

The processing of wax and wax additives with supercritical fluids

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Declaration

I, the undersigned, hereby declare that the work contained in this thesis is my own original work and that I have not previously in its entirety or in part submitted it at any university for a degree.

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16 September 2005

Abstract

Waxes have many potential uses but large-scale application is hampered by their virtual insolubility. By grafting the wax with a polyethylene glycol segment to form an alcohol ethoxylate, the solubility of the wax in commercial solvents is significantly increased. Alcohol ethoxylates are produced by the polymerisation addition of ethylene oxide onto an oxidised wax. Current methods of alcohol ethoxylate production from alcohols lead to wide ethylene oxide addition distribution and large quantities of residual alcohol.

The objective of this study is to provide a method for narrowing the ethylene oxide distribution and to reduce the residual alcohol content. It is proposed to concentrate the alcohol ethoxylate in a post-production separation process using supercritical fluid extraction.

The system is modelled to contain three pseudo-components: an alkane, an alcohol and an alcohol ethoxylate. Propane is selected as the supercritical solvent of choice due to the large solubility difference between the alkane and polyethylene glycol.

Lower molecular weight alkane phase equilibrium data with propane is abundant but extrapolation to higher molecular weights requires further investigation as it may be complicated by molecular folding. Molecular folding occurs in crystalline polyethylene and high molecular weight normal alkanes but information regarding molecular folding in solution is inconclusive.

A model is proposed for molecular folding of normal alkanes in supercritical solution. A high molecular weight alkane mixture is synthesised and phase equilibrium measurement with propane are conducted. A lower molecular weight alkane mixture is used to prove the application of the principle of congruency to high-pressure phase equilibria. In the high wax mass fraction region the measurements are between the no-folding and once-folded relationship, indicating the possibility of partial molecular folding. In the mixture critical and low wax mass fraction region the measurements are similar to the non-folding relationship. Molecular folding in solution is thus dependent on the solution concentration.

No phase equilibria measurements exist for propane with either high molecular weight alcohols or alcohol ethoxylates. Measurements of propane with an alcohol mixture show total solubility below 140barA for temperatures up to 408K. Measurements of propane with an alcohol ethoxylate at temperatures between 378 and 408K shows that for an alcohol ethoxylate mass fraction between 0.025 and 0.5 pressures greater than 275barA are required for solubilisation.

When comparing the solubility of the three pseudo-components, the alkane is the most soluble followed by the alcohol. The alcohol ethoxylate is the least soluble. A counter-current supercritical extraction process is proposed for the concentration of the alcohol ethoxylate. Pilot plant tests were conducted and the proposed set-up shows good separation. An estimate of the energy requirements shows that heating and cooling constitute the majority of the energy required but with the use of heat integration it can be reduced by approximately 33%.

This work thus shows that the proposed process is both technically and economically viable.

Although this work has provided a method for concentrating the alcohol ethoxylate, the process has not been optimised yet and future work includes the fine-tuning of this process.

Opsomming

Sintetiese wasse het baie potensiële gebruike maar die feit dat hulle byna onoplosbaar is belemmer grootskaalse toepassings. Die oplosbaarheid van die was kan beduidend verhoog word deur 'n poliëtileenglikol segment aan die was molekule te bind om sodoende 'n alkohol etoksilaat te vorm. Alkohol etoksilate word produseer deur die polimerisasie addisie van etileenoksied aan geoksideerde was. Huidige alkohol etoksilaat produksiemetodes lei tot 'n wye etileenoksied verspreiding en 'n groot hoeveelheid residuele alkohol.

Die doel van hierdie studie is die ontwikkeling van 'n metode om die etileenoksiedverspreiding te vernou en om die residuele alkohol te verlaag. Daar word voorgestel om die alkohol etoksilaat te konsentreer in 'n stroomaf skeidingsproses deur van superkritiese ekstraksie gebruik te maak.

Die sisteem word gemodelleer as drie pseudokomponente naamlik, 'n alkaan, 'n alkohol en 'n alkoioletoksilaat. Propaan is gekies as die mees geskikte oplosmiddel as gevolg van die groot oplosbaarheidsverskil tussen die alkaan en polietileenglikol in superkritiese propaan.

Fase-ewewigs data van propaan met lae molekulêre massa alkane is volledig verkry, maar verdere ondersoek word benodig voor ekstrapolasie na hoër molekulêre massas kan plaavind aangesien dié fase-ewewig moontlik deur molekulêre vou beïnvloed kan word. Molekulêre vou kom voor in kristallyne polietileen and hoë molekulêre massa alkane maar inligting aangaande molekulêre vou van dié komponente in oplossing is onbeslissend.

'n Model word voorgestel vir molekulêre vou in alkane in superkritiese oplossing. 'n Hoë molekulêre massa alkaanmengsel is gesintetiseer en fase-ewewigsmetings met propaan is gedoen. 'n Lae molekulêre massa alkaanmengsel is gebruik om die toepassing van die beginsel van kongruensie op hoëdrukfase-ewewigte te bewys. In die hoë was massafraksiegebied lê die metings tussen die geen-vou- en enkel-vouverhouding en dui op die moontlikheid van gedeeltelike molekulêre vou. In die mengsel kritiese- en lae was massafraksiegebied is die metings soortgelyk aan die geen-vouverhouding. Molekulêre vou is dus afhangklik van die oplosmiddelkonsentrasie.

Geen fase-ewewigsmetings bestaan vir propaan met of 'n hoë molekulêre massa alkohol of alkoioletoksilaat nie. Metings met propaan en 'n alkoholmengsel wys totale oplosbaarheid onder 140barA vir temperature tot en met 408K. Metings van propaan met 'n alkoioletoksilaat by temperature tussen 378 en 408K toon dat tussen massafraksies tussen 0.025 en 0.5 drukke groter as 275barA benodig word vir totale oplosbaarheid.

Wanneer die oplosbaarheid van die drie pseudokomponente vergelyk word, is die alkaan die mees oplosbare, gevolg deur die alkohol. Die alkoletoksilaat is die minste oplosbaar. 'n Teenstroom superkritiese ekstraktsieproses word voorgestel om die alkoletoksilaat te konsentreer. Proefaanleg skaal toetse is gedoen en die opstelling gee 'n goeie skeiding. 'n Beraming van die energie benodig wys dat verhitting en verkoellings energie die grootste komponente is en dat met die gebruik van energie integrasie die benodigde energie met ongeveer 33% verlaag kan word.

Die werk wys dus dat die voorgestelde proses beide tegnies en ekonomies lewensvatbaar is.

Dié werk het 'n metode vir die konsentring van alkoletoksilaate ontwikkel en verdere werk sal die optimeering van die proses insluit.

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The journey of a thousand miles begins with one step.

Lao-Tsze

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1 Introducing synthetic wax and its derivatives

Wax is as old as mankind. Over 6000 years ago the Egyptians used beeswax in numerous applications, such as the preservation of mummies [1]. With time, numerous different sources and types of wax have been developed with many applications, resulting in a lucrative chemical industry.

1.1 SYNTHETIC WAXES

Synthetic waxes derive their name from their origin: they are generally not found in abundance in nature but are man-made high molecular weight alkanes produced as by-products in the Fischer-Tropsch petroleum synthesis and the production of polyethylene.

In general synthetic waxes are long chain normal alkanes with 30 to 300 carbon atoms, molecules with less carbon atoms classified as paraffin waxes, those with more as polyethylene waxes. Synthetic waxes do not exist as a single mono-disperse molecule, but as a polydisperse mixture, the degree of polydispersity and methyl branching depending on the method of production.

Synthetic waxes are hard, usually white or off-white, tasteless, odourless and non-toxic. They are insoluble in water and most chemicals, and only marginally soluble in strong solvents such as turpentine, naphtha, xylene, toluene and carbon disulphide, the solubility decreasing drastically with increasing chain length. The melting point, ranging between 68 and 140°C depends on the molecular length and, in the case of very long molecules, the crystallisation conditions.

Synthetic waxes are often used as a coating, for example in the printing and paper industry, in the food industry and as polishes. Synthetic waxes are also used as lubricants and linings. Currently the main problem in using synthetic waxes, especially in the aforementioned uses, lies with the difficulty in application. With these waxes being only marginally soluble in even strong solvents application of very thin layers is often difficult, if not impossible.

1.2 WAX DERIVATIVES

To overcome the application problems associated with pure synthetic waxes, either a solvent needs to be developed that is able to dissolve the synthetic wax in large quantities or the chemical structure of the wax needs to be modified so as to improve the solubility. This work concentrates on the latter, modifying the wax to form a wax derivative.

The simplest modification of a normal alkane is the addition of a single functional group, usually an oxygen-containing group such as a hydroxyl or carboxylic group. Typically, either allyl alcohols are grafted to normal alkanes or the alkanes are treated with a peroxide such as hydrogen

peroxide [2] to form long chain alcohols. However, although these simple modifications increase the solubility marginally, the very long hydrocarbon backbone dominates and significant change in solubility is not achieved.

An alternative method of chemical modification is the grafting of a polyethylene glycol segment upon the alkane molecule. This combines the hydrophilic nature of polyethylene glycol with the hydrophobic nature of the alkane and by varying the ratio of the polyethylene glycol segment to the hydrocarbon segment the required solubility can be achieved. This process has the advantage that, although the molecular length is increased significantly, with exception of the solubility, other properties of the alkane are not changed significantly.

These polyethylene glycol modified alkanes, which can either be used in pure form or may be used in combination with normal alkanes acting as a solubilisation agent, are commonly known as alcohol ethoxylates, the name originating from the method of production, and have the following general structure:



Where R is the hydrocarbon backbone and m is a positive non zero integer indicating the average number of ethylene oxide units added

As the name indicates, alcohol ethoxylates are produced through the polymerisation addition of ethylene oxide upon an alcohol in the presence of a suitable catalyst; the value of m thus varying from molecule to molecule. The conversion of the alkane to an alcohol ethoxylate thus proceeds in two steps:

- The conversion of the alkane into an alcohol
- The polymerisation addition of ethylene oxide upon the alcohol

However, as will be shown in this work, the process of the production of alcohol ethoxylates still has major problems, especially with regard to obtaining a high conversion product with a desired variance of m.

Currently wax-like alcohol ethoxylates do not have an excessively wide market application, mainly due to these production problems. Currently it is not possible to produce a narrow enough range wax-like alcohol ethoxylate to find large-scale commercial application. This work aims to suggest a technology whereby it may be possible to produce narrow range ethoxylates and to experimentally test this method. Should this technology be technically feasible and economically viable, it may be possible to commercially produce narrow range wax-like alcohol ethoxylates. A more soluble wax may be produced thus overcoming many of the problems associated with synthetic waxes without losing the character of the wax. New applications may also be found.

1.3 PROBLEM STATEMENT AND ULTIMATE TARGET

Wax-like alcohol ethoxylates can be produced. Alkanes are first converted to alcohols, either by grafting with allyl alcohols or treatment with a peroxide. The resultant alcohol is then ethoxylated with ethylene oxide in the presence of a suitable catalyst to form an alcohol ethoxylate, as described in Equation 1-1. However, in the reaction product a large quantity of unreacted alkane and alcohol is present as well as a wide spread of addition products.

The ultimate goal is to improve the process to such an extent that narrow range alcohol ethoxylates can be produced with little or no residual alkane and alcohol.

1.4 AIMS OF THIS WORK

The ultimate aim is to provide a process for producing an alcohol ethoxylate of a desired product range with little or no residual alkane or alcohol. This is however, beyond the scope of this project and this work aims to provide the basis for this technology and guide the technology in a new direction which would hopefully provide a solution to the ultimate aim.

This work will show that at present the best solution for the production problem is a postproduction separation process. It is envisaged to use supercritical fluid extraction to remove unreacted alkane and alcohol (which can easily be extended to the lower addition products) and to test the suitability of this method on pilot plant scale. The aims of this project can be summarised as follows:

- A detailed investigation of the production of alcohol ethoxylates will be conducted. From this investigation it is envisaged to obtain knowledge on the factors limiting the production of an alcohol ethoxylate with a desired product range and little or no residual alcohol or alkane. Possible solutions to the production-problems will be investigated briefly.
- The use of supercritical fluids for the concentration of alcohol ethoxylates in a postproduction process will be investigated. Preliminary investigations of the technical viability of this process will be based on the phase equilibria of the alkane, the alcohol and the alcohol ethoxylate.
- In the solid-state long chain alkanes undergo molecular folding [3], [4], the onset of molecular folding occurring within the molecular size range investigated in this work. The possibility of molecular folding in supercritical solution will be investigated. This investigation includes the synthesis of very long chain alkanes of low polydispersity and the measurement of the phase equilibria of these normal alkanes in the supercritical solvent. From the measured phase equilibria the presence of molecular folding in supercritical solution will be postulated and the effect, if any, will be determined.
- A process for the concentration of alcohol ethoxylates will be suggested and this process will be tested on pilot plant scale. An order of magnitude economic evaluation based on the energy requirements will be conducted.

The following is beyond the scope of this project:

- It is not envisaged to totally redevelop the process of ethoxylation. It is envisaged to complement the current technology with a post-production process.
- The post-production process will be developed as far as the suggestion and testing of a method for the concentration of the alcohol ethoxylate produced. It will suffice as to provide the basic technology for concentration process, test this technology on pilot plant scale and conduct a preliminary economic evaluation. A detailed optimisation, design and costing is beyond the scope of this project.

A schematic representation of the layout of this work is given in Figure 1-1 illustrating the sequence of presentation and how the aims stated above will be achieved.

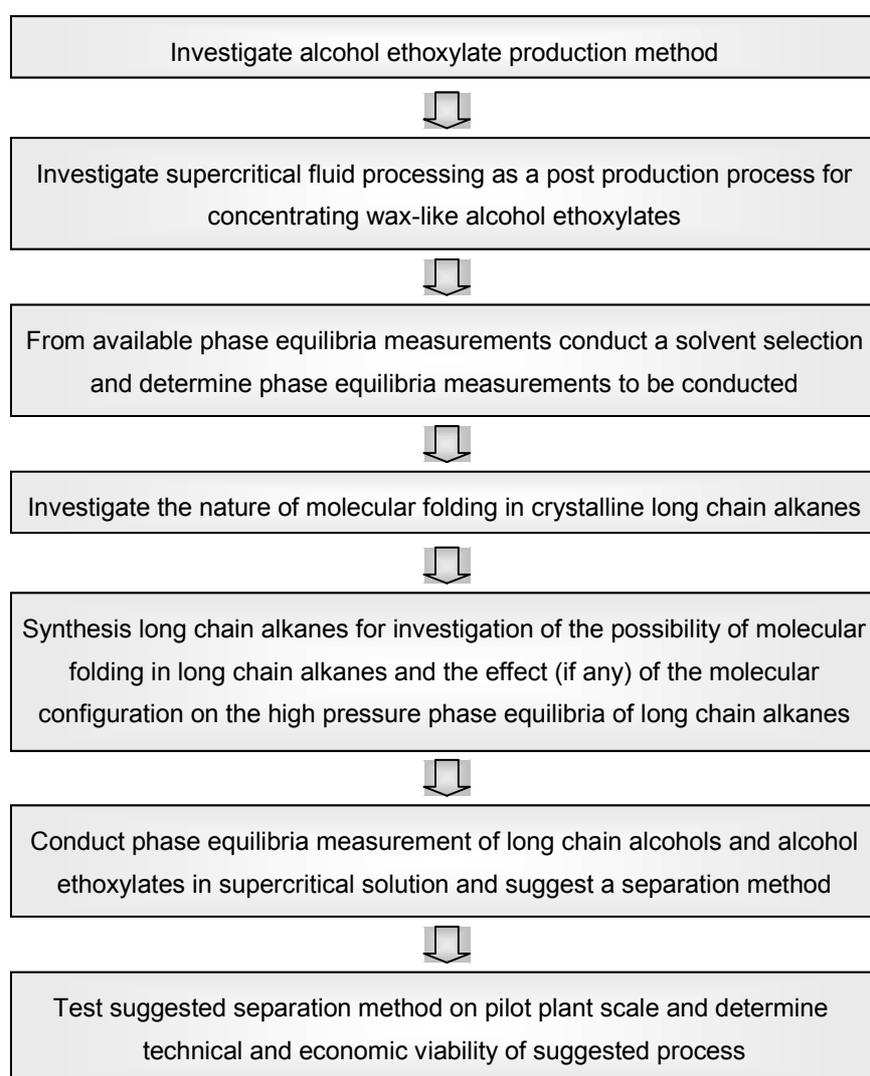


Figure 1-1: Schematic representation of layout of this work

1.5 NOMENCLATURE

Symbol	Description
m	Average number of ethylene oxide groups
R	Hydrocarbon backbone of the alcohol ethoxylate

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2 Alcohol Ethoxylates

In this chapter alcohol ethoxylates will be discussed. The discussion will include a general background of surfactants and alcohol ethoxylates, the uses and production of alcohol ethoxylates and with particular reference to waxy alcohol ethoxylates, problems in the method of production and an outlook on the possible solutions will be given. Upon completion of this chapter the aims of this work will be defined in more detail.

Very little information is available with regard to waxy alcohol ethoxylate and thus lower homologue members are relied upon to provide some of the general information required.

2.1 SURFACTANTS

Surfactant is an acronym for SURFace ACTive AgeNT.

Surfactants generally comprise of two parts:

- Hydrophilic head: This part of the molecules has an affinity for polar compounds and may consist of, for example, hydroxyl groups or a polyethylene glycol chain.
- Hydrophobic tail: This part of the molecule has an affinity for non-polar groups and may consist of, for example, phenol and hydrocarbons.

Surfactants may contain several hydrophilic or hydrophobic groups and are usually classified according to their hydrophilic group.

- Non-ionic surfactant: Non-ionic surfactants are amphiphilic compounds that are unable to ionise in aqueous solutions, i.e. they carry no charge [1]. Non-ionic surfactants comprise of a broad range of over 250 types of surfactants and examples include alkyl polyethylene glycol ethers, alkyl phenol polyethylene glycol ethers, fatty acid alkylolamides, sucrose fatty esters etc. Alcohol ethoxylates fall into this class of surfactants.
- Anionic surfactant: Anionic surfactants are amphiphilic compounds with an anionic hydrophilic residue and a small counter ion such as sodium, potassium or ammonium, the counter ion only slightly influencing the surface-active properties of the substance [1]. Examples of anionic surfactants include alkyl benzene sulphanoates, alkyl phosphates etc.
- Cationic surfactant: Cationic surfactants are amphiphilic compounds with a cationic hydrophilic residue and counter ions such as chlorides, sulphates or acetates that only slightly influence the active properties of the compound [1]. Examples of cationic compounds include tetra-alkyl ammonium chloride, n-alkylpyridinium chloride etc.
- Amphoteric surfactant: Amphoteric surfactants are amphiphilic compounds in which the hydrophilic residue has a zwitterionic group, i.e. a group with both an anionic and a cationic

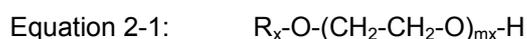
group [1]. Amphoteric surfactants thus have both a positive and negative local charge but the molecule as a whole is usually neutral. Examples of amphoteric surfactants include amino-carboxylic acids, betanes, sulphobetanes etc.

2.2 DEFINING ALCOHOL ETHOXYLATES

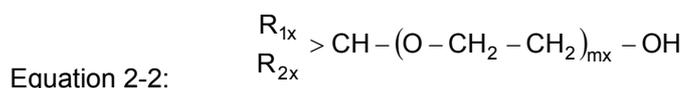
Alcohol ethoxylates, also known as alkyl polyglycol-ethers, are of the most common type of non-ionic surfactants.

2.2.1 CHEMICAL STRUCTURE

Alcohol ethoxylates have the following general formula:



Although the focus of this work is on primary alcohol ethoxylates, secondary alcohol ethoxylates are sometimes included and can be represented as follows:



2.2.2 DEGREE OF ETHOXYLATION AND PERCENTAGE ETHYLENE OXIDE CONTENT

The degree of ethoxylation can be defined as follows:

$$\text{Equation 2-3: } \text{degree of ethoxylation} = \frac{\text{mol ethylene oxide}}{\text{mol fatty alcohol}}$$

An alternative method for describing the amount of ethylene oxide per molecule alcohol is the percentage ethylene oxide content, defined as follows:

$$\text{Equation 2-4: } \% \text{ Ethylene oxide} = \frac{\text{Mass ethylene oxide in molecules}}{\text{Total molar mass of molecule}}$$

Equation 2-4 is usually preferred as analysis results can easily be converted to percentage ethylene oxide content.

2.2.3 HYDROPHOBIC LIPOPHILIC BALANCE

The hydrophobic-lipophilic balance (HLB) is the balance of the size and strength of hydrophilic and hydrophobic, also known as lipophilic, groups in a surfactant. The HLB can be expressed mathematically as follows for an alcohol ethoxylate:

$$\text{Equation 2-5: } \text{HLB} = 20 \frac{M_{\text{hyd}}}{M_{\text{tot}}}$$

In Equation 2-5 M_{hyd} is the molar mass of the hydrophobic fraction of the molecule, M_{tot} being the total molar mass of the molecule. The value of the HLB thus gives a good indication of the behaviour of the surfactant in water and the typical uses. These are summarised in Table 2-1:

Table 2-1: Relationship between HLB, behaviour in water and uses of surfactants [1].

HLB Range	Behaviour in Water	Example of uses
0 – 3	Insoluble	Defoaming agent, dispersant, for solids in oil, co-emulsifier, refatting agent
3 – 6	Insoluble, dispersible	Water-in-oil emulsions, co-emulsifier
6 – 9	Dispersible, giving milky solution	Wetting agent, water in oil emulsions
8 – 10	Soluble, giving milky turbid to translucent solution	Wetting agent
10 – 13	Soluble, giving translucent to clear solution	Oil in water emulsions, detergents and cleansing agents
13 – 15	Soluble, giving clear solution	Oil in water emulsions, detergents and cleaning agents
> 15	Soluble, giving clear solution	Solubiliser, cleansing agent

Using Table 2-1 in conjunction with Equation 2-5 and Equation 2-3, the desired degree of ethoxylation can be determined for a desired application.

2.3 PROPERTIES

All non-ionic surfactants are composed of two connected but distinctly different portions. One end of the molecule is hydrophobic in nature, or water disliking and is strongly attracted to oily hydrophobic substrates. The other end is hydrophilic in nature, or water liking and is strongly attracted to hydrophilic substances or water itself. The properties of the surfactants depend on the combined effect of these two parts of the molecule.

The degree of emulsification required dictates the percentage ethylene oxide required. Generally, an increase in percentage ethylene oxide leads to an increase in solubility. Too few ethylene oxide units lead to a large amount of unreacted alcohol. Too many ethylene oxide units lead to the emulsifier being too soluble in water and thus reduce the aquatic efficiency. Normally a balance between too few and too many ethylene oxide units is required.

The number of carbon atoms in the hydrocarbon backbone depends on the desired properties of the product. Usually it is regarded that too few carbon atoms results in a decrease in the effectiveness of the surfactant while too many carbon atoms are often not able to disperse satisfactorily.

2.3.1 GENERAL PROPERTIES OF NON-IONIC SURFACTANTS

Non-ionic surfactants have the following general properties:

- Good surfactants and emulsifiers.
- Low aquatic toxicity in comparison to other surfactants.
- Range in solubility from complete oil compatibility to complete water solubility and are able to dissolve a water-insoluble substance in an aqueous solution.
- Have the ability to disperse both organic and inorganic particles in both aqueous and non-aqueous solution yet do not absorb on charged surfaces.
- Are some of the most powerful wetting agents available; a narrow range alcohol ethoxylate is a more effective wetting agent than the wide range addition product [2].
- They are moderate to low foamers, yet at an optimum temperature and ethylene oxide content they are quite good foamers. Depending on the system conditions, they are also able to act as foam stabilisers or even as defoamers.
- Generally have excellent stability towards acids, yet are sensitive towards alkali. They are unstable at high pH and in the presence of oxidising agents [3].

The influence of the structure of the alcohol ethoxylate properties are given in Table 2-2:

Table 2-2: Influence of structure on alcohol ethoxylate properties [4]

Property	Effect of increasing hydrocarbon backbone	Effect of increasing % ethoxylation	Other factors
Melting point	Increases melting point	Increases melting point	
Density	Increases density	Increases density	
Viscosity of solution	Increases viscosity	Complex relationship	Concentration
Surface tension		Decreases surface tension	Increasing concentration decreases surface tension
Solubility in water	Decreases water solubility	Increases water solubility	Solubilisation decreases with increasing temperature
Cloud point temperature of solution	Increase in cloud point temperature	Increase in cloud point temperature	

2.3.2 DISTRIBUTION OF ETHYLENE OXIDE UNITS

The distribution of ethylene oxide added to the alcohol has a profound effect on the properties and the applicability of the alcohol ethoxylates. Narrow range alcohol ethoxylates, can be defined as those ethoxylates where the number of ethylene oxide units per molecule is close to the average and the quantity of high ethylene oxide addition products and unreacted alcohol is limited.

Narrow range alcohol ethoxylates have the following advantages:

- Due to the reduced unreacted alcohol content in narrow range alcohol ethoxylates, fewer moles of ethylene oxide are required to be added to achieve a given cloud point than in the wide range alcohol ethoxylate [5].
- Lower aqueous viscosities are also observed for narrow range alcohol ethoxylates compared to broad range products with the same average ethylene oxide content [5].
- Narrow range alcohol ethoxylates produce less stable foams. Where alcohol ethoxylates are used as foam destabilisers, narrow ranges are advantageous [5].
- Narrow range alcohol ethoxylates are more efficient wetting agents [5].
- For the same number of moles of ethylene oxide added, a narrow range alcohol ethoxylate produces a higher polarity. As the function of alcohol ethoxylates as surfactants depends on the polarity of the molecule, an increase in polarity may be advantageous.

Although most applications prefer the use of narrow range alcohol ethoxylates, broad range products do offer some advantage:

- Broad range products provide a more stable foam height for a product with the same cloud point. This is advantageous when one of the functions required of the alcohol ethoxylate is the creation of a stable foam [5].
- Broad range alcohol ethoxylates form a more stable emulsion than narrow range products [5], [6].

2.4 ECONOMIC AND ENVIRONMENTAL CONSIDERATIONS

Although not the main objective of this work, economic and environmental considerations have a significant impact on the selection and application of an alcohol ethoxylate.

2.4.1 ECONOMIC CONSIDERATIONS

Surfactants are mainly marketed as constituents of finished products together with non-surfactant products. In many cases their specific consumption cannot be determined exactly on account of lack of knowledge of their content in commercial products. In addition, most market estimates are limited to specific application sectors. There is thus no accurate data on the total consumption.

In 1987 a series of articles were published concerning the soap and detergent industry in North America [7], China [8], Japan [9], Latin America [10] and Europe [11]. Table 2-3 shows the production of soaps, detergents and cleaning products in 1982. The North American and European production has remained relatively constant when compared to a study conducted regarding soap and detergent production in 1975 [12], yet significantly larger quantities are being produced in the rest of the world. The production of alcohol ethoxylates in 1990 was estimated to be 700 000 tons [1].

Table 2-3: Soap, detergent and cleanser production 1982 (10⁶ kg) [7]

Country / Region	Production	Percentage
Canada	300	1.0%
United States	7700	25.7%
Western Europe	8000	26.7%
Rest of the World	6000	46.7%
World	30000	

2.4.2 HUMAN SAFETY AND ENVIRONMENTAL CONSIDERATIONS

Surfactants are used in many areas of human activity: in the home, in commerce, in agriculture and in industry. A large number of surfactants come into direct contact with human skin as constituents of detergents and cleaning agents, their accidental oral ingestion, even if only as residues on washed dishes, therefore cannot be ruled out. Surfactants must thus be safe for their intended use for the estimated human dosage.

Irrespective of their intended use, human safety and environmental protection is of major importance. The fate and effect of surfactants in rivers and waters are of particular importance in environmental risk assessment, since a large portion of surfactant is discharged after use into effluent and sewage and ultimately flows into rivers, lakes and oceans. Here degradation of surfactants by micro-organisms in natural waters and in sewage plants, which ultimately leads to their complete neutralisation, is particularly important.

2.4.2.1 HUMAN TOXICOLOGY

For alcohol ethoxylates there is no danger of acute lethal toxicity by adsorption of surfactants through the skin or by inhalation. Surfactants can, however, cause skin irritation and damage on prolonged contact since they have the ability to destroy the water-lipid membrane that serves as an external protective layer of the skin by destroying the individual constituents. Faucher et al. [13] found that non-ionic surfactants are weak penetrants of skin. Alcohol ethoxylates can also be used to reduce the negative effects that anionic surfactants have on the skin.

The oral lethal dose of surfactants is usually between several hundreds to several thousands of milligrams per kg body mass [1]. Zerkle et al. [14] assessed the oral safety of alcohol ethoxylates and concluded that alcohol ethoxylate induced anaesthesia is not predicted to occur in humans and general anaesthetic effect in humans is expected to occur only in the case of extremely high volumes of accidental ingestion (> 10ml/kg).

2.4.2.2 BIODEGRADABILITY

Since used surfactants are discharged mainly into effluent streams and sewage, and thus eventually into rivers and the, their aerobic degradation is of primary interest. Surfactants whose hydrophobic group is derived from hydrocarbons can be oxidised enzymatically under aerobic conditions and are thus biodegradable. In anaerobic conditions, alcohol ethoxylates are partially mineralised to CO₂ and CH₄ [15]. With ethoxylates, the degradation rate is influenced by the chain length of the polyethylene glycol chain in so far that an increase in the number of ethylene oxide units leads to a decrease in the rate of degradation for the same hydrophobic residue.

2.4.2.3 AQUATIC TOXICITY

Surfactants have a tendency to collect at the oil/water interface and together with their effect on the interfacial tension make them likely to interfere with the breathing mechanism of aquatic organisms. The toxicity of surfactants to aqueous organisms can only be evaluated if the rate and the degree of their biodegradation are also taken into account. Thus, substances with high toxicity will generally not have any harmful effect on aquatic organisms if they are degraded sufficiently quickly. Aquatic toxicity is strongly dependent on the structure of the surfactant. An increase in the length of the hydrophobic group leads to an increase in aquatic toxicity [1]. In alcohol ethoxylates, it is generally noticed that a decrease in the length of the polyethylene glycol chain leads to an increase in aquatic toxicity [1].

2.5 USES OF ALCOHOL ETHOXYLATES

Alcohol ethoxylates can be used as emulsifiers, dispersants, wetting agents and solvents in many applications. They are active agents that are used widely in products or applications where it is necessary or desirable to improve contact between polar and non-polar media.

2.5.1 GENERAL APPLICATIONS

Historically, the oldest sector of application is the textile industry with numerous processes such as washing, cleaning, lubricating, sizing, filling, bleaching, micronising, carbonising and finishing. Yet, in recent times, considerably wider applications have been found for alcohol ethoxylates. Currently alcohol ethoxylates are used in, amongst others, the following applications:

- Detergent industry: As hard surface cleaners, dishwashing detergents, laundry detergents, fabric softeners and bleach containing compositions.

- Body and hair care products.
- In the agricultural and food sector.
- Removal and reclamation of uncured paint from spray booths.
- As a reaction medium.
- In subterranean applications to remove oil from oil wells [16], [17].
- As a component of disinfectant solutions.
- In tissue paper lotion [18], [19].
- In odour control composition [20].
- Stabilisation agent for peracid [21].
- A dispersing agent capable of suspending solids in liquid medium [22].
- As emulsifiers in the petrochemical industry.

2.5.2 ALCOHOL ETHOXYLATES AS STARTING MATERIAL FOR OTHER SURFACTANTS

By modifying the terminal group of alcohol ethoxylates, the surface properties of the alcohol ethoxylates can be changed. These properties include surface tension, cloud point, critical micelle concentration and foaming properties of the compound [23]. The most common modifications that can be made to alcohol ethoxylates are the following (see section 9.1.1 in appendix A for details):

- Alkyl and aryl terminally blocked alcohol ethoxylates
- Co-polymerisation of alcohol ethoxylates
- Production of alcohol ethoxysulphates and alcohol ethoxysulphate salts
- Production of carboxy methylated alcohol ethoxylates
- Production of carboxylic acid alcohol ethoxylates
- Production of ketone derivatives of alcohol ethoxylates
- Production of alcohol ethoxylated derived diols
- Production of terminal nitrogen derivatives of alcohol ethoxylates

Narrow range alcohol ethoxylates are extremely important when alcohol ethoxylates are used as starting materials for other surfactants, such as sulphated alcohol ethoxylates, as wide range products often contain significant quantities of unreacted alcohol, which leads to unwanted conversion by-products that may be detrimental to the final product [24].

2.5.3 POSSIBLE USES FOR HIGH MOLECULAR WEIGHT ALCOHOL ETHOXYLATES

Large quantities of high molecular weight alcohol ethoxylates are not currently produced mainly due to production problems. Although possible applications may not be as numerous as in the case of lower homologue members, possible uses do exist. A number of possible applications can be proposed, suggestions mainly originating from traditional applications of waxes [25] where alcohol ethoxylate may improve the functions of the wax. The applications listed below are the most obvious, yet possible applications should not be limited to those mentioned in this work.

Louw et al. [26] shows that waxy alcohol ethoxylates can be emulsified or dispersed in water, emulsification referring to the wax in the liquid phase, dispersion to the wax in the solid phase. They also showed that alcohol ethoxylates waxes can also be used to emulsify Fisher Tropsch waxes in water, this being the only known emulsifier that is able to emulsify these long chain molecules. These properties of alcohol ethoxylates can be exploited for future application.

Uses in papermaking and recycling

Waxes are used in the paper industry both during the processing and on the finished goods. One of the major uses of waxes in the paper industry is in the use of coatings. Here waxes improve the water resistance of the paper product and are often used to impart a surface gloss. However, application of thin layers of high molecular weight waxes is difficult due to the insolubility of these waxes in a suitable solvent.

Using high molecular weight alcohol ethoxylates a thin layer with properties similar to the high molecular weight wax could be imparted. The application would be considerably easier due to the increased solubility in solvents and it may even be possible to produce a superior product.

Component of ink

Surfactants are used as a component in the ink for inkjet printers and other applications. Many ink compositions contain, in addition to the surfactant, a wax [27]. It may thus be possible to use a waxy alcohol ethoxylate as (part) replacement for the surfactant and/or wax.

In polishes

Surfactants are used in a wide range of polishes. In addition to the surfactant, the polish usually contains amongst others, wax (paraffin, microcrystalline, beeswax etc) [28]. The surfactant is used in addition to a wax. It may be possible to replace the large quantities, if not all of the surfactant and/or the wax with high molecular weight alcohol ethoxylates.

Pharmaceutical industry

Waxes are used as dispersion agents and surface treatment products in the pharmaceutical industry. High molecular weight alcohol ethoxylates could be applied as superior dispersion

agents due to their improved dispersion ability compared to alkanes. In addition, they could be used to improve surface application compared to alkanes.

Cosmetic industry

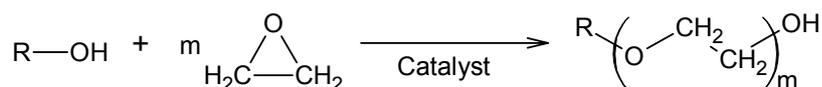
In the cosmetic industry, waxes are used as binders and consistency regulators. High molecular weight alcohol ethoxylates may be superior binder and better consistency regulators due to their surfactant properties and both hydrophilic and hydrophobic nature.

Starting materials for other high molecular weight surfactants

As in the case for lower alcohol ethoxylates, higher molecular weight alcohol ethoxylate members can also be used as starting materials for other surfactants. Production and application of these other molecular surfactants would depend on the surfactant required and an even wider range of applications may be possible.

2.6 PRODUCTION OF ALCOHOL ETHOXYLATES

As their name indicates, alcohol ethoxylates are produced by the polymerisation addition reaction of ethylene oxide to alcohols in the presence of a catalyst:



Equation 2-6:

The ethoxylation process serves to introduce a desired average number of ethylene oxide units per mole alcohol ethoxylate. For example, if a mixture of 3 moles of ethylene oxide per mole alcohol is used, the product has an average of 3 ethylene oxide units per molecule. However, a substantial amount will be combined with less than three units and a substantial amount with more than three units. In a typical ethoxylation process the product mixture also contains an amount of unreacted alcohol, the quantity depending on the degree of ethoxylation, the reaction conditions and the catalyst used.

One of the earliest publications on the production of alcohol ethoxylates was by Johnson in 1927 [29] where the mono-ethers of alcohols were produced by reacting an alkylene oxide with the alcohol in the presence of sulphuric acids or acid compounds thereof, or in the presence of an alkali metal alcolates or alkali metal salts of the lower fatty acids. Many improvements have since been made. This subsection will focus on methods for the production of alcohol ethoxylates.

2.6.1 PRODUCTION OF ALCOHOLS

In many cases, alcohol ethoxylates are required to be produced from the alkane, thus requiring the alkane to be oxidized to an alcohol before the ethoxylation can take place. Although not the primary focus of this work, it will be mentioned briefly here.

Until the early 1960s, alcohols were made almost exclusively from natural sources by saponification of waxes or by the reduction of long chain acids derived from natural oils or fats. Since then significant improvements have occurred and the following methods are currently used:

- Ziegler process [30], [31].
- Oxo process via hydroformylation [30], [32], [33].
- Paraffin oxidation [30].
- Hydrogenation of long chain aldehydes, carboxylic acids and esters [34].
- From natural sources [30].

Details regarding these production methods are given in section 9.1.2 in appendix A. Although the formation of alcohol forms an integral part of the production of alcohol ethoxylates, for the purpose of this work it is assumed that this technology is well known and no further investigations will be conducted.

2.6.2 GENERAL ETHOXYLATION PROCESS

In general many types of surfactants can be produced from petrochemicals. This is illustrated in Figure 2-1 where it is shown that ethylene, paraffin and benzene are the main building blocks for surfactants. The process for the production of alcohol ethoxylates has been highlighted. The rest of this subsection will concentrate on this process.

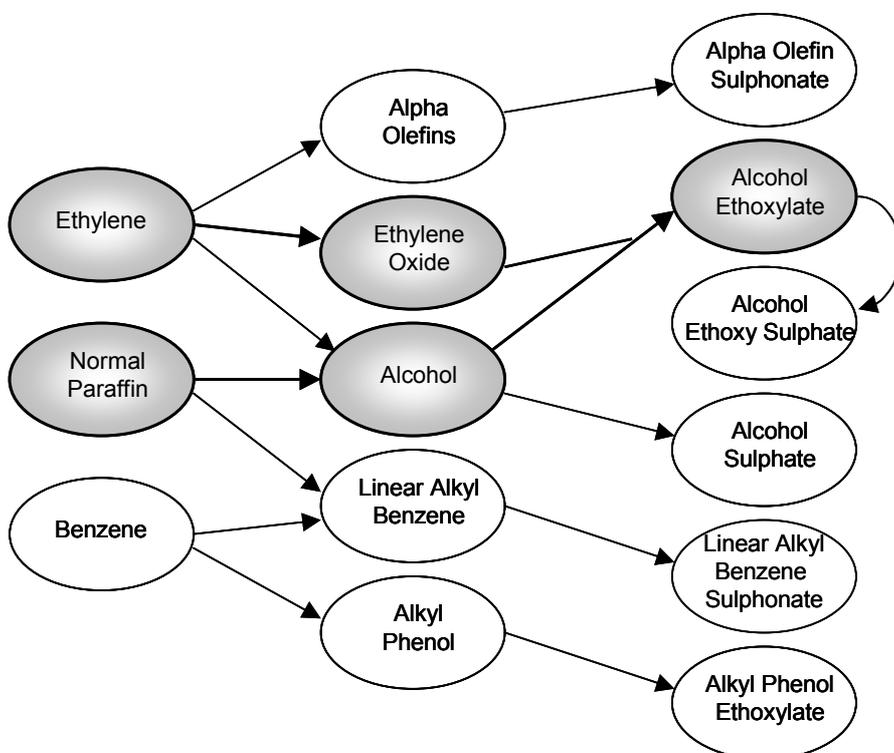


Figure 2-1: Representation of conversion of petrochemicals to surfactants [35]

One of the earliest systematic representations of the process for the ethoxylation of alcohol ethoxylates was published by Satkowski et al. [36] in 1957. In this work various aspects of the ethoxylation reaction were highlighted: Various catalysts were investigated as well as no catalyst and it was found that the reaction required the catalyst to proceed. A reaction mechanism was also proposed and the effect of the basicity of the catalyst was noted. For the basic catalysts the following equation represents the reaction mechanism of the alcoholate formation, the first step in the ethoxylation process:



Where R' = H, -CH₃, -CH₂CH₃ and M = K⁺ or Na⁺

Equation 2-7 is reversible and the basicity of RO⁻ will affect the extent to which the first of the above-mentioned reactions is moved to the right. In addition, the reversibility of the above reactions may explain the delay in the reaction at the beginning.

The second and subsequent steps of the reaction mechanism are those where the ethylene oxide is added to the RO⁻ group and to R(OCH₂CH₂)_nO⁻ respectively.

2.6.3 CATALYSTS USED

The most common catalysts used are strong acids or strong bases, yet the use of other catalysts has also been found. Depending on the catalyst used, problematic by-products may be formed. These include [3] polyglycols if ethylene oxide reacts with water, particularly under basic conditions, catalytic residues, ethylene oxide that is difficult to remove beyond 1 – 25 ppm and 1,4 dioxane.

In addition to by-product formation, the catalyst also determines the alcohol ethoxylate distribution. Selection of a suitable catalyst can minimise the by-products formed and optimise the alcohol ethoxylate distribution required.

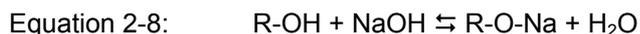
Comparing the performance of the various catalysts is not that easy unless identical experimental conditions are applied. In evaluating the performance of a catalyst in terms of the distribution achieved, this work will concentrate on the following:

- A comparison of the distribution achieved with a Poisson distribution of the same number of ethylene oxide units. The comparison with the Poisson type distribution shows the effect of the activity and acidity of the catalyst. Should all molecules have the same reactivity, a Poisson distribution should be obtained as this a Poisson type process.
- The fraction of the product within $n = \pm 3$ where n = average number of ethylene oxide units added.
- The quantity of unreacted alcohol.

2.6.3.1 BASIC CATALYST

Basic catalysts, the first to be developed, are still the most common and have been studied extensively. Strong bases used include salts of group 1 metals and certain group 2 metals.

Sodium hydroxide is the most common catalyst to be used and industrially it is usually applied to a batch process that takes place in a stirred reactor. In this process the sodium hydroxide (0.1 to 1.0%) and alcohol are placed into the reaction vessel where they are allowed to react according to the following reaction:



Once the reaction is complete, all water is removed either by vacuum or by passing nitrogen through the reactor. This is required to prevent the polymerisation of ethylene oxide into polyethylene glycol.

Ethylene oxide is added to the reaction vessel in the presence of an inert gas such as nitrogen. The reaction is conducted at 130 to 180°C but as the reaction is exothermic, cooling is usually required during the reaction. An increase in temperature results in discoloration and the formation of polydiols. The reaction time required depends on the amount of ethylene oxide added, the temperature and the nature of the hydrocarbon backbone.

Alcohol ethoxylates produced with the use of alkaline catalysts need to be neutralised immediately after production to a pH of 6.5 – 7.5, else serious discoloration due to atmospheric oxygen occurs. The reaction product is usually neutralised with an acid such as acetic anhydride, phosphoric acid, CO₂ [37], [38], glutonic acid, benzoic acid, lactic acid, oxalic acid, citric acid, propionic acid, methane sulphonic acid and diglycolic acid [39]. Strong acids, such as HCl and H₂SO₄ are of no practical significance. During the neutralisation process, the acid reacts with potassium / sodium (or other) alkoxylate to form the corresponding salt. These salts show only a limited solubility in the reaction product and the quantity of the catalyst is limited by the solubility of the neutralised salt in the reaction medium. By substantially increasing the quantity of the catalyst beyond the solubility limit, it is possible to obtain a product with narrower homologue distribution [37], [39], [38]. If the quantity of the catalyst used is so high that the solubility of the salt is no longer guaranteed during the neutralisation process, first clouding and then increasingly salt precipitation occurs, specifically on the surface of the reactor and pipes.

Schmid et al. [39] increased the quantity of the catalyst beyond the solubility limit. The process problems were overcome by neutralising the catalyst in the presence of finely divided solids that are uniformly distributed throughout the reaction mixture. The reaction product can conventionally be filtered to remove the salts formed. An alternative in overcoming the presence of large quantities of precipitated salts is to first partially neutralize the reaction mixture to a pH of about 8, followed by bleaching with hydrogen peroxide and then neutralization can be completed to a pH of 6.5 – 7.5 [39].

Reaction mechanism

The chemistry of the reaction in the presence of basic catalysts can be summarised as follows with sodium hydroxide used as catalyst for illustrational purposes:

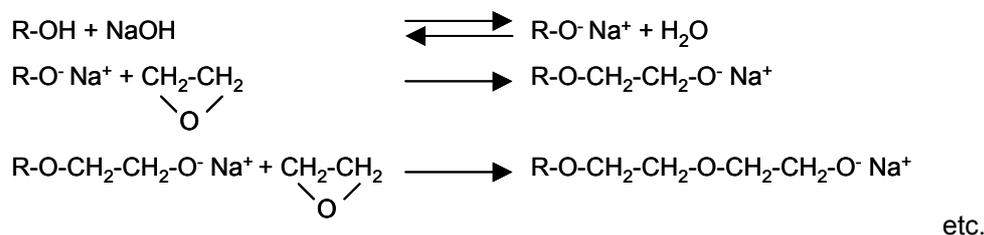


Figure 2-2: Schematic representation of chemistry of ethoxylation process in presence of a basic catalyst illustrated with the aid of sodium hydroxide as catalyst

The reaction rate depends on the ionisation of the active hydrogen. The alcoholate ion formed initially by reaction with the catalyst nucleophilically attacks the ethylene oxide molecule. The resultant anion of the ethylene oxide addition product can undergo an equilibrium reaction with another alcohol molecule or with another ethylene oxide molecule. Schematically the process can be summarised as follows:

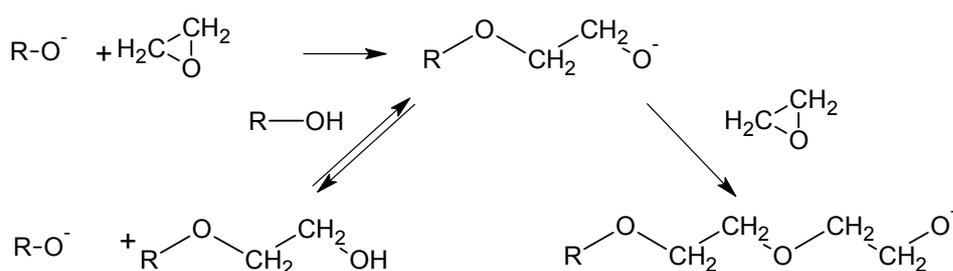
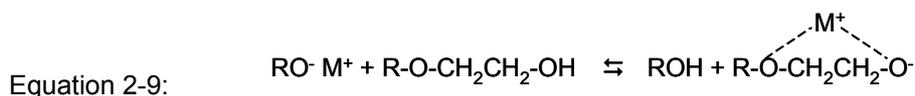


Figure 2-3: Schematic representation of mechanism for ethoxylation reaction in presence of a base catalyst [1]

The pathway that is followed can be determined by considering the acidity of the species. The more basic species preferentially reacts with ethylene oxide. The ether group of the ethoxylated alcoholate increases the acidity of the terminal primary hydroxyl group compared to the initial alcohol [1]. Ethylene oxide thus reacts preferentially with mono-ethoxy alcohols in comparison to the unreacted alcohol, di-ethoxy alcohols preferentially above mono-ethoxy alcohols etc. The net result is a wide distribution of alcohol ethoxylate and a substantial portion of unreacted alcohol.

The reaction mechanism is consistent with the experimental investigation that the distribution tends to sharpen as the strength of the base weakens. A possible explanation of this phenomenon is that with a stronger base, the difference in acidity between the alcohol and the alcoholate becomes less significant. However, it was found that ethoxylation with alkaline earth hydroxides produces a peak sharper than that of alkaline hydroxides [40]. The mechanism thus needs to be modified to incorporate the metal cation-alkoxide anion interaction. The equilibrium reaction is expressed as follows:



For ethoxylation in the presence of an alkaline hydroxide, Equation 2-9 will predict the same results as the mechanism given in Figure 2-3. Yet for divalent metal cations, there will be two bulky ethoxylated alkoxide anions surrounding the metal ion and this overcrowding will reduce the interaction between the cation and the ether oxygen. The equilibrium will be shifted to the left in comparison to the previously stated mechanism and the resulting product is expected to have a sharper peak [41].

Assuming the same acidity of the starting alcohols and all poly-ethoxy alcohols present in the mixture, a Poisson distribution of the individual species must be expected after the ethoxylation reaction. However, due to the difference in acidity of the individual species in the reaction mixture, the homologue distribution that is actually observed in the reaction mixture differs from the Poisson distribution. The deviation is true for all alkaline and alkaline earth catalysts, although deviations in the case of alkaline earth compounds are less strongly pronounced [1].

Examples of Catalysts

Various basic catalysts can be used. Details are given in Table 9-1 in appendix A.

Typical distributions

A plot of a typical distribution attained with NaOH and KOH as catalyst is shown in Figure 2-4 [24] and for comparison purposes, a Poisson distribution of the same average number of ethylene oxide units added is also shown. Figure 2-5 shows typical distributions attained with a calcium ethoxide catalyst with and without an acid promoter [42].

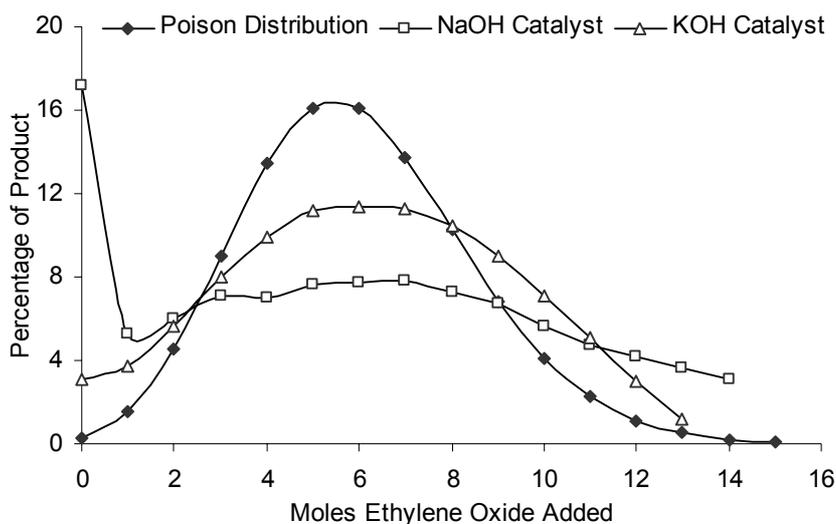


Figure 2-4: Plot of typical distribution attained for NaOH and KOH catalysts and Poisson distribution for same moles ethylene oxide added [42]

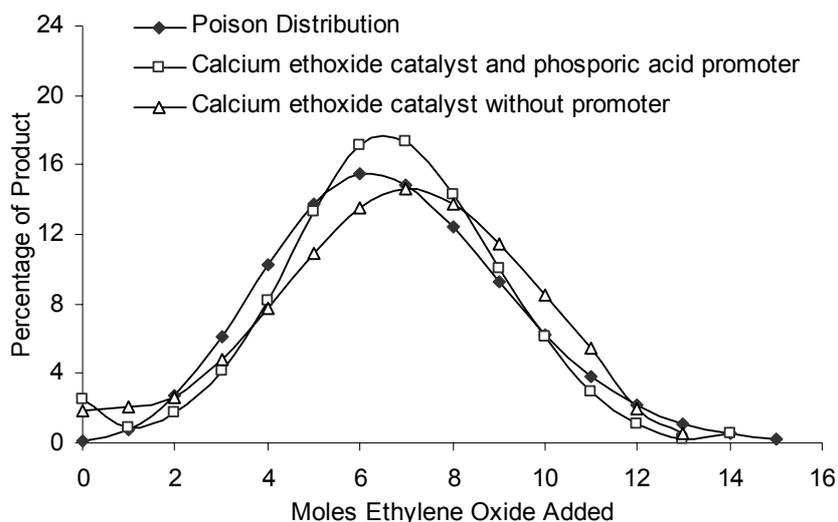


Figure 2-5: Plot of typical distribution attained for calcium ethoxide catalysts with and without a promoter and Poison distribution for same moles ethylene oxide added [42]

The plots shown in Figure 2-4 and Figure 2-5 indicate that the catalyst has a profound influence on the distribution achieved. The values of the residual alcohol and product quantity within $n = \pm 3$ is given in Table 2-4:

Table 2-4: Distribution properties for data shown in Figure 2-4 and Figure 2-5 [42]

Catalyst	Residual Alcohol	$n = \pm 3$
NaOH	17.2%	44.5%
KOH	3.1%	63.2%
Poison Figure 2-4	0.25%	78.6%
Calcium ethoxide with promoter	2.5%	80.2%
Calcium ethoxide without promoter	1.9%	72.1%
Poison Figure 2-5	0.12%	76.0%

From the data it can be seen that the bivalent calcium catalysts provide a significant improvement, especially in the presence of an acid promoter.

2.6.3.2 ACIDIC CATALYST

Acidic catalysts were developed as far back as the 1950's when it was established that alkaline catalysts are not able to produce a narrow enough product range [43].

Acid catalysts used broadly include the Lewis acids [44] such as the fluorides, chlorides and bromides of boron, antimony, tungsten, iron, nickel, zinc, tin, aluminium, titanium and

molybdenum. However, complexes of these Lewis acids with alcohols, ethers, carboxylic acids and amines have also been found. In addition the following are also used as acid catalysts: Sulphuric and phosphoric acids; perchloric acids; perchlorates of magnesium, calcium, manganese, nickel and tin; metal oxalates, sulphates, phosphates, carboxylates and acetates; alkali metal fluoroborates; zinc titanate; and metal salts of benzene sulphonic acid.

Reaction mechanism

When acid catalysts are used, the homologue distribution approximates the Poisson distribution because there is no proton activity and the nucleophilicity of the substrate determines the reaction pathway. The acid, not the alcohol, activates the ethylene oxide. This activation is illustrated with the aid of BF_3 , a Lewis acid:

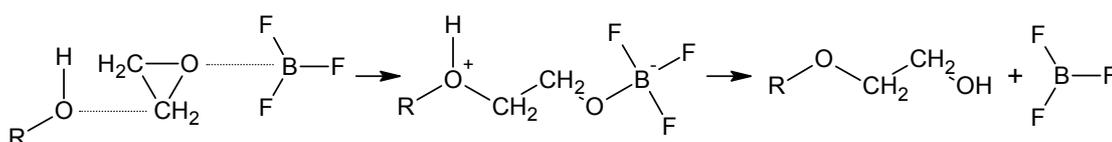


Figure 2-6: Schematic representation of ethoxylation reaction mechanism for acid catalyst illustrated with the Lewis acid BF_3 [1]

Examples of catalysts

Various acid catalysts can be used. Details are given in Table 9-2 in appendix A.

Typical distributions

Typical plots of two acid catalysts are shown in Figure 2-7 and Figure 2-8 and the residual alcohol and the product quantity within $n = \pm 3$ is given in Table 2-5:

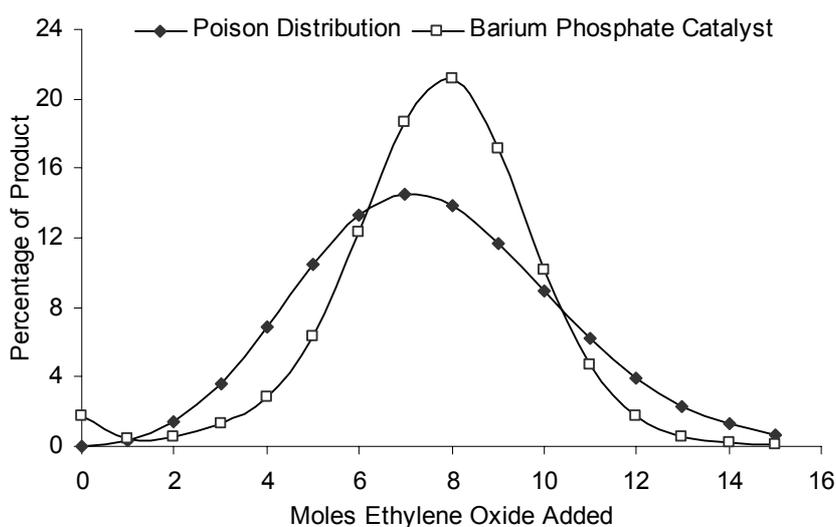


Figure 2-7: Plot of typical distribution attained for barium phosphate catalysts and Poison distribution for same moles ethylene oxide added [45]

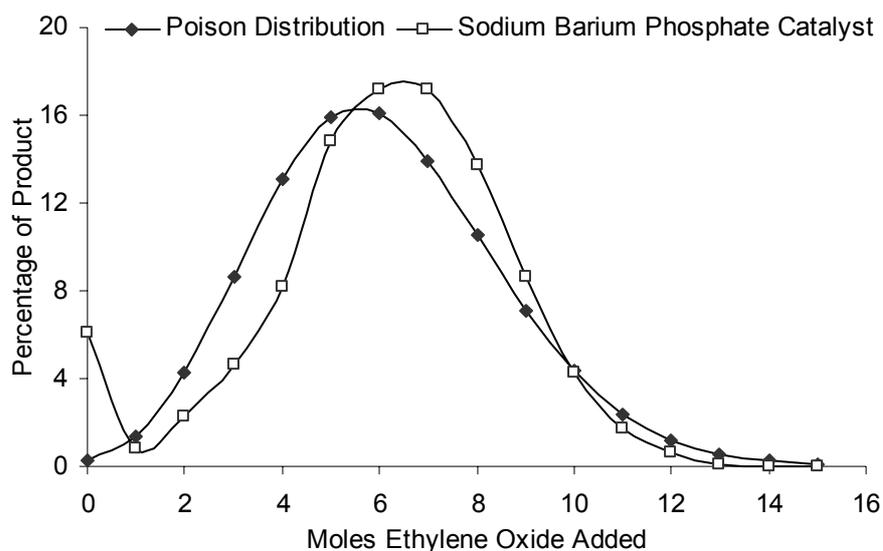


Figure 2-8: Plot of typical distribution attained for sodium barium phosphate catalyst and Poison distribution for same moles ethylene oxide added [45]

Table 2-5: Distribution properties for data shown in Figure 2-7 and Figure 2-8

Catalyst	Residual Alcohol	n = ± 3
Barium phosphate catalyst	1.8%	85.8%
Poison Figure 2-7	0.05%	72.8%
Sodium barium phosphate catalyst	6.1%	76.6%
Poison Figure 2-8	0.23%	79.7%

The acid catalysts perform considerably better than the basic catalysts and in general are able to improve on the poison distribution value of $n = \pm 3$. However, although the residual alcohol content is reduced, the values are still higher than those of the poison distribution.

2.6.3.3 COMBINATIONS AND OTHER CATALYSTS

In the conventional process strongly alkaline or acidic catalysts are used. Acid catalysed reactions produce a sharper peak molecular weight but result in harmful by-products. Base catalysed products produce less by-products but give a much broader molecular weight distribution. A comparison of the properties of acid and basic catalysts is given in Table 2-6:

Table 2-6: Comparison of advantages and disadvantages of basic and acidic catalysts for ethoxylation reaction [46], [45], [47], [48], [1].

Basic Catalysts		Acidic Catalysts	
Examples: NaOH, Na-methylate, Na-ethylate		Examples: BF ₃ , AlCl ₃	
Advantages	Disadvantages	Advantages	Disadvantages
Low by-products Easy catalyst removal	Low selectivity – hydroxy group of starting compound has lower reactivity than hydroxyl group of alcohol ethers formed	Excellent selectivity – Poisson type distribution: $P(n) = \frac{N^n e^{-N}}{n!}$ where N = overall ethylene oxide added. High catalyst activity	Corrosive action on normal metals Stability problems and often unstable with limited life span Undesirable levels of by-products (e.g. PEG, dioxane, dioxolane) May form organic derivatives of acids at unacceptable levels Catalyst needs to be laboriously removed

The difference in the products formed from acid and basic catalysts can be summarised according to an investigation of the ethoxylation of a C16 – C18 alcohol:

Table 2-7: Comparison of products formed from C16 – C18 alcohol using an acid and a basic catalyst [3]

Moles ethylene oxide per mole alcohol	Alcohol ethoxylate		Polyglycols		Others	
	NaOH	BF ₃	NaOH	BF ₃	NaOH	BF ₃
5	96	68	4	19	0	19
20	88	41	12	32	0	27

Examples of catalysts

Various other catalysts were investigated. Details of acid-base combinations and other catalysts are given in Table 9-3 in appendix A.

Typical distributions

Distributions attained for combined catalysts are shown in Figure 2-9 and Figure 2-10 and the residual alcohol and the product quantity within $n = \pm 3$ is given in Table 2-8:

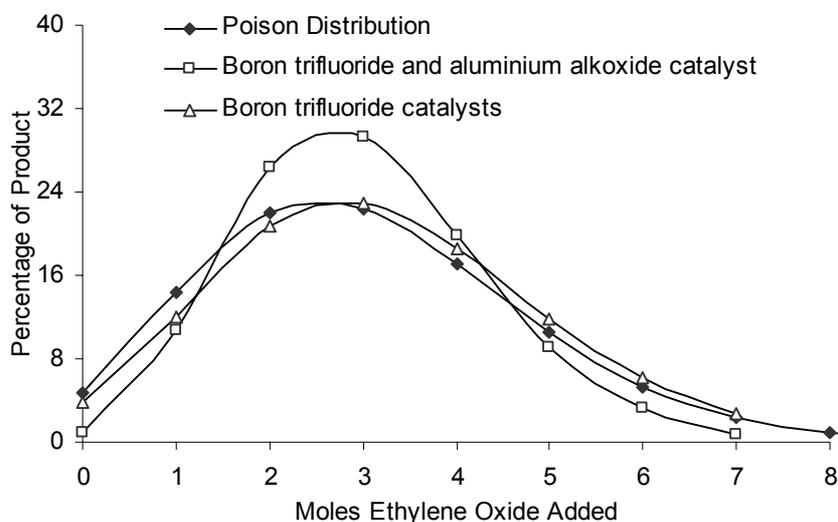


Figure 2-9: Plot of typical distribution attained for boron trifluoride with and without aluminium as catalysts catalyst and Poison distribution for same moles ethylene oxide added [49]

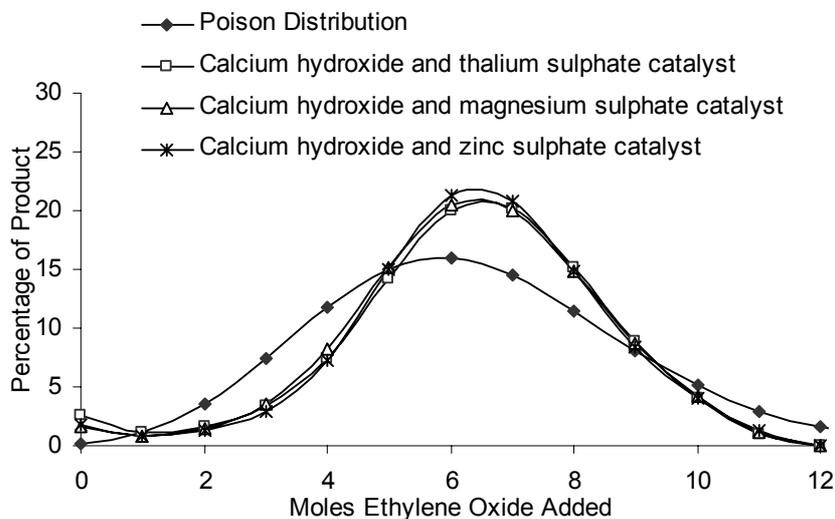


Figure 2-10: Plot of typical distribution attained for calcium hydroxide combined with sulphate salts of thallium, magnesium and zinc as catalyst and Poison distribution for same moles ethylene oxide added [50]

Table 2-8: Distribution properties for data shown in Figure 2-9 and Figure 2-10

Catalyst	Residual Alcohol	n = ± 3
Boron trifluoride with aluminium alkoxide	0.83%	98.5%
Boron trifluoride without aluminium alkoxide	3.8%	92.0%
Poison Figure 2-9	4.7%	91.6%
Calcium hydroxide and thallium sulphate	2.6%	85.9%
Calcium hydroxide and magnesium sulphate	1.6%	87.2%
Calcium hydroxide and zinc sulphate	1.8%	87.7%
Poison Figure 2-10	0.17%	76.7%

From the data it can be seen that the combined catalysts perform well with respect to both the distribution and the residual alcohol content. It should however be noted that the above data is for a relatively low ethylene oxide content added and as in the case with pure acid compounds, by-products such as polyethylene glycol can be formed.

2.6.4 INDUSTRIAL AND LITERATURE PROCESSES FOR PRODUCTION OF ALCOHOL ETHOXYLATES

Various process set-ups have been published. Although these set-ups are formulated for sodium hydroxide, they can be applied universally to most catalysts systems.

In the simplest set-up the alcohol and catalyst are added to a batch reactor, after which the reaction mixture is dried and reactor evacuated. Nitrogen and ethylene oxide are added to the reactor and the mixture is allowed to react [51]. The required post reaction workup is then conducted.

Umbach et al. [52] published an early works on the process of alcohol ethoxylation. In this work a basic continuous process is suggested and can be represented according to Figure 2-11:

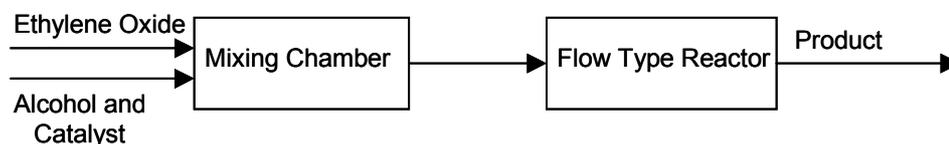


Figure 2-11: Schematic representation of alcohol ethoxylate production according to method of Umbach et al. [52]

The batch process can be improved by continuously circulating the liquid phase, the reintroduction into the reactor being at the top of the reactor. This concept can further be improved by application of a spray type reactor [51]. These concepts improving the contact between the liquid and vapour phase.

Leuteritz [51] proposed a method for ethoxylation with sodium hydroxide catalyst where the process is continuous, has a continuously circulating liquid phase and part of the product stream is constantly recycled. In this process the alcohol, ethylene oxide and catalyst first come into contact with one another in the reactor. This process results in a product with a reduced ethylene oxide and dioxane content and an improved product. The process is illustrated schematically in Figure 2-12:

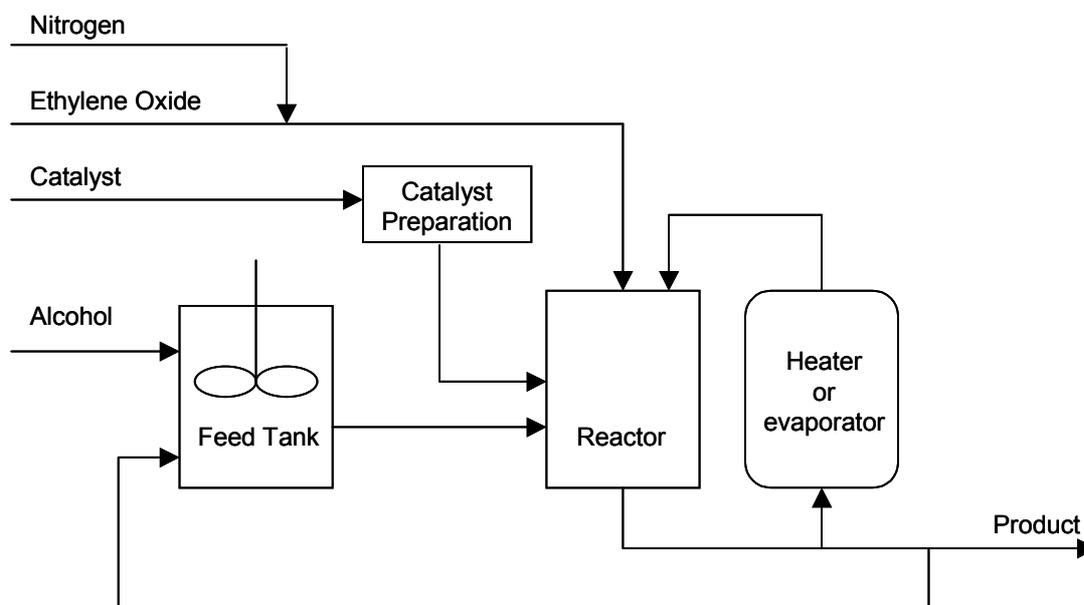


Figure 2-12: Schematic representation of alcohol ethoxylate production according to method of Leuteritz [51]

These are the most basic set-ups being used. Details of some of the most important set-ups will now be discussed:

2.6.4.1 PRESSINDUSTRIA PROCESS

This process is different from the traditional stirred reactor method in that the liquid mixture, circulated at a high speed, is dispersed in the gaseous ethylene oxide phase ensuring rapid adsorption of ethylene oxide [1].

The catalyst and alcohol mixture is passed into the reactor, stirred and then heated to the reaction temperature. The ethylene oxide addition is started, the ethylene oxide being flashed into the gas phase of the mixer. The high speed circulating liquid reaction mixture now absorbs the ethylene oxide allowing the reaction to proceed. When the desired degree of ethoxylation is reached, the product is passed into a neutralisation vessel. The process described above is for a batch operation, however the process can be operated continuously.

This process leads to a high reaction rate and a uniform product quality. Additionally the process reduces safety risks by minimising the quantity of gaseous ethylene oxide and as the reactor does not contain any moving parts, the possibility of ethylene oxide ignition is significantly reduced.

2.6.4.2 PROCESS PROPOSED BY KURATA ET AL.

In their patent, Kurata et al. [53] described a method for the production of alkylene oxide adducts of an aliphatic alcohol from a hydrocarbon. A schematic representation of the reaction process is shown Figure 2-13:

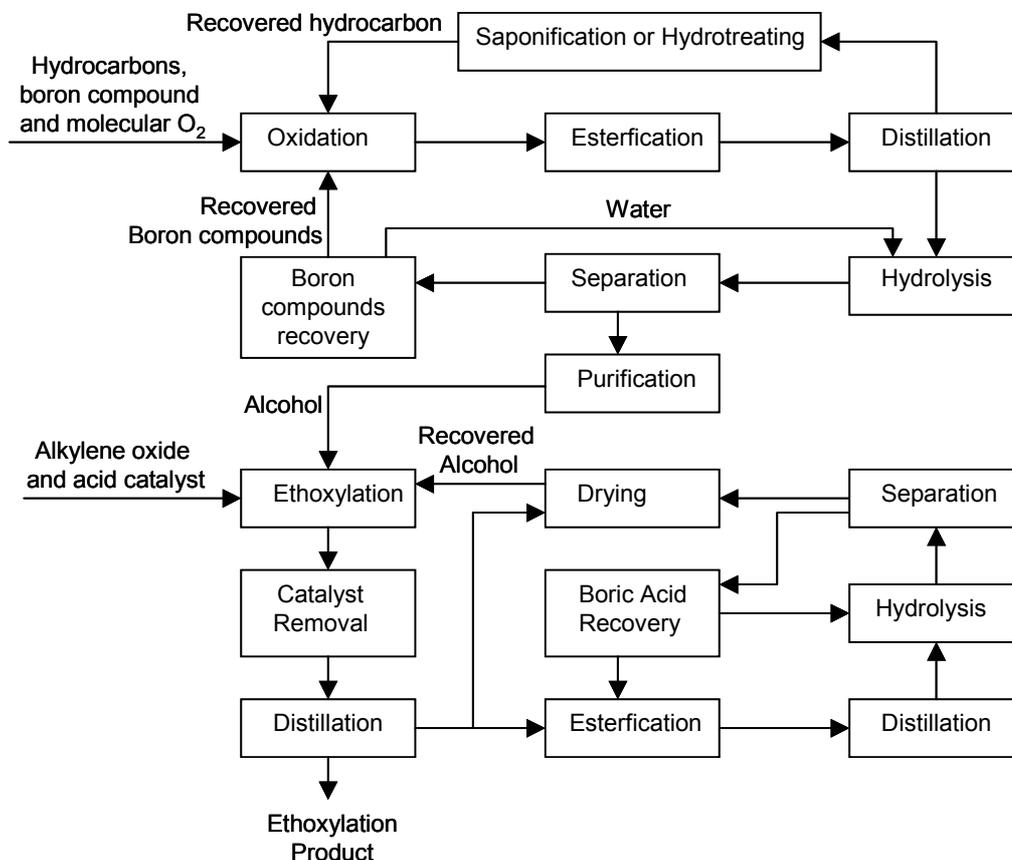


Figure 2-13: Schematic representation of production of alcohol ethoxylates from hydrocarbons [53]

The process can be summarised as follows: An aliphatic hydrocarbon is oxidised in the presence of oxygen with boric acid. The alcohol is esterified to produce to an ester and the ester is separated from the alkane by distillation, with residual hydrocarbon being removed as the distillate. To minimise thermal decomposition, the process is conducted at reduced pressures and thus lower operating temperatures. The distillate is recycled to the oxidation step, preferably after subjecting the mixture to saponification or hydrotreating. The ester is hydrolysed to yield the alcohol. The resultant alcohol is separated from the aqueous boric acid layer, the aqueous boric acid being recycled. Before the alcohol can be subjected to ethoxylation, it needs to be purified. The alcohol is reacted with ethylene oxide in the presence of an acid catalyst. The reaction may be conducted in a batch or a continuous mode. In the batch mode, the alcohol and the catalyst are added first, after which the ethylene oxide is added slowly. In the continuous mode, the alcohol is passed through a tubular reactor while adding the ethylene oxide from two or more points within the reactor. The catalyst can be removed from the reaction product by neutralisation

and subsequent filtration of the reaction mixture. Water-soluble by-products such as polyethylene glycol and dioxanes are removed by water extraction and unreacted alcohol is recovered by means of a separation process such as distillation. The recovered alcohol is reacted with boric acid resulting in the corresponding boric acid ester. The boric acid ester is separated from the remaining impurities. This is usually achieved by distillation, the impurities being removed as distillate, the ester as the residue. The boric acid ester is hydrolysed to form the alcohol. The resultant alcohol is separated from the aqueous boric acid layer and recycled. The boric acid is recovered and can be used for further esterification.

An alternative process is suggested and schematically represented in Figure 2-14:

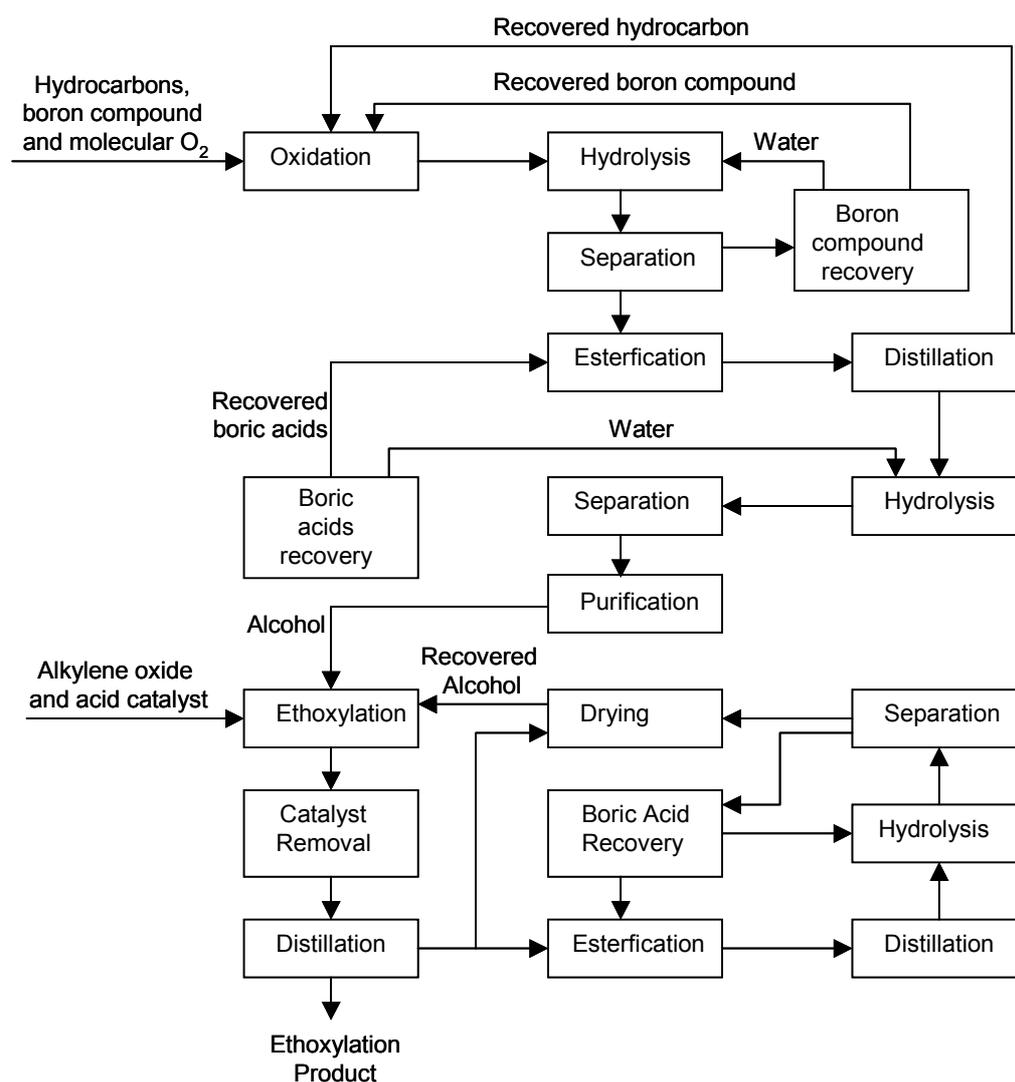


Figure 2-14: Schematic representation of alternative process for production of alcohol ethoxylates from hydrocarbons [53]

The main difference between the processes is that the alternative process has two boric acid recycle streams, one before and one after the separation system whereas the original process only had one boric acid recycle stream. The advantage of the alternative process above the original process is the production of a product with an improved colour and odour.

Advantages of these processes are:

- The concentration of impurities in the recycled alcohol stream increases with continuation of the operation to a certain point, thereafter they remain constant. Thus impurities in the feed stream do not cause as much trouble as in other methods.
- Impurities of the same or similar and lower boiling points as the alcohol can be removed.
- It is possible to produce continuously and commercially ethylene oxide adducts of alcohols having uniform good quality.

Disadvantages of these processes are:

- Various separations are conducted by means of distillation. This process can thus only be applied to the production of surfactants with corresponding alcohols that can be removed under vacuum distillation at temperatures below approximately 200°C. This process can thus not be applied to the ethoxylation of wax derivatives.
- High boiling point impurities are difficult to remove.

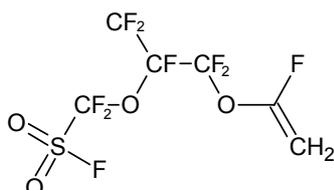
2.6.4.3 VAPOUR PHASE CATALYST PROCESS

This method [54] differs from the traditional production method insofar that ethylene oxide is used in the vapour phase instead of the conventional liquid phase. The result is a product with less flocculants. The reaction takes place under standard temperatures (between 50 and 200°C) with either acidic or basic catalysts. The pressure may be above or below ambient pressure, provided the ethylene oxide is in the vapour form. Typical pressures used are between 0.034 and 3 barA, preferably below 2.4 barA.

2.6.4.4 SOLID CATALYST PROCESS

Vaughan [55] suggested a process for the production of a mono alkoxyated product in the presence of a solid acid catalyst and the process is based on the fact that the oxyated product has a higher boiling point than the hydroxylic product.

A solid perfluorocarbon polymer containing pendant sulphonic groups is the preferred catalyst. The catalyst may have a mixture of chlorine and fluorine substituents, with a maximum of 20 mol% chlorine. The monomer has the following structure:



Alternatively sulphated polystyrene can also be used but it is less stable. The operating temperature is normally determined by the maximum operating temperature of the catalyst,

usually below 200°C. The operating pressure ranges between atmospheric and approximately 70 barA. Schematically the process can be represented as follows:

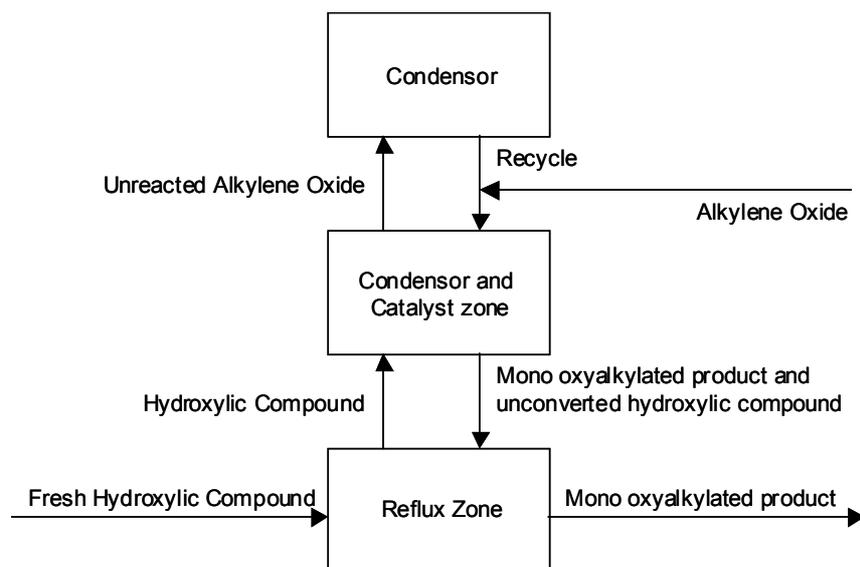


Figure 2-15: Schematic representation of alkoxylation process utilising a solid catalyst

The hydroxylic compound is vapourised in the reflux zone. The vapourised hydroxylic compound passes into the condenser and catalyst zone where it is condensed. Here it comes into contact with the alkylene oxide in the presence of the catalyst to form the mono oxyalkylated product. The liquid product and unreacted condensed hydroxylic compound pass to the reflux zone. Here the unreacted hydroxylic compound is vapourised together with the fresh hydroxylic compound and the remaining mono alkoxyated product is drawn off as a product stream.

This process provides a good method for the production of very narrow range alkoxyated products. However the process, as stated above, has the major limitation that one must be able to vapourise the hydroxy compound.

2.6.4.5 PROCESS FOR ETHOXYLATION OF DI-, TI- AND POLYALCOHOLS

Hreczuch et al. [56] proposed a method for the ethoxylation of solid di-, tri- and polyalcohols. Although in this work emphasis is placed on monohydric alcohols, the work of Hreszuch et al. shows how high melting point compounds can be treated.

The process proposed here is substantially solvent free process to limit the formation of polyethylene glycol and other by-products and consists of two steps: Initial ethoxylation is conducted so as to decrease the melting point below the operating temperature. This part of the process is conducted in a stirred reactor where the solid alcohol, coated with an effective amount of catalyst, is reacted with a quantity of ethylene oxide to produce a product that is a liquid at the reaction temperature. In the second step, further ethoxylation is conducted on the liquid product from the first step in the traditional manner.

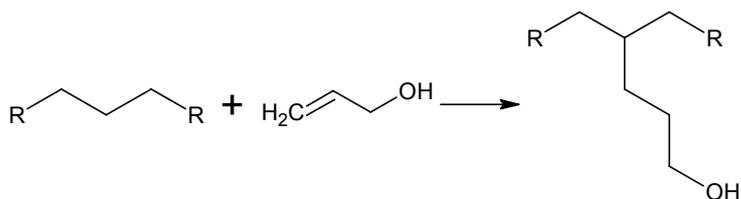
2.6.4.6 FISHER-TROPSCH WAX PROCESS

Louw et al. suggested a process for the ethoxylation of Fisher-Tropsch wax. Here the linear alkane is converted to an alcohol by oxidation, followed by ethoxylation [26]. The process is applicable in particular to normal alkanes with 45 to 85 carbon atoms and an average 75 carbon atoms.

Production of alcohol

Various methods are suggested for production of the alcohol wax from alkanes. These methods are similar to those in section 2.6.1 yet may differ due to the high molecular weight of the compound:

- Via grafting with allyl alcohol: In this method an alkane wax is converted to an alcohol by grafting the alkane with allyl alcohol (2-propene-1-ol). The product wax comprises of an alkane chain with side chains carrying an n-propanol group. Schematically, the process can be represented as follows where R = alkane chain with usually between 40 and 80 carbon atoms:



Equation 2-10:

Typically the reaction is conducted at about 180°C usually in an autoclave as it is at a pressure above atmospheric pressure, yet no indication of the pressure applied is given.

- Via oxidised wax: Waxy alcohols can be produced from paraffin wax by reacting the paraffin wax with air or oxygen enriched air followed by hydrogenation. If auto-oxidised paraffin wax is used, the first step of the process is not required. The oxidised waxes, such as long chain esters, ketones and carboxylic acids can easily be converted into alcohols through hydrogenation. Hydrogenation can be achieved by exposing the wax to hydrogen in the presence of a catalyst such as CuCr and/or Ru/C.
- Via oxidation with peroxide: Normal alkane wax can be converted to alcohols through treatment of the alkane with a peroxide, typically hydrogen peroxide.

Ethoxylation reaction

Ethoxylation is conducted in a batch reactor with sodium ethoxide (2 wt %) as catalyst at a temperature of 130 – 140°C and pressures between 3.5 and 4 barA. A HLB value of between 2 and 18, preferably around 10 is attained. Schematic representations of the suggested processes are given in Figure 2-16 and Figure 2-17. These processes represent the conversion of an alkane

to an ethoxylated wax via the grafting process and the oxidation and hydrogenation process respectively.

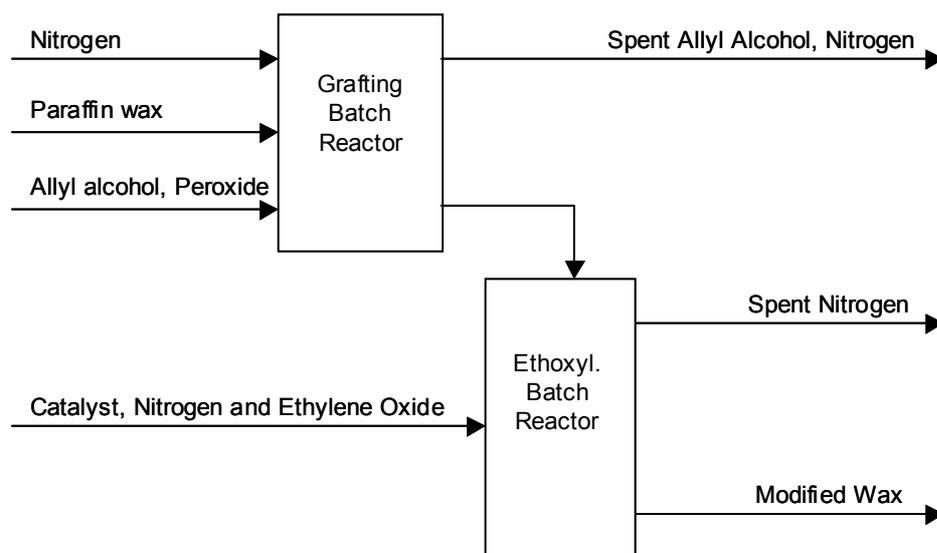


Figure 2-16: Schematic representation of synthesis of alcohol ethoxylates from paraffin waxes via grafting process [26]

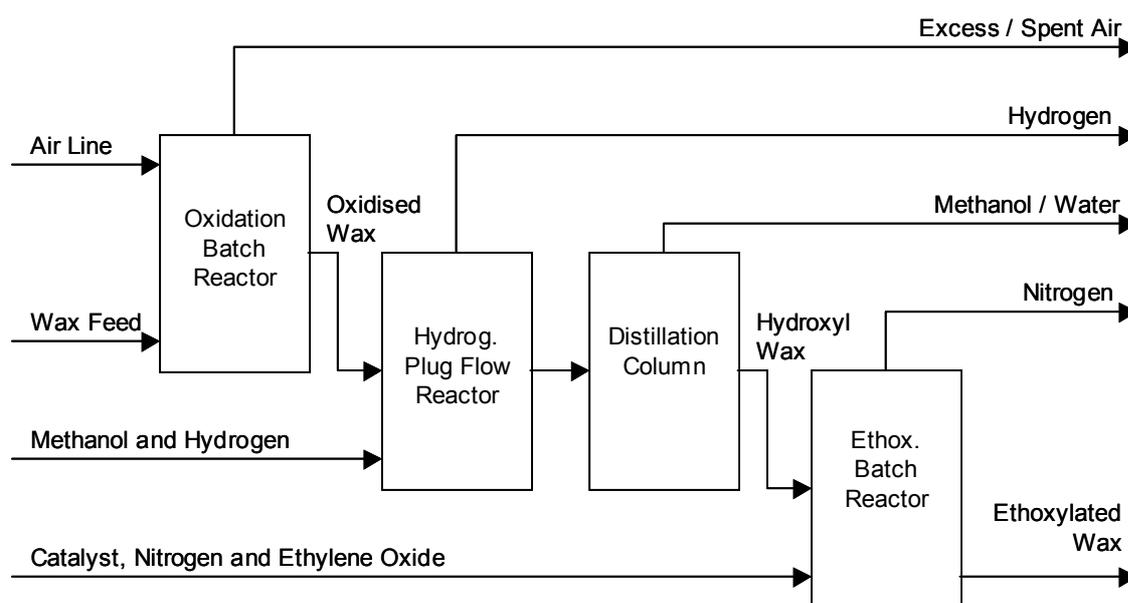


Figure 2-17: Schematic representation of synthesis of alcohol ethoxylates from paraffin waxes via oxidation process [26]

2.7 PRODUCT REQUIREMENTS, PRODUCTION PROBLEMS AND POSSIBLE SOLUTIONS

From the above study the current state of the art for the production of a high molecular weight narrow range alcohol ethoxylate can be critically evaluated.

2.7.1 DEFINING THE PROBLEM

It is shown that waxy alcohol ethoxylates can be produced [26]. Once these products can be produced commercially they will have the advantage that they are able to provide a method to (partially) solublise wax and bypass the problem of the virtual insolubility of synthetic waxes. Once commercially producible, these waxes may find many applications and may improve the quality of finished products currently relying on synthetic waxes.

At this point in time a basic catalysts such as sodium ethoxide are used to ethoxylate the alcohol derivative of the synthetic wax and although the process is technically viable, the following problem still exist: As shown, the distribution achieved during the ethoxylation reaction is very broad and the quantity of residual alcohol in the wax derivative is high.

The aim of this work is provide a way in which the above-mentioned problems can be reduced or even totally circumvented. Solutions to the above problems can be divided into two categories, namely those which concentrate on improving the production method and those which provide a method for post production purification. In the subsequent sections, these two alternatives will be investigated.

2.7.2 IMPROVEMENT THROUGH PRODUCTION CHANGES

Currently the ethoxylation process of the alcohol ethoxylate takes place in a batch mode, usually in a stirred autoclave [26] in the presence of a sodium hydroxide catalyst. In this subsection various improvements through production method changes is suggested.

2.7.2.1 POSSIBLE IMPROVEMENT THROUGH CATALYST IMPROVEMENTS

From the above study it can be seen that sodium hydroxide is not the optimum catalysts. Many improved catalysts can be applied, yet these catalysts often have the problem of either a large quantity of by-products or are difficult to remove from the product. In addition, for waxy alcohol ethoxylates, the removal is complicated by the fact that the alcohol ethoxylate solidifies at high temperatures and cannot be distilled off due to its high molecular weight. A large amount of work has been conducted on the development of new catalysts and it is felt that a new and different approach, other than the development of a new catalysts, is required to solve the problem.

2.7.2.2 POSSIBLE IMPROVEMENT THROUGH SET-UP CHANGES

Currently the alcohol ethoxylate is produced in a batch type system, in a set-up similar to a continuous stirred tank reactor. It is suggested that the quality of the product produced can be improved if a system closer to a plug flow reactor can be used. A packed bed type of system is suggested with an option of two set-ups, depending on the phase of the catalyst used:

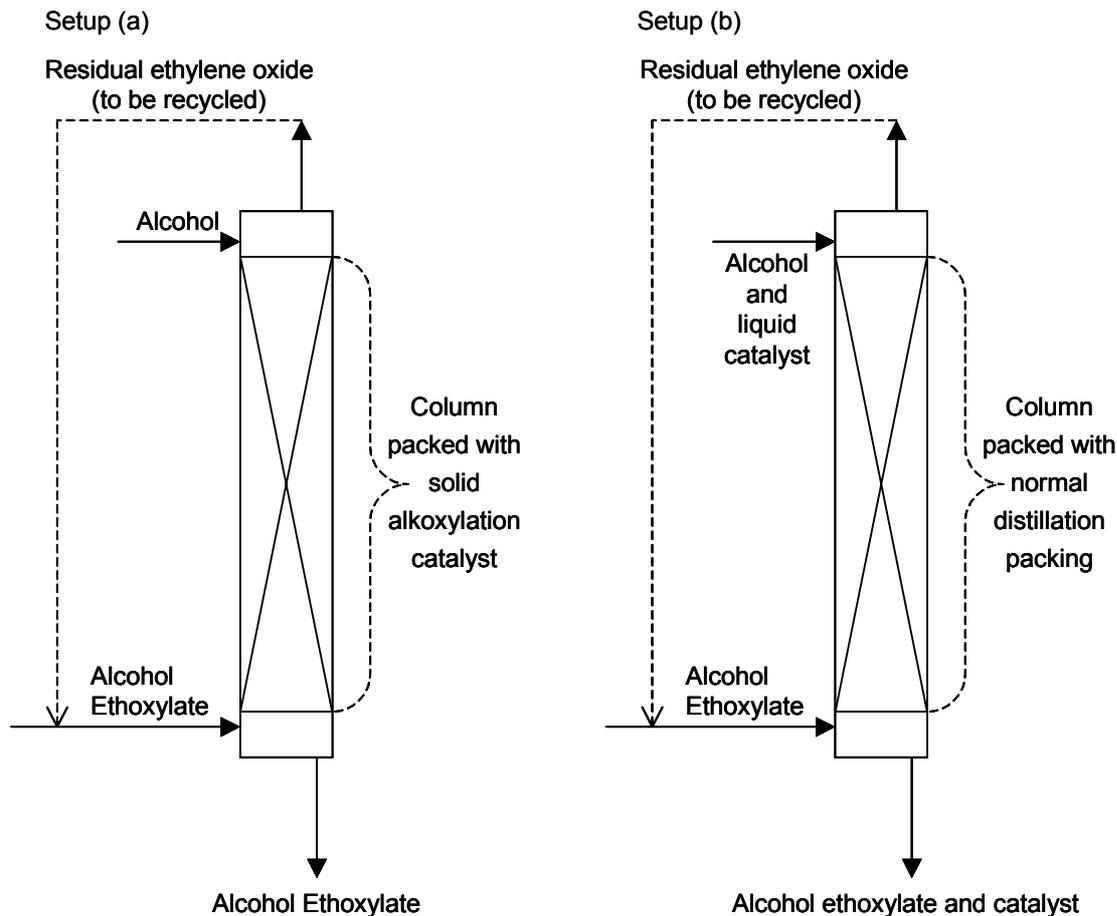


Figure 2-18: Schematic representation of two possible methods for alternative reactor set-ups for alkoxylation process. Set-up (a): Set-up for when catalyst is a solid. Set-up (b): Set-up for when catalyst is a liquid.

The concept behind the idea of the set-ups as illustrated in Figure 2-18 is that the contact between the ethylene oxide and the alcohol/alcohol ethoxyate is improved and at the same time a continuous process is suggested with a relatively large residence time.

Consider set-up (a) where the catalyst is a solid: In this set-up the catalyst is used as a packed bed. The high molecular weight alcohol is fed in at the top of the column and the gaseous ethylene oxide is fed at the bottom. As the alcohol proceeds down the column, it continuously comes into contact with the ethylene oxide in the presence of the solid catalyst and ethoxylation is allowed to occur. Residual ethylene oxide exits the column at the top and can be recycled. It is hoped that in this way that a reduction of residual alcohol and a narrower product can be achieved.

The set-up for a liquid catalyst is similar; the only difference being that the catalyst is fed together with the alcohol at the top of the column and instead of a column packed with catalyst normal distillation packing is used.

The set-ups in Figure 2-18 are merely conceptual and would require a large amount of refining.

2.7.3 IMPROVEMENT THROUGH POST-PRODUCTION PURIFICATION

As an alternative to improvements on the production process, the product can be purified. Although this is not solving the problem but rather treating the symptoms of the problem, it may be a viable solution.

A postproduction separation system would require the following:

- Depending on the catalyst used, catalyst residue may be required to be removed.
- The system would be required to remove the majority of the residual alcohol.
- The system would be required to remove the low ethoxylates and high ethoxylates from the peak molecular weight products.
- The process would be required to remove any unwanted by-products formed.

Due to the temperature sensitivity of the alcohol ethoxylate, the operating temperature should be below 200 °C. Additionally, the process needs to be both economically and technically viable and should be able to be implemented in a safe manner without great danger to the environment. Although ideally all the above requirements should be fulfilled, the product quality can be significantly improved if the residual alcohol can be removed.

2.7.3.1 TRADITIONAL SEPARATION METHODS

Traditional separation methods for organic compounds include liquid-liquid extraction, distillation and crystallisation.

Liquid-liquid extraction: Johnson suggested a method for separating alcohol ethoxylates from high molecular weight compounds such as ketones, aldehydes and esters [46]. Firstly the mixture and a water insoluble organic solvent, such as benzene, ethers, high molecular weight alcohols, carboxylic acids and chlorohydrocarbons etc is mixed. A water-soluble organic solvent, such as low molecular weight alcohols, is added followed by water. Two resultant layers are formed. In the aqueous layer, the water, the water-soluble organic solvents and the alcohol ethoxylate is to be found. In the organic layer, the organic solvent and the high molecular weight compounds are found. The aqueous layer may be extracted once more with the water insoluble organic solvent to remove the last traces of the high molecular weight compounds. Extraction may be simpler if the extraction can be attained without the use of water. Although it is referred to as high molecular weight compounds, very high molecular weight compounds, as those used in this work, are not really soluble in the water insoluble organic phase and thus this method is not suited to the type of separation required in this work.

Distillation: Many of the processes mentioned in section 2.6.4 and its subsections, allows for alcohol ethoxylates to be separated from alcohols and alkanes and used distillation as its preferred method of separation. Distillation works well for low molecular weight compounds, yet for high molecular weight alcohol ethoxylates distillation cannot be used as, even at high vacuum,

temperatures above the thermal stability range, are required. With particular reference to this project, distillation is thus not a viable separation method for the separation of the alkane, alcohol and the alcohol ethoxylate.

Crystallisation: Crystallisation works on the basis of a difference in melting point. The melting points of the alcohol ethoxylates differ with too small a margin from the alcohols to implement a viable crystallisation process. In addition, fractionation of the alcohol into lower and higher molecular weight fractions may occur; the same also being true for the alcohol ethoxylate. It also needs to be remembered that the alcohol ethoxylate has the ability to dissolve the wax and entrainment may occur.

2.7.3.2 SUPERCRITICAL FLUID PROCESSING AS AN ALTERNATIVE

Traditional separation methods cannot be applied to this problem. An alternative method is required where a distinction can be made between the alcohol and the alcohol ethoxylate. Supercritical fluid processing is proposed as an alternative separation method.

It is hoped that the supercritical solvent is able to separate the alcohol and the alcohol ethoxylate due to a difference in solubility of the two compounds in supercritical solvent. It is aimed that a difference in solubility can be achieved due to the presence of the polar ethylene oxide groups in the alcohol ethoxylate, which are absent in alkanes and alcohols.

Eckert et al. [57] used supercritical fluids to remove unreacted dodecanol from ethoxylated dodecanol. Various solvents, such as pure carbon dioxide, carbon dioxide with 3.5% methanol, propane and ammonia were investigated and economic considerations aside, carbon dioxide with 3.5% methanol and propane were found to provide a high selectivity and loading at moderate temperatures. These results indicate that supercritical fluid extraction is in fact a promising method for separating long chain alcohols from their corresponding alcohol ethoxylates, yet it must be remembered that the alcohol to be used in this work has a hydrocarbon backbone of 3 or more times the length than that of Eckert et al. and thus the effect of the long hydrocarbon backbone needs to be investigated.

2.7.4 SELECTION OF A METHOD FOR PRODUCT IMPROVEMENT

Various methods have been mentioned above for the possible improvement of the production process of waxy alcohol ethoxylates. Ideally a combination of improving the production process and a postproduction separation process should be implemented. To implement both the above mentioned improvements with complete details is beyond the scope of this work. This work aims to provide an improvement on the current product and does not require the entire technology to be reinvented.

A choice is thus required as which of the process improvement should be implemented: Although improvements with regard to the production process are required it is chosen to rather follow the postproduction separation route. This choice can be justified by the fact that a considerable

amount of work has already been done on the production of surfactant in general but very little time and effort has been applied to a separation process. It is hoped that with the time and effort invested in this work, a separation process can be designed that is able to fulfil or partly fulfil the requirements of a separation process. It is decided that merely a concentration of the alcohol ethoxylate is enough of an improvement at this point in the investigation.

The aim of this work is thus to develop a separation process where the alcohol and alkane can be removed from the alcohol ethoxylate to such an extent that the properties of the alcohol ethoxylate can be improved. It is envisaged to use supercritical fluid processing in the development of this process.

2.8 NOMENCLATURE

Symbol	Description
HLB	Hydrophilic lipophilic balance
M	Metal ion
M_{hyd}	Molar mass of hydrophilic fraction of molecule (g/mol)
M_n	Number average molecular weight (g/mol)
M_{tot}	Molar mass of entire molecule (g/mol)
M_w	Weight average molecular weight (g/mol)
m	Average number of ethylene oxide groups
P(n)	Poisson distribution function
R	Alkyl group
R_1	Alkyl group
R_2	Alkyl group
X	Alkaline metal ion, an alkaline earth metal ion, alcohol ammonium ion or an ammonium ion
y	Average number methylene groups added
Subscripts	
x	Refers to compound x in a multi-component ethoxylate mixture – only used where applicable

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3 Supercritical phase equilibrium data and solvent selection

From the discussion in section 2.7, supercritical fluid extraction is selected as the method of choice to separate alkanes and alcohols from alcohol ethoxylates. In order to design a separation process, a detailed knowledge of supercritical fluids and the phase equilibrium of the components in supercritical solution is required. This chapter aims to provide some details with regard to supercritical fluid processing, high-pressure phase diagrams and the literature data available for the selected process. Ultimately a solvent will be selected and it will be determined which phase equilibrium measurements are required before a separation process can be designed.

The aim of this chapter is to scan possible solvents and determine which solvents may be suitable. A literature survey of the phase equilibrium measurements of these solvents with alkanes, alcohol and polyethylene will indicate what measurements are available and assist in determining the most suitable solvent.

The components in the mixture that needs to be fractionated can be divided into three groups: alkanes, alcohols and alcohol ethoxylates. Within each of these groups a distribution of molecular weight will be present. For the purpose of this evaluation, it is assumed that the mixture consists of three pseudo components: an alkane, an alcohol and an alcohol ethoxylate. The hydrocarbon backbone length in each component is represented by the peak molecular weight and, in the case of the pseudo alcohol ethoxylate, the average degree of ethoxylation determines the number of ethylene oxide units present.

3.1 SUPERCRITICAL FLUID PROCESSING

In this subsection the basic concepts of supercritical fluids will be introduced. Further information can be obtained in sources such as books by Brunner [1] and McHugh [2] and other studies involving supercritical fluids [3], [4], [5].

3.1.1 DEFINITION OF A SUPERCRITICAL FLUID AND THE CRITICAL POINT

A supercritical fluid is substance that is above both the critical pressure and temperature. Mathematically the critical point can be defined as the temperature and the pressure where:

$$\text{Equation 3-1: } \left(\frac{\partial P}{\partial V} \right)_T = 0$$

$$\text{Equation 3-2: } \left(\frac{\partial^2 P}{\partial V^2} \right)_T = 0$$

3.1.2 TRANSPORT PROPERTIES

Supercritical fluids have the following transport properties:

- Diffusion: The diffusion lies between that of a liquid and a gas. The value of the diffusion coefficient approaches that of a liquid at very high pressure. This implies that the mass transfer rate in a supercritical fluid is higher than that in a liquid.
- Viscosity: The viscosity lies between that of a liquid and a gas, therefore allowing more favourable hydrodynamic properties than for liquids. In contrast to a gas, for a supercritical fluid, an increase in temperature will lead to a decrease in viscosity.
- Thermal conductivity: The thermal conductivity shows enhancement in the critical region.
- Density: Although the density lies between that of a liquid and a gas, the value tends towards that of a liquid. The density is dependent on the pressure and the temperature and as in liquids and gases, the density increases with increasing pressure and decreases with increasing temperature. It is important to note that just above the critical point for reduced temperatures of 1.0 to 1.2, a very small increase in pressure results in a dramatic increase in density. From Equation 3-1 it can be seen that at the critical point, the gradient of the density with respect to pressure is infinitively large.
- Interfacial tension: The interfacial tension between the two phases in a supercritical phase equilibrium situation depends strongly on the system conditions, such as the temperature, pressure and composition as well as the characteristics of the solute. Near the mixture critical point the interfacial tension will be low while far away from the mixture critical point the interfacial tension may be large.

The properties of supercritical fluids therefore favour mass transfer using supercritical fluids as extraction solvent.

3.1.3 PRINCIPLES OF SUPERCRITICAL PROCESSING

As in all separation processes with an auxiliary medium, separation with supercritical fluids requires two basic steps. In the first step the desirable extraction is achieved while in the second step the supercritical fluid is removed from the feed, regenerated and recycled.

The removal of the supercritical fluid from the solute is generally a relatively simple procedure, usually conducted by a decrease in pressure and/or an increase in temperature. Supercritical extraction processes are usually operated as counter-current extraction processes, either in a manner similar to liquid-liquid extraction with the solute feed at the top, the solvent feed at the bottom and no reflux or similar to distillation with the solvent feed at the bottom, the solute feed in the middle and reflux at the top of the column.

3.1.4 ADVANTAGES AND DISADVANTAGES

Supercritical fluid processing holds the following advantages:

- Supercritical fluids show good solvating power that depends strongly on the temperature and pressure.
- The solvating power can be varied so that the dissolved material can be removed from the solvent and allow regeneration of the solvent with low solvent residue in the product.
- The operating temperature is determined by the critical temperature of the solvent (and possibly the melting temperature of the solute) and is usually considerably lower than the boiling temperature of the solute. This allows the processing of temperature sensitive materials.
- Supercritical fluids offer an alternative to liquid solvents. Liquid solvents are often hazardous in terms of toxicity and flammability and conducive to solvent residue problems. Supercritical fluids often do not pose these problems.

As in all processes, disadvantages also exist:

- Supercritical processes operate at much higher pressures than traditional processes. Due to unfamiliarity with high pressures there is little tendency to come to terms with the high operating pressures.
- The phase behaviour of supercritical processes is complicated due to the fact that the systems are highly non-ideal in both the liquid and the vapour phase.

It has been postulated that supercritical processes are less energy intensive than traditional processes, yet conflicting reports exist in this regard [6].

3.1.5 COST OF SUPERCRITICAL PROCESSING

A perception exists that supercritical processing is expensive and not financially viable due to the high investment cost in comparison to classical low-pressure equipment. When considering the investment costs of supercritical processes, Perrut [6] suggests that large capacity processes are financially viable. The investment cost grows slowly with increasing capacity and large plants are thus not excessively expensive. Additionally, although the equipment costs, and thus the initial capital outlay, is high, yet these figures depend drastically on the type of equipment used. The operating costs can also vary from process to process and thus the cost of supercritical processes cannot be defined in general.

Nieuwoudt et al. [7] studied the economic viability of supercritical fractionation of paraffin waxes. They compared supercritical fractionation to recrystallisation and short path distillation. The analysis showed that supercritical fractionation is economically viable, yet depends strongly on the design of the auxiliary equipment. Contrary to other studies and general belief, the capital cost

for a supercritical fractionation plant is less than that for a recrystallisation plant. The utility costs depend on the amount of energy integration and, with correct equipment choice and energy integration, the utility costs are similar to the recrystallisation and short path distillation plants.

3.2 PHASE DIAGRAMS IN THE CRITICAL REGION

For a clear understanding of the fundamentals of processing with supercritical fluids, an understanding of phase behaviour of the mixtures in the critical region is necessary.

3.2.1 GENERAL PHASE DIAGRAMS

Phase behaviour of fluids at moderate to high pressures is very complex and difficult to understand. Figure 3-1 shows a binary phase diagram with good solvation characteristics:

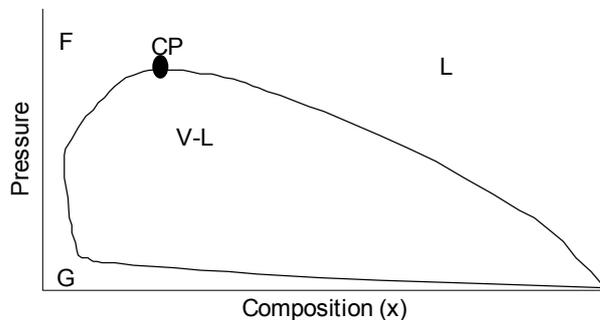


Figure 3-1: Phase diagram for a solvent-solute system with a solvent showing good solvation characteristics

The binary solvent solute phase diagram can be considered to show desirable solvation characteristics due to the fact that the phase behaviour is simple without a three-phase region. These types of systems can usually produce a high vapour loading at moderate pressure.

The phase diagram shown in Figure 3-2 shows some less desirable solvation characteristics.

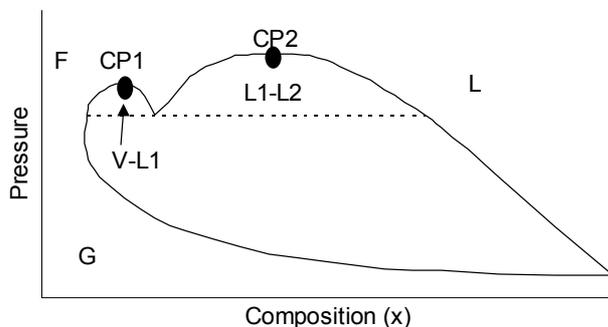


Figure 3-2: Phase diagram for a solvent-solute system with a solvent showing intermediate solvation characteristics

It can be seen that two liquid phases can occur, and at a specific pressure, three phases may occur. The three-phase region should be avoided, yet a relatively high vapour loading can still be achieved. Although phase behaviour as illustrated in Figure 3-1 is preferred, components showing this type of phase behaviour can also be extracted successfully, provided the three phase region is avoided.

The phase diagram may also exhibit poor solvation characteristics shown in Figure 3-3.

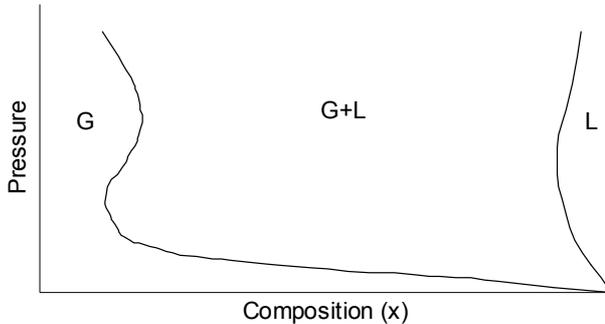


Figure 3-3: Phase diagram for a solvent-solute system with a solvent showing poor solvation characteristics

These characteristics may however be desirable when it is envisaged to separate two components, one with characteristics such as those illustrated in Figure 3-1 or Figure 3-2, the other with characteristics such as those illustrated in Figure 3-3. The component with good solvation characteristics is preferentially extracted, the one with poor solvation characteristics occurring mainly in the raffinate.

3.2.2 BINARY PHASE DIAGRAM CLASSIFICATION BY TYPE

Binary mixtures can be divided into the six different types, these six types describing all phase behaviour occurring in nature. This classification is currently widely accepted and based on the work of van Konynenburg et al. in 1980 (as referenced by Brunner [8]). Classification is done according to the nature of their pressure – temperature projections. The first five types can be qualitatively predicted by the van der Waals equation of state while, with the aid of a simple Carnahan-Starling type equation of state type VI can be predicted [9]. Type VI is only found in aqueous mixtures and complex interactions may play a significant role in this type of system.

The pressure – temperature projections of the six types of phase diagrams can be summarised by Figure 3-4 (a) through (f).

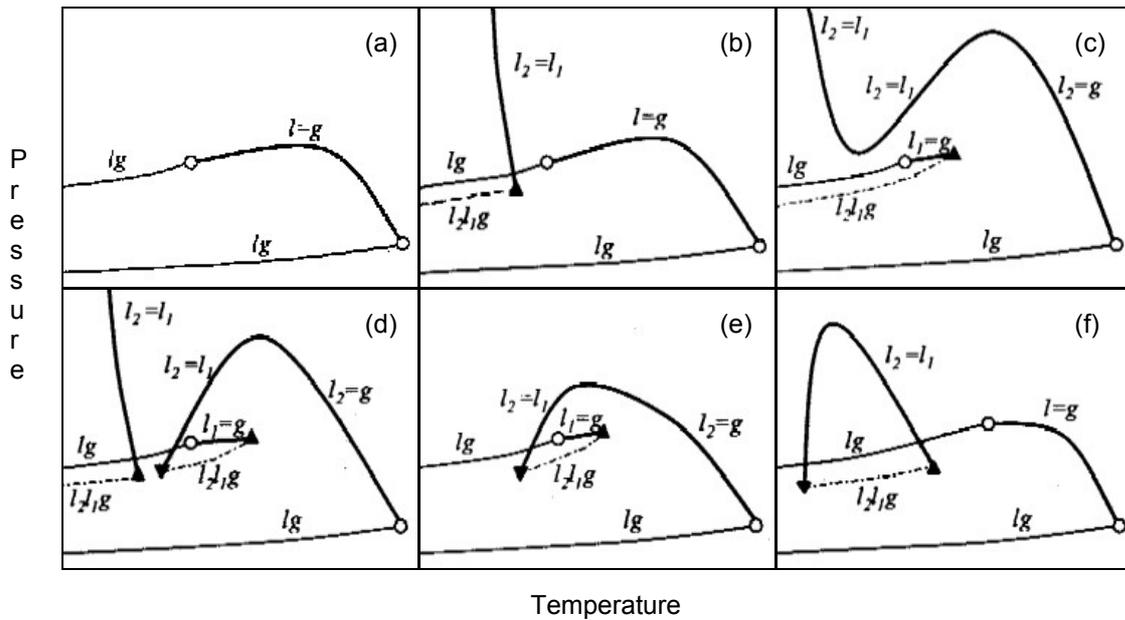


Figure 3-4: Pressure-temperature projections of the six main types of possible binary phase diagrams for fluids. (a) Type I, (b) Type II, (c) Type III, (d) Type IV, (e) Type V, (f) Type VI [10]

In Figure 3-4 the curves lg are the vapour pressure curves of the pure components that end at the pure component critical point, illustrated by the symbol O . The curves $l=g$, $l_1=g$ and $l_2=g$ are vapour-liquid critical curves and the $l_2=l_1$ curve is where on which two liquid phases become critical. The point of intersection of a critical curve with a three-phase curve l_2l_1g is a critical end point (CEP). At the CEP, two phases in a three-phase equilibrium become identical. The critical end point is also the end point of the critical solution temperature line.

Consider the liquid-liquid behaviour of type VI phase behaviour. In Figure 3-5 the location of the definitions on the phase diagrams is illustrated.

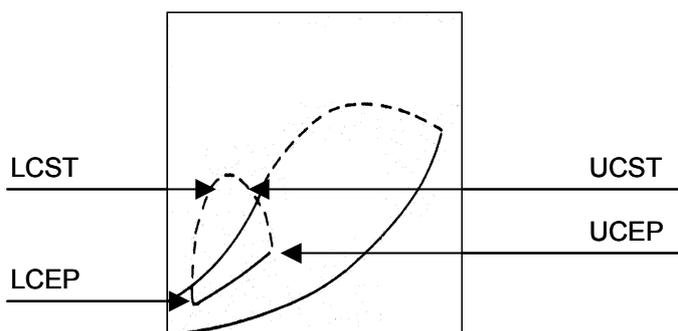


Figure 3-5: Type VI phase behaviour illustrating the definitions discussed.

The lower critical solution temperature (LCST) at a set pressure is the temperature at which two liquids critically merge to form a single liquid phase as the system temperature is isobarically lowered. The LCST forms a continuous line on the PT diagram.

The upper critical solution temperature (UCST) at a set pressure is the temperature at which two liquids critically merge to form a single liquid phase as the system temperature is isobarically raised. The UCST forms a continuous line on the PT diagram.

The upper critical end point (UCEP) is the upper temperature limit of the three-phase equilibrium where two liquid phases become identical. The UCEP is also the end point of the UCST line. In Figure 3-4 the UCEP is illustrated by the symbol ▲.

The lower critical end point (LCEP) is the lower temperature limit of the three-phase equilibrium where the two liquid phases become identical. The LCEP is also the end point of the LCST line. In Figure 3-4 the LCEP is illustrated by the symbol ▼.

When the UCEP and LCEP temperatures are plotted as a function of temperature, the tricritical point is the point where the LCEP and UCEP merge. The tricritical point is thus not a point on a phase diagram but rather the point where a homologous series changes from one type of phase behaviour to another. To illustrate the concept of the tricritical point, the UCEP and LCEP temperatures of the homologous series of propane with normal alkanes are plotted in Figure 3-6.

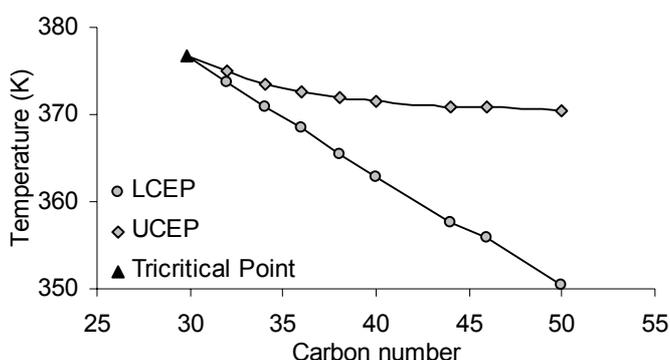


Figure 3-6: Illustration of tricritical point of normal alkanes homologous series with near critical propane [11]

The mixture critical point for a set temperature can be defined as the composition and pressure where the properties of the liquid and the vapour phase are identical. These properties include density, composition, viscosity and other thermodynamic properties. Graphically, the mixture critical point can be represented as follows:

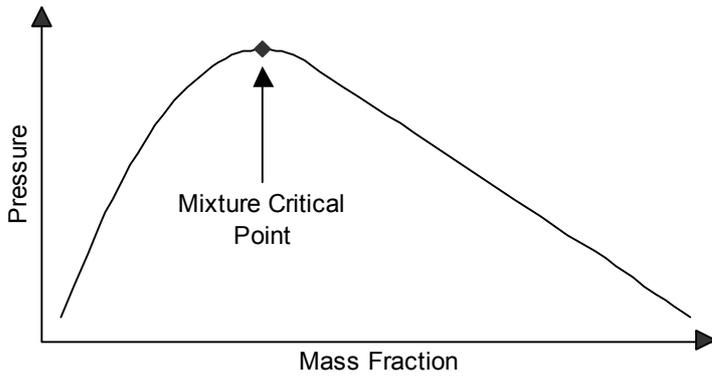


Figure 3-7: Mixture critical point at constant temperature

The various types of phase behaviour will now be discussed. To aid in explanation and at the same time hold true to the original classification, the types will be discussed in the sequence type I, type II, then type V, type IV and type III and finally type VI.

3.2.2.1 TYPE I

Type I is the simplest possible phase behaviour for a binary mixture. This type of phase diagram is distinguished by the fact that only one liquid phase exists throughout the phase diagram and that a single critical curve runs continuously from the critical point of the more volatile component to the critical point of the less volatile component. A pressure-temperature composition phase diagram is given in Figure 3-8:

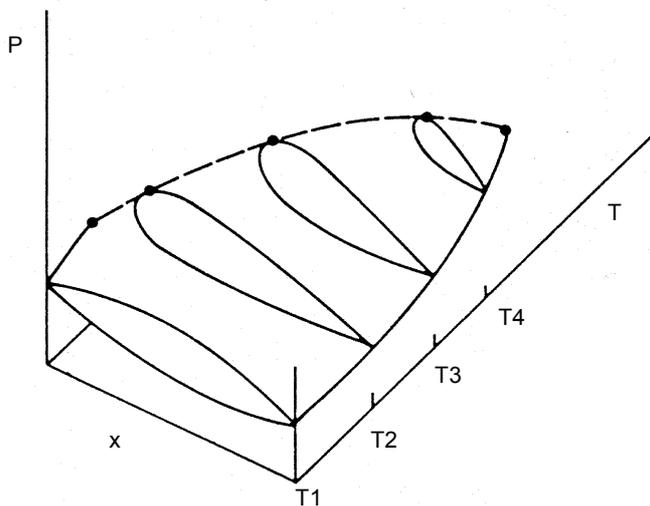


Figure 3-8: PTx phase diagram for type I binary mixtures [2]

This type of phase diagram usually occurs when the components have similar molecular size or diameters and similar interaction strengths, or have critical properties of comparable magnitude. Examples of this type of phase behaviour is methane + ethane, carbon dioxide + oxygen, benzene + cyclohexane [10], carbon dioxide + ethane and carbon dioxide + propane [12].

Components of a particular homologous series, such as normal paraffins (as studied in this project) often show this type of trend, unless the size difference exceeds a particular value.

3.2.2.2 TYPE II

Type II phase behaviour is similar to that of type I, with the exception of the existence of two liquid phases at specific temperatures and pressures, i.e. a $l_2=l_1$ critical curve and a three phase curve l_2l_1g . These two curves intercept at the upper critical end point. In the pressure-temperature-composition space, the two-phase region ($l_2 + l_1$) is found at temperatures lower than the $l_2=l_1$ curve and at pressures higher than the three phase curve.

This phase behaviour can be seen in Figure 3-9 where three pressure-composition sections are shown:

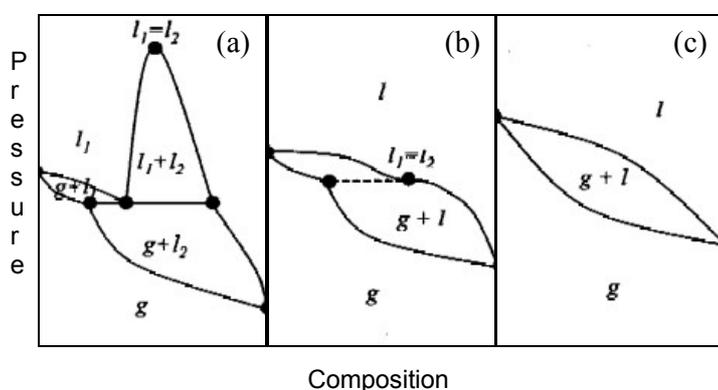


Figure 3-9: Pressure-composition sections for type II at (a) $T < T_{UCEP}$, (b) $T = T_{UCEP}$, (c) $T > T_{UCEP}$ [13]

From Figure 3-9 it can be seen that the two liquids become critically identical in the presence of a gas phase at the UCEP. At temperatures above T_{UCEP} the phase behaviour is the same to that in type I. Examples of type II phase behaviour include n-octane + carbon dioxide and n-hexane + nitrobenzene [12].

3.2.2.3 TYPE V

Type V phase behaviour contains a three phase curve l_2l_1g . The three-phase curve extends from the LCEP to the UCEP and the critical curve shows two branches. The first branch, $l_1=g$ runs from the critical point of the low boiling point component to the UCEP. The second branch starts at the LCEP and ends at the critical end point of the higher boiling point component. This branch of the critical curve is at low temperatures, $l_2=l_1$ in character while at higher temperatures the character changes to $l_2=g$. Figure 3-10 shows the general PTx diagram for type V systems.

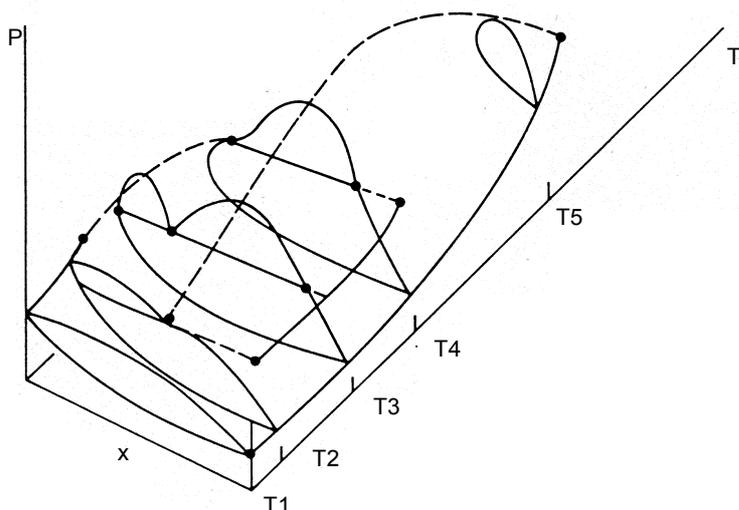


Figure 3-10: Pressure-temperature-composition phase diagram for type V binary mixtures [2]

Figure 3-11 shows pressure-composition sections for type V behaviour.

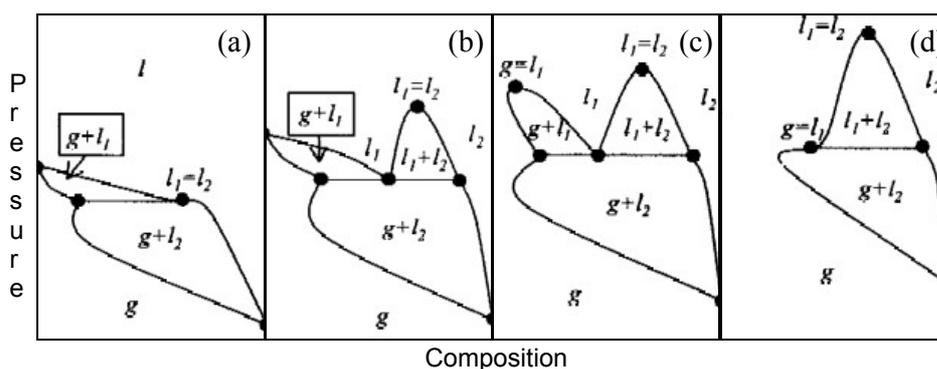


Figure 3-11: Pressure-composition sections for type V at (a) $T = T_{LCEP}$ (b) $T_{LCEP} < T < T_{c,a}$ (c) $T_{c,a} < T < T_{UCEP}$ (d) $T = T_{UCEP}$ [13]

At temperatures below the T_{LCEP} and above T_{UCEP} , type V phase behaviour is the same as that for type I systems.

Type V phase behaviour usually occurs when the critical properties of the two components differ significantly or if the species differs considerably in the strength of the intermolecular potential. When examining the homologous series of normal alkanes type V behaviour occurs when the ratio of the carbon atoms exceeds a certain value.

It can be argued that some systems can be incorrectly classified as type V when they are in fact type IV (see section 3.2.2.4) with the liquid-liquid critical curve being hidden by the solidification of one of the components. Although of academic interest, it is of no practical importance if a system is classified as type IV with the liquid-liquid critical curve hidden by solidification or a type V with no liquid-liquid critical curve. In various publications Peters and co-workers did not report a liquid-

liquid critical curve and by implication thus classified these systems into type V [14], [15], [16]. For the purpose of this project it will be assumed that if the liquid-liquid critical curve cannot be observed, including when it is hidden by solidification, a system will be classified as type V.

Leder et al. [17] found no region of immiscibility for propane-nC36 and stated that nC37 is likely to be the lowest possible normal paraffin that could display liquid-liquid immiscibility in the phase behaviour with propane. However, Peters et al. [11] conducted experiments and found that regions of immiscibility occur for the C3 - nC32, C3 - nC34, C3 - nC36, C3 - nC38, C3 - nC40, C3 - nC44, C3 - nC46 and C3 - nC50 systems and classified all these systems as type V. Extrapolation from the lower and the upper critical solution temperatures leads to a prediction that the transition from type I to type V may occur at hydrocarbons between 29 or 30 carbon atoms (See Figure 3-6).

3.2.2.4 TYPE IV

Type IV phase behaviour is a combination of type V and type II phase behaviour. These systems show two branches of the l_2/l_1g curve, three branches of the critical curve and three critical end points (two UCEPs and one LCEP). At low temperatures (below T_{LCEP}) the phase behaviour is similar to that of type II phase behaviour. Above T_{LCEP} the phase behaviour is similar to that of type V. Pressure-composition sections of type IV phase behaviour is shown in Figure 3-12:

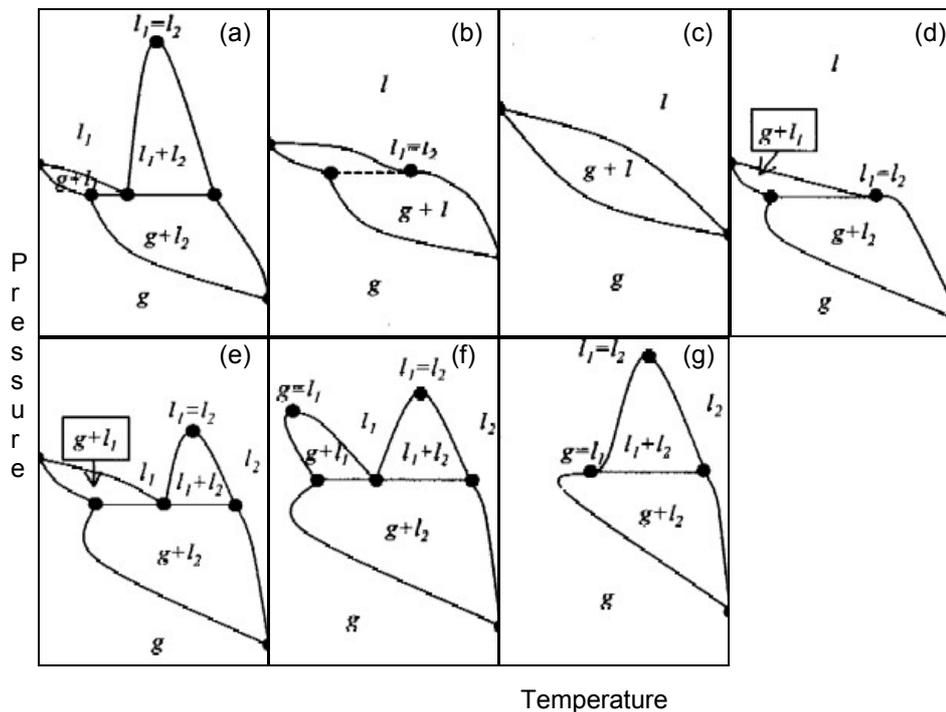


Figure 3-12: Pressure-composition sections for type IV at (a) $T < T_{UCEP1}$, (b) $T = T_{UCEP1}$, (c) $T > T_{UCEP1}$ (d) $T = T_{LCEP}$ (e) $T_{LCEP} < T < T_{c,a}$ (f) $T_{c,a} < T < T_{ucep}$ (g) $T = T_{UCEP2}$ [13]

Examples of type IV phase behaviour include ethylene + nitromethane, methane + n-hexene [13] and carbon dioxide + n-tridecane [18].

3.2.2.5 TYPE III

Using type IV phase behaviour as a starting point, in type III phase behaviour the two branches of the l_2/l_1g are combined and the two branches of the $l_2=l_1$ critical curve are united. Only one critical end point, an UCEP, remains. A three dimensional representation of a type III system is given in Figure 3-13:

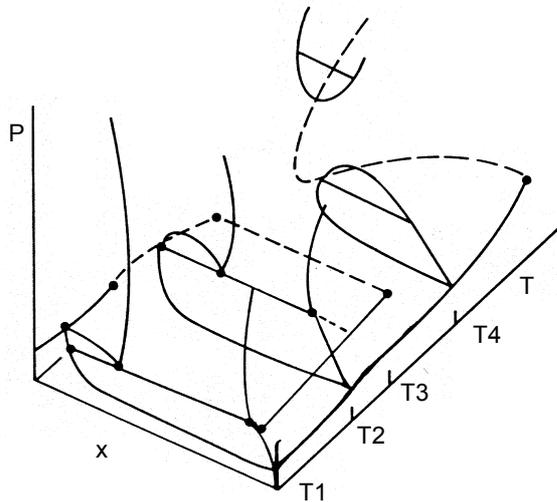


Figure 3-13: PTx phase diagram for type III binary mixtures [2]

Examples of type III systems include carbon dioxide + nC24 [19], carbon dioxide + nC16 and carbon dioxide + squalene [18].

3.2.2.6 TYPE VI

Type VI is type I with the addition of a liquid-liquid immiscibility region. This can be seen in Figure 3-14:

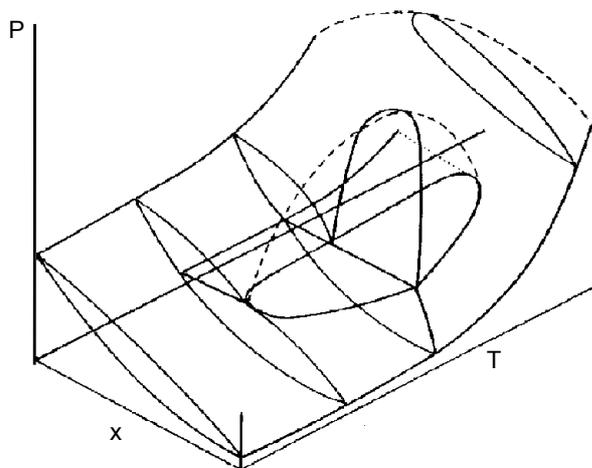


Figure 3-14: PTx phase diagram for type VI binary mixtures [10]

To clarify the above diagram a series of points at 3 different temperatures is given in Figure 3-16:

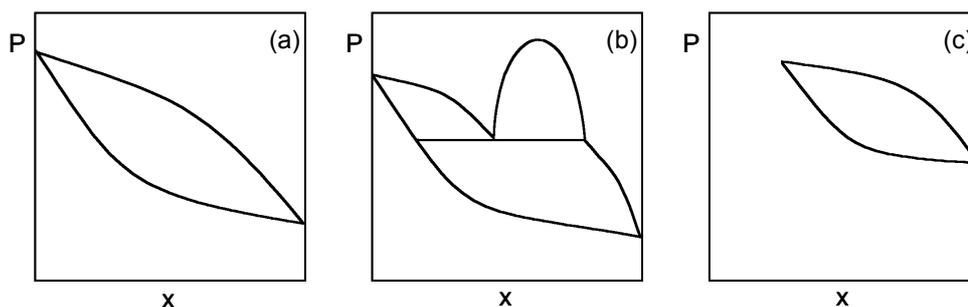


Figure 3-15: Px phase diagrams for type VI or binary mixtures at various temperatures
(a) $T < T_{LCEP}$ (b) $T_{LCEP} < T < T_{UCEP}$ (c) $T > T_{UCEP}$ [13]

The region of liquid-liquid immiscibility is limited to a limited temperature range. Below the LCST and above the UCST the system is miscible. Type VI system is only found in mixtures with chemically complex substances where one or more of the pure components exhibit self association due to hydrogen bonding. Examples include water + n-butanol and water + 2-butanol.

3.2.3 IMPLICATION OF PHASE BEHAVIOUR ON SUPERCRITICAL FLUID EXTRACTION

When considering the phase behaviour of a solute in a supercritical solvent, it is important to know the characteristics in the operating region. These include, in addition to the solubility of the solvent in the solute and the solute in the solvent, if a three-phase region occurs and if so, the temperatures and pressures where it occurs.

None of the above mentioned types are either good or bad, yet some have regions to be avoided. These include all three-phase regions and regions close to the three phase regions. When separating two components, the greater the phase behaviour differs, the better: This will allow one component to be preferentially extracted, the other remaining in the raffinate.

Simple phase behaviour, such as type I, is often preferred. The preference is not due to this behaviour being superior to all other but rather due to easier comprehension and thermodynamic modelling. Separation systems with types other than type I can be implemented as long as sufficient knowledge of the phase behaviour exists.

3.3 PRELIMINARY SOLVENT SCREENING

Various possibilities exist for supercritical solvents and many factors need to be considered. Before considering the solvents, the requirements for the ideal solvent need to be defined:

- The solvent should dissolve either the alkane and alcohol above the alcohol ethoxylate or visa versa. This will allow for the alkane and alcohol to be recycled.
- The solubility difference between the alkane, alcohol and alcohol ethoxylate should be as large as possible to accomplish easy separation.

- The process should be conducted at a temperature where all components are in the liquid phase.
- To prevent excessive decomposition of all products, the operating temperature should be kept as low as possible.
- The process needs to be conducted as close to the critical point of the solvent as possible. The closer the operating point is to the critical point, the easier it is to manipulate the solubility of the solute in the solvent, thus facilitating easier solvent removal.
- To keep the costs at a minimum and to simplify the engineering, the pressure should be as low as possible.

Carbon dioxide is the most widely used supercritical fluid due to its convenient critical parameters, its cheapness, non-flammability and non-toxicity. Although carbon dioxide is a non-polar molecule it may be applied as a weak polar solvent due to its large quadrupole moment. Carbon dioxide is not such a good solvent for high molecular weight alkanes and polymers without functional groups, yet carbon dioxide may be superior in dissolving the alcohol ethoxylate due to the presence of the ethylene oxide residue. Carbon dioxide as a solvent thus warrants further investigation as a possible solvent.

Low molecular weight saturated alkanes, such as ethane, propane, butane and LPG may also be used as supercritical solvents. As shown in the literature [3], [4], these compounds are able to dissolve the hydrocarbon chain considerably better than carbon dioxide and thus need to be considered for further investigation. When selecting a low molecular weight alkane for further investigation, the melting points of the solute and the critical properties of the solvent need to be considered. Ideally, the process should be operated just above the critical temperature of the solvent and the melting point of the solute. The solute melts at approximately 373 K, and propane has a critical temperature of 369.8K. Thus for a low molecular weight alkane, propane is the most suited solvent and will be investigated further.

3.4 VAPOUR-LIQUID EQUILIBRIA: CARBON DIOXIDE AS SOLVENT

Carbon dioxide is the most common supercritical fluid available. Of all systems, the ones with the most abundant literature data available are those concerning carbon dioxide as solvent. In this section, a selection of the data is presented to illustrate the solubility of the solutes in carbon dioxide and possible trends that exist.

3.4.1 CARBON DIOXIDE – ALKANE DATA

A large amount of data exists for the systems carbon dioxide with normal alkanes. Comprehensive lists are provided by Dohrn et al. [20], Christov et al. [21], du Rand [4] and Schwarz [3] amongst others. The purpose of this subsection is not to replicate all published data but to use the published data to illustrate suitability of carbon dioxide as solvent for this system.

A large amount of data exists for systems with 36 or less carbon atoms either as solubility data or even as vapour-liquid equilibria data. Temperatures of measurement range between 300 and 580 K, most of the data just above the critical temperature of carbon dioxide (304.15K) and pressures up to 300barA. Figure 3-16 shows the vapour-liquid equilibria for a selection of alkanes at constant temperature:

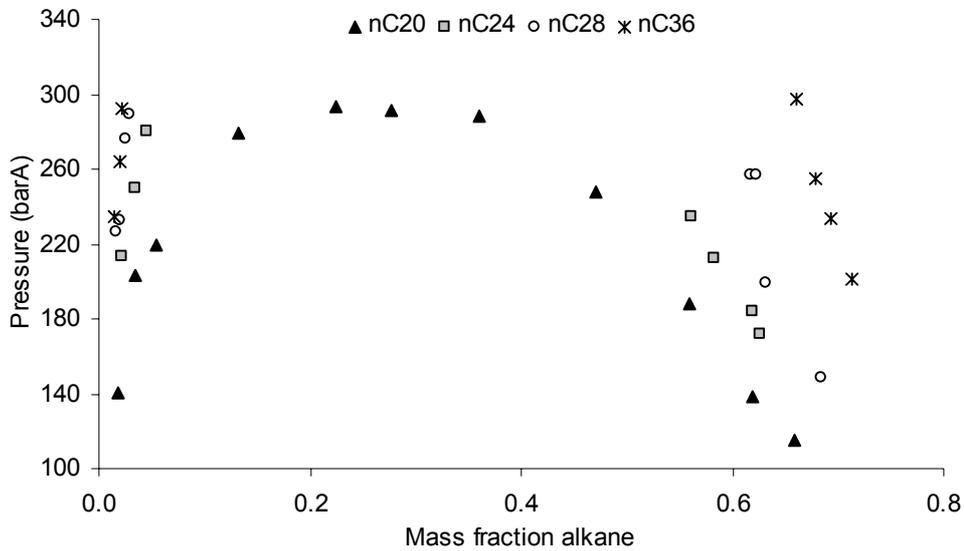


Figure 3-16: Isothermal (348K) plot of solubility as a function of mass fractions for various n-alkanes in supercritical carbon dioxide [4]

From Figure 3-16 it can be seen that the solubility increases quite sharply with increasing molecular weight. High-density polyethylene is a mixture of ultra high molecular weight alkanes and to determine the limit of the solubility, equilibrium data for these high molecular weight compounds is studied. The only available data for solubility of carbon dioxide in polyethylene is illustrated in Figure 3-17:

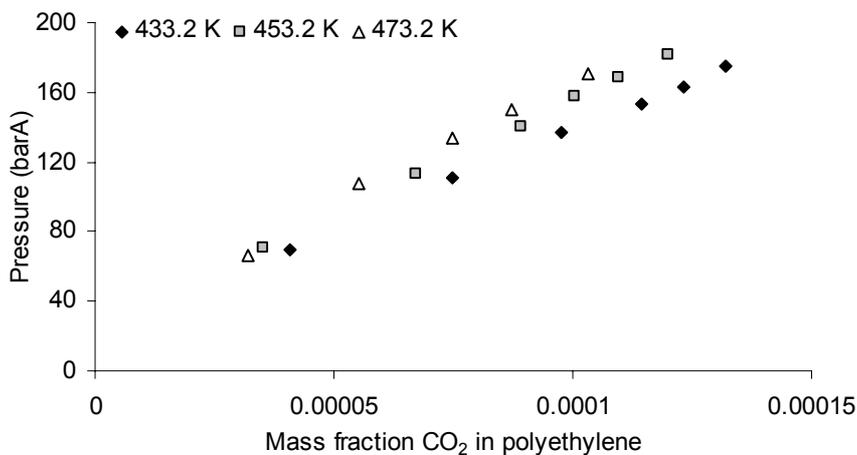


Figure 3-17: Solubility of carbon dioxide in high-density polyethylene [22]

Although a linear relationship is shown, attention is drawn to the magnitude of the axis. For a mere mass percentage solubility of 0.01 % carbon dioxide in polyethylene a pressure of over 120barA is required. The insolubility can be further illustrated by comparing the above data with solubility data of carbon dioxide in nC36:

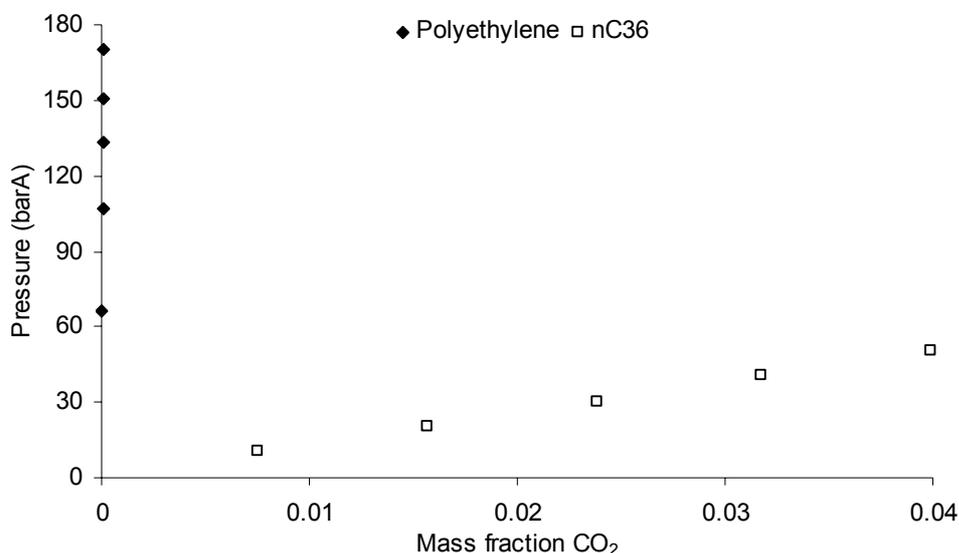


Figure 3-18: Comparison of the solubility of carbon dioxide in polyethylene [22] and in nC36 [23] at 473.2 K

As can be seen above, when compared to nC36, excessive pressures are required to solubilise carbon dioxide in polyethylene. Thus for the higher alkanes (above nC36) pressures well in excess of 300barA are required to obtain a reasonable solubility.

3.4.2 CARBON DIOXIDE – ALCOHOL DATA

Numerous data sets exist for solubility phase equilibria measurements between normal alcohols and carbon dioxide. These data sets are, however, limited to lower hydrocarbon backbones, mainly due to the limited availability of the alcohols (many are found or derived from natural products such as palm oil), yet enough data exists to determine trends in solubility.

Phase equilibria and solubility data exists for systems containing carbon dioxide and alcohols up to 20 carbon atoms. Figure 3-19 illustrates the dependence of the solubility on the hydrocarbon backbone. it can be seen that a limited solubility of the alcohol in carbon dioxide is achieved, yet moderate to high pressures are required. Due to scatter in the data it is not possible to determine a mathematical relationship between the hydrocarbon backbone and the phase transition pressure, yet a general trend of an increase in pressure with an increase in hydrocarbon backbone is noted.

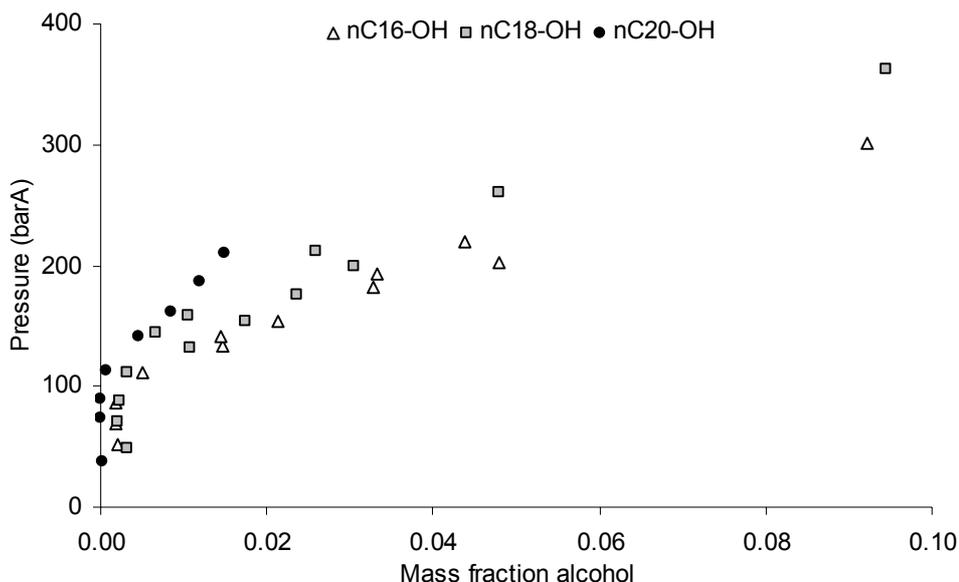


Figure 3-19: Plot of phase transition pressure as a function of mass fractions for various n-alcohol in supercritical carbon dioxide at 328K [24], [25], [26], [27]

When comparing the data in Figure 3-19 with that in Figure 3-16 it can be seen that the alcohols require a high pressure for solubilisation than alkanes.

3.4.3 CARBON DIOXIDE – POLYETHYLENE GLYCOL DATA

The hydrophilic group of the alcohol ethoxylate consists of a polyethylene glycol chain. As no phase equilibrium data is available for alcohol ethoxylates, the solubility of polyethylene glycol in the supercritical fluid can be investigated to determine the effect of the polyethylene glycol chain:

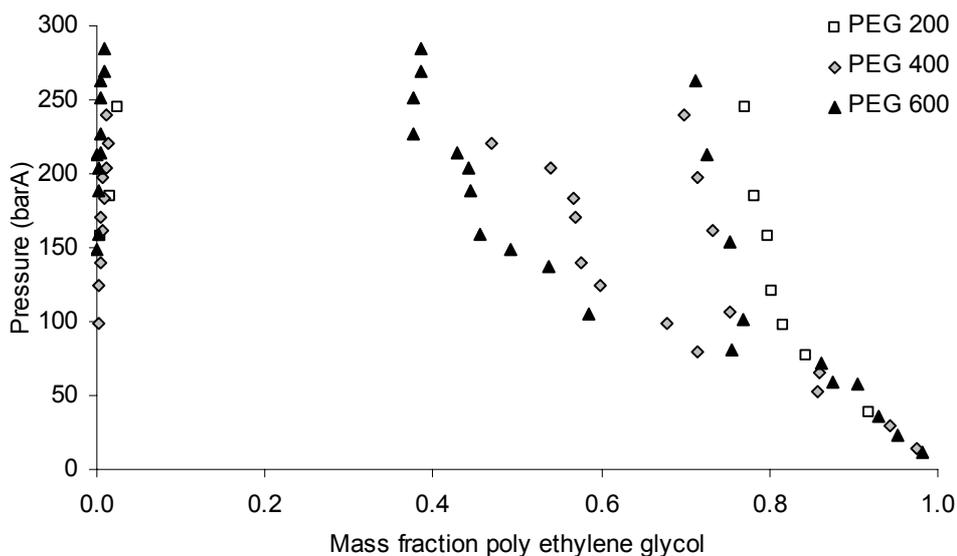


Figure 3-20: Plot of the equilibria of various polyethylene glycol fractions in carbon dioxide at 313.15K [28], [29]

Although there is a significant scatter in the data (possible due to data originating from different sources) a general trend of an increase in molecular weight leading to an increase in solubility is noted. This may be attributed to the increasing effect of the oxygen atoms in the ether bonds with increasing molecular weight. At higher molecular weights this trend seems to have diminished and the effect of the increasing molecular weight, leading to a decrease in solubility, is noted, as seen in Figure 3-21.

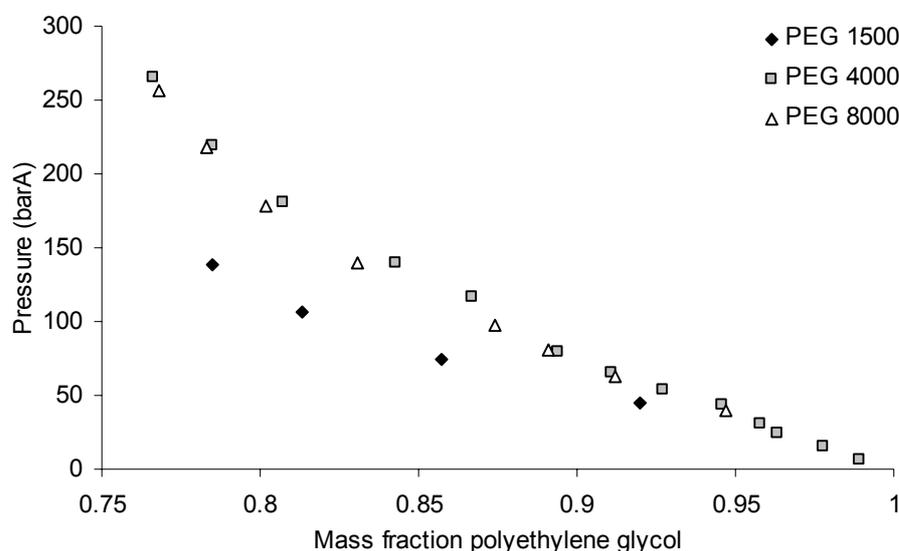


Figure 3-21: Plot of the phase equilibrium pressure as a function of mass fraction for various fractions of polyethylene glycols at 353.15K [30]

Figure 3-22 shows the effect of temperature on the phase equilibrium pressure:

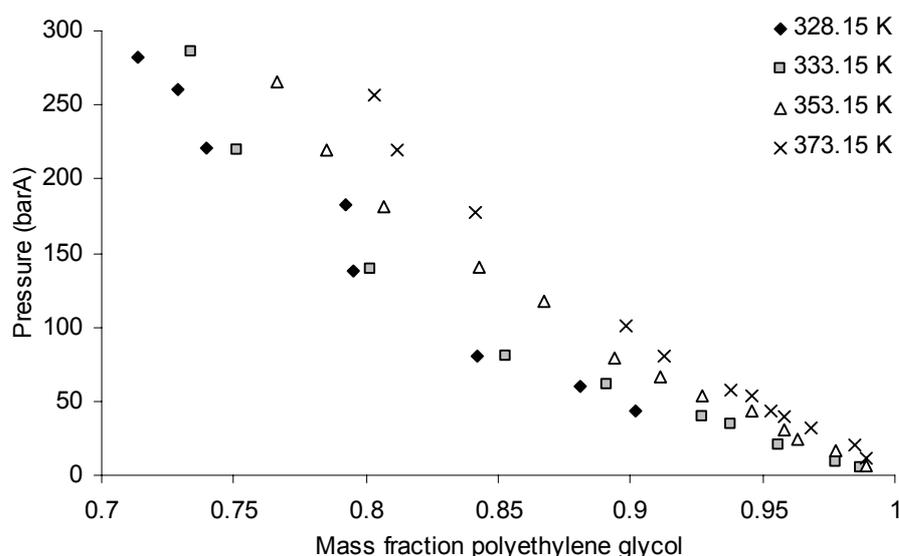


Figure 3-22: Plot of the phase equilibrium pressure as a function of mass fraction for PEG 1500 at various temperatures [30]

As in the case of the alkanes and alcohols, an increase in temperature leads to an increase in phase equilibrium pressure.

Supercritical carbon dioxide also has the ability to fractionate polyethylene glycol. Lopes et al. [31] and Daneshvar et al. [32] published data concerning the fractionation of polyethylene glycols with supercritical carbon dioxide. The data published by Lopes et al. shows that the polyethylene glycol in the CO₂ rich phase has a lower molecular weight and a decreased polydispersity. However, no indication was given as to the fraction of the polymer absorbed in the CO₂ rich phase or the ratio of the two phases, so it is not possible to determine the extent of fractionation that can be achieved. The data published by Daneshvar et al., as shown in Table 3-1 provides a better indication of the ability of carbon dioxide to fractionate polyethylene glycol:

Table 3-1: Experimental data for the fractionation of polyethylene glycol with carbon dioxide [32]

Process Conditions	Temp (K)	313.15	313.15	323.15	323.15	313.15
	Pres (barA)	204.1	202.6	183.5	264.3	270.3
Parent phase	M _n	406	406	406	406	538
	M _w	433	433	433	433	588
	M _w /M _n	1.067	1.067	1.067	1.067	1.093
Overheads	M _n	384	383	385	399	538
	M _w	400	401	402	415	562
	M _w /M _n	1.042	1.047	1.044	1.040	1.045
Bottoms	M _n	455	465	439	417	570
	M _w	480	493	464	441	617
	M _w /M _n	1.055	1.060	1.057	1.058	1.082

From the data in Table 3-1 it can be seen that the polyethylene glycol in the overheads, i.e. the CO₂ rich phase, has a lower molecular weight and that in the bottoms, i.e. the polymer rich phase, has an increased molecular weight. Both fractions have a decreased polydispersity. Carbon dioxide thus has the ability to fractionate polyethylene glycol according to molecular weight.

3.4.4 COMPARISON

A comparison of the ability of carbon dioxide to dissolve the alkane, the corresponding alcohol and polyethylene glycol is given in Figure 3-23:

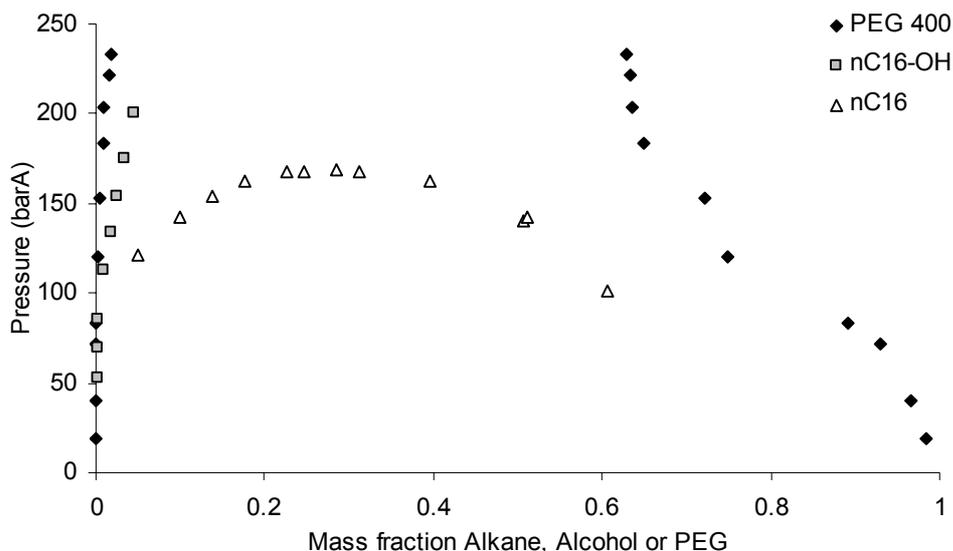


Figure 3-23: Comparison of the phase equilibrium pressure for PEG 400 [28], nC16-OH [26] and nC16 [4] in carbon dioxide at 323.15K

As can be seen, the solubility of the alkane is the best, followed by the alcohol and then the polyethylene glycol. However, there is not such a large distinction between the alcohol and the polyethylene glycol and a fractionation system to distinguish between these two components, although possible, require many theoretical stages.

3.5 VAPOUR-LIQUID EQUILIBRIA: PROPANE AS SOLVENT

Propane is investigated as an alternative solvent to carbon dioxide. Although data is not as abundant as for carbon dioxide, enough data is available to investigate the suitability of propane as a solvent for the intended application.

3.5.1 PROPANE – ALKANE DATA

Propane – n-alkane data has been measured up to nC60 and a large part of the composition range is covered at reduced temperatures up to approximately 1.1. Comprehensive lists are provided by Dohrn et al. [20], Christov et al. [21], and Schwarz [3] amongst others.

A selection of data measured by Schwarz et al. [33], [34] is illustrated in Figure 3-24:

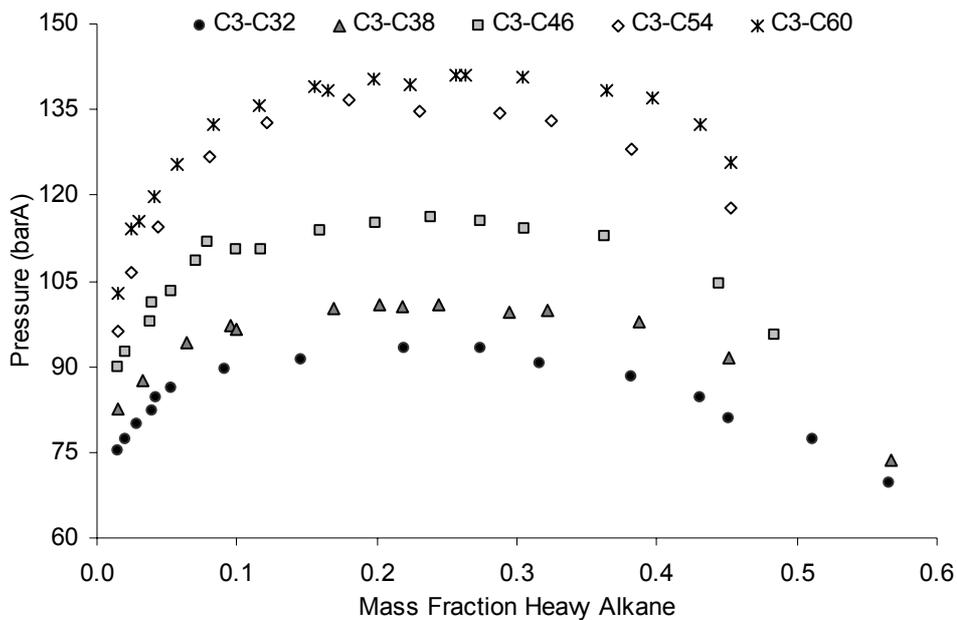


Figure 3-24: Pressure-composition plot for propane with various heavy alkanes at 408.2K [33], [34]

From Figure 3-24 it can be seen that an increase in phase transition pressure occurs with an increase in the hydrocarbon chain length. More importantly, however, it can be seen that for nC60 the hydrocarbon is fully soluble in propane at pressures of 150barA and 408K. Significant solubility of the alkane in the solvent is thus possible at moderate pressures.

When plotting the phase transition pressure as a function of carbon number at constant temperature and composition (mass based) a linear relationship is realised in the region from nC32 through nC60:

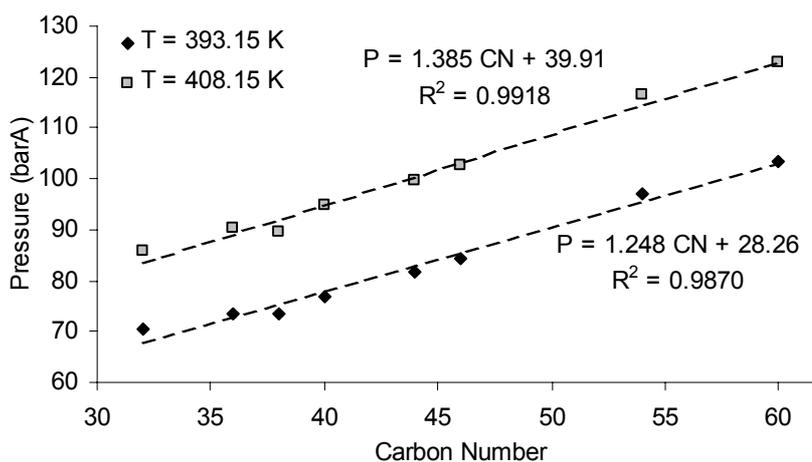


Figure 3-25: Pressure-carbon number plot for wax mass fraction 0.050 (propane rich phase) [34]

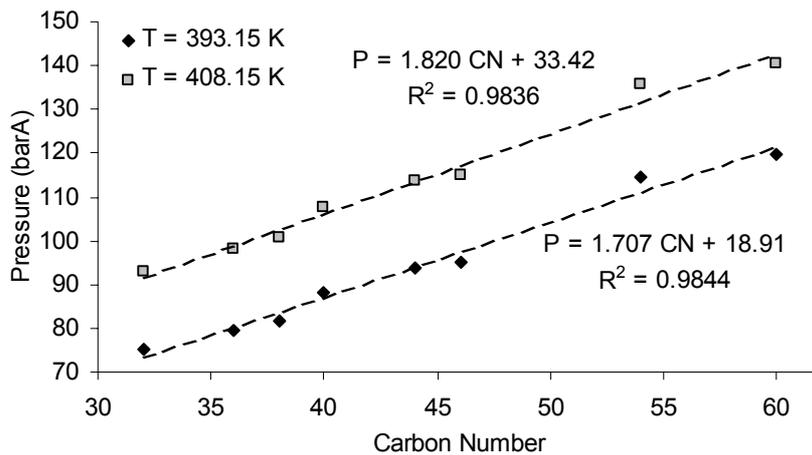


Figure 3-26: Pressure-carbon number plot for wax mass fraction 0.200 (mixture critical region) [34]

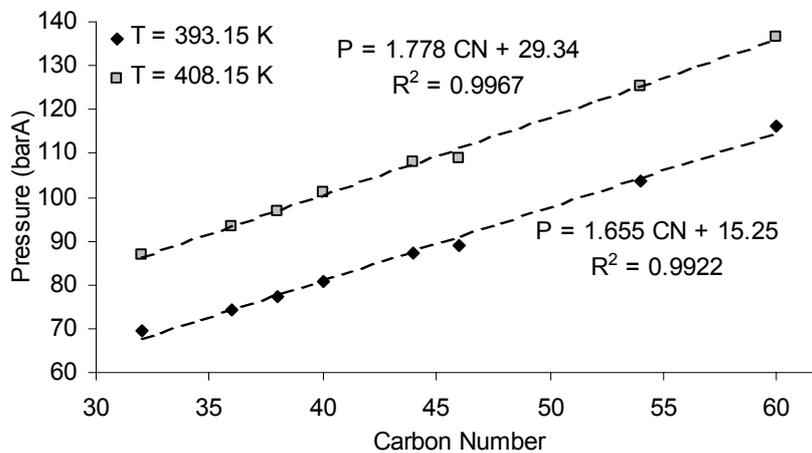


Figure 3-27: Pressure-carbon number plot for wax mass fraction 0.400 (heavy alkane rich phase) [34]

As shown in Figure 3-25 through Figure 3-27 this relationship holds true in the propane rich phase (Figure 3-25), in the mixture critical region (Figure 3-26) and in the heavy alkane rich phase (Figure 3-27). In addition, the relation is valid for various temperatures, the gradient increasing with increasing temperature. On a macroscopic scale, this is explained as follows: As the temperature increases, the system becomes more asymmetric, the increase in the asymmetry being more profound for a larger size difference. Thus the pressure required for on phase behaviour becomes larger and the gradient in Figure 3-25 through Figure 3-27 increases with increasing temperature.

From a range of pressure-carbon number plots such as those in Figure 3-25 through Figure 3-27 [34] the phase transition pressures for various systems not measured can be calculated. Figure 3-28 shows some of these plots:

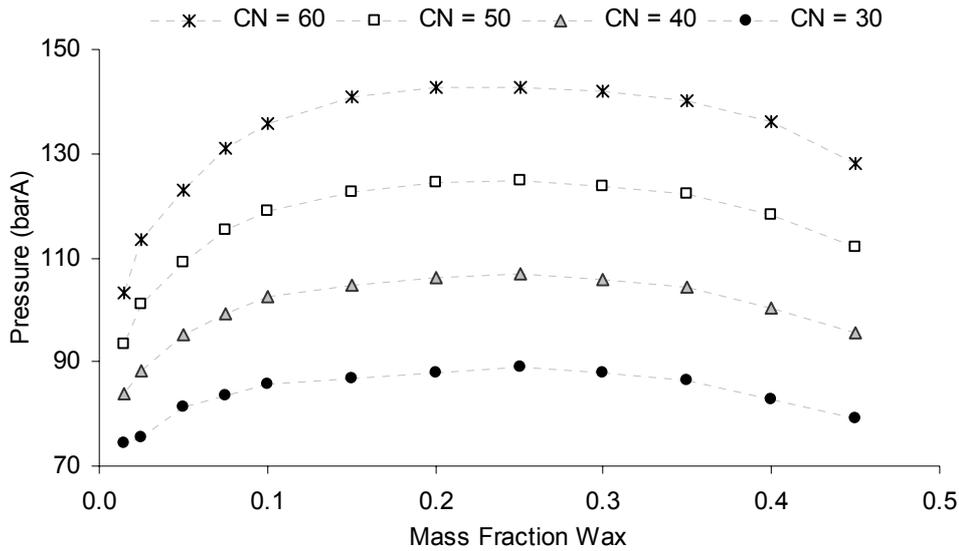


Figure 3-28: Predicted pressure-carbon number plots for nC30, nC40, nC50 and nC60 at 408.1K [34]

The data available for the pressure-carbon number plots is limited to mass fractions of heavy alkane 0.45 and less. Peters et al. [35] published high mass fraction data for propane with nC60 and, as illustrated in Figure 3-29, it was found that for high mass fractions a linear relationship exists between the pressure and mass fraction:

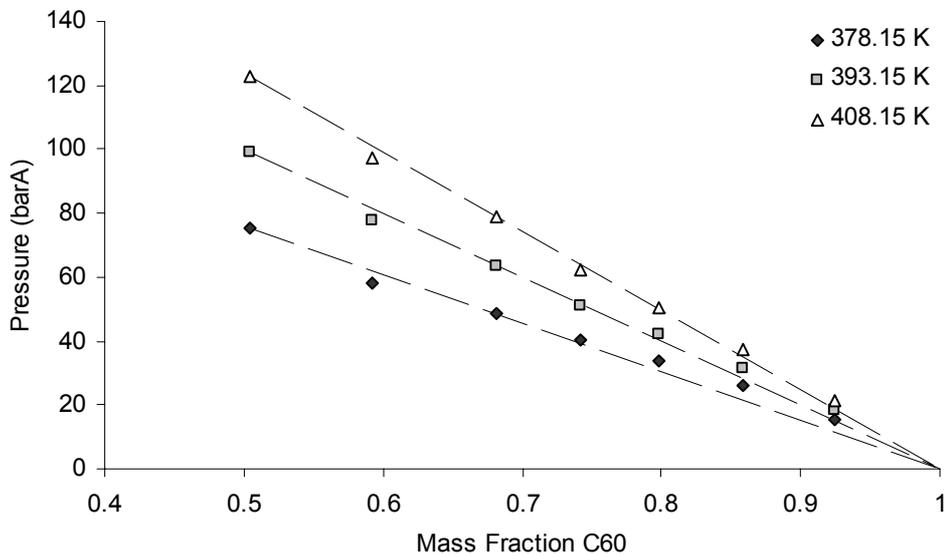


Figure 3-29: Pressure-composition plot for high mass fraction data, propane-nC60 data [35]

This linear relationship, together with the relations from the pressure-carbon number plots can be used to predict the phase transition pressure in the entire concentration range. The ability of this method of prediction is illustrated in Figure 3-30:

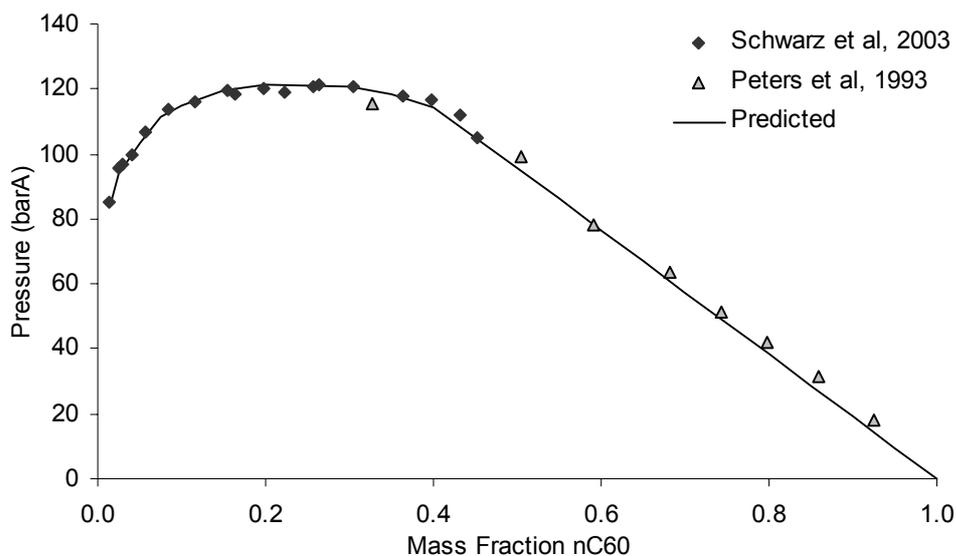


Figure 3-30: Comparison of literature data [34], [35] and predicted phase equilibrium data at 393.15 K

This method is thus able to predict data well in the region nC32 to nC60, the region in which this method was developed. The question now arises as to the possibility of extrapolating the above method to lower and higher carbon number alkanes. Limited lower carbon number data exists and the applicability is illustrated in Figure 3-31:

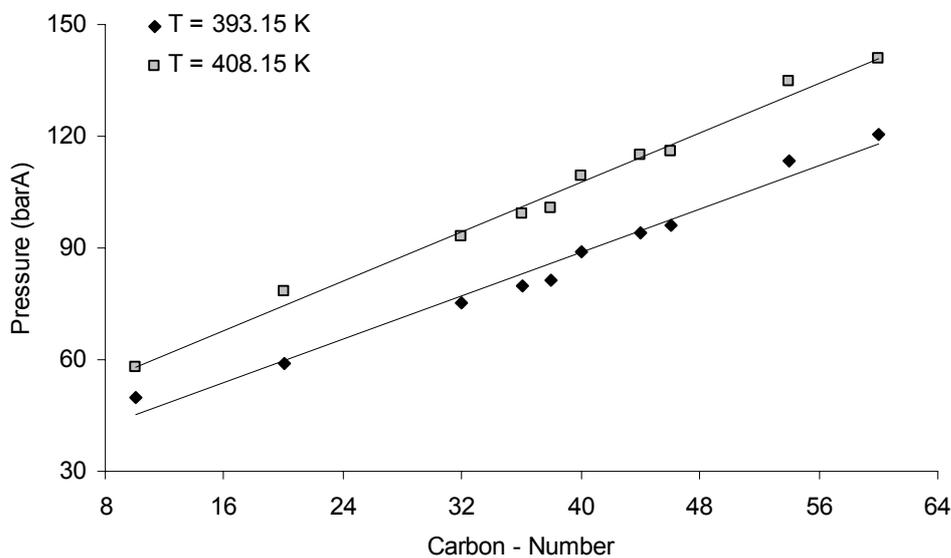


Figure 3-31: Pressure-carbon number plot at $x = 0.25$ with data between nC30 and nC60 [3] extrapolated to lower mass fractions [36], [37]

As the method can be used to predict lower carbon number data, one wonders if the relation can be extrapolated to higher carbon numbers and if so, to what extent. The limiting solubility would be that of high-density high molecular weight polyethylene, but no solubility or vapour liquid equilibria data could be found. Fractionation data is however available. Watkins et al. [38]

published both isothermal and isobaric polyethylene fractionation data. The extent of the fractionation achieved is shown in Figure 3-32 and Figure 3-33 for the isothermally and isobarically fractionated data respectively with the aid of the number and weight average molecular weights of the individual fractions and the parent:

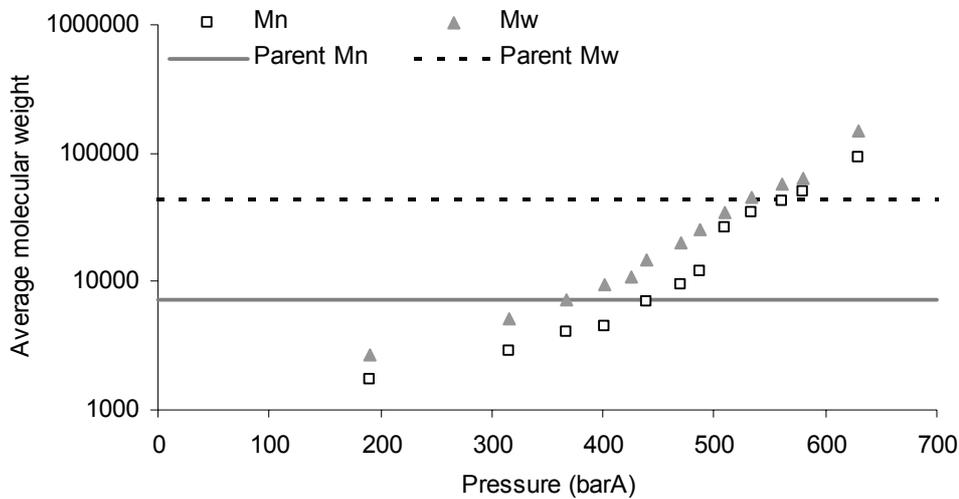


Figure 3-32: Number and weight average molecular weight of fractions of isothermally fractionated polyethylene as a function of pressure [38]

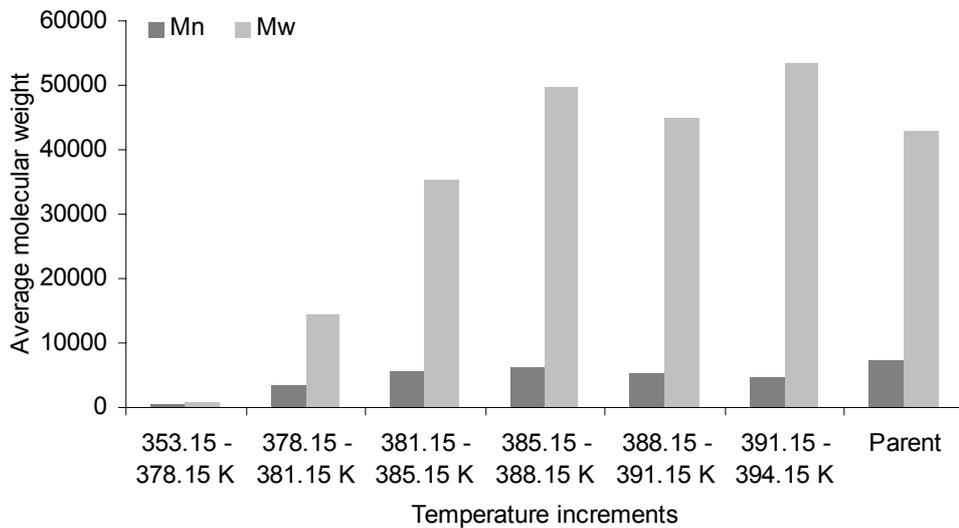


Figure 3-33: Number and weight average molecular weight of temperature increments of isobarically fractionated polyethylene [38]

While the isothermal fractionation resulted in increasing molecular weight fractions and each fraction having a reduced polydispersity compared to the parent, isobaric fractionation, with possible exception of the first two fractions, gave little improvement, in some cases even resulting in more polydisperse product. This may be explained in terms of entropy: At isobaric conditions, with an increase in temperature, the entropy increases and an increase in entropy results in an increase in the 'disorder' of the system. As a more polydisperse system has a higher degree of

disorder, it has a higher entropy. Therefore an increase in temperature, which results in higher entropy of the system, favours a more polydisperse system.

Due to the fact that isothermal fractionation can lead to molecular weight fractionated fractions up to pressures as high as 700barA, it can only be assumed that the relations in Figure 3-25 through Figure 3-27 hold true to some extent at higher mass fractions. Yet, when the phase transition pressure, at say $x = 0.050$ and 408.15 K, is calculated for the lowest and highest fractions based on the number average molecular weight, values of 207.5barA and 9279barA are calculated, compared to extraction pressures of 82.7barA and 630.4barA. It can be noted that at some point the curve may no longer follow the same trend and will start to flatten to an asymptotic value.

It is well known that in the crystalline phase normal alkanes undergo molecular folding once a limiting size is reached [39], [40]. The question now arises as to whether the molecular folding also occurs in solution, particular in supercritical solution. Further investigations with regard to the behaviour of high molecular weight alkanes are thus required.

3.5.2 PROPANE – ALCOHOL DATA

Despite a detailed search, no propane - high molecular weight alcohol data is found in the open literature. If propane is selected as solvent, phase equilibrium measurements are required. It is expected that phase equilibrium measurements of propane-alcohol would result in pressures a few bar above that of the corresponding alkane due to the presence of the hydroxyl group, the difference diminishing with increasing molecular weight.

3.5.3 PROPANE – POLYETHYLENE GLYCOL DATA

Wiesmet et al. [30] measured the solubility of propane in various grades of polyethylene glycol. The effect of the degree of polymerisation is shown in Figure 3-34:

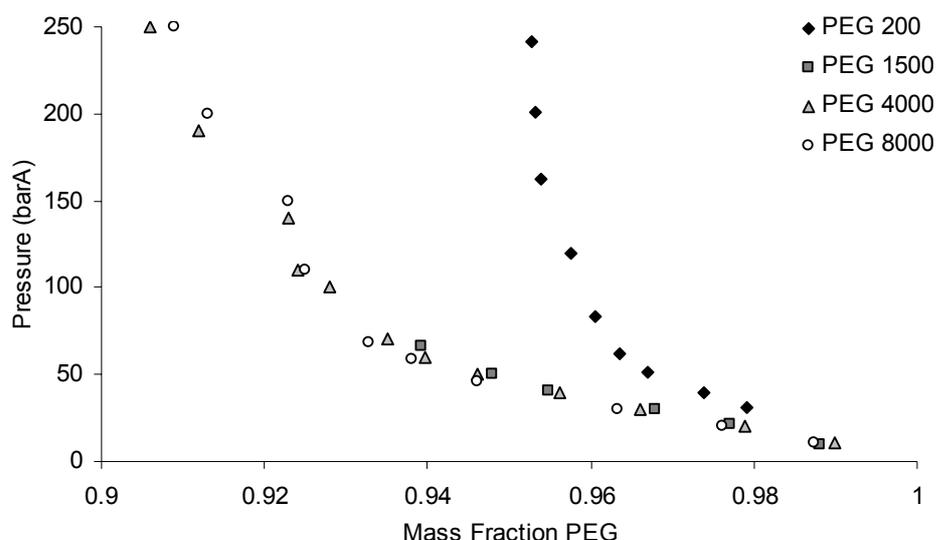


Figure 3-34: Solubility of propane in various grades of PEG at 393.15K [30]

From Figure 3-34 it can be seen that up to a certain point an increase in average molecular weight leads to an increase in solubility after which an increase in average molecular weight has little or no more effect. This may be attributed to the fact that as the molecule weight increases the effect of the terminal hydroxyl groups is diluted by the increasing molecular weight and it is speculated that beyond a certain molecular weight, the solubility is dominated by the oxygen atom of the ether group.

The effect of temperature is shown in Figure 3-35:

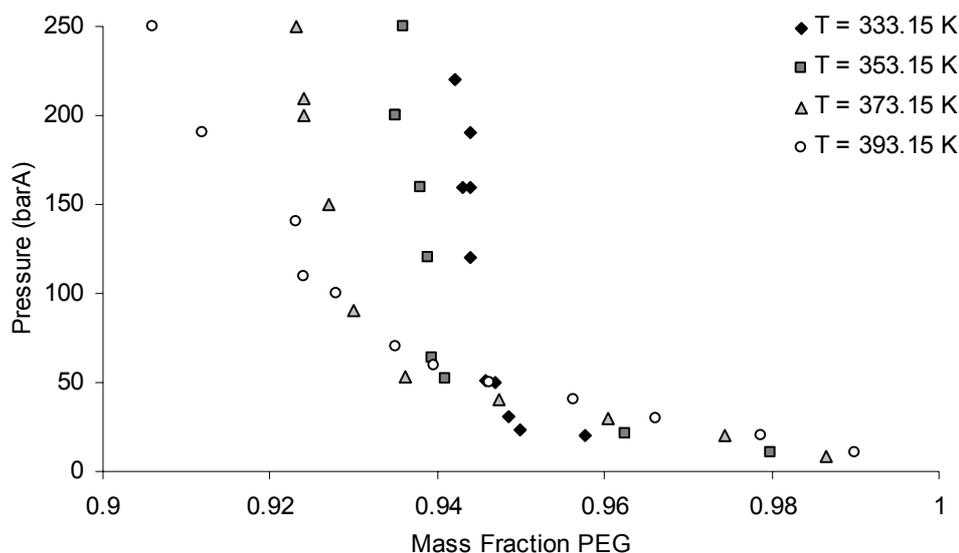


Figure 3-35: Solubility of propane in PEG 4000 at various temperatures [30]

As seen above, an increase in temperature leads to an increase in solubility. This effect may be attributed to the fact that as the temperature increase the polarisability of the ether and the hydroxyl groups decreases, thus increasing the ability of the non-polar propane to dissolve the polyethylene glycol.

3.5.4 COMPARISON

A comparison between the solubility of nC60 and PEG 1500 at constant temperature is shown in Figure 3-36 and as can be seen, the solubility of the alkane and the PEG differ considerably. This difference in solubility may be used to fractionate the alkane and the alcohol ethoxylate. It is envisioned that the alcohol solubility will lie between the alkane and the PEG but closer to the alkane due to the dominating effect of the hydrocarbon backbone.

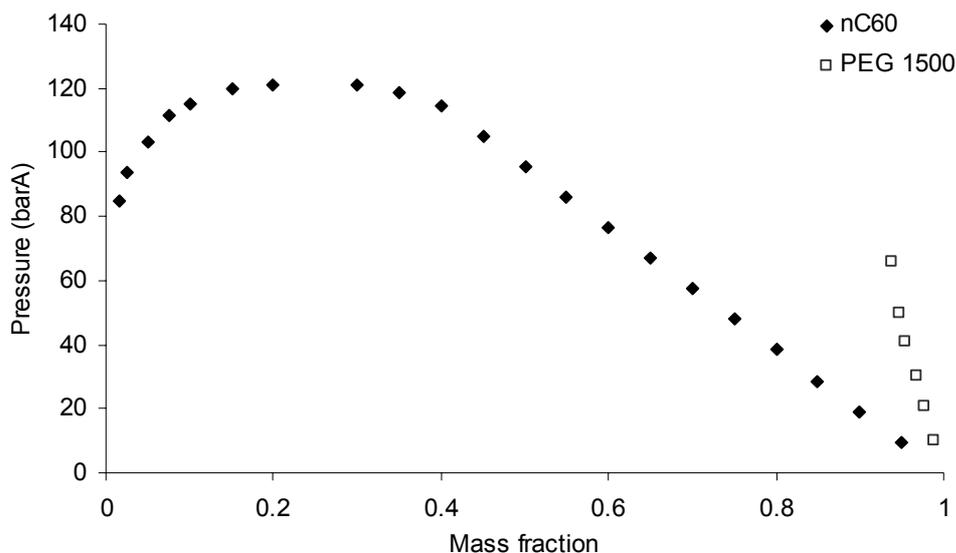


Figure 3-36: Comparison of the solubility of nC60 (predicted data – see section 3.5.1) with PEG 1500 [30] at 393.15 K in propane

3.6 SOLVENT SELECTION

The solvent requirements, as set out in section 3.3, need to be taken into account while comparing the solvents, after which a decision will be made as to the most suitable solvent.

3.6.1 COMPARING SOLVENTS

To compare the solvent, the solubility difference of the solute in the two different solvents is compared. Figure 3-37 shows the difference in the solubility of the alkane in propane and carbon dioxide while Figure 3-38 shows the difference in solubility of PEG in propane and carbon dioxide.

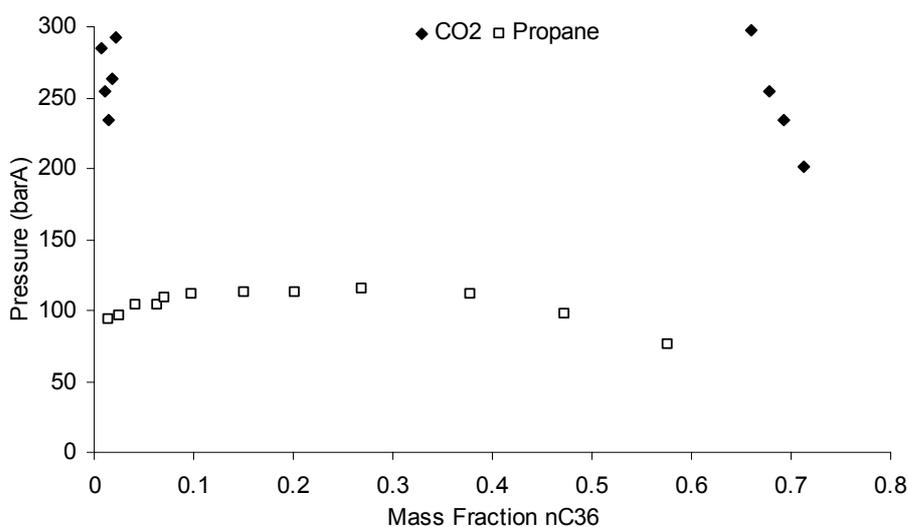


Figure 3-37: Comparison of the solubility of nC36 in carbon dioxide at 348K [4] and in propane at 420K [34] – Reduced temperatures are similar (~ 1.14)

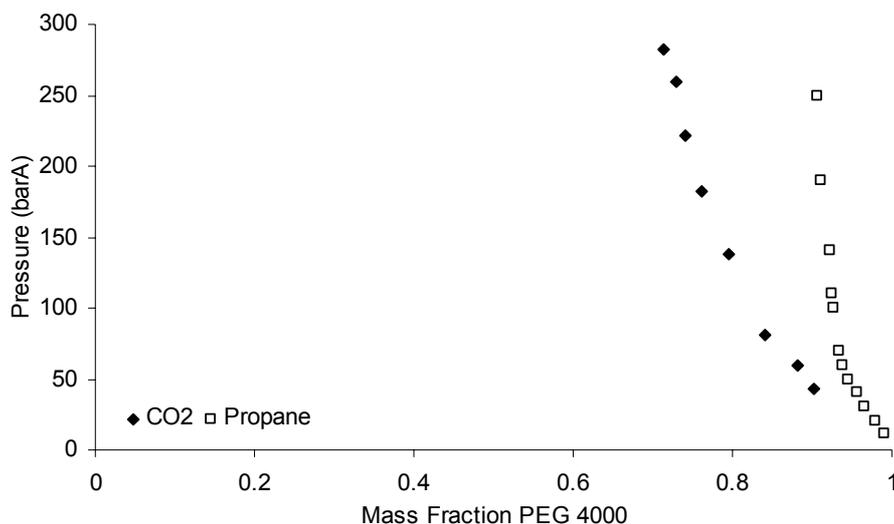


Figure 3-38: Comparison of the solubility of PEG 4000 in carbon dioxide at 328K [30] and in propane at 393K [30] – Reduced temperatures are similar (~1.07)

From Figure 3-37 and Figure 3-38 it can be seen that propane is a much better solvent of the alkane but a poorer solvent for PEG. For carbon dioxide the solubility difference between the alkane and the PEG is not as great as for propane.

3.6.2 EVALUATING SOLVENTS

From the solvent requirements listed in section 3.3, the phase equilibria measurements available (sections 3.4 and 3.5) and the comparison of the solvent in section 3.6.1 propane is selected as the suitable solvent. The choice can be justified as follows:

- A significant solubility of alkane in propane can be achieved. It is expected that a significant solubility of alcohol in propane may also be achieved. This will allow for a significant solvent loading.
- Propane is a better solvent of the alkane and not a good solvent for polyethylene glycol. It thus provides a larger difference in solubility compared to carbon dioxide.
- A process can be operated where all the components are in the liquid phase, yet the temperature is not too high. In this temperature range (approximately 390 – 423 K) propane is at a reduced temperature of 1.06 to 1.15, a range where the solubility can easily be changed due to a small change in pressure.
- A process with propane as solvent would be able to operate at a much lower pressure than a process with carbon dioxide as the solubility of the alkane (and possibly also the alcohol) in propane is much better.

3.7 VAPOUR-LIQUID EQUILIBRIA MEASUREMENTS REQUIRED

Although a significant quantity of data is already available for propane as solvent, some additional data needs to be measured before a scheme for a separation process can be designed. The following data is required:

- High molecular weight alkanes need to be synthesised and the phase equilibrium pressure of these alkanes needs to be measured.
- The phase equilibrium pressure of a long chain primary alcohol needs to be measured so as to investigate the influence of the hydroxyl group.
- The phase equilibrium pressure of an alcohol ethoxylate needs to be measured to determine the order of magnitude of the solubility of the alcohol ethoxylate.

In addition, an analysis of the principle of molecular folding is needed to determine the factors driving molecular folding and the possibility of molecular folding occurring in supercritical solution.

The above should suffice to determine if propane will in fact be a suitable solvent and provide enough information for the design of a pilot plant set-up for the separation process.

3.8 NOMENCLATURE

Symbol	Description
C3	Propane
CEP	Critical end point
CN	Carbon number, i.e. number of carbon atoms in an alkane
CP	Mixture critical point
CP1	Mixture critical point 1
CP2	Mixture critical point 2
F	Fluid phase
G	Gas / vapour phase
L	Liquid phase
L1	Liquid phase 1
L2	Liquid phase 2
LCEP	Lower critical end point
LCST	Lower critical solution temperature
M_n	Number average molecular weight (g/mol)
M_w	Weight average molecular weight (g/mol)
nCX	Refers to a normal alkane where X is the number of carbon atoms in the compound
nCX-OH	Refers to a linear primary alcohol where X is the number of carbon atoms in the hydrocarbon

	backbone
P	Pressure (Pa, barA)
PEG	Polyethylene glycol
PEGX	Refers to polyethylene glycol where X is the average molecular weight of the sample
T	Temperature (K)
T _c	Critical temperature (K)
T _{c,a}	Critical temperature of the more volatile component (K)
T _{c,a}	Critical temperature of the less volatile component (K)
T _{LCEP}	Temperature at the LCEP (K)
T _{UCEP}	Temperature at the UCEP (K)
T _{UCEP1}	Temperature at the UCEP (K) at the lower of the two UCEPs
T _{UCEP2}	Temperature at the UCEP (K) at the higher of the two UCEPs
v	Specific volume (m ³ /kg)
UCEP	Upper critical end point
UCST	Upper critical solution temperature
x	Composition (g/g)

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4 Molecular conformation in long chain normal alkanes

Usually, in chemical formulas written for chain polymers the successive units are projected as co-linear sequences on the surface of the sheet of paper. This form of representation fails to convey what is perhaps the most significant structural characteristic of a long polymer chain: its capacity to assume an enormous array of configurations. This configurational versatility is a consequence of the considerable degree of rotational freedom about single bonds of the chain and an almost limitless variety of irregular shapes may be realised. This chapter concentrates on the configuration of long chain normal alkanes and polyethylene in various states and under various conditions. At the core of this analysis is possibly one the most intriguing questions concerning the transition from the traditional behaviour of the short chain molecule to that of a typical polymer.

The purpose of this chapter is to investigate molecular folding in normal alkanes. The analysis will include the discovery of molecular folding, the factors influencing molecular folding and driving forces behind molecular folding. An investigation of the mechanisms involved in molecular folding in crystalline polyethylene and normal alkanes may then shed some light on the possibility of molecular folding in molten or solution-dissolved alkanes.

4.1 INTRODUCING MACROMOLECULES

Polymer molecules possess the unique structural feature of being composed of a very large number of units covalently linked to one another. Their large size results in some unique properties different from ordinary low-molecular weight compounds, mainly due to their large molecular weight and highly non-spherical shape.

4.1.1 AVERAGE MOLECULAR MASS

Various methods can be used to describe the average molecular mass. The number average molecular weight and the weight average molecular weight are defined as in Equation 4-1 and Equation 4-2 respectively [1]:

$$M_n = \frac{\sum_i n_i M_i}{\sum_i n_i}$$

Equation 4-1:

$$M_w = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i}$$

Equation 4-2:

The range of molecular weights is usually defined in terms of the polydispersity, which can be defined in terms of the number average and weight average molecular weight:

Equation 4-3:
$$\text{Polydispersity} = \frac{M_w}{M_n}$$

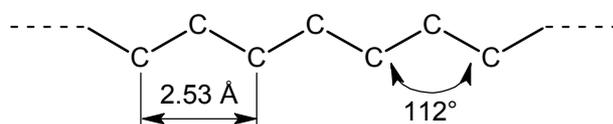
A further, less used, average molecular weight is the z-average molecular mass, which is related to the higher moment of the distribution [2]:

Equation 4-4:
$$M_z = \frac{\sum_i n_i M_i^3}{\sum_i n_i M_i^2}$$

4.1.2 GEOMETRY OF POLYETHYLENE

As an investigation of molecular folding concentrates on the geometry of the molecule on a molecular scale, the geometry of classical polyethylene is important.

The length of a C-C single bond has been determined to be about 1.54Å. Carbon atoms covalently bonded to 4 atoms involves a tetrahedral geometry with bond angles of 109.5°. Yet, due to the non-equivalence of the C-C and C-H bonds, the C-C-C bond angle is expanded to approximately 112°. The repeat distance, i.e. the distance along the chain in the crystal between groups of identical orientation, is 2.53Å. The bond angle and repeat distance can be illustrated schematically as follows:



4.2 EARLY STUDIES ON LONG CHAIN MOLECULES

Various early studies were conducted on long chain molecules and although these studies do not prove or disprove the concept of molecular folding in alkane type molecules, they are the foundation of the development of the understanding of the concept of molecular folding.

4.2.1 EXPERIMENTAL OBSERVATIONS

Various early experimental studies were conducted on both pure compounds as well as mixtures of alkanes and polyethylene.

Early work on pure compounds

One of the earliest works on the conformation of long molecules in crystalline form was conducted by Müller and co-workers. Müller [3] found that fatty acids with 10 or more carbon atoms crystallised into flakes, the molecules being oriented parallel to the surface of the flakes. The

same results were found for long chained esters [4]. In these studies the distance between two consecutive planes was measured and it was found that the continued addition of a $-\text{CH}_2-$ group results in a linear increase in the distance of the plane, suggesting that the molecules are arranged in a constant angle to the plane. Similar results were obtained for hydrocarbons [5].

Dawson [6] studied the crystallisation of nC100 and although no direct mention of the molecular arrangement was made, it was found that nC100 has an orthorhombic structure when crystallised from xylene.

Anderson et al. [7] measured over two hundred step heights in twenty-three different crystals of nC39 and found an average step height of $45 \pm 10\text{\AA}$. These measurements compare well to the molecular length of approximately 48\AA . X-ray diffraction measurements of the crystals showed that the crystals were of orthorhombic form.

From these early studies it can be concluded that long chain n-alkanes molecules are packed approximately parallel to the crystal surface in an orthorhombic structure.

Early work on alkane mixtures and polyethylene

Early work was also conducted on alkane mixtures such as paraffin wax and polyethylene. Bunn [8] conducted an x-ray analysis of very long chain paraffin with more than 130 carbon atoms per molecule and found that the linear chains are arranged parallel to one another. Alfred et al. [9] postulated that a single polyethylene molecule may extend through several crystalline and amorphous layers, the constituents of semi-crystalline polyethylene. Charlesby et al. [10] found that if a thin film of polyethylene is heated up to 40°C above its melting point and re-cooled, its initial orientation appears. They came to the conclusion that this can only be due to the survival in the liquid state of some of the memory of its initial structure, this survival best explained by the retention within the liquid of some part of the crystal structure.

4.2.2 MODELS OF SEMI-CRYSTALLINE POLYETHYLENE

Parallel to experimental observations, models of semi-crystalline polyethylene were developed.

Fringed micelle theory

Once the crystalline nature of many polymers was recognised, it was determined that the crystals were invisibly small, their sizes ranging from tens to a very few hundred Angstrom. In addition, the crystallinity was imperfect. Properties such as density and heat of fusion indicated that only a fraction of the material was crystalline. All these factors can be accounted for by the so called fringed micelle theory [11], as illustrated in Figure 4-1:



Figure 4-1: Fringed micelle theory representation of crystalline polymers [11]

In this theory the crystalline order is restricted to small regions with only portions of chains being part of the lattice. The crystalline regions can be regarded as junctions acting as stiffeners within an otherwise amorphous network of disordered chains. Later studies [11] revealed that this theory cannot account for the spherulitic morphology of bulk-crystallised polymer.

Theory of Flory

In 1949 Flory [12] proposed a theory on the crystalline states, the fusion of polymers and the mixture of polymers with diluents. This theory does not prove or disprove molecular folding but it provides valuable information with regard to understanding the process of crystallisation of polymers. According to the theory the percentage crystallinity and the average dimensions of the crystallites define the state of the unoriented, semi crystalline polymer. Crystallite thickness should be independent of the molecular size and the regularity of the polymer chain; it may be expected to be dependent on the kinetic factors governing crystallite growth and, under ideal considerations, may be relatively large. The crystal plane size will, however, depend on the structural regularity i.e., on the regularity with which the crystallising unit is repeated successively along the chain. For a detailed description, the reader is referred to Flory [12].

4.2.3 SIGNIFICANCE OF EARLY WORK

These early works facilitated later work by developing the basic concepts of crystallisation of alkanes: It was determined that alkanes are aligned parallel to the crystal surface and for low molecular weight species the crystal thickness is roughly equal to the molecular length. In addition, attempts have been made to describe the molecular structure, these models forming the basis of future models.

4.3 MOLECULAR FOLDING IN CRYSTALLINE POLYETHYLENE

Molecular folding of alkanes was first discovered and the concepts developed in crystalline polyethylene and an excessive amount of information is available on molecular folding in crystalline polyethylene. The purpose of this section is not to repeat all information but to present

the evidence of molecular folding, explain the morphology of crystalline polyethylene and to study the factors influencing molecular folding and the models pertaining to molecular folding.

Studies in the field of polyethylene crystallisation fall into two main classes, usually defined by sample type and origin: The first is the spherulite resulting from bulk-crystallised material and the second the single crystal obtained from dilute solution crystallisation.

4.3.1 EVIDENCE OF MOLECULAR FOLDING

4.3.1.1 IN SOLUTION CRYSTALLISED POLYETHYLENE

The discovery of molecular folding in solution crystallised polyethylene occurred in 1957 and is generally attributed to Keller and O'Conner [13], [14], yet the work of Till [15] and Fisher [16] played an important role.

In 1957 Till [15] investigated the effect of the long chain and a polydisperse nature of low molecular weight polyethylene during the crystallisation of polymers. From his study it is seen that polymers can crystallise in single crystals in a similar form to that shown by simple organic molecules. The crystals formed had a crystal thickness of 100Å.

Fischer [16] studied the crystallisation of linear polyethylene from dilute xylene and, as in the work of Till [15], single crystal sheets were formed. Fisher found that the molecules are orientated with the chain axes perpendicular to the face of the crystal. The recognition of single crystals immediately raised the problem of how the long chain crystals can be accommodated within the crystal entity. Keller [13] was the first to mention molecular folding:

"The observed orientation and the minimum thickness of the crystals leads to the inescapable conclusion that the molecules must bend sharply back on themselves forming a regular folded configuration."

This statement was justified by experimental results where the crystal thickness had an average of 100Å, varying between 60 and 150Å while the 83% of the polymer has a chain length greater than 200Å and 29% greater than 7000Å. Keller also suggested that the bending back must be sharp as the orientation of the molecules is perfect.

So far the argument of molecular folding is irrefutable and from the beginning the model was more specific: Molecular folding is considered a regular structural feature.

4.3.1.2 IN BULK CRYSTALLISED POLYETHYLENE

The first study considering the morphology and molecular orientation of bulk-crystallised polyethylene was conducted by Keller and co-workers in 1955 [17], [18], [19]. The existence of large X-ray spacings of 80 – 200Å was discovered, these large spacings being attributed to the alternation of amorphous and crystalline regions.

In 1956 Mandelkern [20] found that the size of the crystallites in polymers is much smaller than the extended length of a typical polymer molecule. It is suggested that only a portion of the molecule participates in a given crystallite, the remaining portion of the molecule being either in the amorphous region or in another crystallite. This structure suggested is illustrated in Figure 4-2, the straight-line parts illustrating the crystalline part, the remainder the amorphous part:

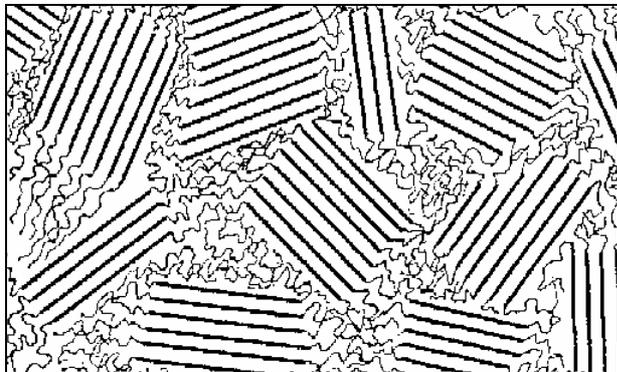


Figure 4-2: Schematic representation of a semi-crystalline polymer [20]

At the Discussions of the Faraday Society in 1958 the topic of molecular folding in bulk-crystallised polyethylene arose. Westrik et al. [21] compared the crystalline structure obtained from the melt with single crystals from solution crystallisation and stated:

“It is very tempting to suppose that these layers have similar structure to the lozenge shaped single crystals which can be obtained from dilute polyethylene solutions. This would mean that also polyethylene chains crystallised from melt must have a folded configuration.”

Keller and O’Conner’s comments, also at this meeting, included [22]:

“Low angle x-ray studies have revealed spacings of 100 – 200Å in most polymers during the last 14 years, and these spacings have never been fully explained. It is very tempting to connect this phenomenon with chain folding. We think there must be some connection between the large spacings in melt crystallised specimens and those found in single crystals prepared from solution where it is undoubtedly due to chain folding ... it is to be expected that crystallisation from melt would lead to a less regular configuration owing to the closer entanglement of the chains, which is in agreement with observation ...”

In 1961 Mandelkern [23] conducted low angle x-ray diffraction studies on crystallised linear polyethylene. He found it extremely difficult to reconcile the level of crystallinity and the observed first order reflections with the concept that the crystallites are composed of pleated chains unless the highly improbable situation of chain ends meeting in juxtaposition within the crystallite occurs. Mandelkern thus found it extremely difficult to conclude that in bulk systems the crystallites are composed of pleated polymer chains. However, these considerations do not preclude the possibility of back-looping or partial folding of an individual chain so that different crystalline sequences from the same molecule could occur in non-adjointing positions within a given crystal.

Unlike solution-crystallised polyethylene, conflicting reports as to the presence of molecular folding in bulk crystallised polyethylene exists. It is expected that the answer to this question can be found in a detailed analysis of the morphology of crystalline polyethylene.

4.3.2 MORPHOLOGY OF CRYSTALLINE POLYETHYLENE

4.3.2.1 MORPHOLOGY OF SOLUTION CRYSTALLISED POLYETHYLENE

Since the discovery of molecular folding, the morphology of solution-crystallised polyethylene has become clearer: Keller et al. [13], [14] found that the thinnest parts of solution-crystallised polyethylene were about 100Å thick, thickening taking place by stepwise addition of similar layers. The molecular chains were found to be perpendicular to the surface of the plates, the thickness of the first layer and that of successive steps thus corresponding to the distance between successive folds along the molecule.

Various models for the loop structure have been proposed. Initially crystallised cyclo-alkanes with forced loop structures were used to examine the loop structure of polyethylene [24], [25] but although the analysis of cyclo-alkanes added to the understanding of the loop structure, a direct superposition was fruitless: Cyclic alkanes require a reversal in the chain direction with a minimum number of closure atoms, whereas for long chain polymer molecules more closure atoms are involved in the directional reversal. Initially it was thought that molecules may pack in a random re-entry or switchboard type model Figure 4-3 (a) or in an adjacent re-entry fold model Figure 4-3 (b):

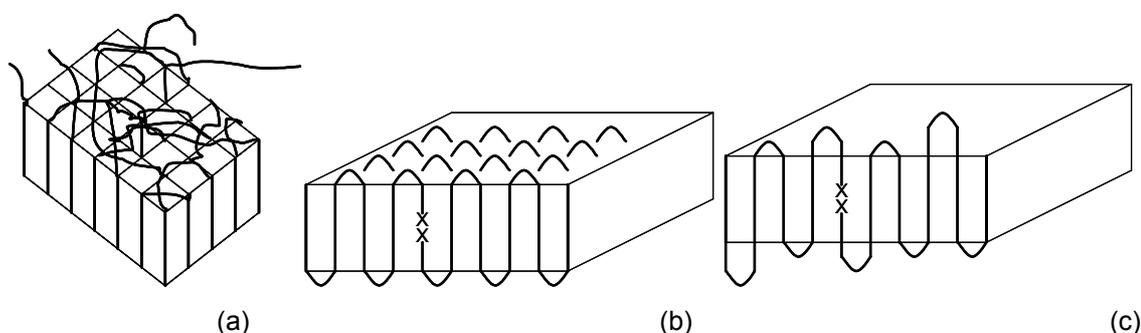


Figure 4-3: Models for polymer crystals formed in dilute solution [26]: (a) Random re-entry or 'switchboard' fold model; (b) Adjacent re-entry fold model with smooth chain folded surface; (c) Adjacent re-entry fold model with rough chain folded surface

In the adjacent re-entry fold model (Figure 4-3 (b)), each molecule crystallises to the maximum possible extent and its crystallisation is virtually complete. In the other extreme (Figure 4-3 (a)), sequences are connected more or less at random in "switchboard" fashion. Intermediate situations can be envisaged such as one in which sequences from a given molecule occur within the same layer of the crystal but with varying loop length (Figure 4-3 (c)).

Flory [27] proposed an alternative theory regarding the shape of the fold. He suggested that the regularity of arrangement of chains within the crystal cannot be dissipated abruptly at the crystal interfaces. Consider an infinite interface illustrated in Figure 4-4:

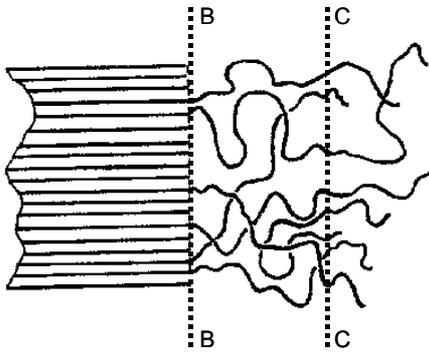


Figure 4-4: The interfacial zone transverse to the c-axis. In the interest of clarity only a few of the chain trajectories emanating from crystal face BB are shown [27]

Chains emerging from the crystal pass through the plane BB into the adjoining region. No more than half the flux of chains in plane BB can be accommodated in the plane CC and the flux of chains must somehow be dissipated. An obvious possibility for dissipation is the return of a considerable fraction of the chain trajectories to the crystal surface with re-entry into crystals. However, it does not follow that the polymer chain needs to be regularly folded or pleated and chains that re-enter the same crystallite need not do so immediately, but may enjoy a brief sortie into the amorphous region.

The concept of the disordered fold surface conflicts with the crystallographic treatment of the chain folds. However, the existence of disorder has a special appeal as it brings back the random element, traditionally believed to be intrinsic of true polymers. One thus needs to have disordered amorphous material along the basal plane of the lamellae where some kind of crystallographic regularity occurs along the fold surface.

4.3.2.2 MORPHOLOGY OF BULK CRYSTALLISED POLYETHYLENE

Information on melt-crystallised polymers is extensive but even more controversial and less precise than solution crystallised material. The major problem in the examination of the fine structure is the inability of obtaining representative interior structure elements [28], [11]. A bulk crystalline polymer consists essentially of spherulites, these being the largest observable structural units. A typical spherulite can be seen in Figure 4-5:

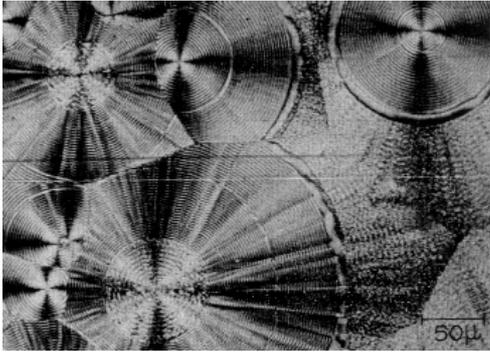


Figure 4-5: Banded spherulite of poly(trimethylene glutarate) grown between two glass surfaces as seen between crossed polaroids [11]

Figure 4-5 illustrates rather well developed examples of spherulitic morphology. Figure 4-6 suggests a method for spherulite formation:

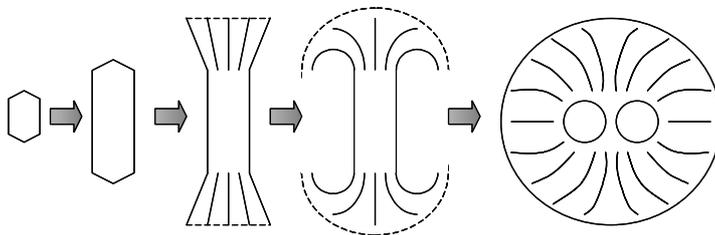


Figure 4-6: Diagrammatic representation of the formation of spherulites [29]

Initially fibrous or needle like crystals are formed which develop lengthwise by a branching or fanning mechanism. The spherical shape is gradually approached through the formation of sheaves. The long axis of the molecules are arranged perpendicular to the radii of the spherulites, however, this orientation is rather imperfect. A replica of a typical initial sheaf formed from nylon 6 is shown in Figure 4-7 (a) and lamellar crystals in a spherulite are shown in Figure 4-7 (b):

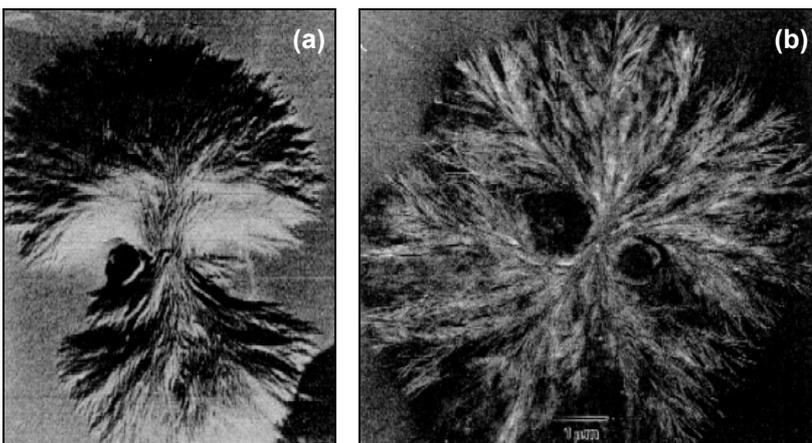


Figure 4-7: Photographs of the formation of spherulites (a) Replica of a typical initial sheaf of nylon [11] (b) Lamellar crystals in a spherulite [30]

Initially it was assumed that the nature of the molecular re-entry process in the crystallites of the spherulite is similar to that of the re-entry occurring in single crystals. However, this model is inconsistent with neutron scattering evidence for bulk-crystallised polyethylene and an alternative model is proposed namely the interzonal model, as illustrated in Figure 4-8:

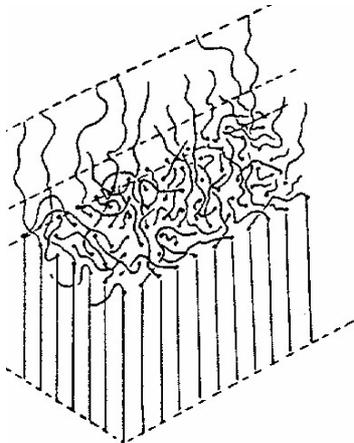


Figure 4-8: The interzonal model of molecular re-entry [30]

When the lamellar are stacked, the possibility of chains passing from one lamellar to the next pertains. Nevertheless, they cannot all pass through and remain straight; otherwise the identity of the lamellae of the particular thickness would be lost, neither can all tie molecules become random as there is no room. Thus a certain number of chains must fold back on themselves into the same layer. Such a model is illustrated schematically in Figure 4-9:

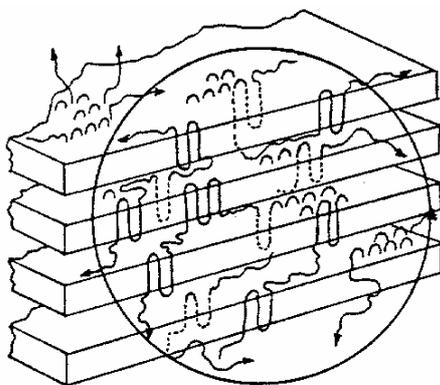


Figure 4-9: The synoptic model of molecular re-entry. The circle represents the radius of gyration of a typical high-molecular weight polymer. [30]

This model combines the features of adjacent and non-adjacent re-entry folds.

4.3.3 FACTORS INFLUENCING MOLECULAR FOLDING

In order to determine the forces behind molecular folding, an investigation needs to be conducted as to the factors influencing the formation of the fold and the fold period.

4.3.3.1 IN SOLUTION CRYSTALLISED POLYETHYLENE

Dependence on temperature

Kawai et al. [31] investigated the effect of the solvent by comparing the fold length produced by xylene, octane and hexadecane a common temperature range. The curves of the fold length as a function of the crystallisation temperature are approximately parallel. In order to generalise the data, the data is plotted as a function of supercooling, where the supercooling is calculated from the infinite fold length dissolution temperature. The infinite fold length dissolution temperature for the three solvents shown is given in Table 4-1 while the plot of the fold length as a function of supercooling is shown in Figure 4-10:

Table 4-1: Polyethylene infinite fold length dissolution temperatures [32]

Solvent	Infinite fold length dissolution temperature
Xylene	110.5 ± 1.0
Octane	120.2 ± 1.4
Hexadecane	128.1 ± 1.6

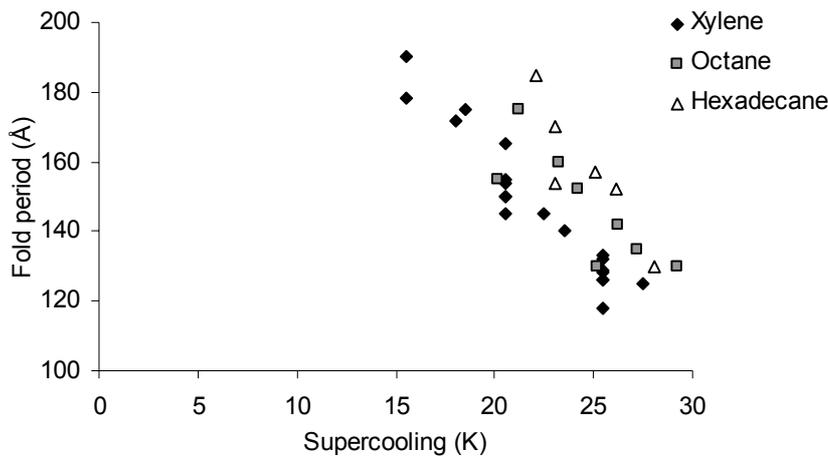


Figure 4-10: Plot of the fold period as a function of supercooling for various solvents

The fold period is thus a function of supercooling rather than of absolute temperature.

Dependence of concentration

Bassett [33] found the fold period to be indistinguishable between preparations crystallised at the same temperature but from various different concentrations. Although the fold period is independent of the solution concentration, the morphology is not. As the concentration is increased, the crystals form gradually more and more complex aggregates. At very low crystallisation temperatures and high concentrations, the crystals tend to simulate the early stages of spherulitic growth [33].

Dependence of molecular weight

Bassett [33] and Mandelkern [34] found the fold period to be independent on the molecular weight of the polymer used. As in the case of the concentration of the solution, the molecular weight does not affect the fold period but it does influence the morphology: Lower molecular weight material gives a smoother face development.

Dependence of other crystals of other fold period

With the aid of seeding experiments Bassett [33] determined that the presence of other crystals with a different fold length does not affect the fold length of the fold in the newly crystallised material.

4.3.3.2 IN BULK CRYSTALLISED POLYETHYLENE

Effect of time

The crystallisation time has an effect on the crystallite thickness, generally the crystallite thickening with time [35], [36], [37]. A faster rate was observed for higher crystallisation temperatures while the process was retarded for higher molecular weights. McCready et al. [36] concluded that competition exists between the thickening of existing crystals and the formation of new crystallites. At least a portion of the crystallite thickening occurs by the growth of some crystallites, accompanied by dissolution of others.

Effect of temperature

When the fold period is plotted as a function of temperature a similar shape curve as that found in solution crystallised polyethylene is found for bulk-crystallised polyethylene:

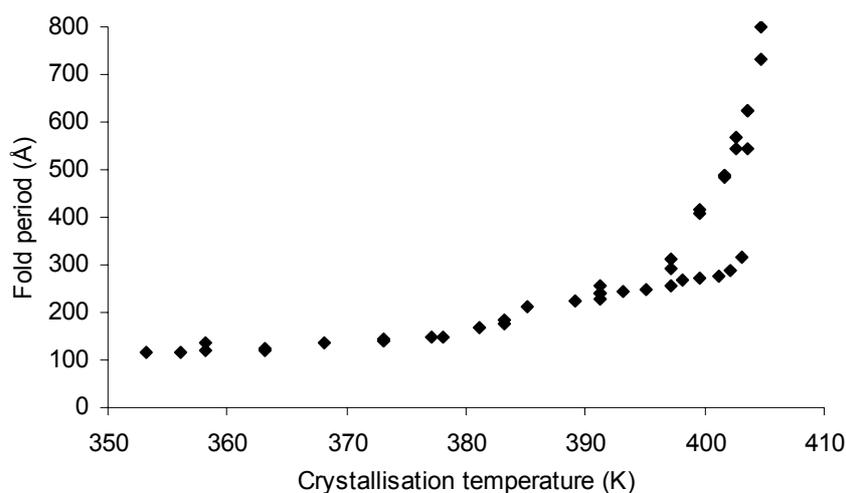


Figure 4-11: Plot of the fold period as a function of crystallisation temperature [36], [35], [38], [39], [40]

The data shown in Figure 4-11 is data for all crystallisation times. The scatter observed, especially at temperatures above 390K can be attributed to the difference in crystallisation time, the data in the low branch of the plot being initial crystallisation data, the rest after some crystallisation time. It is clear that the fold period is dependent on some type of temperature relationship. However, from the data generated here it is not clear if in bulk crystallisation the fold period is a function of absolute temperature or supercooling, as all the data is generated from a medium with the same extended chain melting/dissolution temperature.

Effect of molecular weight

Martinez-Salazar [40] found that, as in the case for solution-crystallised polyethylene, the crystal thickness is essentially independent of the molecular weight.

4.3.4 THEORETICAL MODELS

Upon accepting the presence of molecular folding one needs to ask the question as to why it occurs. It did not take very long following the discovery of molecular folding in normal alkanes before it was attempted to explain why molecular folding occurs. At the Discussion of the Faraday Society in 1958 various people commented on possible reasons for molecular folding:

Frank stated [41]: "... Before we can attempt to understand it [chain folding] in quantitative detail, we have to find something which can cause it in principle. I do not yet know what this is ... question to ask is whether it is a kinetically determined structure or whether it is conceivable that crystals with folded molecules can be a state of lowest free energy for the material ..."

Keller and O'Conner commented on the requirements of a model [42]: "... any explanation of the regular folding will have to be consistent with the dependence on the fold period on the temperature of crystallisation ..."

4.3.4.1 FOR SOLUTION CRYSTALLISED POLYETHYLENE

There are two main types of theories for solution-crystallised polyethylene:

- According to the equilibrium approach [43], the state of maximum stability in a polymer crystal is that of the folded configuration.
- According to kinetic theories [44], [45], [46] the structure of the crystals will have a folded configuration with a narrow distribution of fold length, to favour the rate with which crystallisation can take place.

The question exists as to whether the periodicity of the crystal thickness is caused by a kinetic or thermodynamic cause. Each of these theories will now be evaluated.

Equilibrium theory (thermodynamic driving force)

The starting point of this theory [43] is the fact that linear polymers undergo molecular folding while low molecular weight compounds do not. Molecular folding must thus be based on a property that is not common to low molecular weight crystals.

In contrast to the low molecular weight compound lattice, lattice defects in high polymers do not heal easily with increasing distance. In high polymer lattice defects may be caused by various phenomena such as branchings, hydrogen bonds wrongly fitted and distorted or entangled crystals. In a crystal the long-range order in the chain direction breaks down by introduction these defects and thus the crystal is no longer stable after it has exceeded a certain length.

The model proposed here is based on the fact that the surface energy contribution favours infinite thickness while the smearing out of defects favours thin crystals. The resultant thickness of the crystal is thus a balance of these two opposing energy considerations.

In spite of good qualitative agreement with experimental data, the model is far from being satisfactory: Folding is not a direct consequence of the theory; it is only one possible way that the lattice continuity along the chain can be interrupted. The theory certainly accounts for a dominant layer thickness and for the variation of this thickness with crystallisation temperature. However, it does not account for the observed dependence of the fold length on supercooling rather than on the absolute temperature of crystallisation.

Kinetic theory (kinetic driving force)

According to kinetic theories the observed chain folded crystals correspond to the structure with maximum crystallisation rate. In general, crystallisation occurs via primary nucleation followed by growth. In polymers, primary nucleation could take place intramolecularly by folding up for the same molecule. Further growth occurs with the molecules folding up along the existing crystal faces. It is this growth process that determines the fold length in the crystals formed [44]. From the analysis of Basett [33] where it is proven that the presence of other crystals do not affect the fold length, it can be concluded that it is essentially secondary nucleation along the existing face that controls the fold length. This is the starting point of all kinetic based theories.

Consider an existing crystal substrate and now the deposition of a new chain of infinite length. The deposition of a new chain segment results in a protrusion, the protrusion giving rise to two new side surfaces. The reduction of the free energy due to the attachment of a chain segment is insufficient to balance the free-energy gain due to the corresponding new surface. Thus the free energy of the system will increase as the chain keeps depositing along a straight line. Should a chain happen to bend back on itself, after a large free-energy increase associated with the bend, the deposition will proceed without the creation of a new surface. There will thus be a drop in free energy as long as the chain segment covers up the side of the first deposited segment. This theory assumes that the supercooling is nearly proportional to the distance from the melting point.

Various mathematical models have been proposed by Price [47], Lauritzen et al. [44], Frank et al. [46] and Lauritzen et al. [48] and for detailed information the reader is referred to these sources.

Evaluation of theories

In the kinetic theory the fold length depends on the supercooling while in the equilibrium theory it is a function of the absolute temperature and thus it may appear to be a simple matter to decide between them. However, the true melting point of the crystal with an infinite fold length in the solvent is uncertain.

Holland et al. [49] found that the kinetic theory cannot account for the observed variation on the crystal thickness with temperature unless it is assumed that crystal thickness exceeds the critical nucleus dimension by an amount that varies with temperature. When considering the thermodynamic theory it was found that the temperature variation to be expected is not sufficiently well defined by Peterlin et al. [43] to be confirmed or denied by the work of Holland et al. [49].

Neither theory can fully explain solution crystallisation of polyethylene, yet both have their merits and until a theory is proposed to improve these two proposals, combined they remain the best explanation of molecular folding available.

4.3.4.2 FOR BULK CRYSTALLISED POLYETHYLENE

Spherulitic formation is not unique to polymers, yet the main difference lies in the formation of the primary nucleus.

The free energy of formation of a nucleus of critical size for a linear homopolymer was studied [50] and the chain molecules are assumed to be normal to the radius because this is the most reasonable manner for a bundle-like nucleus to form spontaneously from an array of linear molecules.

The rapid growth of the primary nucleus in the radial direction is almost certainly nucleation controlled. Its rapidity suggests that the secondary growth nucleus is comparatively easy to form in the temperature range of interest here. During early growth more or less parallel bundles of fibres are observed to fan out gradually like wheat sheaves. Later these sheaves assume a spherical or cylindrical shape at some finite, though frequently small, size. Radial growth then continues uniformly in all directions until spherulites impinge upon one another and form polyhedral inter-spherulite boundaries.

4.3.5 LINK BETWEEN SOLUTION AND BULK CRYSTALLISED POLYETHYLENE

The link between solution and bulk crystallised polyethylene is virtually as old as the technology itself. At the Discussions of the Faraday Society in 1958 Keller and O'Conner made the following comment [22]:

“... there are indications that crystallisation from the melt and that from solution may not proceed along entirely different lines ... we think there must be some connection between the large spacings in melt crystallised specimens and those found in single crystals prepared from solution where it is undoubtedly due to chain folding ... “

Barham et al. [39] attempted to link the behaviour of solution grown and bulk crystallised polyethylene by constructing the full relationship between the primary fold length and the supercooling covering a wide range of crystallisation temperatures. Comparison of bulk-crystallised polyethylene with crystallisation from solution revealed that the primary fold length against supercooling curves are completely superimposable thus removing the gap between melt and solution crystallisation:

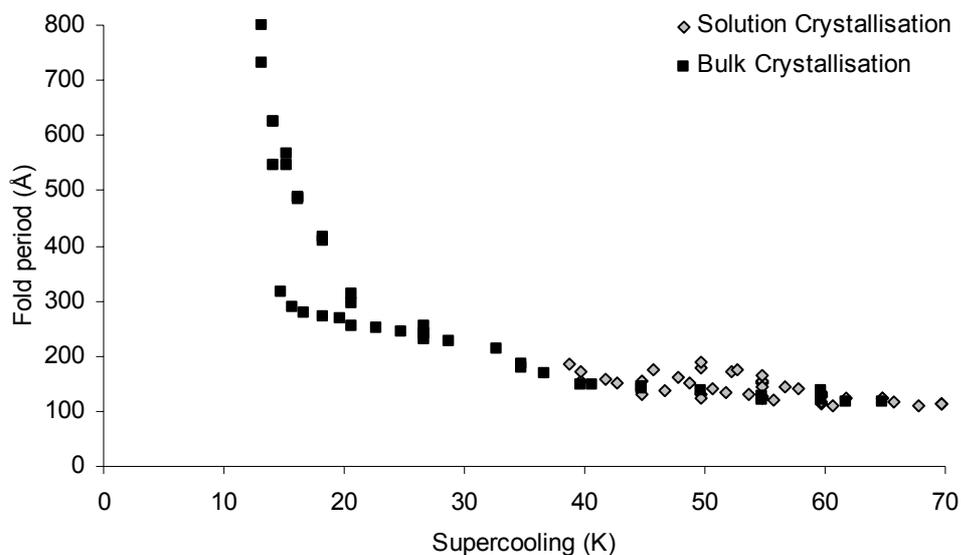


Figure 4-12: Plot of comparison of fold period in bulk crystallised polyethylene with solution-crystallised polyethylene as a function of supercooling (Melting temperature = 413.4K – See section 4.6)

4.3.6 MOLECULAR FOLDING IN LOW MOLECULAR WEIGHT POLYETHYLENE

Although most investigations have shown that the crystallisation features of polyethylene are independent of molecular weight, deviations may start to occur in low molecular weight polyethylene when the molecular length starts to approach the fold length.

Kloos et al. [51] and Leung et al. [52] studied the fold period for various narrow range polyethylene fractions. The results are summarised in Figure 4-13 and Table 4-2:

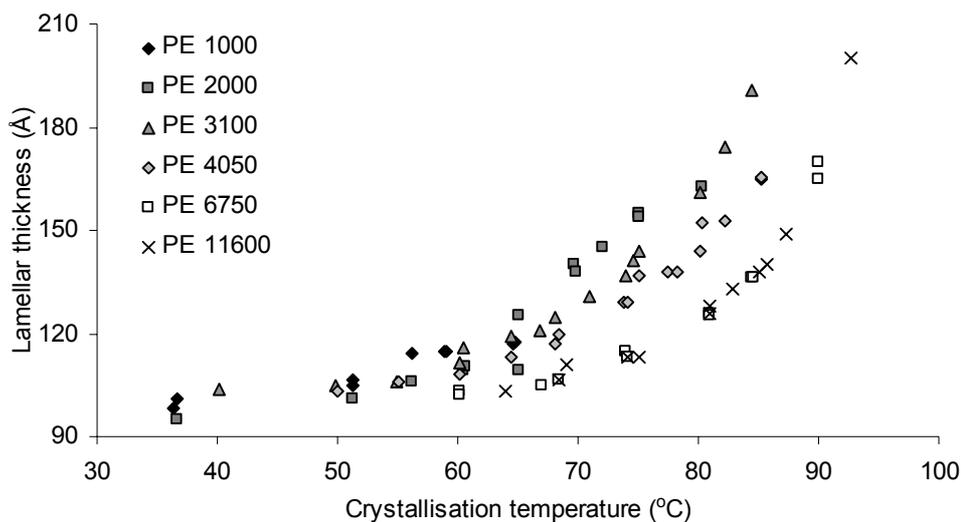


Figure 4-13: Plot of the lamellar thickness as a function of the crystallisation temperature for various fractions of polyethylene crystallised from a dilute xylene solution [52]

Table 4-2: Effect of molecular weight and crystallisation temperature on the fold length for narrow range low molecular weight normal alkanes [51]

Sample characteristics	Crystallisation temperature (°C)	Fold period (Å)
$M_n = 1055$ $M_w = 1142$	25	97 (0.75 extended chain)
	45	125 (extended chain)
	55	125 (extended chain)
	60	125 (extended chain)
$M_n = 1586$ $M_w = 1756$	25	85 (0.55 extended chain)
	70	153 (extended chain)
$M_n = 2859$ $M_w = 3140$	25	81 (0.29 extended chain)
	60	109 (0.39 extended chain)
	70	125 (0.45 extended chain)
	75	140 (0.50 extended chain)

Although the data in Figure 4-13 is quite scattered, generally it can be seen that up to a certain value, the lamellar thickness decreases with increasing molecular weight for fractions crystallised at the same temperature. Above a certain molecular weight, the molecular weight seems to have little, if any, impact on the lamellar thickness. Leung et al. [52] postulated that this value is approximately 5000 g/mol. The data measured by Kloos [51] verifies the trends found by Leung et al..

4.3.7 EFFECT OF PRESSURE

All the data discussed above has been generated at atmospheric pressure. As this project aims to use moderate pressures, the effect of pressure is significant in any investigation regarding this project.

A study [53] investigating the effect of pressure up to 6000 barA on solution crystallised polyethylene found that very little, if any variation occurs in the crystal thickness with pressure for solution crystallised polyethylene. The relationship seems to be constant yet may show a slight increase with increasing pressure.

The effect of pressure on bulk-crystallised polyethylene shows that the two different types of crystals are formed, depending on the pressure and temperature [54], [55].

- For pressures below 2000 barA: The main portion of the polymer crystallised in the chain folded regime, the crystal thickness increasing from about 400 to 600Å.
- For pressures above 3500 barA: The character of the polymer was totally different from that at low pressures. Almost perfect extended chains were present, all the samples were extremely brittle and high crystallinity ones could easily be powdered.
- Intermediate region: 2000 – 3500 barA: In this region a mixed crystallisation took place.

The reason for extended chain type crystals forming under pressure is believed to lie in the increased rate of isothermal thickening under these conditions [11]. Accordingly, chain folded crystals would form in the first usual manner. However, at much higher crystallisation temperatures that can be achieved by virtue of melting point depression due to pressure increase, isothermal thickening that follows would proceed much faster and accordingly lead to much greater chain extensions.

4.4 MOLECULAR FOLDING IN CRYSTALLINE LONG CHAIN NORMAL ALKANES

From the analysis of the crystallisation of polyethylene it can be seen that molecular folding in high molecular weight normal alkanes is possible. The purpose of this section is to investigate molecular folding in pure normal alkanes and to estimate the point of onset of molecular folding.

4.4.1 MORPHOLOGY OF CRYSTALLISED NORMAL ALKANE

Linear polyethylene has an orthorhombic crystalline form at the melting point yet many of the lower alkane waxes have a hexagonal structure at the melting point. From the literature it is not entirely clear exactly when the transition occurs, yet it occurs somewhere between the hexagonal nC29 [56] and the orthorhombic nC44 [57], [58]. Although, for this analysis it is not of significant value if a crystal is hexagonal or orthorhombic, it is essential that similar crystals should be

investigated in a similar manner and thus the region with a hexagonal structure should be avoided.

In general the morphology of alkanes is similar to that of polyethylene. Electron diffraction studies show that the chains are substantially perpendicular within the crystals in all cases [59].

In the case of bulk crystallisation, the morphology depends on the presence of molecular folding. Bassett et al. [60], [61] investigated the morphology of melt crystallised long chain normal alkanes and found that spherulites occur only when the molecules in the crystals adopt a folded configuration. When the lamellae contain molecules that are in the extended form, the resulting textures are quite different. There is thus a clear difference in organisation between chain-folded, spherulitic textures and the extended chain morphologies.

4.4.2 EXPERIMENTAL OBSERVATIONS

From the results of Lee et al. [62] there seems to exist a critical chain length above which chain folding occurs in crystalline linear hydrocarbons. Data for solution and bulk crystallised alkanes is shown in Figure 4-14:

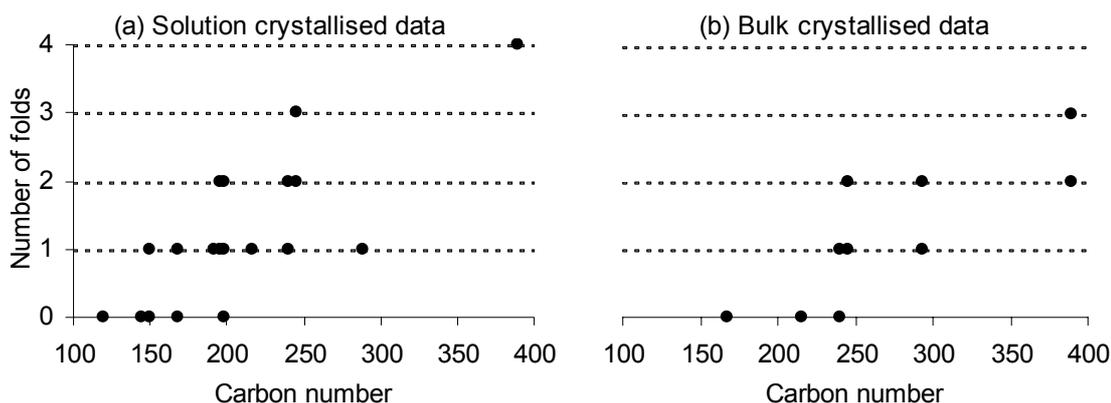


Figure 4-14: Data for number of folds per molecule for (a) Solution crystallisation [62], [59], [63], [64], [65], [66] and (b) Bulk crystallisation [62], [63], [64]

From Figure 4-14 it is concluded that chain folding can be found in all n-alkanes with more than 150 carbon atoms and chains fold in integral reciprocals of the extended chain length, within a limit of 5 % in most cases. Although not shown in Figure 4-14 the greater the supercooling, the larger the number of folds per molecule, a feature that parallels the situation in crystalline polymers.

There is thus a tendency for chain-folded crystallisation to occur in linear molecules beyond a certain chain length, this length being less than 150 carbon atoms. The tendency increases with increasing chain length. Folded chain crystals of 150 could be grown only at large supercoolings. In contrast, the long paraffins, such as nC390, tended to fold so readily that special measures are required to obtain the extended form.

The tendency of pure alkanes to fold in integral reciprocals of the extended chain length indicates the exclusion of the chain ends from the crystal interior. Such end group exclusion modifies the lamellar thickness versus supercooling relation by making it a step function for any given paraffin instead of the continual function observed in polyethylene. It is unlikely that any appreciable portion of the chain is anywhere but in the straight stem, with only a small residual set aside for an adjacent re-entry fold when a fold is present.

The number of folds also depends on the concentration. For example, Alamo et al. [67] found that for nC168 once folded molecules occurred below about 77°C at high concentrations while for low concentrations extended conformation crystals were found as low as 68°C. Thus for solution crystallised alkanes, the transition from once folded to twice folded configurations (and in the same manner for all other transitions) does not occur at a single temperature but over a temperature range. However, for bulk-crystallised alkanes a single transition temperature occurs, the temperature being dependent on the molecular weight, as shown in Figure 4-15:

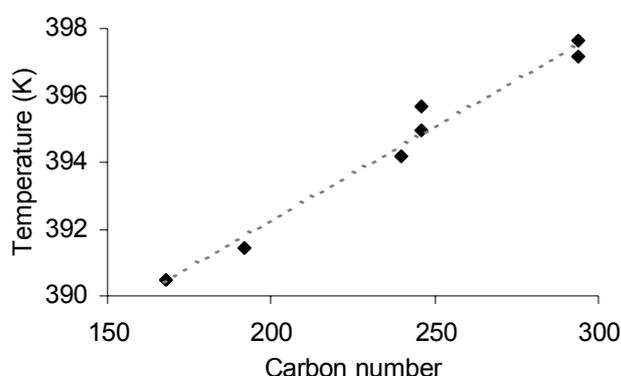


Figure 4-15: Plot of the temperature of transition from extended chain conformation to once folded conformation as a function of carbon number for bulk crystallised alkanes [64], [68], [69]

It is expected that the transition from once-folded to twice-folded conformation will follow a similar pattern, only at a lower temperature.

4.4.3 THEORETICAL MODELS

Hoffman [70] found that flux based nucleation theory can deal with the major aspects of extended chain crystallisation and the extended chain to once folded transition in specific systems in a straightforward manner. The onset of once folding for molecules of a fixed length occurs when the kinetically determined surface nucleus length is close to half the length of the molecules. The value of the kinetically determined surface nucleus length depends on the undercooling and the effective fold surface free energy.

For a complete understanding of when molecular folding occur, Alamo et al. [64] suggested that both the thickening or the thinning that occurs during the isothermal crystallisation as well as the isothermal transformation with time from one discrete state to another has to be explained. To

simultaneously explain these two phenomena a free energy diagram of the following shape is postulated:

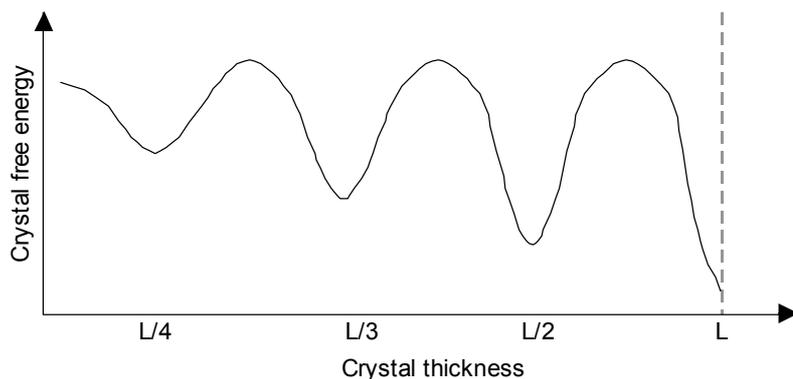


Figure 4-16: Schematic representation of the crystal free energy versus crystal thickness. L indicates the thickness of the extended chain crystal [64]

The free energy function of the crystallite has a set of minima energy wells. The lowest energy well corresponds to the extended chain crystallites. The progressively higher energy wells correspond to the folded chain crystallites with thicknesses approximately half, one third etc of the extended molecular length. During isothermal crystallisation the critical nucleus dimension in the chain direction will determine the initial crystallite thickness and thus its position relative to a given well. After initial crystallisation the chains will seek the nearest local free energy minima without having to overcome the barrier energy. Figure 4-16 thus explains in a straightforward manner, the thinning or thickening that is observed during the initial isothermal crystallisation.

4.4.4 BINARY SOLUTIONS OF NORMAL ALKANES

The phase behaviour of solid binary alkane mixtures is complicated by the many different phases present. The purpose of this investigation is not to describe the phase diagram in detail but to briefly investigate the behaviour just below the melting temperature and to determine if, when and where molecular folding occurs.

Hosier and co-workers [71], [72], [73] studied the crystallisation behaviour of dilute solutions of various compounds in nC122, nC162 and nC246. Blend behaviour depends on the guest molecule, whether it is shorter or longer than the host. When studying the morphology of a longer guest molecule, it is seen that the longer molecules co-crystallise with the host forming permanent cilia with increased splaying angles and enhanced spherulitic growth. On the other hand, for solutions with shorter guest molecules, segregation of the shorter molecule occurs thus disfavours spherulitic growth.

When considering the effect of chain folding, the effect of nC122 in a host of nC246 and nC246 in a host of nC122 is investigated. Four possible methods of crystallisation were found:

- Co-crystallisation of chain folded nC246 in extended nC122

- Co-crystallisation of extended nC122 in chain folded nC246
- Chain folded growth of nC246 with segregation of nC122
- Extended growth of nC246 with segregation of nC122

The method of crystallisation depends on mainly on the crystallisation temperature but to a lesser extent also on the concentration of the guest. Generally co-crystallisation occurs at lower crystallisation temperatures while segregation occurs at higher temperatures (generally above the crystallisation temperature of nC122).

From the analysis of binary alkane crystallisation it can be seen that impurities can significantly influence the molecular conformation of alkanes in the crystalline phase.

4.5 LINK BETWEEN CRYSTALLINE STATES OF PURE N-ALKANES AND POLYETHYLENE

There is no clear-cut boundary between polymer chemistry and the rest of chemistry. As a rough guide molecules with either a molar mass of more than 1000 g/mol or at least 100 repeating units are regarded as polymers. However, due to their similarity in chemical structure there must be some link between the crystalline state of pure normal alkanes and polyethylene. Yet due to the polydispersity present in polyethylene and absent in pure alkanes there must also be some differences.

4.5.1 MORPHOLOGY

When studying the morphology of melt-crystallised samples it is seen that, providing the molecules of the pure alkane fold, the morphological structure of the pure alkane and that of polyethylene is the same. In the absence of molecular folding in melt crystallised pure alkane, a significant difference in the morphology is noted. Similar morphology occurs in solution crystallised alkanes and polyethylene irrespective of the presence of molecular folding.

4.5.2 MOLECULAR FOLDING

The main difference between crystals of polyethylene and pure alkanes is the occurrence of discrete crystal thickness close to integral fractions of the extended chain length in pure alkanes compared to a continuous change in crystal thickness with crystallisation temperature for polyethylene crystals. Thus inhomogeneity in a sample results in the crystal thickness as a function of temperature being a continuous function.

When the data in Figure 4-12 is plotted together with the extended chain length of alkanes as a function of the highest supercooling (based on the infinite length extended chain melting point) where extended chains can occur (see Figure 4-15), the data fits well on one curve:

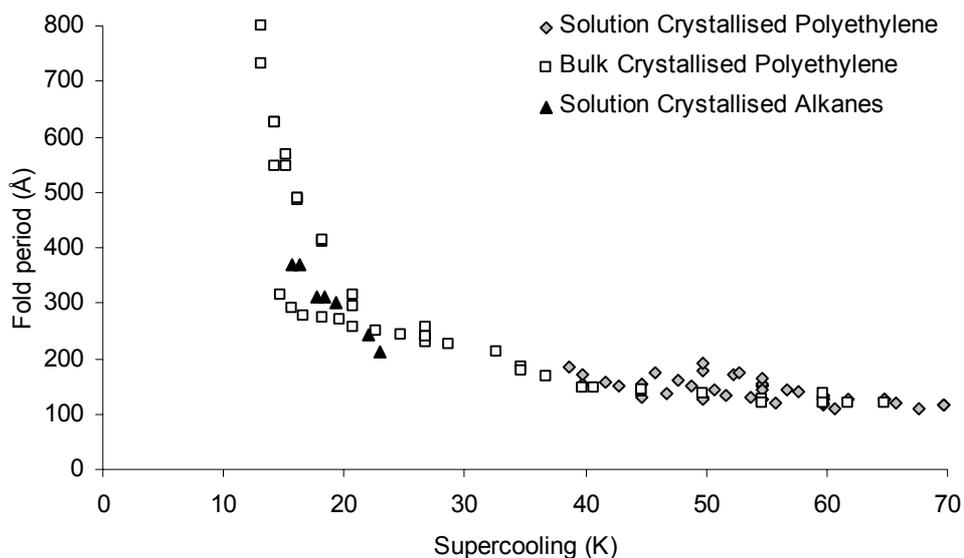


Figure 4-17: Plot of fold period as a function of supercooling for bulk and solution crystallised polyethylene and maximum supercooling as a function of molecular length for alkanes

Thus, despite the difference due to polydispersity, there seems to be a strong link between the fold period of the pure alkane and that of polyethylene.

4.6 MELTING TEMPERATURE OF LONG CHAIN ALKANES AND POLYETHYLENE

Following the above study a brief investigation regarding the melting point of long chain alkanes and polyethylene will be conducted. The melting point of alkanes is required in some of the investigations conducted above as well as in subsequent chapters and as molecular folding has a significant effect on the melting point, its inclusion at this point is justified.

No clear-cut relations presently exist for the melting point of pure alkanes and polyethylene as a function of molecular weight. Various methods have been found in the literature, yet these methods, although consistent for lower alkanes, show significant variations for long chain values. In this section it is attempted to obtain a mathematical expression of the melting point as a function of carbon number for both extended and folded crystals.

4.6.1 MEASURED DATA

4.6.1.1 RELATIONSHIP BETWEEN MELTING TEMPERATURE AND CARBON NUMBER

In a homologous series there must exist a relationship between the number of carbon atoms and the physical properties. The relationship between the melting temperature and the carbon number for normal alkanes is shown in Figure 4-18:

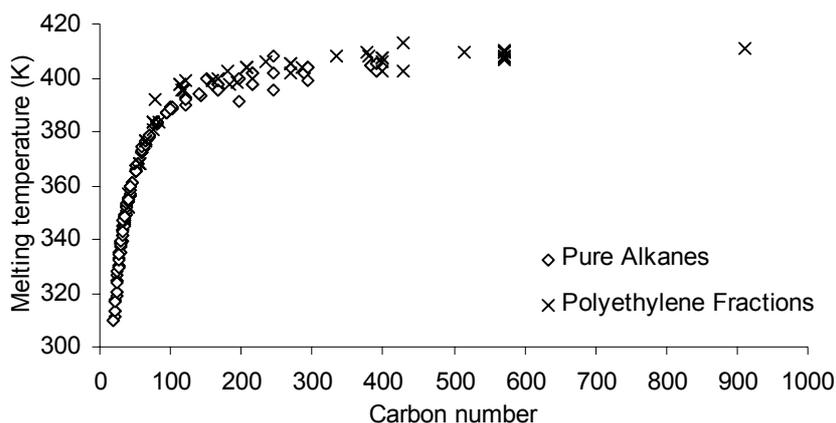


Figure 4-18: Plot of melting temperature of pure alkanes [57], [58], [63], [74], [75], [76], [77], [78], [79], [80] and polyethylene [77], [80], [81], [82], [83], [84] as a function of temperature

At high molecular weight the data converges and there exists melting range. There seems to be a non-linear relationship between the carbon number and the melting temperature. The melting points seem well defined with little variation for the lower carbon numbers, yet for higher carbon numbers considerable scatter seems to be present. This scatter can be attributed to the inclusion of data of both extended and folded samples, the folded samples resulting in lower melting points.

4.6.1.2 DATA SET FOR FITTING TO MODEL

When selecting data to be used to fit a model, it is important that the data be consistent. As seen in Figure 4-18, the presence of molecular folding affects the melting point. Only extended chain data will be used. Melting points of samples containing molecular folding will be treated separately (See section 4.6.3).

Normal alkanes are found in 4 different crystalline forms: Hexagonal, orthorhombic, monoclinic and triclinic. It is well known that polyethylene and the higher alkane members melt from the orthorhombic form, with the lower members, combinations of the remaining forms. As the melting point is dependent on the crystal form, only members of the homologous series melting from the orthorhombic form will be considered. The exact point above which members only crystallise in the orthorhombic form is not clear: Gray et al. [75] suggest above 36 carbon atoms; Anderson et al. found nC_{39} to be orthorhombic [7]; Flory et al. [57] suggests above 44 carbon atoms; Broadhurst et al. [58] also suggests above 44 carbon atoms. To ensure only orthorhombic crystals are considered, only data with 44 or more carbon atoms will be included in the data set.

A data set to be used for fitting models is given in Table 9-4 in appendix A.

4.6.1.3 EXTENDED CHAIN MELTING TEMPERATURE

The limiting value for the melting point must be consistent with the infinite length extended chain melting point. Various predictions of the extended chain melting temperature exist:

Table 4-3: Predictions of infinite length extended chain-melting temperature

Infinite length extended chain melting temperature (K)	Reference
408.1	[74]
410.2	[75]
414.3	[58]
414.4	[79]
415.2	[85]
417.5	[84]
418.7	[57]
419.0	[76]
422.4	[77]

There is exists no clear extended chain melting temperature. With exception of Wunderlich et al. [80] no experimental observations of the extended chain melting point have been published. Wunderlich et al. measured this temperature to be 414.6K. Although this value will not be used in fitting the model, it will be used as an indication of the ability of a correlation to predict the infinite chain length.

4.6.2 PREDICTING EXTENDED CHAIN MELTING TEMPERATURE

Various correlations exist to predict the extended chain melting temperature. These models will be discussed and fitted to the data, after which the ability of the models will be assessed to determine the correlation most able to predict the data.

4.6.2.1 CORRELATIONS BASED ON CARBON NUMBER

The correlation required should be simple, easy to fit and be dependent solely on the carbon number. For simplicity, only correlations where the melting temperature can be calculated explicitly and containing only two parameters to be fitted will be considered.

Correlation of Garner et al. and Broadhurst

Garner et al. [74] proposed a correlation and fitted the data to alkanes with 20 to 35 carbon atoms:

Equation 4-5:
$$T_m = \frac{An + B}{Cn + D}$$

With the parameters A = 0.6085, B = -1.75, C = 0.001491 and D = 0.00404

Broadhurst [58] applied a different form of the same correlation to alkanes with 44 or more carbon atoms:

$$\text{Equation 4-6: } T_m = A \frac{n+B}{n+C}$$

With the parameters $A = 414.3$, $B = -1.5$ and $C = 5$

The correlation in the form as proposed by Broadhurst will be fitted to the data. As only two parameters are to be fitted, a value of $C = 5$ will be accepted.

Correlation of Gray et al.

Gray et al. [75] proposed the following correlation:

$$\text{Equation 4-7: } T_m = A + \frac{B}{n-1}$$

With the parameters $A = 410.6$ and $B = 2266.7$ for $n > 37$.

Correlation of Hay et al.

Hay et al. [76] proposed a correlation for the melting of polymers based on the equilibrium thermodynamics of Flory et al. [57] but redefining the parameters:

$$\text{Equation 4-8: } T_m = A - B \frac{\ln(n)}{n}$$

With the parameters $A = 419$ and $B = 760$

Correlation of Mandelkern et al., Feng et al. and Höhne et al.

Mandelkern et al. [84], Feng et al. [77] and Höhne [79] all proposed a correlation that can be reduced to the following form:

$$\text{Equation 4-9: } \frac{1}{T_m} = A + \frac{B}{n}$$

With Mandelkern et al. predicting $A = 0.002396$ and $B = 0.01667$

With Feng et al. predicting $A = 0.002368$ and $B = 0.01741$

With Höhne et al. predicting $A = 0.002413$ and $B = 0.0162$

4.6.2.2 FITTING OF DATA TO CORRELATION

The four above-mentioned correlations have been fitted to the data and the predictions are shown in Figure 4-19 (a) through (d):

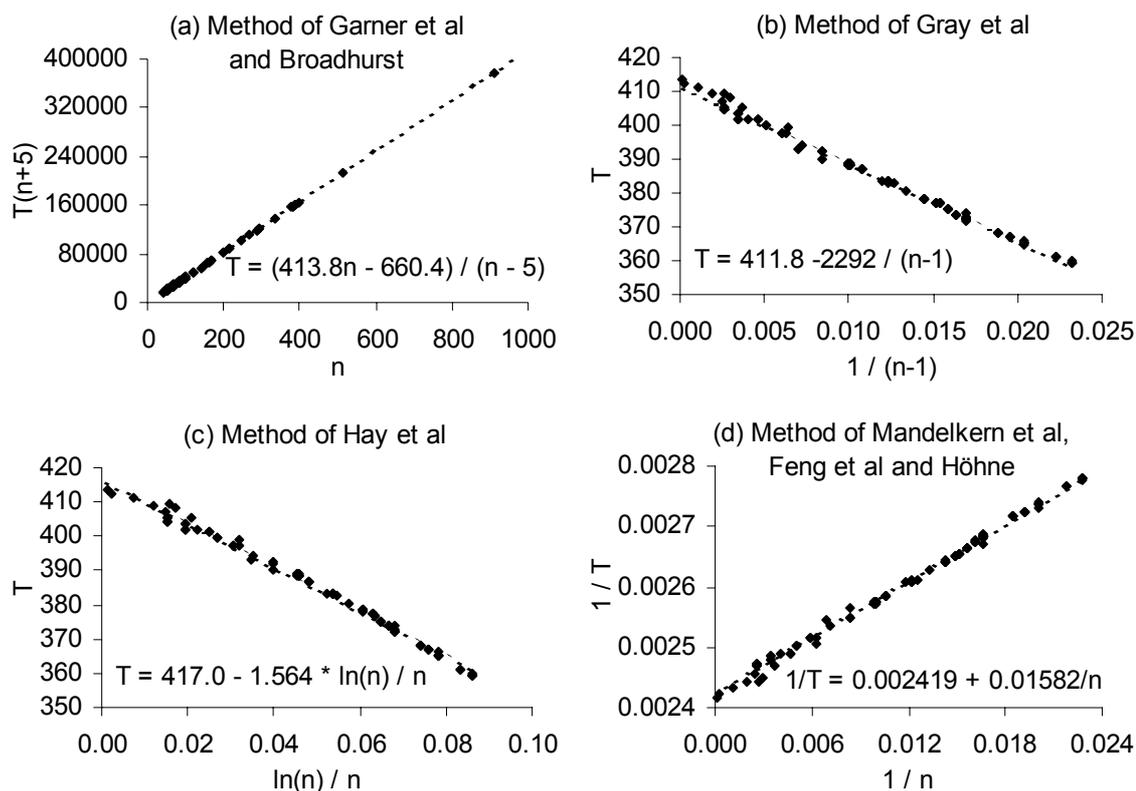


Figure 4-19: Prediction of the melting point with various correlations proposed in the literature: (a) Correlation according to Garner et al. [74] and Broadhurst [58]; (b) Correlation according to Gray et al. [75]; (c) Correlation according to Hay et al. [76]; (d) Correlation according to Mandelkern et al. [84], Feng et al. [77] and Höhne [79]

All four correlations seem to provide a good fit for the data. The infinite length extended chain-melting temperature, the R^2 values of the fit as well as the error are shown in Table 4-4:

Table 4-4: Data comparing the fit of the various correlations shown in Figure 4-19

Correlation	T_{inf}	R^2 of fit	Error average *	Absolute error average **
Garner et al. and Broadhurst	413.8	>0.9999	-0.51	1.04
Gray et al.	411.8	0.9955	-0.02	0.68
Hay et al.	417.0	0.9927	-0.25	1.09
Mandelkern et al., Feng et al. and Höhne	413.4	0.9966	-0.02	0.67

* Defined as the average of the predicted value minus the actual value

** Defined as the average of the absolute value of the predicted value minus the actual value

The R^2 values of all the correlations are excellent indicating there is no significant difference between the correlations. The correlation of Gray et al. and that of Mandelkern et al., Feng et al. and Höhne provide the lowest errors, the latter providing a better approximation of the infinite

length extended chain melting temperature. The correlation of Mandelkern et al., Feng et al. and Höhne with the parameters fitted in this work will thus be used:

$$\text{Equation 4-10: } \frac{1}{T_m} = 0.002419 + \frac{0.01582}{n}$$

4.6.3 RELATIONSHIP OF MELTING TEMPERATURES OF FULLY EXTENDED AND CHAIN FOLDED CRYSTALS

It is important to be able to predict the folded chain melting temperature and a relationship for the folded chain melting temperature as a function of the extended chain melting temperature and the crystal thickness is required.

4.6.3.1 EXPERIMENTAL DATA

Melting temperatures of folded crystals as a function of their crystal thickness (as published in the literature) is plotted together with the extended chain melting temperature.

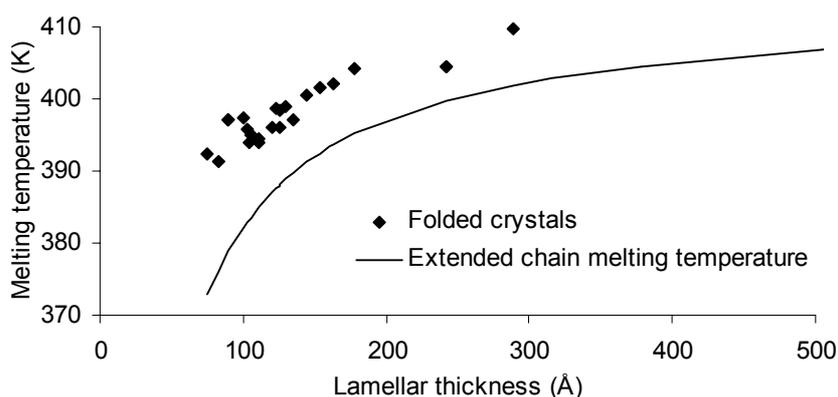


Figure 4-20: Plot of melting temperature of alkane and polyethylene folded crystals [86], [77], [78], [79] as a function of lamellar thickness versus extended chain melting thickness (calculated from Equation 4-10)

The data indicates that the melting temperature of chain folded crystals is higher than the melting temperature of extended chain molecules with the same molecular length, yet the data hints towards some relationship.

4.6.3.2 CORRELATION FOR PREDICTING LAMELLAR THICKNESS

Weeks et al. [85] proposed a correlation to relate the melting temperature of chain folded crystals with the extended chain melting temperature:

$$\text{Equation 4-11: } T_{mf} = \frac{(c - A)T_m}{c}$$

By rearranging Equation 4-11:

$$\text{Equation 4-12: } c = A \frac{T_m}{T_m - T_{mf}}$$

By plotting the crystal thickness as a function of $T_m / (T_m - T_{mf})$, the gradient A can be determined:

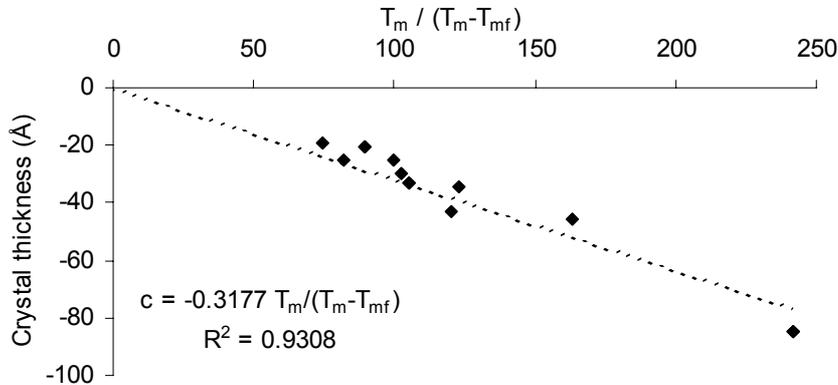


Figure 4-21: Plot to determine the value of A in Equation 4-12

The value of A is thus -0.3177 . Using this value of A in Equation 4-12 the folded chain melting temperature can be predicted with an average deviation of 2.3 K:

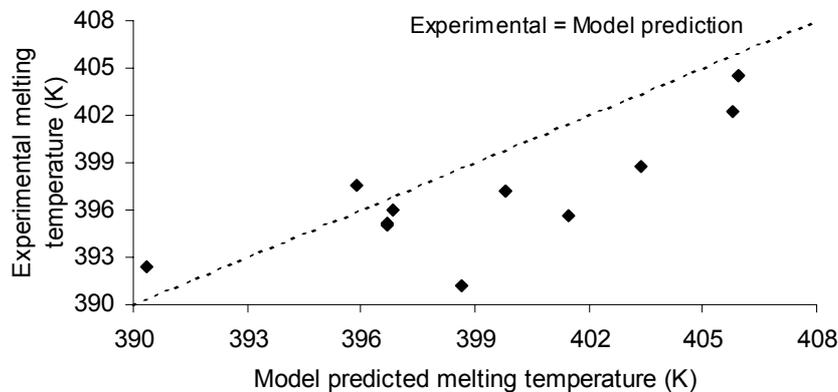


Figure 4-22: Comparison of experimental data and the correlation predicted

Although not perfect, with a single parameter this correlation is able to provide a reasonable approximation of the melting temperature.

4.7 MOLECULAR ORIENTATION OF POLYETHYLENE IN THE FLUID STATE

From the analyses above it is clear that in the crystalline state, linear polymeric molecules undergo molecular folding. However, the molecular formation in the molten and/or solution state is less well understood and, although various theories exist, to date general consensus with regard

to molecular configuration in solution or in the liquid form has not been reached. In this section it is aimed to present the information available regarding conformation of polyethylene in this state.

The analysis of the molecular orientation of polyethylene in the liquid or dissolved solution state can be divided into two sections, depending on the concentration of polyethylene. The configuration of the polymer molecule thus depends on its environment:

- Firstly, in dilute systems the concentration of polyethylene is such that the individual polymer molecules behave independently of one another, i.e. the configuration and behaviour of one molecule has little or no effect on another molecule.
- Secondly, in the pure melt the molecules have a significant effect on one another. Although no direct information on the general conformation of polyethylene molecules in concentrated solution is available, it is envisaged that the conformation will be similar to that of pure melt.

4.7.1 POLYMER SOLUTIONS IN GENERAL

Polymers are unusual solutes in that they take up relatively large volumes for low molar concentrations. Two parts of a given polymer molecule cannot occupy the same space and experience increasing repulsion as they move closer together.

Dissolution of polymers is a very slow process. It may take days, even weeks for high molar mass polymers to dissolve. The typical shape of most polymer molecules in solution is the random coil [2]. This is due to the relative ease of rotation around the bonds of the molecule and the resulting large number of possible conformations that the molecule can adopt. However, the polymer may not adopt a random coil conformation until higher temperatures.

4.7.2 MOLECULAR ORIENTATION IN DILUTE POLYMER MOLECULES

Very little information is available regarding the molecular orientation of dilute polymer molecules and details in this regard depend on the fact that the melting or dissolution of a crystalline polymer at high dilution is widely observed as the inverse process of a polymer crystallising out of a dilute solution. The dissolution process results in the separation of the constituent molecules and is usually accompanied by a simultaneous change in molecular configuration. However, Mandelkern [87] postulated that it is also possible, at high dilution, for the individual polymer molecules to maintain the configuration typical of the crystalline state. This is particularly true if steric requirements favour the perpetuation of a preferred bond orientation or if the crystalline structure is maintained by intramolecular bonding.

4.7.3 MOLECULAR ORIENTATION IN PURE MELT

Considerably more information, although not conclusive, is available on the molecular orientation of polyethylene in the melt. Shortly after the discovery of molecular folding in polyethylene by

Keller and O'Conner in 1957 [13], [14], Bunn [88] proposed that there may be some type of structure in the molten state of polyethylene:

“The regular folding of chain molecules in crystals grown from solution is surprising enough; if it occurs in crystals grown from melt [which subsequently has been proven] ... this is still more surprising, because we suppose the melt to be a tangle of long chain molecules. Either the rate of disentanglement is much larger than we imagined, or else the molecules in the melt are to some extent folded up on themselves and are not so completely entangled with others as we imagined. The degree of entanglement would be expected to depend on the temperature of the melt, and on the time spent in the liquid state; it is therefore important to correlate observations on crystal structure with thermal history in the melt ... it is therefore relevant to ask whether the layer [folded-molecule] structures which have been observed in melt grown crystals are survivals of structures in existing crystals before melting – structures which perhaps arose in previous crystallisation from solution or during the polymerisation reaction ...”

Westrik et al. proposed an alternative [21]:

“ ... it is of course difficult to imagine how such a highly ordered structure is formed if the melt is assumed to consist of an entangled mass of chains. A possible explanation is that in the melt the chains are already ordered to a certain degree ... ”

Early indications were thus that the melt may contain a total random configuration but be more structured than initially assumed.

Ovchinnikov et al. conducted some of the earliest studies on the configuration of molten polyethylene. Their calculations showed that the short-range order in polyethylene melt is represented by hexagonal packing of molecular chain fragments [89]. They conducted a study of molten polyethylene between 136 and 211°C and their results indicated that molten polyethylene consisted of ordered regions of approximately 50Å in diameter in which the chains were essentially parallel. Later they found that the intermolecular distance of polyethylene and nC16 were similar and showed a continuum. However, the structure of the melt could not be related to the intermolecular distances [89]. Since the publications of Ovchinnikov et al. various publications have contested their results:

In 1972 Mitchell et al. [90] studied the local structure of molten polyethylene and concluded that the chains in molten polyethylene are irregular in shape. The measurements confirmed a chain conformation of 60 % trans bonds, 40 % gauche bonds and indicated no substantial correlation in orientation between neighbouring chains.

In 1976 Voigt-Martin et al. [91] studied liquid polyethylene between 140 and 200°C and concluded that the polyethylene melts have a high degree of structural randomness.

Longman et al. [92] attempted to resolve the difference between the works of Voigt-Martin et al. [91] and Mitchell et al. [90] and that of Ovchinnikov et al. [89]. Longman et al. found a considerable liquid-like order caused by packing of polymer chains with an effective diameter of ~

5Å. However, the oscillations observed are damped fairly quickly and cannot clearly be resolved beyond 15Å. They thus concluded that any pseudo-crystalline parallel ordering of polymer chains does not persist over large distances.

Lovell et al. [93] found that molten polyethylene chains do not lie parallel to one another.

The above analysis seems to indicate a general random configuration yet the 'memory' of the melt also needs to be taken into account: Aitken et al. [94] investigated the influence of the structure of molten high-density polyethylene on that of the crystalline material produced by rapid cooling of its melt. The study shows that the structure of the crystal depends on its melt precursor. Gao et al. [95] found that for ultra-high-molecular-mass polyethylene both elevated pressures and long annealing times are required in order to remove complete memory of interface within the melt. It appears that pressure alone may be insufficient for the whole memory of the interface to be lost.

4.7.4 POSSIBILITY OF MOLECULAR FOLDING IN SUPERCRITICAL SOLUTION

As seen above, very little information is available regarding molecular folding in solution. Yet it should be remembered that for the applications intended in this work, non-dilute concentrations of polymer will be employed. The molecular configuration in the melt will thus probably be able to give the best outlook as to the possibility of molecular folding in supercritical solution.

Many factors, both favouring molecular folding and a random configuration, have been mentioned in the literature: Mitchell et al. [90], Voigt-Martin et al. [91], Longman et al. [92] and Lovell et al. [93] all found that the melt has a generally random conformation. Yet the following needs to be remembered:

The total loss of structure of the melt is generally a slow process, an increased rate favoured by high temperatures. As the intended operating temperatures are not very high above the melting temperature, the envisioned process may not allow sufficient residence time for complete loss of memory of the solid state. Additionally, the rate of crystallisation is rapid and as pointed out already in 1958 [88], [21] there may not be sufficient time for the molecules to disentangle themselves and align themselves as perfectly in the crystal as observed. As proven by Aitken et al. [94] the crystallised solid may thus contain a memory of the liquid.

To date no mention has been made regarding the possibility of molecular folding in supercritical solution. The high pressures applied may favour an extended conformation yet the proximity of the melting point and low residence time favours a folded configuration. It can thus not be said with any certainty if molecular folding in the supercritical state exists or not.

A last point to note is that the analysis done in this section concerns stationary liquids / fluids. When liquids flow, the molecular orientation tends to change, especially for high molecular weight compounds. The orientation during flow is a lot more complicated than in a stationary liquid / fluid, dependent on velocity, molecular weight, temperature, flow duct characteristics etc and for the purpose of this work it will suffice to merely mention that the molecular configuration in a flow situation may be different to that in a stationary liquid / fluid.

4.8 APPLICATION TO HIGH PRESSURE ENGINEERING

From the above analysis of the crystalline state it can be seen that if an alkane folds, the nature of the polymer changes. Should an alkane of 300 carbon atoms fold, it behaves closer to that of an alkane of 150 carbon atoms. However, the behaviour of alkanes in solution is considerably less defined. Conflicting theories exist as to the presence of molecular folding in solutions and no information is available on the behaviour of long alkanes in supercritical solution.

From the crystallisation analysis the following is proposed:

If an alkane of n carbon atoms folds while in (supercritical) solution, then it will no longer behave as one alkane molecule of n carbon atoms but rather as two alkane molecules of $n/2$ carbon atoms. Similarly if the same alkane should fold twice, it will now behave as three alkanes of $n/3$ carbon atoms.

If the above premise is true and can be applied to, for example $nC150$, the pressure-mass fraction carbon number plot would have the following shapes for the extended, once folded and twice folded molecules (generated according to method set out in section 3.5.1):

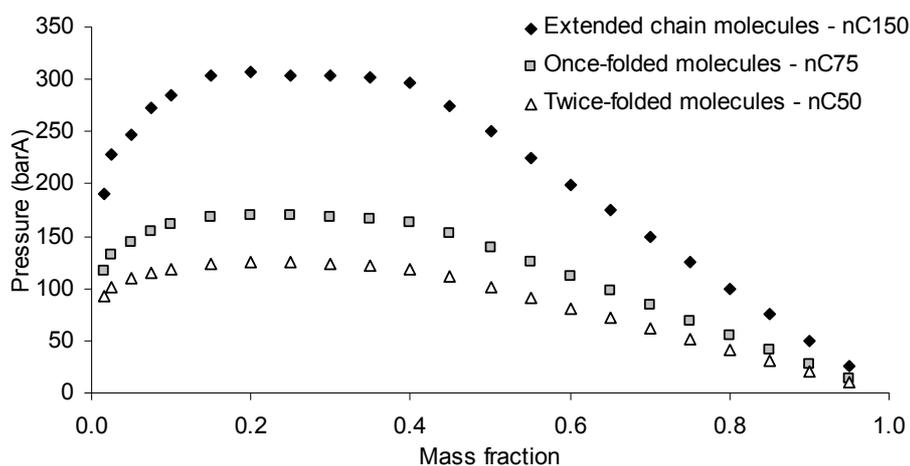


Figure 4-23: Possible phase behaviour for normal alkanes with 150 carbon atoms

Molecular folding may thus significantly influence the phase behaviour in supercritical solution: The plots illustrated in Figure 4-23 consider the situation where all molecules have the same configuration. A more realistic situation may be one where a mixture of for example extended and once folded molecules occur thus resulting in a phase transition pressure intermediate between that of, for example, extended and once folded molecules.

In order to test the above premise, phase equilibrium measurements with high molecular weight alkanes need to be conducted. High molecular weight alkanes need to be synthesised and their phase behaviour investigated. Should the measured phase equilibrium pressure compare well with the generated data for the same molecular weight, it can be assumed that either molecular folding does not occur or even though it does occur it does not significantly influence the phase

equilibrium pressure. Although the occurrence of molecular folding is of scientific interest, for engineering purposes it is more important to determine what type of phase behaviour occurs.

4.9 NOMENCLATURE

Symbol	Description
A	Parameter in extended chain melting temperature equation
A	Parameter in folded chain melting temperature equation
B	Parameter in extended chain melting temperature equation
C	Parameter in extended chain melting temperature equation
c	Final crystal thickness (Å)
CCX	Refers to a cyclic alkane where X is the number of carbon atoms in the compound
D	Parameter in extended chain melting temperature
L	Extended chain crystal length (Å)
M _n	Number average molecular weight (g/mol)
M _w	Weight average molecular weight (g/mol)
M _z	Z-average molecular weight (g/mol)
n	Number of carbon atoms per molecule for a pure alkane or the equivalent number of carbon atoms calculated from M _n for polyethylene mixtures
nCX	Refers to a normal alkane where X is the number of carbon atoms in the compound
PE	Polyethylene
PEX	Refers to a polyethylene mixture where X is the weight average molecular weight
T ₁₂	Temperature where transition from regime I to regime II occurs (K)
T ₂₃	Temperature where transition from regime II to regime III occurs (K)
T _{inf}	Infinite length extended chain melting temperature (K)
T _{mf}	Folded chain melting temperature
T _m	Extended chain melting temperature

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5 Fluid-liquid equilibria

measurements of propane and

long chain normal alkanes

The aim of this chapter is to investigate the high-pressure phase equilibria of propane with long chain alkanes. These investigations will assist in determining the possibility of molecular folding in long chain alkanes in supercritical solution and more importantly, its effect on the high-pressure phase equilibria.

5.1 SYNTHESIS OF LONG CHAIN ALKANES

Long chain alkanes are commercially available up to nC60. As phase equilibrium measurements with propane and nC60 have already been conducted [1], a higher normal alkane is required and thus needs to be synthesised.

5.1.1 SYNTHESIS METHODS INVESTIGATED

Various methods for the synthesis of long chain molecules will be compared, both for pure products and for alkane mixtures. The advantages of obtaining a pure compound versus the ease of obtaining a mixture will be considered.

Various methods exist for the lengthening of the chain by successive increments of one or two carbon atoms, however, these methods become exceedingly tedious for molecules larger than 30 carbon atoms and numerous repetitions will be required before chains of the desired length are attained. Only methods with additions of 5 carbon atoms or more per cycle will be considered.

5.1.1.1 STARTING MATERIALS AVAILABLE FOR SYNTHESIS

All methods investigated required an alkane chain with either one or two active ends. These species usually include but are not limited to alcohols, carboxylic acids, methyl esters of carboxylic acids and haloalkanes. With the aid of amongst others, reduction, oxidation, halogenation and esterification most of these species can easily be converted to the species that may be required. A search of molecules with a hydrocarbon backbone of 10 or more carbon atoms is conducted, however above 20 many members of these series become scarce with virtually no members above 30 carbon atoms. A summary of the highest suitable member i.e. the member used for the actual synthesis (determined by a trade off between cost and chain length), and the member of the homologous series used for testing the method is given in section 9.3.1 in appendix A. For a hydrocarbon with a single active end a hydrocarbon backbone with up to 22

carbon atoms easily available. For a hydrocarbon with two active ends 12 carbon atoms are generally available.

5.1.1.2 UNSUITABLE SYNTHESIS METHODS

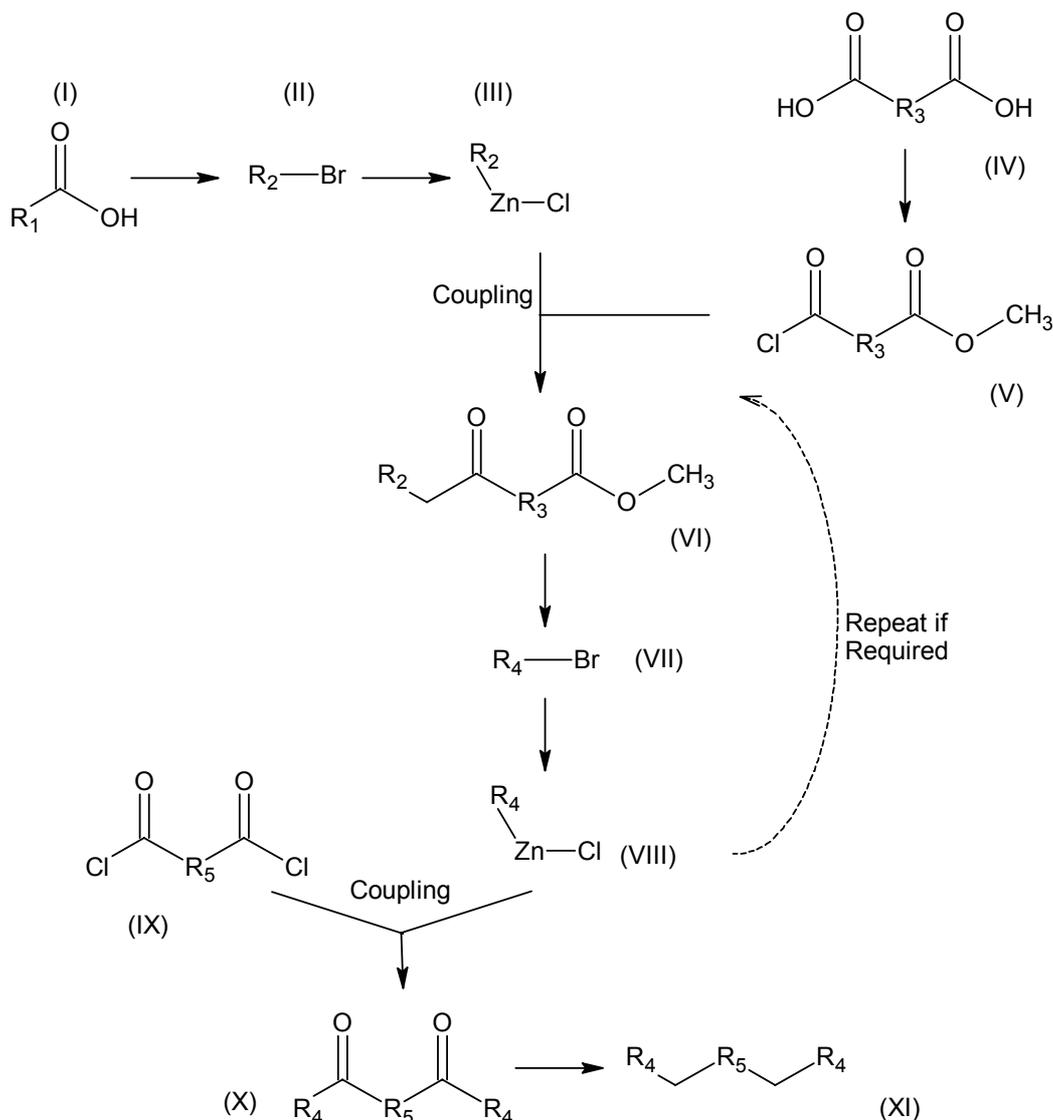
Many synthesis methods were investigated and found not to be suitable. These methods are listed in Table 5-1 together with the reasons for their unsuitability and are described in detail in section 9.3 in appendix A.

Table 5-1: Synthesis methods found to be unsuitable and the reasons for unsuitability

Method	Reasons for unsuitability
Method of Robinson and co-workers [2], [3], [4], [5]	The method has not been tested at high enough molecular weights, has solubility problems in diethyl ether and low overall conversion.
Method of Jones [6]	The conversion is low, a lack of information with regard to reaction rates of high molecular weights compounds exists and the possibility of water poisoning is high.
Method of Doolittle et al. [7]	The method cannot be applied repeatedly and require higher molecular weight 1-bromo alkanes than commercially available.
Method of Ställberg et al. [8]	A low conversion and the inability to obtain large enough β -keto diesters handicaps this method.
Method of Rama Rao [9]	Doubt exists as to whether the coupling reaction may occur at higher carbon numbers.
Method of Maruyama et al. [10] and Singh et al. [11]	A very difficult, if not impossible separation is required to remove the by-products from the main product.
Miller et al. [12] and Bhalerao et al. [13]	The possibility of by-products and lack of information regarding the influence of molecular weight on the reaction kinetics and the conversion handicaps this method.
Villemin [14]	A water sensitive Grignard coupling is used and lack of information regarding the conversion at higher molecular weights exists.
Iyer et al. [15]	The inability to repeat the process impedes its application.
Brown et al. [16]	The method requires extreme reaction conditions, little available information regarding kinetics and α -benzoxy- ω -alkenes are not easily obtainable.
Method of Urabe et al. [17]	Undesirable by-products may be formed that are difficult to remove.
Method of Whiting and co-workers [18], [19], [20], [21], [22], [23]	The process is water sensitive, the reaction time for the formation of the ylide is very long and a refrigeration system is required.

5.1.1.3 METHOD OF REINHARD ET AL.

Reinhard et al. [24] proposed a method for the synthesis of long chain n-alkanes and illustrated the method with the synthesis of nC94:



where

- R_1 = Alkane chain with a $-CH_2-$ groups, terminated with a H atom
- R_2 = Alkane chain with b $-CH_2-$ groups where $b = a + 1$, terminated with a H atom
- R_3 = Alkane chain with c $-CH_2-$ groups
- R_4 = Alkane chain with d $-CH_2-$ groups where $d = b+c+2$, terminated with H atom
- R_5 = Alkane chain with e $-CH_2-$ groups

Figure 5-1: Schematic representation of the reaction scheme according to Reinhard et al. [24]

In this method chain lengthening is obtained through the coupling of an organo zinc chloride compound with an acid chloride half ester or a double acid chloride. The total number of carbon atoms in the product (XI), f, is calculated as follows:

Equation 5-1: $f = 2a + 2c + e + 8$

where a, b, c, d and e are defined in Figure 5-1.

According to this method, an acid (I) and a dibasic acid (IV) are used as starting materials, and a double acid chloride (IX) is used in the final coupling reaction.

As starting material, either a 1-alkanol, a carboxylic acid or a 1-bromoalkane is required. A dicarboxylic acid or a dimethyl diester can be used as the starting material containing two functional groups. Alternatively, an acid chloride half ester can be used and although the acid chloride half ester is more expensive than the corresponding dicarboxylic acid the choice can be justified as in the process for the formation of the acid chloride half ester significant by-products may be formed. These by-products are difficult to remove.

According to Reinhard et al. [24] the following conversions are attained:

Table 5-2: Conversion of various steps in synthesis according to Reinhard and Dixon

Reactant	Product	Conversion
Carboxylic acid (I)	Bromide (II)	72 %
Dibasic carboxylic acid (IV)	Acid chloride half ester (V)	78 %
Bromide (II) + acid chloride half ester (V)	Keto ester (VI)	80 %
Keto Ester (VI)	Bromide (VII)	74 %
Bromide (VII) + double acid chloride (X)	Alkane (XI)	51 %

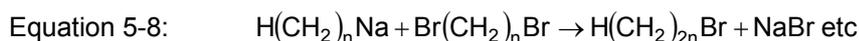
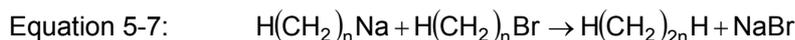
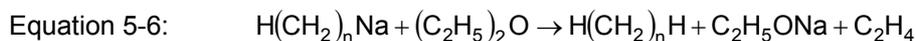
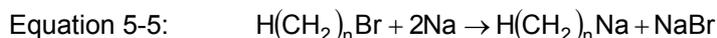
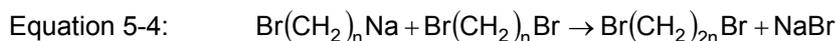
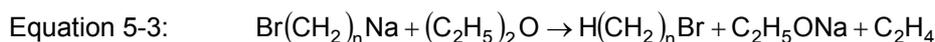
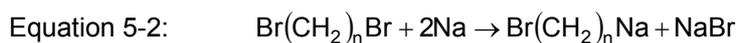
The overall conversion depends on the starting products. Using the conversion given by Reinhard et al. and assuming 1-bromodecosane (a = 21), methyl-10-chloro-10-oxodecanoate (c = 8) and azelic acid dichloride (e = 7) are used as reagents, an nC73 alkane can be synthesised with a single pass and an overall conversion of about 30 %.

Advantages: The chemistry involved in this process is simple and the methods are well documented, a single product is produced and although the conversion is not excessively good, it is acceptable.

Disadvantages: The process uses an organometallic coupling. These type of couplings are not very reactive and are very sensitive to the presence of water, even trace amounts thereof. Thus extreme care needs to be taken to prevent poisoning due to water.

5.1.1.4 METHOD OF CAROTHERS ET AL. AND HEITZ ET AL.

In 1930 Carothers et al. [25] proposed a method for the synthesis of long chain alkanes by using a bifunctional Wurtz reaction. This method consists of the reaction of sodium with α - ω -dibromoalkane in diethyl ether and the reactions can be formulated as follows:

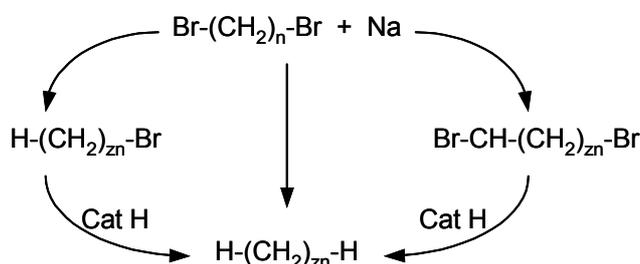


Where n = number of $-\text{CH}_2-$ groups per molecule of dibromoalkane initially used

As can be seen in Equation 5-2 through Equation 5-8 no single reaction occurs, rather a sequence of reactions. The reactions shown represent the reactions for the first set of reactions and are repeated for $2n$, $3n$, $4n$, etc. The product of the reaction system can thus be represented by the general formula $\text{H}(\text{CH}_2)_{zn}\text{H}$ and possibly similar chains terminated at one or both ends with bromide atoms, i.e. $\text{H}(\text{CH}_2)_{zn}\text{Br}$ and $\text{Br}(\text{CH}_2)_{zn}\text{Br}$ where n = number of $-\text{CH}_2-$ groups per starting molecule and z = integer 1, 2, 3, 4, 5, etc. The reaction is thus a polymerisation of an α - ω dibromoalkane.

Although theoretically possible, Carothers et al. stated that in the reaction scheme neither alkenes nor cyclic molecules are formed, this indicating that no intermolecular or elimination reactions occur. Heitz et al. [26] investigated the possibility of the formation of intermolecular reaction, but due to the absence of cyclodecane and with the aid of gas chromatography of the lower homologues they confirmed the statement by Carothers et al. that no intermolecular reactions occur.

In short the process can thus be summarised according to the following scheme:



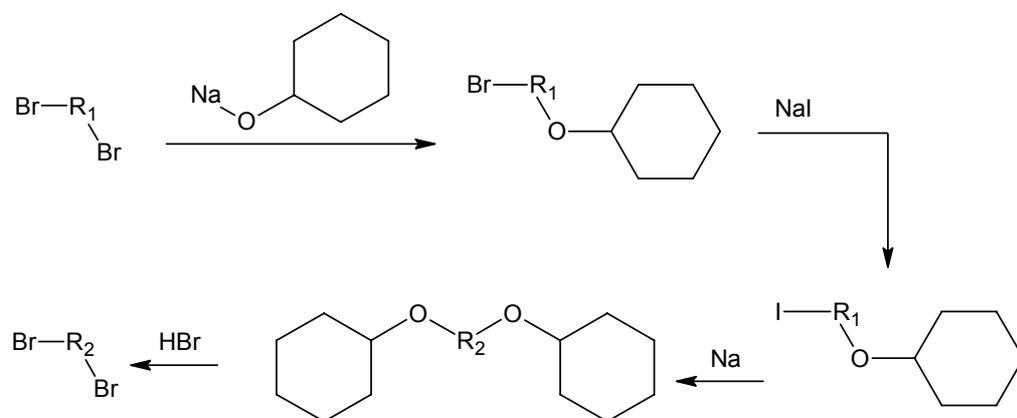
where n is the number of $-\text{CH}_2-$ groups in the initial α - ω dibromoalkane.
 z is an integer of 1 or larger

Figure 5-2: Schematic representation of reaction scheme

Carothers polymerised 1-10-dibromodecane ($n = 10$) and produced a mixture of alkanes with 10x alkanes, i.e. decane, eicosane, triacontane, tetracontane, pentacontane, hexacontane etc. It was found that 25 % of the product mixture is alkanes higher than heptacontane ($nC70$).

Heitz et al. polymerised 1,10-dibromodecane ($n = 10$) and as in the work of Carothers et al. a mixture of alkanes with 10x alkanes was found with a melting range of $106 - 109^{\circ}\text{C}$. Heitz et al. also polymerised 1,20-dibromoeicosane ($n = 20$) and found a melting range of $107 - 113^{\circ}\text{C}$. With the aid of the model proposed in section 4.6.2 these melting ranges correspond to alkanes with an average of $72 - 80$ carbon atoms for the mixture from 1,10-dibromodecane and $74 - 92$ for the mixture from 1,20-dibromoeicosane.

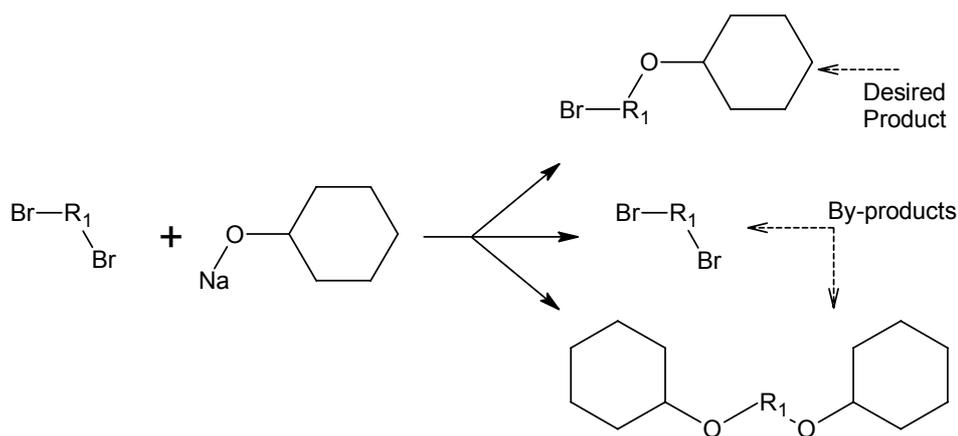
Heitz et al. proposed a method for the synthesis of 1,20-dibromo-eicosane from 1,10-dibromodecane so as to double the size of n . Schematically the method can be represented according to Figure 5-3:



where $\text{R}_1 =$ Alkane chain with a $-\text{CH}_2-$ groups
 $\text{R}_2 =$ Alkane chain with b $-\text{CH}_2-$ groups, where $b = 2a$

Figure 5-3: Schematic representation for doubling of dibromoalkane chain length according to Heitz et al. [26]

In the method for the doubling of the hydrocarbon chain length of the dibromoalkane one of the dibromoalkane groups are protected. This method is simple and all steps occur readily, however, during the protection of the one active end, by-products may be formed. If a stoichiometric amount of sodium cyclohexanoate is added to the dibromoalkane as well as the desired product that is formed, some dibromoalkane molecules are not protected and some molecules undergo double protection.



where $R_1 = \text{Alkane with a } -\text{CH}_2- \text{ groups}$

Figure 5-4: Schematic representation of products and by-products formed during protection of one bromide group

The products and by-products need to be separated and according to Heitz et al. separation is achieved through vacuum distillation at 1 Pa between 120 and 130°C.

Advantages: Although Equation 5-2 through Equation 5-8 suggest a complicated combination of products, the reaction procedure is simple and the polymerisation process consists primarily of a single experimental step. The reaction is exothermic and unlike other organo-metallic reactions, it occurs readily and an increase in molecular weight does not impede the reaction rate to the extent that the reaction does not occur. Sodium will neutralise any trace amounts of water directly on contact and the presence of trace amounts of water will thus have very little, if any effect on the reaction save slightly reducing the sodium content.

Disadvantages: A mixture of products is formed. The procedure of doubling the hydrocarbon chain length of the dibromoalkane requires a very difficult separation process. Very low pressures are required and although the separation may be conducted at slightly higher pressures, this will result in higher temperatures, which in turn increases the chance for thermal decomposition. The doubling procedure will not be investigated further due to the formation of difficult to remove by-products. Further investigation of this method will thus only include the polymerisation reaction.

5.1.1.5 METHODS OF HYDROGENATION

Both synthesis methods considered require the final product to be hydrogenated, albeit the hydrogenation of a ketone or dehalogenation of a halo-alkane. Possible methods of hydrogenation will now be investigated.

Metal catalysed hydrogenation

Catalytic hydrogenation allows for the reduction of various functional groups. Typical metallic catalysts used include platinum, palladium, nickel and ruthenium yet Raney-nickel is one of the most popular catalysts.

Catalytic hydrogenation allows for the dehalogenation of halo-alkanes. In neutral or acidic medium, unactivated primary and secondary bromides and chlorides are not hydrogenolysed over palladium but iodides and tertiary chlorides and bromides are hydrogenolysed at room temperature and atmospheric pressure. However, in the presence of methanol alkyl halides can easily be hydrogenolysed [27]. As the compounds to be dehalogenated have a high melting point and should be hydrogenated in the liquid form, high operating temperatures may be required. This will result in considerable safety considerations being required, specifically due to the high temperature use of hydrogen with a highly active catalyst.

Catalytic hydrogenation of ketones usually leads to the formation of secondary alcohols. This reaction holds true for numerous metallic catalysts [28], [29]. As an alkane, not an alcohol, is required, catalytic hydrogenation is not a suitable method for the direct removal of a ketone group. However, by converting the alcohol into a halo alkane [30] and in turn hydrogenating the halo-alkane will result in an alkane. This method is quite tedious and should another, shorter method be available, it should be favoured.

Hydrogenation by lithium aluminium hydride and other metal hydrides

Lithium aluminium hydride (LAH) is an excellent reducing agent for many organic compounds and has the ability to convert halo-alkanes into alkanes, however the reaction with halo-alkanes is more sluggish than other reductions with LAH and an equimolar mixture of LAH and halo-alkane is suggested. Other metal hydrides, such as aluminium hydride [31], sodium borohydride [32], [33] and zinc borohydride [34] have been suggested in the literature and although their selectivity and reaction rates may differ, the resultant compounds are the same and thus do not justify further investigation.

As in the case of catalytic hydrogenation, hydrogenation of ketone groups with LAH leads to the formation of secondary alcohols. Once again, this method cannot be implemented for a direct hydrogenation but can be used in conjunction with halogenation and then hydrogenation to result in an alkane.

LAH is inert towards ethers and the reaction is thus usually conducted in either diethyl ether or tetrahydrofuran. The compounds to be hydrogenated here have a melting point above the boiling point of both diethyl ether and tetrahydrofuran and in addition to the fact that the reaction would be sluggish for the high molecular weights required here, this method is not ideal for the intended purpose.

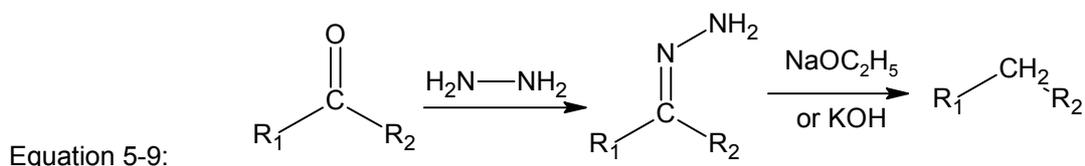
Clemmensen Reduction

Clemmensen reduction [35] can be summarised as the replacement of an oxygen atom in an aldehyde or ketone by two hydrogen atoms through the use of amalgamated zinc and hydrochloric acid. Aliphatic and cyclic ketones of low molecular weight are reduced smoothly yet those of higher molecular weight are attacked slowly [35] and it is thus doubtful if this method can be used for the reduction of a keto group.

Although some sources [35] have indicated that this method can be used to reduce some halides, their inability to reduce long chained ketones implies that halides may also be difficult to reduce. This method thus requires no further investigation.

Wolf-Kishner reduction

Hydrogen atoms can replace the oxygen atoms of a carbonyl group of a ketone by heating the ketone and hydrazine in the presence of an alkaline catalyst:



Huang-Minlon [36] proposed a method where 85% hydrazine hydrate in water (i.e. 55% hydrazine in water) and either sodium or potassium hydroxide is used resulting in a conversion in excess of 90%. In comparison to other methods, the Wolff-Kishner method performs well, especially for high molecular weight aldehydes and ketones.

Method according to Carothers et al.

Carothers et al. [25] dehydrogenated an alkyl bromide with molten sodium in boiling dibutyl ether. The same reaction scheme as set out in section 5.1.1.4 in Equation 5-2 through Equation 5-8 is followed, except that the reaction for the dehalogenation is favoured.

Due to the fact that molten sodium in boiling dibutyl ether (normal boiling point = 413.4K [37]) is above the melting point of the alkane/bromoalkane mixture, the reaction may proceed with considerable ease. In addition, sodium is a strong reducing agent and is used in excess, thus ensuring complete dehalogenation, as proven by Carothers et al. [25].

Selection of a hydrogenation method

The method of hydrogenation used depends on the functional group to be hydrogenated.

- Should a ketone or a keto-acid be required to be reduced to an alkane or acid, the Wolff-Kishner [36] method is suggested. This method work well for the hydrogenation of a high molecular weight ketone or keto acid without the formation of an alcohol.
- Should a bromide be required to be dehalogenated, the method according to Carothers et al. [25] should be favoured. This method has a high reactivity and works well even for high molecular weight compounds.

5.1.2 SELECTION OF A SUITABLE METHOD

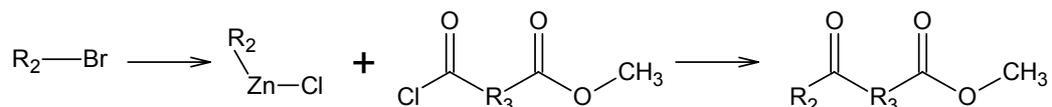
As discussed above, the method of Carothers et al. and Heitz et al. as well as the method as proposed by Reinhard et al. warrant further investigation. The next step in the investigation of the methods is to test the coupling reaction. The aim of the testing is:

- To determine if the coupling reaction occurs
- In the method of Reinhard et al., to determine if any side products occur
- In the method according to Carothers et al. and Heitz et al., to estimate the molecular weight of the product obtained.

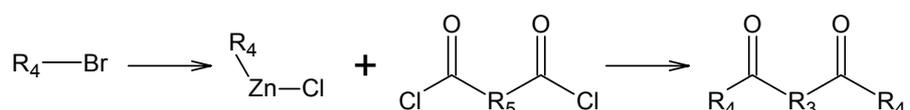
This testing may be conducted with slightly lower molecular weight components as these components are generally cheaper and the reaction may proceed easier. If the reaction does not work with these compounds, it is unlikely that it will work for higher molecular weight compounds.

5.1.2.1 PRELIMINARY TESTING OF METHOD ACCORDING TO REINHARD ET AL.

In the method according to Reinhard et al. there are two coupling reactions. The chain lengthening reaction, resulting in a product with one active end group can be expressed as follows, R_2 and R_3 defined as in Figure 5-1:



The last coupling, resulting in a diketone with no active end groups can be expressed as follows:



The mechanism of these two reactions is similar and it can be assumed if the first reaction works, the second will also proceed. The first coupling is thus investigated. To allow for the analysis to be conducted accurately the product is reduced to the alcohol. It is important that an active functional end group exists and that chain lengthening occurred.

This method was tested twice with 1-bromododecane ($b = 12$) and 5-methyl-5-chloro-oxovalerate ($c = 3$). In each test run the resultant product was dodecane, with trace amounts of 1-heptanol, the desired product, in the second test. This indicates that the coupling reaction did not occur readily. This method will not be used in this work.

5.1.2.2 PRELIMINARY TESTING OF THE METHOD ACCORDING TO CAROTHERS ET AL. AND HEITZ ET AL.

The method of Carothers et al. and Heitz et al. is tested to determine if the polymerisation reaction occurs readily and if a high enough molecular weight alkane is formed. The method was tested with 1,10-bromodecane. The reaction occurs readily and the results showed that a product with a melting point of about 110°C (equivalent to average of 82 carbon atoms per molecule) is produced. (See section 5.1.4 for details of testing). This method can thus be used to produce a mixture of alkanes of high enough molecular weight.

5.1.2.3 SELECTION OF A METHOD

The method according Carothers et al. and Heitz et al. will be used to synthesise the high molecular weight alkanes.

5.1.3 EXPERIMENTAL SET-UP AND PROCEDURE

The polymerisation and hydrogenation reactions are carried out in a 2L reaction flask equipped with an argon inlet, a dropping funnel and a condenser. As diethyl ether, with a normal boiling point of 35°C [38], is used as the solvent for the polymerisation reaction, a large condenser is required. A schematic representation of the set-up is shown in Figure 5-5:

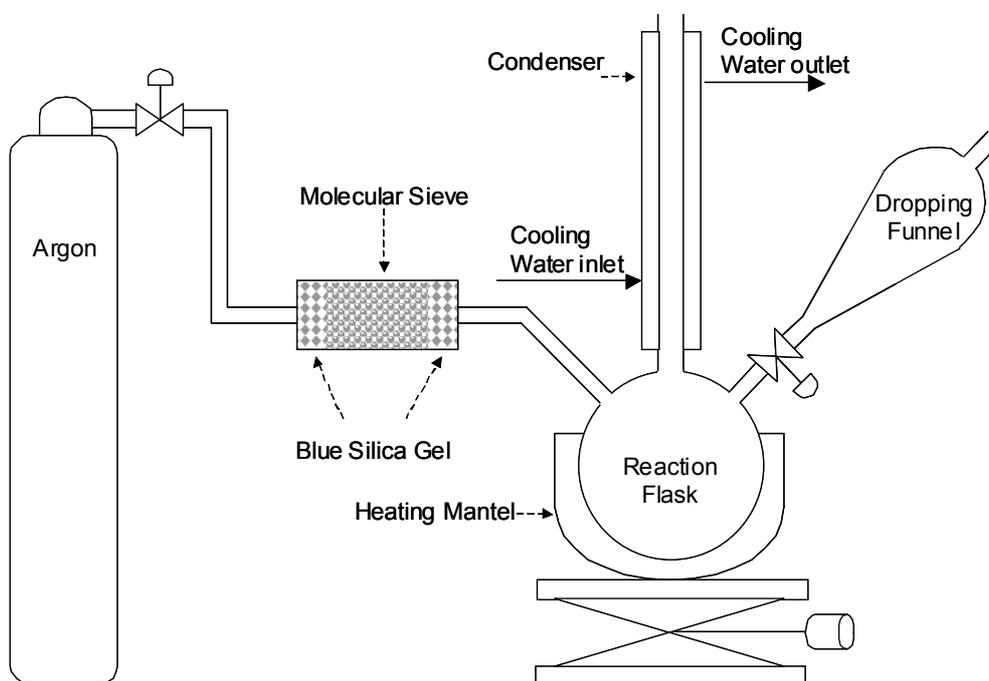


Figure 5-5: Schematic representation of the experimental set-up for the sodium preparation and polymerisation reaction

The reaction flask is supported independently from the heating mantel and jack. This has the advantage that if required, the heat can quickly be removed from the system quickly, and that during the dibromoalkane addition and the neutralization process, both of which are exothermic, the heating mantel does not act as insulation. For the part of the experiment where the heating mantel is not required, the heating mantel is replaced by a piece of insulation material lying flat in the jack, acting not as insulation but as a cushion between the jack and the reaction flask.

Various safety precautions need to be taken into account. As temperatures and pressures are either moderate or atmospheric, these do not play a significant role. However, the chemicals used are often highly flammable and in the case of sodium, highly reactive. A detailed list of the hazards associated with and safety precautions required for the various chemicals is given in section 10.1.2 in appendix B.

The experimental procedure for the synthesis of high molecular weight wax used here can be divided into the following steps:

- The sodium dispersion in diethyl ether can be prepared from a sodium dispersion in toluene or in a low molecular weight paraffin wax. The preparation differs according to the starting material of the dispersion, which varies according to availability. Details are given in section 10.1.1.1 in appendix B.
- The α - ω -dibromoalkane is polymerised to a high molecular weight alkane with the aid of sodium suspended in diethyl ether. Details are given in section 10.1.1.2 in appendix B.
- To isolate the polymer from the reaction mixture, three steps are required: Firstly, a solid-liquid separation of polymer and reaction mixture, secondly a cold water washing and drying and thirdly a hot water washing and drying. Details are given in section 10.1.1.3 in appendix B.
- Hydrogenation of the polymer. Details are given in section 10.1.1.4 in appendix B.

The chemicals used and where applicable and available the important impurities are given in Table 5-3:

Table 5-3: Chemical used for synthesis for polymer mixture, their suppliers, product number and important impurities

Product	Supplier	Product Number	Purity
Argon – UHP grade	Afrox	-	Max 1 ppm H ₂ O
Cyclohexane	Protea Industrial Chemicals Company	-	± 100 ppm H ₂ O by KF analysis
1,10-dibromodecane	Aldrich	D39800	-
1,12-dibromododecane	Aldrich	174866	-
	Fluka	34150	-
Dibutyl ether (different products used due to availability)	Riedel de Haën	32203	0.1 % H ₂ O
	BDH (via Merck)	BB 100946B	0.05 % H ₂ O
	Merck	100921	0.05 % H ₂ O
	Fluka	31680	0.01 % H ₂ O
Methanol	Fluka	24228	0.2 % H ₂ O
	SASOL	-	-
Sodium dispersion in paraffin wax (30 – 35 % weight)	Aldrich	244686	-
Sodium dispersion in toluene (30 % weight)	Aldrich	472263	-
THF	Fluka	87368	0.05 % H ₂ O
p- Xylene	Fluka	95682	-
Xylene – mixture of isomers	Protea Industrial Chemical Company	-	-

5.1.4 TESTING OF METHOD AND VARIATION OF EXPERIMENTAL METHOD

Before a large amount of time, effort and money is spent on the synthesis of large amounts of wax, the method needs to be tested. The testing of the method will allow for the following:

- To test if the method works.
- To determine the optimum operating conditions by varying certain parameters.
- To determine the typical conversion attained.

5.1.4.1 EXPERIMENTAL METHOD

The experimental method, as set out in section 5.1.3 is used as is with the exception that 1,10-dibromodecane is used instead of 1,12-dibromododecane. For the purpose of the preliminary experiments, sodium dispersed in paraffin wax is used.

5.1.4.2 TESTING OF METHOD FOR POLYMERISATION

The experiment is conducted and a hard whitish substance is obtained as the product. For this run, a sodium charge of 130 grams of sodium per mole dibromoalkane is used. A conversion of 85 % of the theoretical is attained, assuming no bromide molecules being present in the product.

The product is analysed by a differential scanning calorimetry (DSC). This method of analysis gives a plot the energy liberated as a function of increasing temperature. A change in phase will thus result in a significantly larger energy change in comparison to the energy required for heating. In this work the energy liberated is plotted as the normalised energy where the normalised energy is defined as the energy liberated divided by the absolute value of the largest energy uptake, thus resulting in a scale from 0 to -1. The resultant plot for the product is given in Figure 5-6:

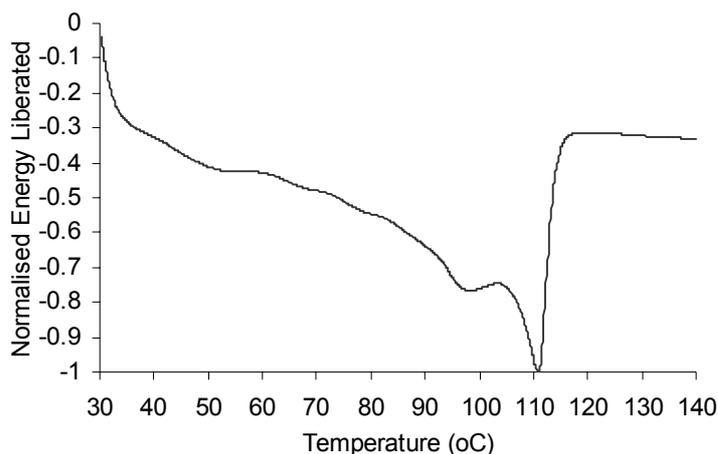


Figure 5-6: DSC plot of normalised energy liberated as a function of temperature: Base case results

The results show a single melting point of 110.8 °C, corresponding to alkane with an average of 85 carbon atoms. The bump in the curve just below 100°C can be attributed to the presence of residual water remaining from the hot water washes.

5.1.4.3 TESTING OF METHOD FOR HYDROGENATION

The hydrogenation is conducted and an even harder off-white product is formed. The mass is slightly reduced and the following DSC plot was obtained:

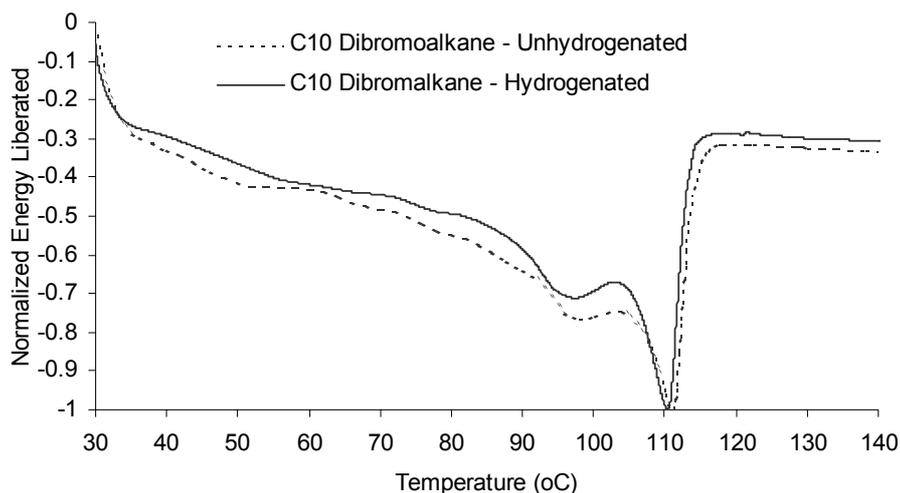


Figure 5-7: DSC plot of normalised energy liberated as a function of temperature: Hydrogenated versus un-hydrogenated sample.

From the DSC analysis, a melting point of 110.3°C is observed. This is lower than for the original sample, yet a decrease in melting point due to the removal of the bromide group can be expected. This melting point corresponds to an alkane with an average of 84 carbon atoms.

5.1.4.4 VARIATION OF PARAMETERS

The aim of the investigation of varying the parameter is not to optimise and fine-tune the synthesis process in detail but to quickly determine if alternative experimental conditions may produce a superior product. The following parameters are varied in attempt to improve the experiment and to increase the peak molecular weight:

- Sodium charge.
- Solvent – Try using THF (tetra hydro furan) instead of diethyl ether as THF has a higher boiling point and increase the reaction temperature.

From the results, the optimum experimental conditions will be applied and the effect of molecular weight on the product will be investigated. This will be done by conducting an experiment with 1,12 dibromododecane instead of 1,10 dibromodecane with an equivalent number of moles of dibromoalkane.

Effect of Sodium Charge

The effect of the sodium is investigated by firstly doubling the quantity of sodium used and then using 30% of the base case sodium charge. When increasing the sodium, no visual difference was noted in the experimental process. However, it was found that the product contained a large amount of sodium hydroxide as more foaming was observed during filtration and thus additional rinsing water was required. When decreasing the sodium, it was found that the reaction took longer to start, as solution took longer to turn blue and the product was softer.

All three runs gave similar conversions but the difference in the final products can be seen in the DSC plots, as shown in Figure 5-8:

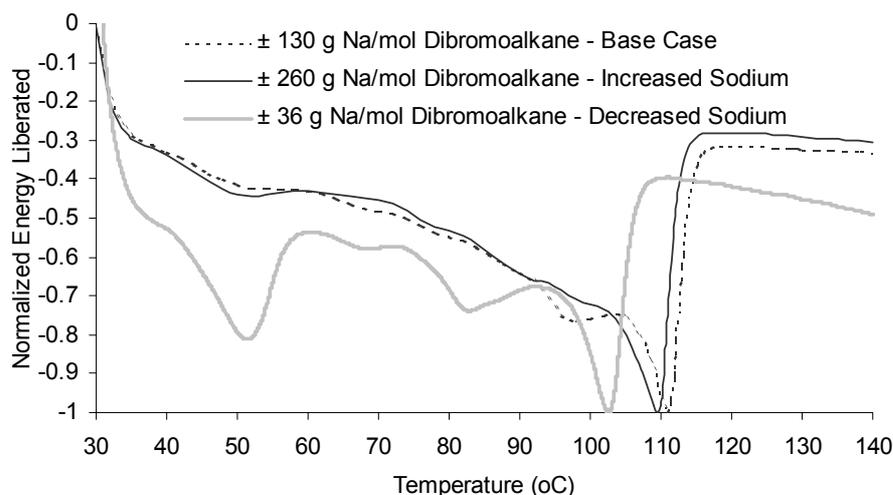


Figure 5-8: DCS plot of normalised energy liberated as a function of temperature: Effect of sodium charge

As seen in Figure 5-8 there is an optimum sodium charge. The decrease in the molecular weight when the sodium is doubled can be attributed to the fact that the reaction occurs faster and it may be that hydrogen terminated molecules are preferentially formed (see Equation 5-2 through Equation 5-8 for possible reactions) and these molecules can no longer polymerise. The decrease in the molecular weight with decreasing sodium can be attributed to insufficient sodium to allow complete polymerisation. A sodium charge similar to the base case should thus be used. The base case thus provides the optimum sodium charge.

Alternative solvent

THF is proposed as an alternative solvent. It has a normal boiling point of 388 K [37] compared to 308 K for ether [38] and thus the reaction temperature will be increased, the experiment will be easier to control and the solvent losses will be decreased. It was found that the reaction mixture went dark blue very quickly. However, with time, the reaction mixture started displaying a dark green colour. After neutralization the colour of the mixture was a light brown / orange colour compared to white in ether and it was found that the aqueous and organic phases did not split easily and the product was very difficult to filter.

Effect of molecular weight of dibromoalkane

To investigate the effect of the molecular weight of the dibromoalkane, an experiment is conducted with 1,12-dibromododecane as dibromoalkane and results compared to the base case.

Visually there is no difference in the experiments, but once the results are compared by DSC analysis, as shown in Figure 5-9, it can be seen that there exists an increase in molecular weight

when the molecular weight of the dibromoalkane is increased. In addition, the peak is sharper, possibly indicating a narrower distribution product.

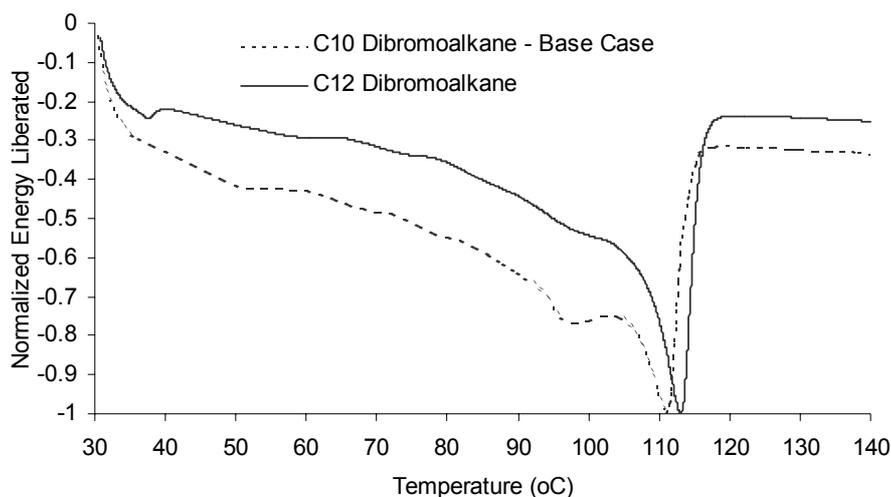


Figure 5-9: DCS plot of normalised energy liberated as a function of temperature: Effect of molecular weight of dibromoalkane

The polymerised C12 dibromoalkane has a melting point of 113.1 °C, corresponding to an alkane with an average of 93 carbon atoms.

5.1.4.5 CONCLUSIONS FOR TEST RUNS

It has been proven that the experiments work and can be conducted safely. Using 1,12-dibromododecane in diethyl ether as solvent with the base case sodium charge the polymer can now be synthesised.

5.1.5 SYNTHESIS OF ALKANE MIXTURE

It is aimed to produce a total of 800 grams of paraffin mixture. Assuming a conversion of 70% for the polymerisation reaction and 80% for the hydrogenation reaction, an initial quantity of approximately 2800 grams of dibromoalkane needs to be polymerised.

5.1.5.1 POLYMERISATION

A total of 2903 grams of dibromoalkane was polymerised resulting in 1007 grams of unhydrogenated polymer. An average conversion of 67.7 % was attained. Although not the focus of this work, the different sodium sources resulted in slightly different products: Where sodium in toluene was used, a conversion of 56.8% was attained with a peak melting point of 110.3°C (alkane with average of 84 carbon atoms) while when sodium in paraffin wax was used, a conversion of 82.7% was attained with a peak melting point of 112.0°C (alkane with average of 90 carbon atoms). The difference in the product is attributed to the difference in particle size of the sodium, the sodium dispersion in toluene being a lot finer than sodium dispersion in paraffin wax.

5.1.5.2 HYDROGENATION

Due to cost and availability sodium dispersion in paraffin wax is used. The un-hydrogenated polymer was hydrogenated (conversion of 85.9%) resulting in 865 grams of hydrogenated polymer.

5.1.5.3 ANALYSIS OF FINAL SYNTHESISED PRODUCT

Linear alkane samples of molecular weight studied here are often very difficult to analyse. Due to their high molecular weight, traditional methods, such as gas chromatography cannot be applied. However, due to their general insolubility, methods often used for larger molecules, such as HPLC and normal GPC can also not be applied. Additionally methods relying on ionisation of molecules are neither applicable as the molecules do not ionise easily or they fragment giving no indication of molecular weight. The only methods applicable are those where the sample is dissolved at high temperature or where a pure sample is used. High temperature GPC and DSC are thus the best analysis techniques available and are used.

A DSC plot of the normalised energy liberated for both the unhydrogenated and hydrogenated is shown:

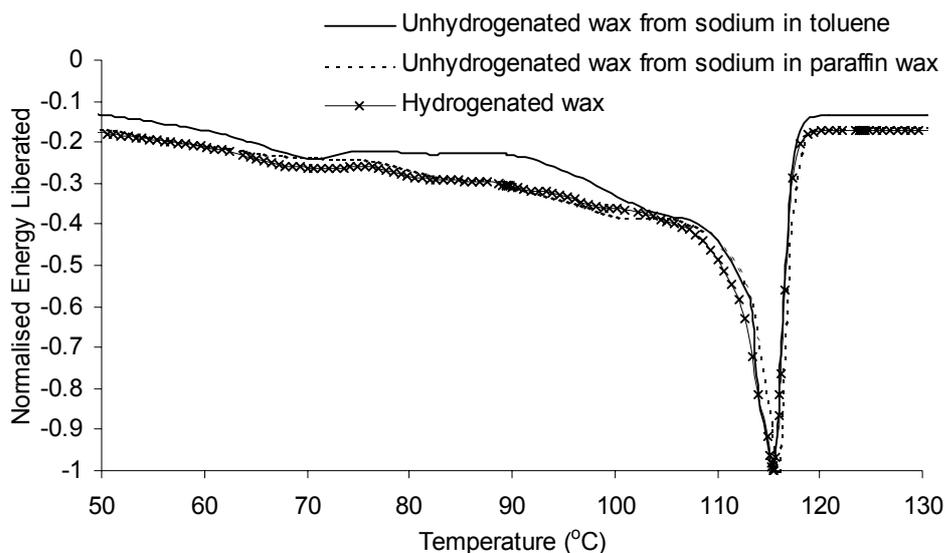


Figure 5-10: DSC plot of normalised energy liberated as a function of temperature: Unhydrogenated synthesised wax (from both sodium in toluene and sodium in paraffin wax) and hydrogenated synthesised wax

From these results it can be seen that the samples are of high enough molecular weight to give an indication as to whether molecular folding occurs or not yet are low enough so that molecular folding will not significantly influence the melting point. Estimations of the carbon number of a pure alkane with the same melting point is shown in Table 5-4:

Table 5-4: Estimation of carbon number of an alkane with the same melting point

Sample	Melting point (K)	Carbon number
Unhydrogenated wax from sodium in toluene	388.49	102.0
Unhydrogenated wax from sodium in paraffin wax	389.08	104.6
Hydrogenated wax	388.65	102.7

Clearly the molecular weights calculated in Table 5-4 are an estimation of the molecular weight present in the alkane. The question now exists as to whether it corresponds to the number average, weight average or peak molecular weight of the sample. Feng et al. [39] investigated the use of DSC to estimate the molecular weight of a sample and published M_n , M_w , peak molecular weight and melting point data for 9 polyethylene samples. The method developed to link the melting point and the molecular weight is similar to that developed in this work in section 4.6.2, yet samples from nC16 through nC60 were used. The method in this work is thus superior as it takes into account the solid state from melting (developed from nC40 upwards only, as these samples melt from the orthorhombic crystal structure) and higher alkanes were used for the fit and will thus be used. Table 5-5 shows the calculated CN from the melting point and compared this value with the M_n , M_w and peak molecular weight carbon number from the GPC results.

Table 5-5: Comparison of carbon number calculated from melting point with M_n , M_w and Peak MW [39]

Sample	M_n *		M_w *		Peak M_{tot} *		T_m		CN difference: T_m -		
	g/mol	CN	g/mol	CN	g/mol	CN	K	CN	M_n	M_w	Peak
A **	4006	286	8192	585	6834	488	404.2	286	0	-299	-202
B **	2536	181	4328	309	3628	259	402.3	236	55	-73	-23
C **	2326	166	3586	256	3278	234	400.0	195	28	-62	-40
D	1682	120	2788	199	2228	159	398.9	179	59	-20	20
E	2718	194	3824	273	2620	187	398.2	171	-23	-102	-16
F	2550	182	4398	314	2872	205	397.4	162	-20	-152	-43
G	1626	116	2312	165	1878	134	395.8	147	31	-18	13
H	1108	79	1654	118	1402	100	392.3	121	42	3	21
I	548	39	688	49	506	36	356.8	41	2	-8	5
Average of samples									19.3	-81.3	-29.5
Average of sample D – I									15.1	-49.6	-0.1

* M_n , M_w and Peak M_{tot} calculated relative to polystyrene standards

** Samples A, B and C have very high molecular weights and polymer folding may influence molecular weight estimation from melting points

Except for very low molecular weight samples, the carbon number from the melting point gives an underestimate of M_w . When all samples are compared, the carbon number from the melting points gives the best correlation to M_n , but when the heavy samples are omitted (samples where molecular folding may occur), the carbon number from the melting point corresponds best to the peak molecular weight. From this analysis alone, it seems as if the carbon number obtained from the melting point on the DSC results on the samples synthesised in this work, will give a good indication of the peak molecular weight.

Regarding the question as to the distribution of the molecules, a comparison of the 'sharpness' of the DSC melting plot will give an indication of the distribution. A DSC plot around the melting point of the pure alkane, a wax mixture and the synthesised mixture is compared in Figure 5-11:

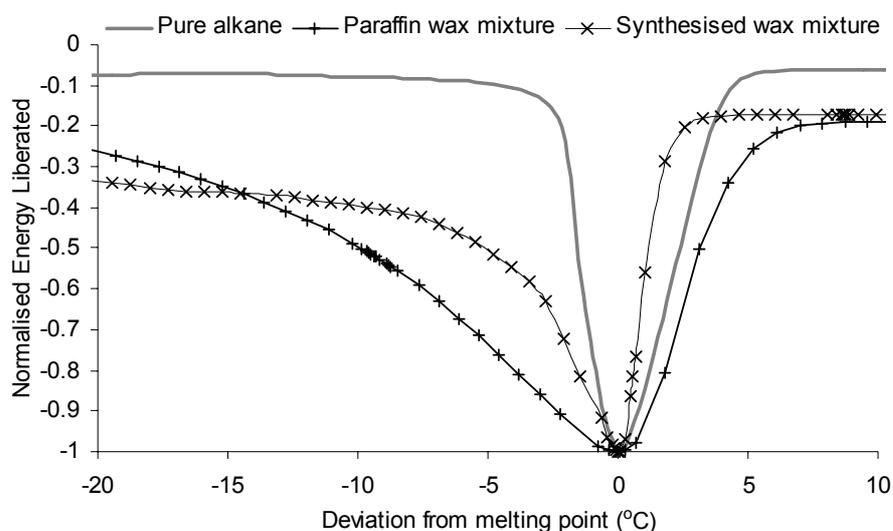


Figure 5-11: DSC plot of the normalised energy of pure alkane nC40, a commercial paraffin wax mixture (Paraflint C80 from Schümann-Sasol) and the synthesised hydrogenated wax around the melting point

Although not as sharp as the pure alkane, the plot shows a sample that is probably sharper than the commercial wax.

A high temperature GPC analysis was conducted on the sample by PSS, Mainz, Germany with a Mixed E type column. It is very difficult to accurately determine the molecular mass distribution for ultra low molecular weight polymers, such as the polymer studied in this work, from general GPC analysis. Even when columns for low molecular weight polymers are used, such as the Mixed E column used in this work, resolution at low molecular weights is not very good [39]. However, the results do give a fair indication of the molecular weight range present but should be used with caution. The following results were obtained:

Table 5-6: Analysis results of final hydrogenated product

Calibration Standard	Universal (Polystyrene and polyethylene standards)	Polystyrene
M_n (g/mol)	333	903
M_w (g/mol)	2840	5530
M_z (g/mol)	10300	18900
Polydispersity (M_w/M_n)	8.53	6.12
Weight % < 500 g/mol	16.07	14.54
Weight % 500 – 1000 g/mol	34.88	13.34
Total weight % < 1000 g/mol	50.95	27.88

A comparison of the molecular weight range present as estimated with the DSC and the GPC results is given in Table 5-7:

Table 5-7: Estimation of carbon number of synthesised polymer

Method of Estimation	Estimate of CN
Melting point from DSC	102.7
GPC: Universal standard M_n	23.8
GPC: Universal standard M_w	202.8
GPC: Polystyrene standard M_n	64.5
GPC: Polystyrene standard M_w	395.0

As seen, the estimations of the molecular weights range considerably. The estimation of CN = 24 from the mole average molecular weight from the universal standard is not realistic. An alkane with 23 carbon atoms is a solid at room temperature but is generally soft and melts at approximately 50°C. The other extreme, the estimation of CN = 395 from the weight average molecular weight from the polystyrene standard is also not realistic. This alkane would melt in the range of 140°C and thus this result is neither realistic. The true peak molecular weight thus most probably lies between CN = 65 and CN = 203.

For the purpose of this work, the melting point will be used to estimate the peak molecular weight, yet results will also be compared in the range of nC80 - nC150. The use of the melting point for estimation of the peak molecular weight will further be justified in section 5.3.2.

5.2 EQUIPMENT AND METHOD OF MEASUREMENT OF HIGH PRESSURE PHASE EQUILIBRIUM

Various methods for the measurement of phase equilibrium data can be used. The methods can be divided into static and dynamic methods: In dynamic methods the solute is continuously swept with the supercritical solvent, the supercritical phase being sampled and the solubility measured. On the other hand, in static methods the solvent and solute are loaded in a high-pressure cell and the phase transition pressure is measured. No analysis is required as the quantity of solvent and solute is known. Both methods have their advantages and disadvantages [37] and taking these into account a static method is chosen.

5.2.1 EQUIPMENT

A variable volume high-pressure phase equilibrium cell is used to conduct the measurements. The phase equilibrium cell had the following specifications:

Table 5-8: Specification and accuracy of high-pressure phase equilibrium cell

Minimum volume	10 cm ³
Maximum volume	50 cm ³
Maximum operation pressure	250 barA
Maximum design pressure	500 barA
Maximum test pressure	290 barA
Maximum temperature	150 °C
Maximum design temperature	200 °C
Phase transition detection method	Visual
Accuracy of temperature measurement	± 0.2 K
Accuracy of pressure measurement	± 0.5 barA
Accuracy of volume measurement	± 0.2 cm ³
Accuracy of phase transition pressure measurement	± 1 barA

A schematic representation of the experimental set-up is shown in Figure 5-12:

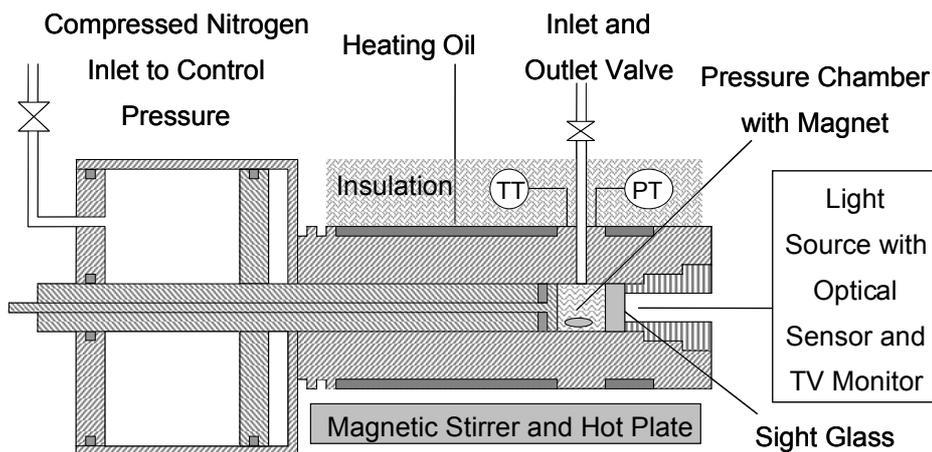


Figure 5-12: Schematic representation of high-pressure phase equilibrium cell

For details regarding the design, experimental procedure and safety requirements, the reader is referred to Schwarz et al. [40] and Schwarz [37]. A summary of the experimental procedure is given in section 10.2 in appendix B.

5.2.2 DATA OBTAINED

For each loading of solvent and solute the phase equilibrium is measured at three temperatures. As the data is not at exactly the same temperature, a method had to be devised to obtain isothermal data. It has been proven [40] that, within a limited temperature range the isopleths are a straight line, as seen in Figure 5-13:

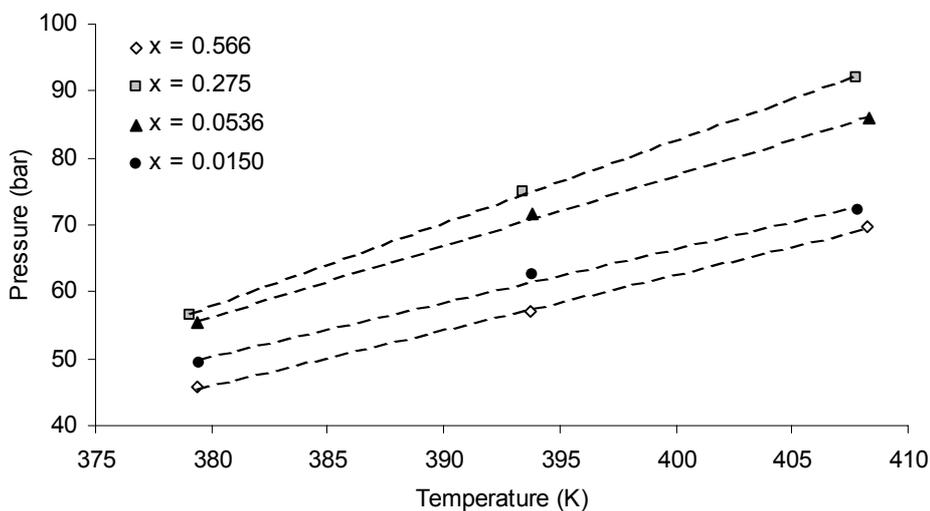


Figure 5-13: Isopleths for the system propane – nC32 as measured with the phase equilibrium cell [40]

For each mass fraction a linear equation is constructed in the form:

$$\text{Equation 5-10: } P = A * T + B$$

The values of A and B are determined from the data and by using this equation, the phase equilibrium pressure at any temperature within the measured temperature range can be determined. A similar method is used to determine density as a function of temperature.

5.3 THE PRINCIPLE OF CONGRUENCE, THE PROOF AND ITS APPLICATIONS

There must be some relationship between the phase equilibrium pressure of a pure alkane and an alkane mixture with a similar melting point or composition. In this sub-section this relationship is investigated. This investigation can be justified by the fact that the alkane generated is not pure but rather a mixture of varying polydispersity and the aim is to determine a correlation between the behaviour of pure alkanes and equivalent alkane mixtures.

5.3.1 THE THEOREM OF CORRESPONDING STATES AND THE PRINCIPLE OF CONGRUENCE

Originally proposed by van der Waals in 1873 [41], the law of corresponding states expresses the generalisation that equilibrium properties, which depend on intermolecular forces, are related to the critical properties in a universal kind of way. The relationship of pressure to volume at constant temperature is different for different substances. However, the corresponding states theory asserts that the function relating the reduced pressure to reduced volume is the same for all substances. On a macromolecular scale, the theory can thus be formulated as follows [42]:

“All fluids at the same reduced pressure and reduced temperature have the same compressibility factor.”

The corresponding states theory holds well for fluids containing simple molecules and, upon semi-empirical extensions, such as the inclusion of the acentric factor, it also holds for many other substances where molecular orientation is not important, i.e. for molecules that are not strongly polar or hydrogen bonded. The molecules of interest in this work are not simple molecule yet they are neither polar nor hydrogen bonded. Thus despite their chain-like nature, the theory of corresponding states may thus be applied with some amount of success.

The principle of congruence developed from the concept of corresponding states and allows us to equate the thermodynamic and transport properties of a mixture of normal alkanes to that of a pure alkane of the mole-fraction-averaged carbon number. The principle was first mentioned by Brønsted et al. in 1946, as cited by Peters et al. [43].

In 1981 Creek et al. [44] introduced the concept of a quasi-binary approximation: This approximation assumes that a ternary mixture, with two non-volatile components only slightly different in chain length or structure, effectively behave like a binary mixture. The criterion for the validity of this hypothesis is that the mole fraction ratio of the two non-volatile components is the same in the three coexisting phases.

Peters et al. [43] studied the application of the principle of congruence on the bubble and dew points of alkane mixtures. The study was conducted by calculating the bubble and dew point curves for various ternary mixtures with the simplified perturbed hard chain theory equation of state (SPHCT EOS) [45], an equation of state that inherently obeys the principle of congruence. In testing the application of the principle of congruence to the bubble point curve, Peters et al. [43] compared the SPHCT EOS predictions of various quasi-binary mixtures with both experimental and SPHCT EOS predictions of the equivalent binary mixtures.

From the results obtained, it was seen that the quasi-binary SPHCT EOS prediction is close to the binary SPHCT EOS prediction, yet, especially in the case of systems with methane as solvent, the binary SPHCT EOS prediction is not in complete agreement with the experimental data. However, from the good agreement between the quasi-binary and binary SPHCT EOS predictions, Peters et al. [43] came to the conclusion that, for predicting the bubble points of mixtures of long alkanes in short-chain solvents, the principle of congruence in terms of pressure and temperature provides an excellent approximation.

In a similar manner, the application of the principle of congruence in predicting the dew points was also tested. From the results obtained it can be seen that the SPHCT EOS provides a poorer prediction of the binary system dew points than the bubble points, especially at higher temperatures. In addition, the SPHCT EOS prediction of the quasi-binary system departs from the binary prediction yet, not mentioned by Peters et al. [43], it can be seen that the departure from the experimental data, in most cases shown, is of the same order of magnitude for the binary and the quasi-binary prediction.

It should be noted in the analysis of Peters et al. [43] of the application of the principle of congruence to the dew point curve, the SPHCT EOS is not able to provide a good description of the dew point curve of the binary. Thus errors inherent in the EOS may hamper the application of the principle of congruence in the dew point curve. However, their reasoning, namely that the predictions fail due to the mixture being in the compressible vapour phase, also deserves merit. Should this reasoning hold true, the application of the principle of congruence may not hold true in the mixture critical region either.

Thus although predictions in the bubble point area of the solubility curve are thought to adhere to the principle of congruence, doubt exists as to the adherence in the dew point area of the solubility curve and no mention has been made regarding the application of the principle of congruence to the mixture critical region. To test the application of the principle of congruence in the bubble point, dew point and mixture critical region experimental measurements are required.

5.3.2 PRESSURE COMPOSITION MEASUREMENT

To test the principle of congruence experimentally, a plot of the solubility pressures (at constant temperature) of an alkane mixture is compared to that of a pure alkane with the same melting point. Using Equation 4-10 the melting point of 82.1°C (Measured by DSC) corresponds to a pure

alkane with 40 carbon atoms. The phase equilibrium measurements (for data see section 11.1.1 in appendix C) of the alkane mixture is plotted in Figure 5-14 together with a plot of the phase equilibrium data for nC40 generated according to the method as set out in section 3.5.1.

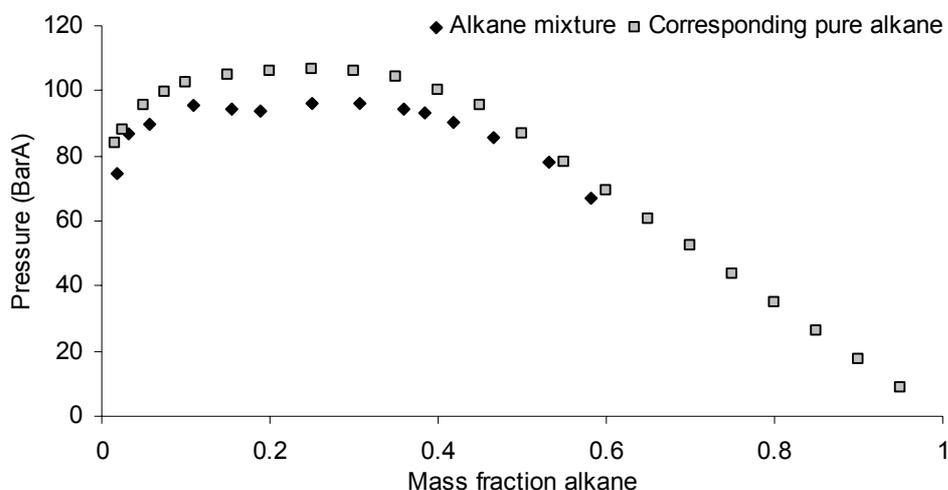


Figure 5-14: Solubility pressure of alkane mixture and pure alkane with same melting point as a function of mass fraction at 408 K

Although not identical, the plot is very similar and the pure alkane measurements would give a good approximation of the estimated phase equilibrium pressure of a corresponding melting point mixture. Additionally, the fact that these two plots correspond well, indicate that the choice of using the melting point as a method for determining the molecular weight of the corresponding alkane can be justified.

5.3.3 APPLICATION OF PRINCIPLE OF CONGRUENCE

By comparing the data in Figure 5-14 it can be seen that the pure alkane shows a slightly higher pressure required for solubility compared to the mixture, the degree varying in different regions in the graph.

In the bubble point region there seems to be good agreement between the data, thus confirming the SPHCT EOS predictions as proposed by Peters et al. [43].

When considering the dew point predictions, there seems to be good prediction, the data indicating better predictions at lower mass fractions. The principle of congruence seems to hold true in this region.

The largest errors seem to occur in the mixture critical regions. A difference in solubility of 10 bar is noted, this difference translating to approximately 10 %. The difference may be attributed to large polydispersity of the mixture and the presence of significant quantities of low molecular weight compounds.

Thus in the dew and bubble point areas the principle of congruence seems to hold true, yet deviations seem to occur in the mixture critical region. Yet, even in the mixture critical region application of the principle of congruence leads to a good order of magnitude estimation of solubility pressure, an estimation that is good enough to determine if molecular folding occurs or not.

5.4 BINARY PHASE EQUILIBRIUM DATA OF PROPANE WITH HIGH MOLECULAR WEIGHT ALKANES

Binary phase equilibrium measurements were conducted with the sample prepared as mentioned above. A measurement of this set of data was extremely difficult. Due to the high melting temperature, measurements were required to be conducted at higher temperatures than for which the alkane data was measured [40], [1]. In addition, due to the higher molecular weight of the alkane, the wax is a lot more viscous than the pure alkane and thus more difficult to mix. To ensure a pseudo-two phase region does not occur, the wax needs to be compressed into the one phase region and the phase transition point is then approached from the one phase region. Due to the high viscosity a large over pressure was often required to obtain the single-phase region and in some cases over pressurisation beyond the 275 barA limit of the equipment was required and thus no meaningful results were obtained for these data points. In the low mass fraction region, samples were left for up to 15 minutes to allow baric equilibrium to be attained.

However, a number of meaningful data points were attained and results thereof shown below. The data is given in section 11.1.2 in appendix C.

5.4.1 PRESSURE-COMPOSITION DATA

A pressure composition plot of the measured data is shown in Figure 5-15:

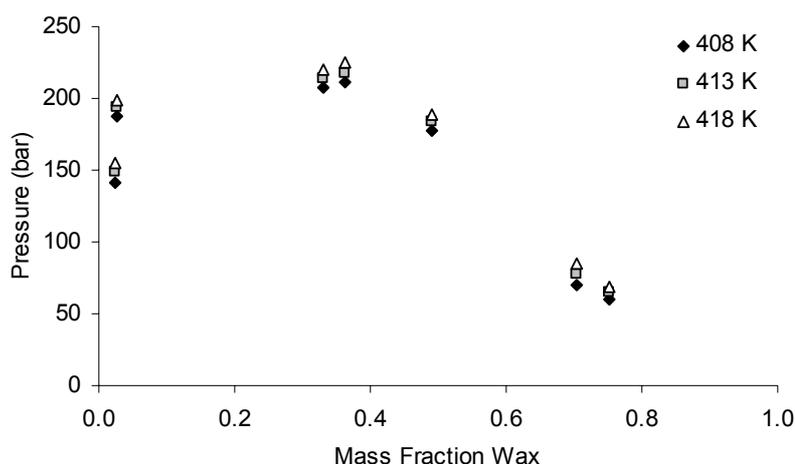


Figure 5-15: Pressure-composition plot of synthesised wax as a function of mass fraction at 408 K, 413 K and 418 K

At 408 K the data measured above is compared to data generated by the method as set out in section 3.5.1 for a pure alkane with the same melting point and shown in Figure 5-16:

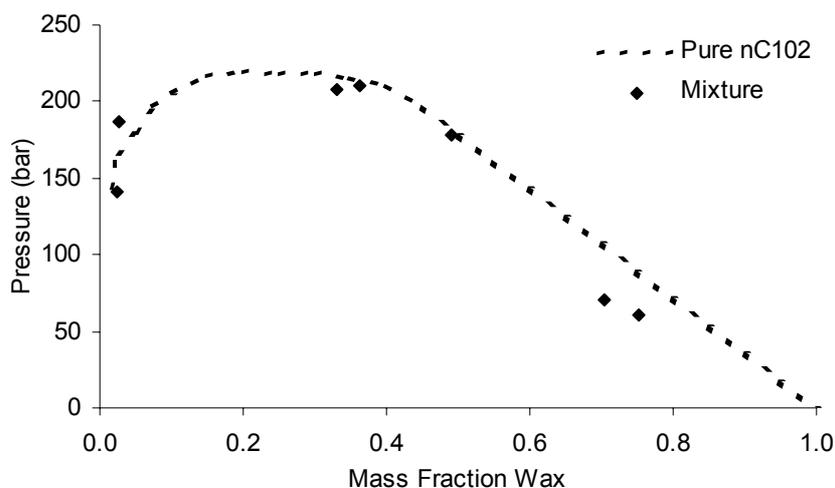


Figure 5-16: Comparison of experimentally measured data with predicted values for pure nC102 at 408 K

When comparing Figure 5-14 and Figure 5-16, the data in the latter shows that the method, as set out in section 3.5.1 provides a good indication of the phase behaviour expected for nC102. Deviations do occur, yet it should be remembered that, as shown in Figure 5-14, due to the polydisperse nature, a mixture shows a slightly lower phase transition pressure. The individual regions will be discussed in more detail in section 5.5.

5.4.2 DENSITY-COMPOSITION DATA

In addition to measuring the phase transition pressure, the phase equilibrium cell also measures the phase transition density. Density measurements at 408 K are shown in Table 5-9:

Table 5-9: Measured density of synthesised wax in propane at 408 K

Mass fraction of wax	Density (kg/m ³)
0.0231	322
0.0275	354
0.330	598
0.362	468
0.491	530
0.705	605
0.753	593

Although the density is not very accurate [37] it does provide a good estimation of the density of the phase investigated. As expected, the data measured is liquid like in dimension. It has previously been proven [37] that the density is only weakly dependent on the molecular weight of the alkane, a slight increase in density observed with an increase in molecular weight. For comparative purposes, the densities measured here are compared to that of nC60:

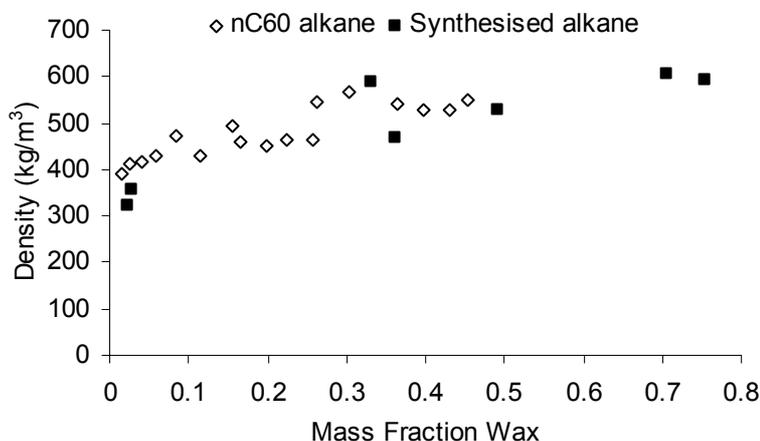


Figure 5-17: Comparison of densities measured for the synthesised alkane with that of nC60 at 408 K as a function of mass fraction wax

Figure 5-17 shows that the densities compare well with those measured for the pure alkane, variations being attributed to the increase in molecular weight of the alkane and experimental accuracies.

5.5 SUPERPOSITION OF HIGH MOLECULAR WEIGHT ALKANE MEASUREMENTS ON PRESSURE-CARBON NUMBER PLOTS

The results from Figure 5-17 show a good correlation between the predicted pure alkane and the synthesised mixture. However, before any comment can be made regarding molecular folding, the measured data should be superimposed on the pressure-carbon number plots. The high, mixture critical and low wax mass fraction ranges will now be considered individually.

5.5.1 HIGH WAX MASS FRACTION RANGE

Two data points were measured in the high wax mass fraction range. The data has been superimposed on a pressure carbon number plot of the same mass fraction. As no alkane data has been measured for mass fractions above approximately a fraction of 0.5, a combination of the methods set out in section 3.5.1 is used to predict the data: the data is first extrapolated to zero, as illustrated in Figure 3-29, and subsequently data is collected for various alkanes at the desired mass fraction and the linear non-folding relationship is determined. The data used in the generation of the measured pure alkane data as well as the straight line data for both the no folding relationship and the one fold relationship in Figure 5-18 and Figure 5-19 is given in section

11.2 in appendix C. The experimental data point is shown for a carbon number of 102. However, it should be remembered that the analysis results indicate that the carbon number may be between 80 and 150 and this range is also shown.

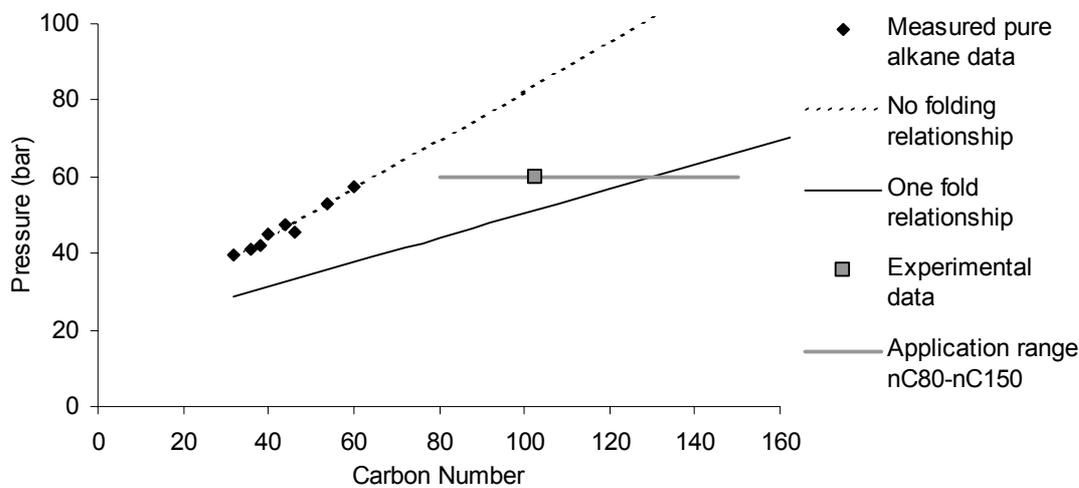


Figure 5-18: Pressure carbon number plot for $x = 0.753$ with measured pure alkane data, the no folding relationship, the single fold relationship and experimental data and application range ($T = 408.15$ K)

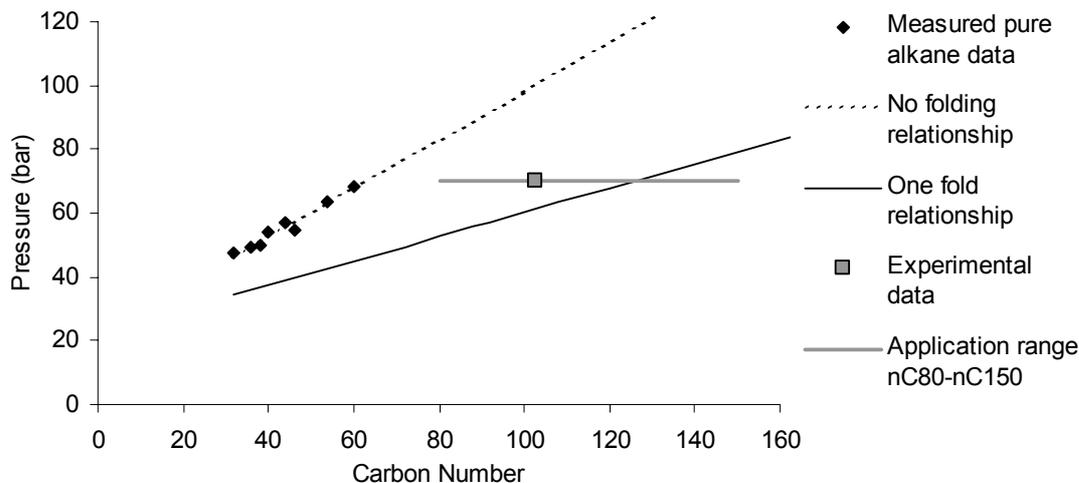


Figure 5-19: Pressure carbon number plot for $x = 0.705$ with measured pure alkane data, the no folding relationship, the single fold relationship and experimental data and application range ($T = 408.15$ K)

Before commenting on the results shown in Figure 5-18 and Figure 5-19 a couple points need to be highlighted: Although the mass fractions measured here can be determined quite accurately, the measurements were really difficult. The liquid phase is extremely viscous and a large difference in viscosity exists between the liquid and the vapour phase. This may result in small quantities of undetectable propane in crevices and mixing may not be perfect, especially at low temperatures. In order to limit the afore-mentioned problems, a relatively long time was allowed

for the experiments to reach baric equilibrium. Additionally it should be noted that the method of generation of the pure alkane data points, although the best available, is not without fault. Extrapolation is used twice: First the nC32 through nC60 data is generated and then to extrapolate to higher carbon numbers. In this range carbon number lines are thus more of an indication than an accurate description of what may be happening.

Yet, despite the above, it is noted that the measured data is at lower pressures than expected. Two factors may be at play:

- The observed lower pressures may be attributed to the nature of the light phase in the two-phase region just below the solubility pressure: This phase will consist mainly of propane but contain a limited amount of dissolved alkane. The alkane dissolved in the light phase will be of the lower members. The lower members have a lower solution pressure and will thus lower the phase transition pressure than for the corresponding pure alkane.
- Although the data point measured is above the single fold area, the application range extends within the range of molecular folding. It may thus be that a limited quantity of the higher molecular weight compounds do undergo molecular folding and this folding influencing the phase transition pressure.

5.5.2 MIXTURE CRITICAL REGION

Three data points were measured in the mixture critical region. The measured pure alkane data is generated by linear interpolation between data points of measured data and extrapolated to higher carbon number and the data plotted in Figure 5-20 through Figure 5-22 is given in section 11.2 in appendix C.

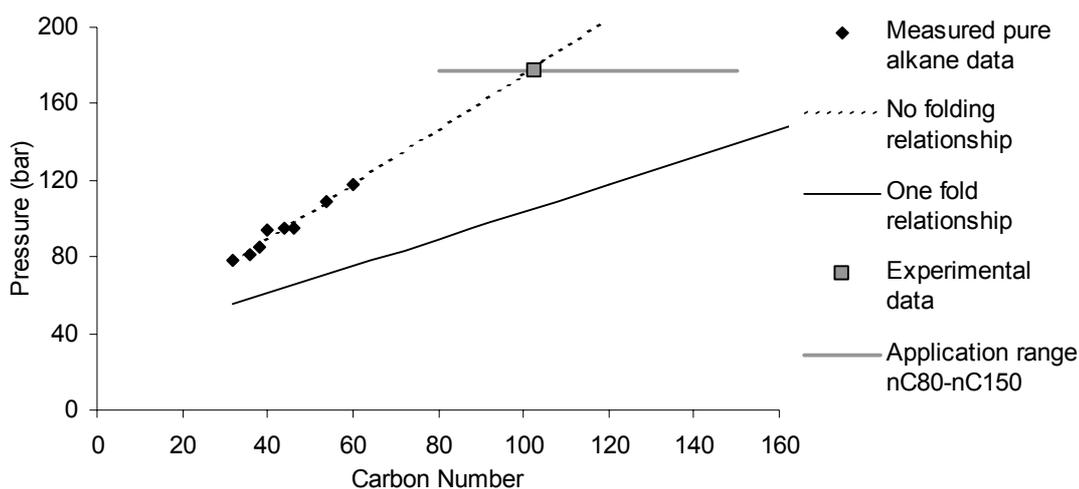


Figure 5-20: Pressure carbon number plot for $x = 0.491$ with measured pure alkane data, the no folding relationship, the single fold relationship and experimental data and application range ($T = 408.15$ K)

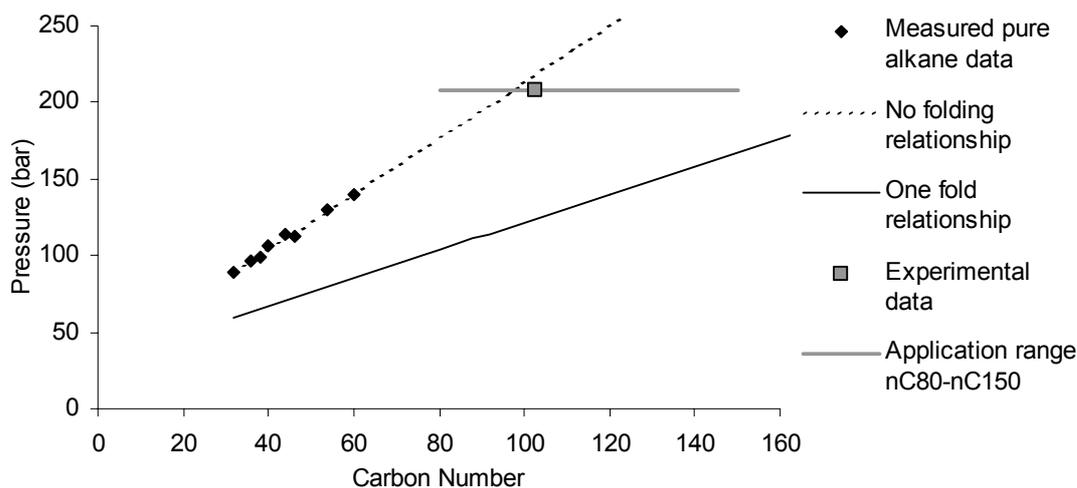


Figure 5-21: Pressure carbon number plot for $x = 0.363$ with measured pure alkane data, the no folding relationship, the single fold relationship and experimental data and application range ($T = 408.15$ K)

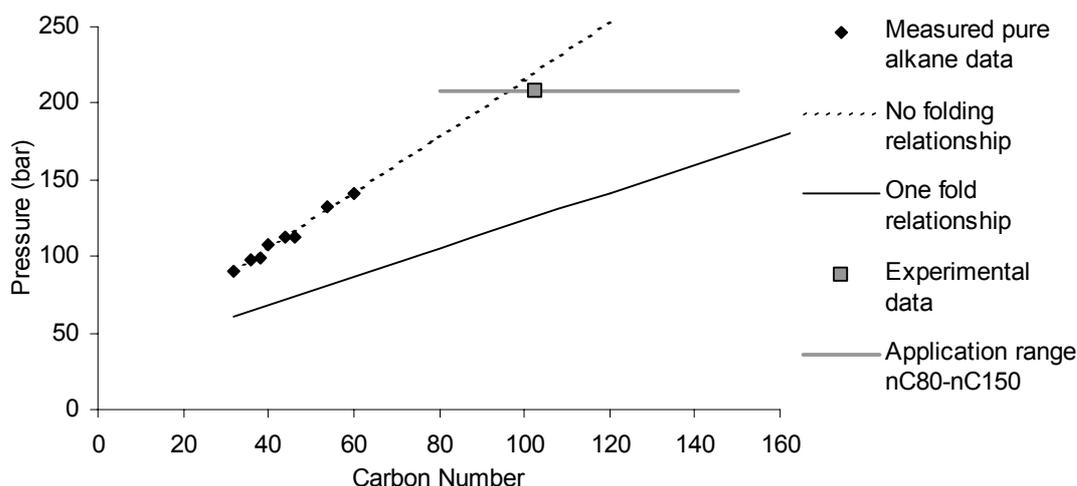


Figure 5-22: Pressure carbon number plot for $x = 0.330$ with measured pure alkane data, the no folding relationship, the single fold relationship and experimental data and application range ($T = 408.15$ K)

Although the viscosities of the co-existing phases are similar due to similar composition, it was still difficult to measure the data points as the viscosities were still high and the pressures approached the limit of the equipment. However, the results in the mixture critical region compare well. The phase transition pressure measured is a few bars (13 barA) below the predicted pressure of the pure alkane. This is less than the 10 % difference observed in the mixture critical region in Figure 5-14 and thus it is expected that molecular folding has not occurred.

5.5.3 LOW WAX MASS FRACTION RANGE

Two data points were measured. The measured pure alkane data was generated in the same manner as for the mixture critical region and the data shown in Figure 5-23 and Figure 5-24 is given in section 11.2 in appendix C.

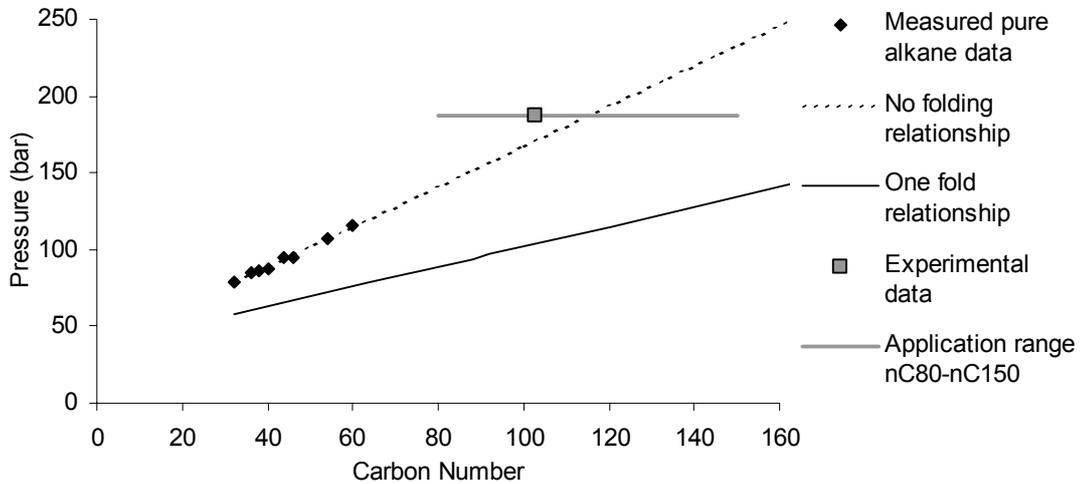


Figure 5-23: Pressure carbon number plot for $x = 0.0273$ with measured pure alkane data, the no folding relationship, the single fold relationship and experimental data and application range ($T = 408.15$ K)

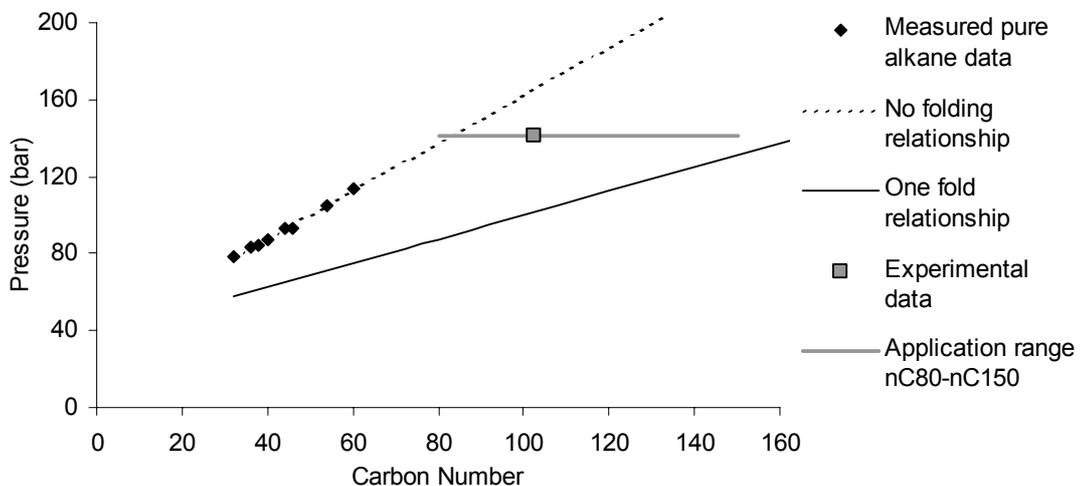


Figure 5-24: Pressure carbon number plot for $x = 0.0231$ with measured pure alkane data, the no folding relationship, the single fold relationship and experimental data and application range ($T = 408.15$ K)

As in the high wax mass fraction and the mixture critical region, the data measurement was quite difficult. The slope of the P-xy plot is quite steep and a large difference in the viscosities and nature of the two co-existing phases made for difficult measurements. However, meaningful results can be obtained from the data measured. Both fractions are close to the no-folding

relationships, the one above, the other below and in all probability molecular folding thus does not occur in this region.

5.6 APPLICATION OF RESULTS TO CONCEPT OF MOLECULAR FOLDING

The only way molecular folding can be proven or disproven beyond doubt is with the aid of physical measurements, such as molecular orientation measurements. However, the results obtained in section 5.5 gives a good indication as to whether it is present and more importantly, the effect (if any) it has on the phase equilibria.

The results in the low mass fraction and mixture critical region indicate that under these conditions for this alkane molecular folding either does not occur or has no effect on the phase equilibria. However, in the high wax mass fraction region, some effect comes into play. A possible explanation of the lower than expected phase transition pressure of the synthesised wax is the presence of molecular folding in the higher molecular weight compounds. It is clear that not all molecules undergo molecular folding, yet should a couple of the higher members undergo molecular folding, thus behaving similar to the lower homologue members, they will lower the effective molecular weight and thus lower the phase transition pressure.

To quantify the above-mentioned phenomena is difficult but a qualitative proposal for molecular folding in alkanes can be given. It is proposed that two phenomena are at play:

- Firstly, the concentration of the solvent in wax: At higher wax fractions, the wax molecules no longer behave independently of one another.
- Secondly, the molar concentration of the molecules undergoing molecular folding.

At low wax mass fractions the alkanes behave in a similar manner as expected, i.e. in the no fold region. This can be attributed to the fact that sufficient solvent is present to allow the molecules to act independently of one another and if a molecule does undergo molecular folding, the effect the folded molecule has on lowering the pressure is negligible due to the low concentration of molecules undergoing molecular folding.

At high wax mass fractions, deviation seems to occur. The molecules are starting to influence one another and the assumption of no interaction no longer hold true (assumption of the principle of congruence). Additionally it may be that the higher members start to fold and due to their high concentration, these molecules start to have a noticeable effect on the phase transition pressure.

Exactly where the transition occurs between the two regions, it is not know. In light of the nature of the phenomena occurring here, it is expected that the transition is not at a single point, but rather a gradual change. The point where the effect becomes significant is thus dependent on the accuracy required. Which of the two above mentioned effects, is the major contributing factor cannot be determined from these measurements. Most likely, it is a combination thereof.

In conclusion, for wax mixtures in this range, the phase behaviour of the alkanes mixture critical and low mass fraction range, the pure alkane behaviour can be used to predict the data. However, with increasing mass fraction, it seems like deviations occur and for very high wax mass fractions, a significant effect is present and needs to be taken into account.

5.7 NOMENCLATURE

Symbol	Description
a	Number of carbon atoms in hydrocarbon backbone R ₁
A	Coefficient of isopleth in Equation 5-10
b	Number of carbon atoms in hydrocarbon backbone R ₂
B	Coefficient of isopleth in Equation 5-10
c	Number of carbon atoms in hydrocarbon backbone R ₃
CN	Carbon number
d	Number of carbon atoms in hydrocarbon backbone R ₄
e	Number of carbon atoms in hydrocarbon backbone R ₅
EOS	Equation of state
f	Total number of carbon atoms in alkane produced in Reinhard et al. synthesis method.
M _n	Number average molecular weight (g/mol)
M _w	Weight average molecular weight (g/mol)
T _m	Melting point (K)
M _{tot}	Molecular weight (g/mol)
n	Number of carbon atoms in a dibromoalkane used as starting material in Carothers et al. and Heitz et al. synthesis method
nCX	Refers to a normal alkane where X is the number of carbon atoms in the compound
P	Pressure (barA)
R ₁	Hydrocarbon backbone section in Reinhard et al. synthesis method
R ₂	Hydrocarbon backbone section in Reinhard et al. synthesis method
R ₃	Hydrocarbon backbone section in Reinhard et al. synthesis method
R ₄	Hydrocarbon backbone section in Reinhard et al. synthesis method
R ₅	Hydrocarbon backbone section in Reinhard et al. synthesis method
SPCHT	Simplified perturbed hard chain theory
T	Temperature (K)
x	Mass fraction wax in wax-propane mixture
z	Integer > 1 indicating the number of monomers in polymer synthesised by Carothers et al. and Heitz et al. method

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6 Solubility measurement of propane with waxes and wax derivatives

In this chapter the solubility data for a typical long chain alcohol and the corresponding alcohol ethoxylate will be measured. The measured data will be compared with that of the corresponding alkane and from the solubility data a method of separation for alkanes, alcohols and alcohol ethoxylates is suggested.

6.1 SOLUBILITY MEASUREMENTS OF PROPANE WITH ALCOHOL

Triacosanol ($C_{30}H_{61}-OH$) is the highest commercially available primary alcohol. Thus in order to investigate the phase equilibria of primary alcohol in propane, a mixture of alcohols is relied upon. In this project, Unilin 550 from Baker-Petrolite is used. The number 550 refers to the average molecular weight of the hydrocarbon backbone, thus translating into an average of 39 carbon atoms. The alcohol comprises of approximately 80% narrow range primary alcohol, the remainder being saturated alkanes, and the hydroxyl groups are evenly distributed amongst all carbon chain lengths.

6.1.1 EXPERIMENTAL MEASUREMENTS

Phase equilibrium measurements, as described in section 5.2.1 and by Schwarz [1] and Schwarz et al. [2], are measured for Unilin 550 in propane. Experimental data is given in section 11.1.3 in appendix C.

6.1.1.1 PRESSURE – COMPOSITION PLOT

A pressure-composition plot for the solubility of unilin 550 at various temperatures in propane is shown in Figure 6-1:

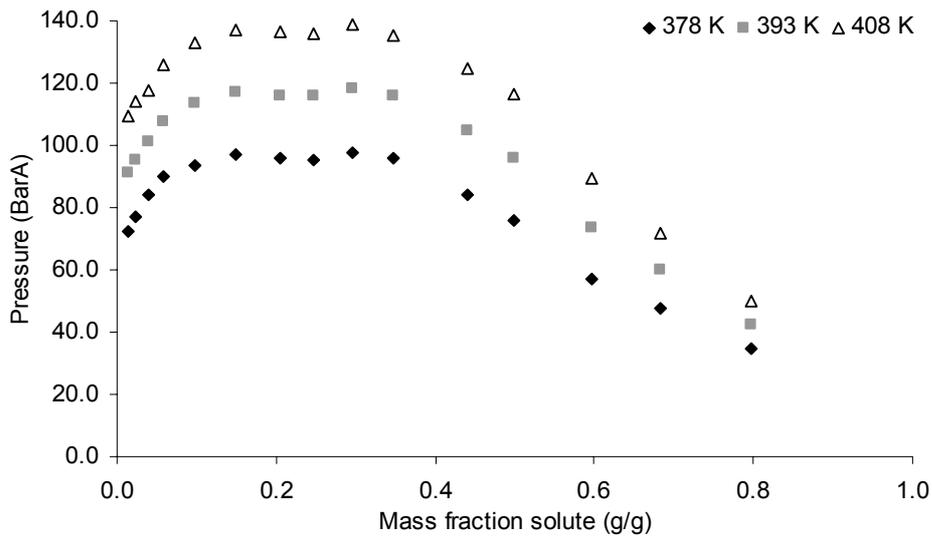


Figure 6-1: Plot of the pressure required for complete solubility as a function of mass fraction solute at 378K, 393K and 408K for the system propane-unilin 550

As seen in Figure 6-1 the alcohol is completely miscible in propane at moderate pressures and no two-phase region is observed within the temperature and composition range measured. Generally an increase in temperature leads to an increase in solubility pressure, the solubility pressure peaking between an alcohol mass fraction of 0.15 and 0.35. Critical opalescence is observed in the mixture critical region.

6.1.1.2 DENSITY – COMPOSITION PLOT

A plot of the density as a function of composition is shown in Figure 6-2:

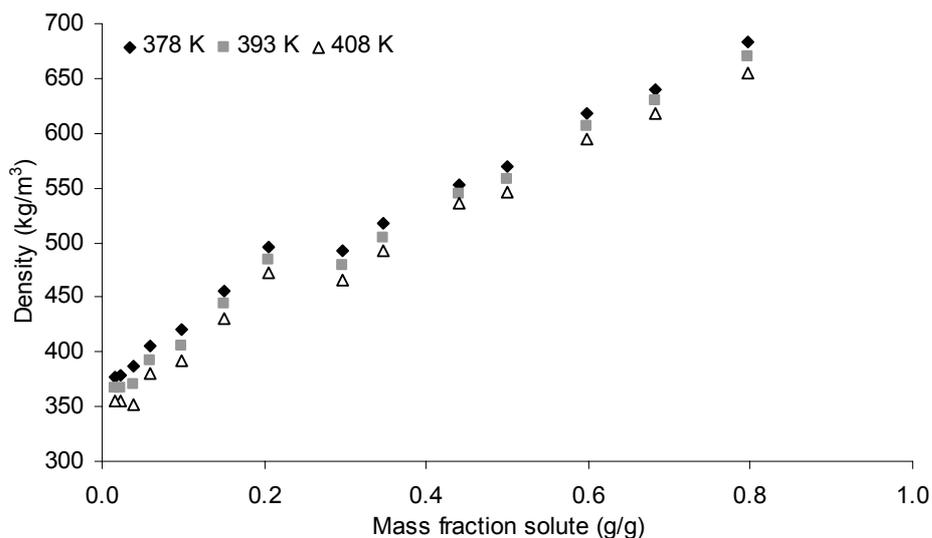


Figure 6-2: Plot of the density at solubilisation pressure as a function of mass fraction solute at 378K, 393K and 408K for the system propane-unilin 550

Figure 6-2 shows a liquid like density at the bubble point as well as in the mixture critical region and in the dew point region, the magnitude of densities being typical in supercritical solvent-solute systems. Additionally, as expected, it is noted that an increase in mass fraction alcohol as well as a decrease in temperature leads to an increase in density.

6.1.1.3 PRESSURE – DENSITY PLOT

In order to achieve a phase separation, a significant difference in density is required between the co-existing phases. A plot of pressure as a function of density will show the densities of two phases in equilibrium:

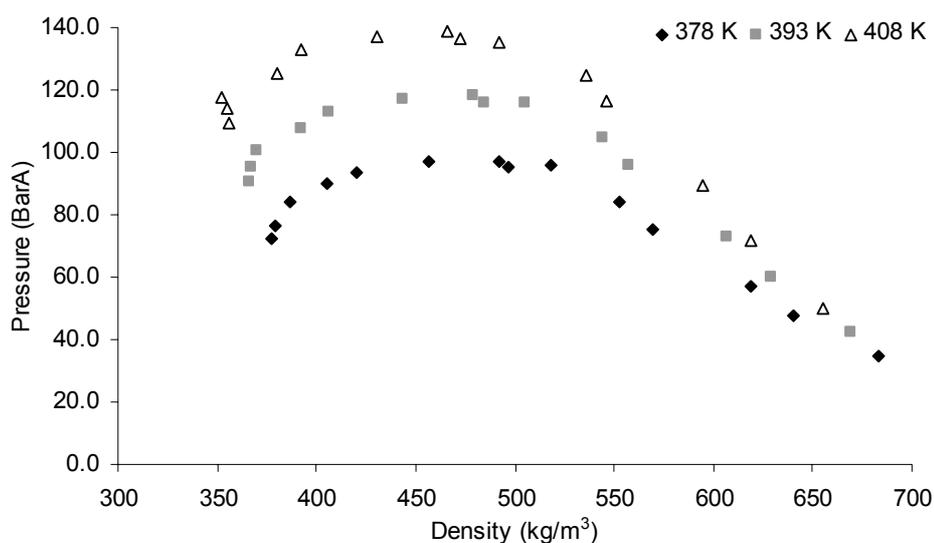


Figure 6-3: Plot of the pressure required for complete solubility as a function of density at 378K, 393K and 408K for the system propane-unilin 550

As seen in Figure 6-3 unless one is working in the mixture critical region, a significant difference in density can easily be achieved.

6.1.2 SOLUBILITY AND TYPE OF SYSTEM

From the description of the types of phase behaviour given in section 3.2.2 it cannot clearly be determined to which type of phase behaviour the alcohol-propane system belongs. Only a limited region of the phase diagram has been measured yet with the aid of this region it is suggested that the measured phase diagram is either type I or type V. It may be type I with no region of immiscibility or it may be type V where the region of immiscibility has not been measured. For alkanes of the same hydrocarbon chain length it is suggested, not with certainty though, that the phase diagram is type V [1]. As the alcohol-propane system is less symmetric than the corresponding alkane-propane system, it is suggested that this system is also of type V.

Whichever type of phase behaviour it is, albeit type I or type V, it is important to note that for the conditions measured in this work no three-phase region exists and total solubility of the alcohol can be achieved.

6.2 SOLUBILITY MEASUREMENTS OF PROPANE WITH ALCOHOL ETHOXYLATE

Unithox 550, also obtained from Baker-Petrolite, is used as a model alcohol ethoxylate. This is a 50 % ethoxylated unilin 550, the 50% ethoxylation referring to the fact that 50% of the average molecular mass of the alcohol ethoxylate is the polyethylene glycol chain and the 550 to the average molar mass of the hydrocarbon backbone. This translates to an average ethoxylation of 12.5 ethylene oxide units per molecule and an average molecular weight of 1100 g/mol.

6.2.1 EXPERIMENTAL MEASUREMENTS

Phase equilibrium measurements, as described in section 5.2.1 and by Schwarz [1] and Schwarz et al. [2], are measured for Unithox 550 in propane. Experimental data is given in section 11.1.4 in appendix C.

6.2.1.1 PRESSURE – COMPOSITION PLOT

A plot of the solubility pressure as a function of mass fraction at various temperatures is shown in Figure 6-4:

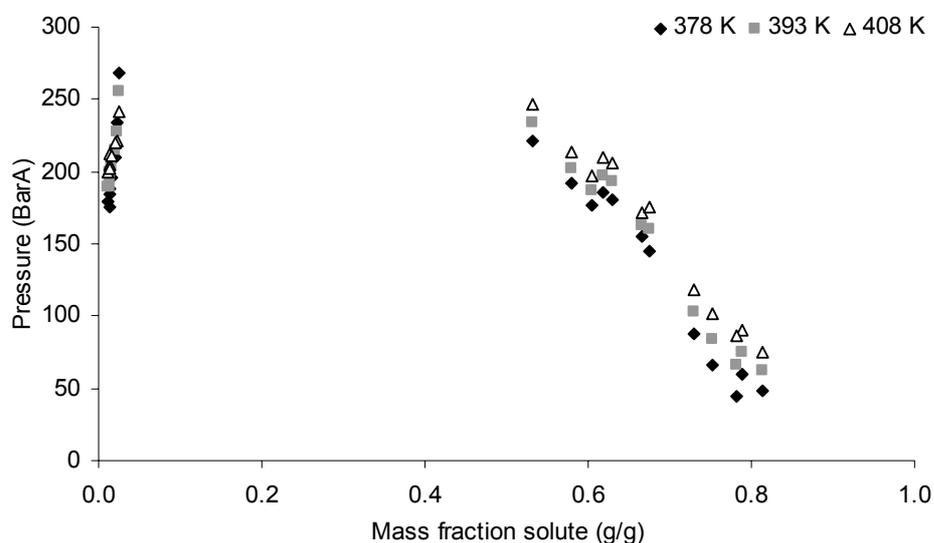


Figure 6-4: Plot of the solubility pressure as a function of mass fraction solute at 378K, 393K and 408K for the system propane-unithox 550

From Figure 6-4 it can be seen that the alcohol ethoxylate is not very soluble in propane. In the solute mass fraction region of approximately 0.025 to 0.5 the pressure required for solubility exceeds 275barA for the temperatures measured here. In addition, the measurements were quite

difficult, both in the bubble point region (due to high viscosity) and in the dew point region (steep gradient of curve) and thus a slightly larger scatter is noted. In the bubble point region a general trend of an increase in fraction solute and an increase in temperature resulting in an increase in solubility pressure is observed. To obtain better clarity in the dew point region, the data for solute mass fractions between 0.01 and 0.025 is shown in Figure 6-5:

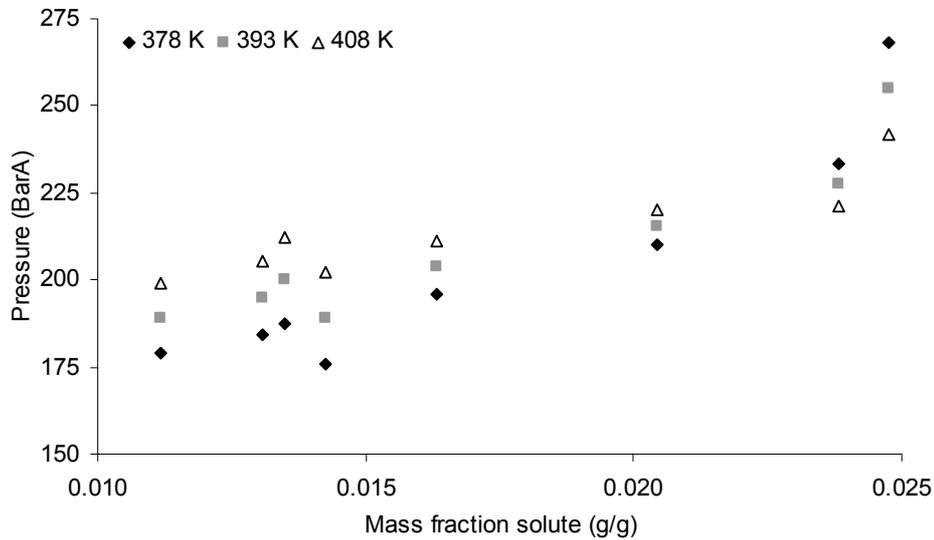


Figure 6-5: Detail of low mass fraction measurements shown in Figure 6-4

As expected, an increase in solute fraction in this region leads to an increase in phase transition pressure. However, the phase behaviour with regard to temperature is interesting. At approximately 0.022 a temperature inversion has occurred; this indicates that at even higher temperatures the solubility plot may close. This temperature inversion may aid in understanding the type of phase behaviour present.

6.2.1.2 DENSITY – COMPOSITION PLOT

A plot of the density as a function of composition is shown in Figure 6-6:

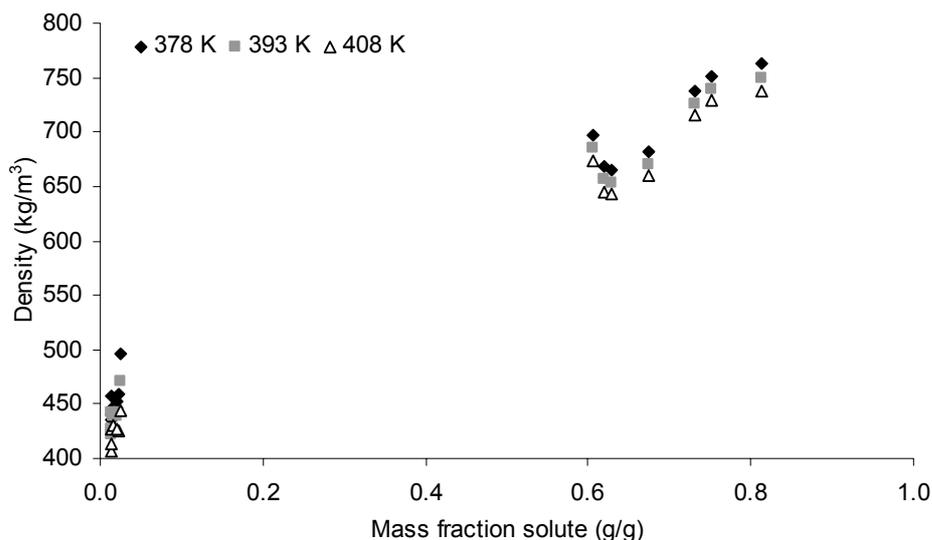


Figure 6-6: Plot of the density at solubilisation pressure as a function of mass fraction solute at 378K, 393K and 408K for the system propane-unithox 550

The densities measured here are, as in the case of the alcohol, liquid-like densities typical of supercritical solvent-solute systems with a generally decreasing trend with increasing solvent content. A plot of the low solute mass fraction densities is shown in Figure 6-7:

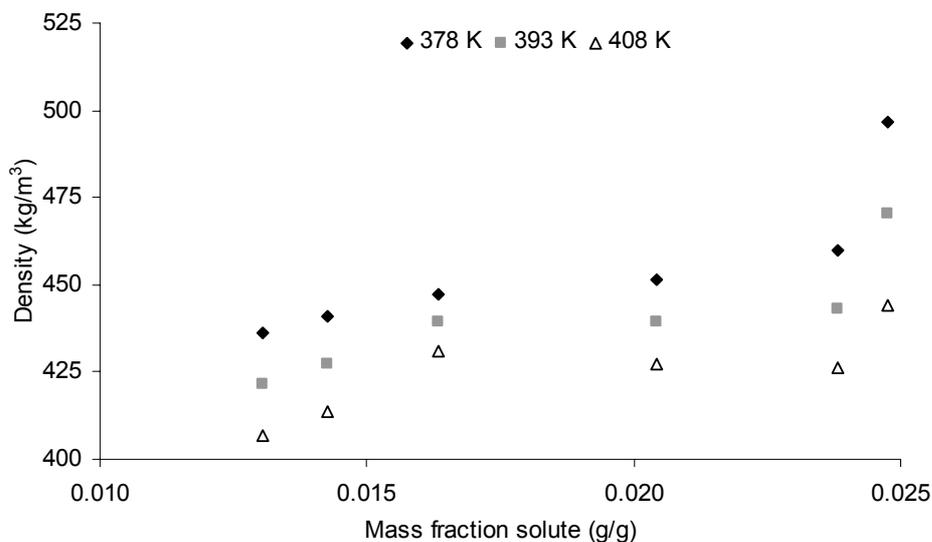


Figure 6-7: Detail of low mass fraction measurements shown in Figure 6-6

Figure 6-7 shows the same general trends that are seen in Figure 6-6 with no density inversions and generally no special or unexpected behaviour.

6.2.1.3 PRESSURE – DENSITY PLOT

Although only a limited quantity of data is available for this system, a plot of the solubility pressure as a function of density is shown in Figure 6-8:

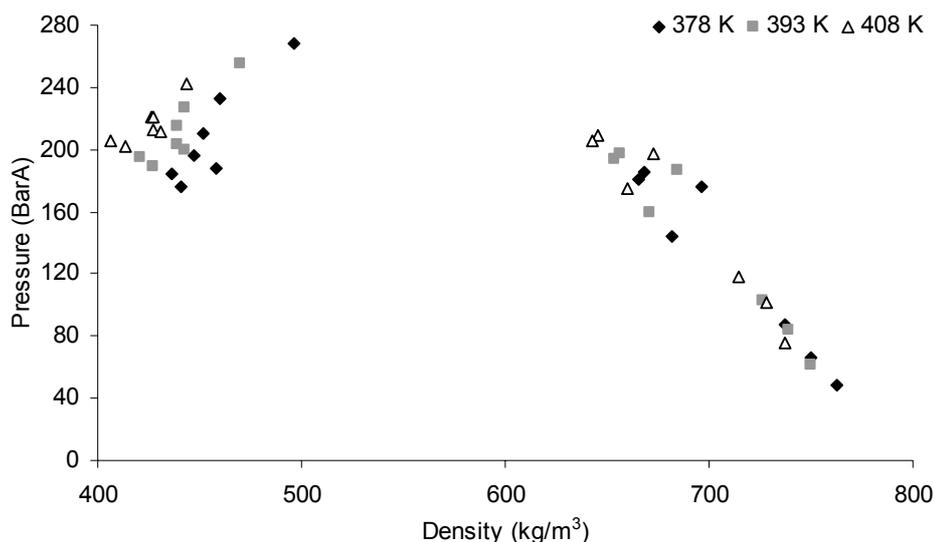


Figure 6-8: Plot of the pressure required for complete solubility as a function of density at 378K, 393K and 408K for the system propane-unithox 550

Figure 6-8 shows a significant difference in the density of the two co-existing phases. Additionally, by extrapolating the dew point (low density) data and the bubble point (high density) data to form a single curve at a given temperature, it can be estimated that the pressures required total solubility are not orders of magnitude larger than those measured here and may possibly be below 400barA.

6.2.2 SOLUBILITY AND TYPE OF SYSTEM

The solubility of alcohol ethoxylates with propane is far less than that of alcohols or alkanes in propane. This may be used advantageously so as to preferentially dissolve the alcohol and the alkane from a mixture.

When considering the phase diagram of the system studied here, as in the case of the alcohol and the alcohol ethoxylate, it cannot be said with absolute certainty to which type this system belongs yet from the data available, a well-educated guess can be made. The most important information with regard to the type of phase exhibited can be regarded as the temperature inversion that occurs at low mass fractions. By superimposing this behaviour on pressure-composition plots of type IV, as shown in section 3.2.2.4, it is suggested that type IV phase behaviour is exhibited. At low temperatures the solvent and solute are generally immiscible, yet as the temperature increases, so does the miscibility.

6.3 COMPARISON OF VAPOUR-LIQUID EQUILIBRIA OF PROPANE WITH ALKANE, ALCOHOL AND ALCOHOL ETHOXYLATE

A comparison of the solubility data of an alkane and the corresponding primary alcohol and alcohol ethoxylate in propane is required to determine if separation with supercritical propane is

possible and if so, the comparison will give an indication of the ease of separation and a set-up that is required.

6.3.1 PRESSURE – COMPOSITION COMPARISON

A comparison of the solubility of an alkane and the corresponding alcohol and alcohol ethoxylate in propane is shown in Figure 6-9. The alkane data is generated according to the method as set out in section 3.5.1 for a hydrocarbon with 39 carbon atoms.

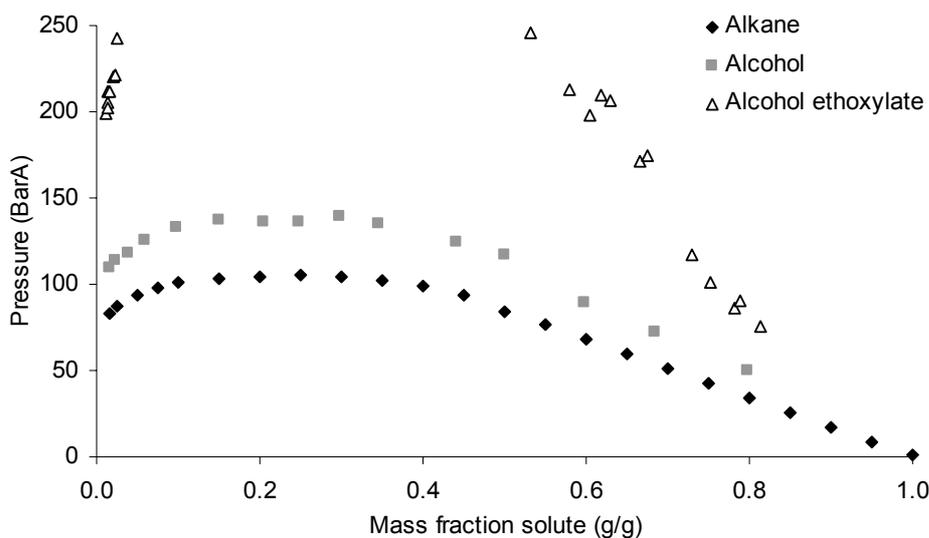


Figure 6-9: Comparison of pressure required to solubilise an alkane, an alcohol and an alcohol ethoxylate with the same hydrocarbon backbone at 408 K

As seen in Figure 6-9 there is a significant difference in the solubility of the alkane and alcohol compared to the alcohol ethoxylate. This will allow quite an easy separation only requiring a few theoretical steps.

6.3.2 RELATIVE SOLUBILITY

To obtain an indication of the separation that can be achieved by a solvent for one component relative to another from solubilisation data, the relative volatility can be calculated [3]:

Equation 6-1:
$$\alpha_{n/m} = \frac{K_n}{K_m}$$

where K_n and K_m are defined as follows:

Equation 6-2:
$$K_n = \frac{y_n}{x_n}$$

Equation 6-3:
$$K_m = \frac{y_m}{x_m}$$

In Equation 6-2 and Equation 6-3 y_n and y_m refer to the fraction of component n and m in the vapour phase and x_n and x_m refer to the fraction of component n and m in the liquid phase. Separation can generally be achieved for a relative volatility greater than 1.05.

In the analysis given above, all components are present in the vapour-liquid equilibria measurement. However, in the phase equilibria measurements conducted in this work, (pseudo) binary measurements were conducted. From the data available the separation factors can not be calculated, but an indication of the solubility of one component with respect to another can be obtained by defining the relative solubility $a_{n/m}$ of component 'n' with respect to component 'm' in a particular solvent:

$$a_{n/m} = \frac{K_n}{K_m} = \frac{y_n/x_n}{y_m/x_m}$$

Equation 6-4:

For the purpose of this work, the K value of the more soluble compound (n) is always divided by the K value of the less soluble compound (m), this ensuring a value of greater than one. The greater the value of the relative solubility, the greater the difference in solubility and the easier separation can be achieved.

This analysis has, however, some limitations. Due to the fact that the fractions originate from (pseudo) binary results, they do not take the interactions of the heavy components with one another into account. Although it is believed that the interactions will be small, they may still have an influence. The relative solubility of the alkane to alcohol ethoxylate, alkane to alcohol and alcohol to alcohol ethoxylate is calculated at various temperatures as a function of pressure and are shown in Figure 6-10 to Figure 6-12. Calculations are conducted up to approximately 5bar from the mixture critical point.

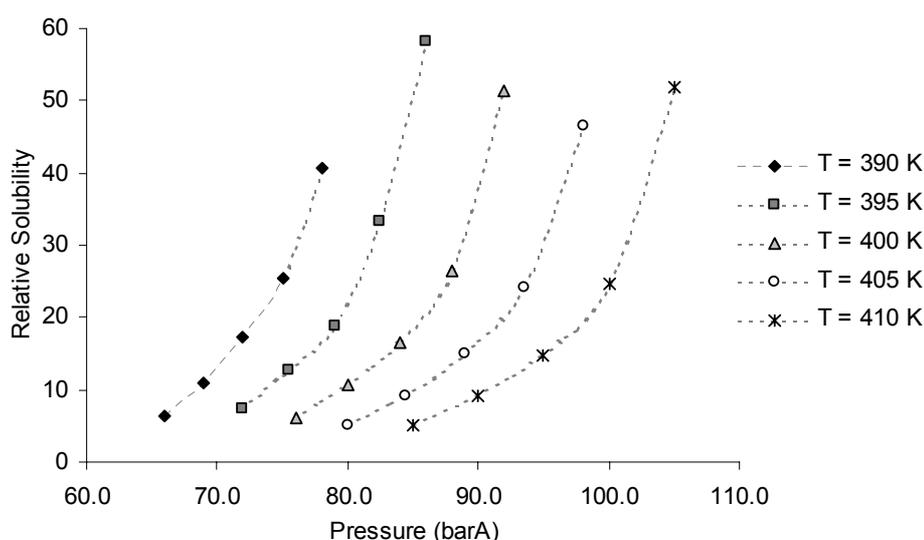


Figure 6-10: Relative solubility of alkane-propane to alcohol ethoxylate-propane at various temperatures as a function of pressure

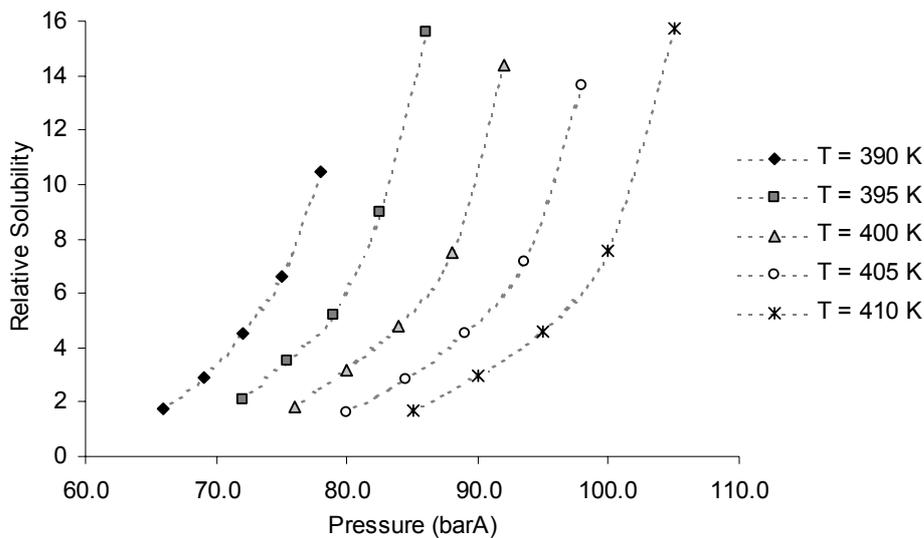


Figure 6-11: Relative solubility of alkane-propane to alcohol-propane at various temperatures as a function of pressure

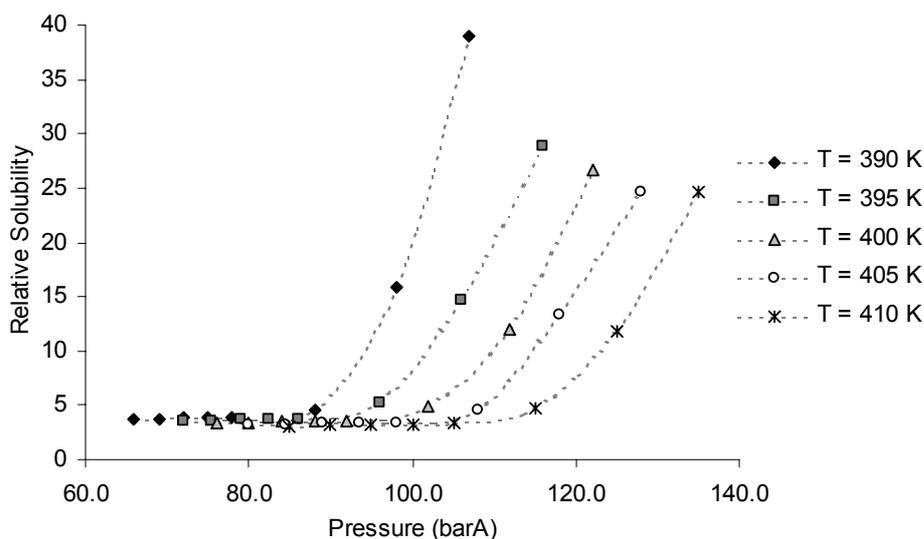


Figure 6-12: Relative solubility of alcohol-propane to alcohol ethoxylate-propane at various temperatures as a function of pressure

The relative solubility values are very high and thus separation should easily be achieved. Additionally, it can be seen that an increase in pressure leads to an increase in relative solubility while an increase in temperature leads to a decrease in relative solubility. Figure 6-13 shows a comparison of the relative solubility at 395K.

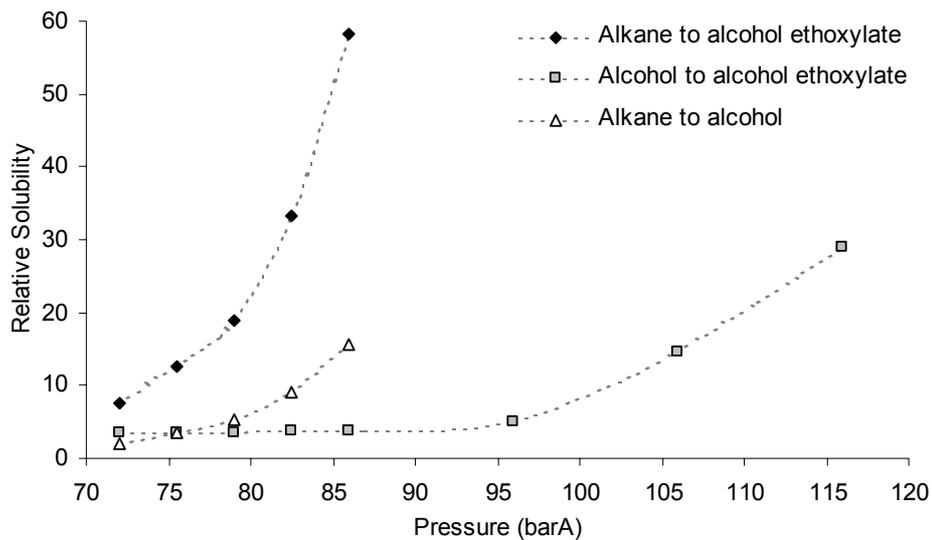


Figure 6-13: Comparison of relative solubility of alkane-propane to alcohol ethoxylate-propane, alcohol-propane to alcohol ethoxylate-propane and alkane-propane to alcohol-propane at 395 K

From these results, it can be seen that a process should be operated at a pressure just above the mixture critical pressure of the alkane in propane. Here the solubility of the alkane and the alcohol in propane is relatively high while the solubility of the alcohol ethoxylate is still low. For the process conditions shown in Figure 6-13 a pressure of about 100barA is recommended.

With respect to a suitable separation process, it is suggested that firstly the alkane and alcohol are extracted from the alcohol ethoxylate, followed by separation of the alkane and the alcohol.

6.3.3 DENSITY – COMPOSITION COMPARISON

A comparison of the densities of the alkane, alcohol and alcohol ethoxylate is made. No density data for an nC39 alkane is available yet, as the density is not highly dependent on the number of carbon atoms [1], the density of the alkane can easily be approximated with that of nC40.

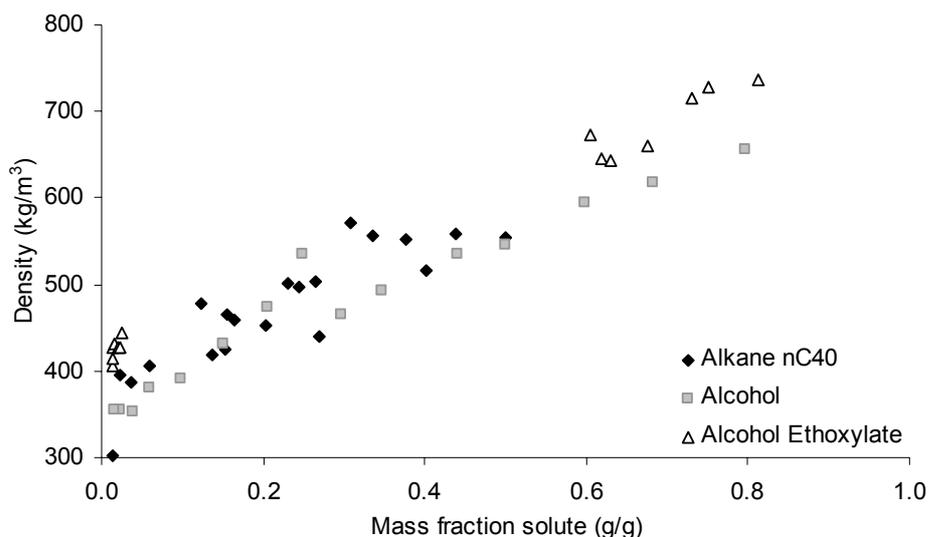


Figure 6-14: Comparison of density at solubilisation pressure of an alkane, an alcohol and an alcohol ethoxylate with the same hydrocarbon backbone at 408 K

As shown in Figure 6-14 there is no significant difference in the densities of the alkane, the alcohol and the alcohol ethoxylate. The data does indicate though that the density of the alcohol ethoxylate may be higher but it must be remembered that the system pressure is higher. A system based on a density difference alone will thus not suffice in separating this system.

6.4 IMPLICATIONS OF SOLUBILITY DATA

From the phase equilibrium data it can be concluded that a significant difference exists between the solubility of the alkane and alcohol compared to the alcohol ethoxylate (as shown in the relative solubility analysis).

This large solubility difference can be used firstly to remove significant quantities of the alkane and alcohol from the alcohol ethoxylate thus concentrating the system. Due to the large difference in solubility a counter current extraction set-up is suggested where the parent liquid is fed at the top of the column, the alkane and alcohol is dissolved in the solvent and removed in the overheads while the concentrated alcohol ethoxylate is removed at the bottom of the column.

Secondly, it is also possible to separate the alcohol, and the alkane with supercritical propane. The separation will, however, not be as easy as the removal of the alkane and the alcohol from the alcohol ethoxylate: A column with reflux and a feed approximately in the middle is required.

The remainder of this work will concentrate on the former, i.e. the concentration of the alcohol ethoxylate in the alcohol ethoxylate, alcohol and alkane mixture.

From the data measured and presented in this chapter a quantitative estimation of the possible operating range can be made.

6.4.1 SELECTION OF OPERATING TEMPERATURE RANGE

The operating temperature is determined by the characteristics of the wax and the effect of the temperature on the relative solubility.

From the relative solubility analysis presented in Figure 6-10 through Figure 6-12 it can be seen that for a set pressure, an increase in temperature leads to a decrease in relative selectivity. Thus in order to keep the operating pressure as low as possible, lower operating temperatures are suggested.

The properties of the wax also have a significant effect on the operating temperature. The wax should be in the liquid form and has a melting point of approximately 100°C. In order to prevent solidification of the wax in lines due to cold spots etc., the operating temperature should be 120°C or higher. However, the operating temperature should be kept as low as possible in order to prevent thermal decomposition.

Combining the above, it is suggested that 120°C is selected as the operating temperature of choice, with an analysis of the effect of operating temperature up to about 130°C.

6.4.2 SELECTION OF OPERATING PRESSURE RANGE

The analysis of the relative solubility conducted in section 6.2.2 is done with a system with a hydrocarbon backbone of 550 g/mol (equivalent to 39 carbon atoms) yet the feed used in the pilot plant runs has a hydrocarbon backbone of 750 g/mol (equivalent to 53 carbon atoms). Due to the increase in the hydrocarbon backbone length, the solubility of the alkane, alcohol and alcohol ethoxylate will be less at the same pressure and temperature.

In order to quantify the increase, the alkane phase equilibrium behaviour of an nC39 hydrocarbon and an nC53 hydrocarbon is compared at 393.15K (generated by method described in section 3.5.1):

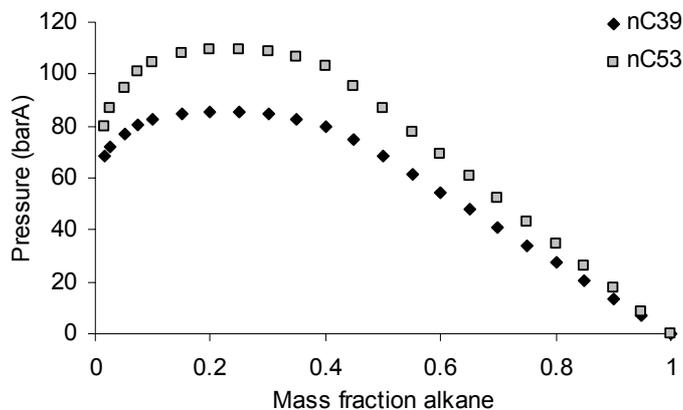


Figure 6-15: Comparison of phase equilibria of nC39 and nC53 in propane at 393.15K

From a comparison of the relative solubility it is suggested that a separation process be operated at pressures about 10 - 15bar above the mixture critical pressure of the alkane. For nC39 this would be about 100barA and with the aid of Figure 6-15 for nC53, this pressure should be about 120barA.

It is thus suggested that the process is operated in a pressure range of 115barA to 150barA at 120°C.

6.5 NOMENCLATURE

Symbol	Description
a	Relative solubility
K	Ratio of vapour to liquid fraction of specified component
x	Mass fraction in liquid phase of component (in propane)
y	Mass fraction in vapour phase of component (in propane)
α	Relative volatility

Subscripts

m	Refers to component m (less soluble compound)
n	Refers to component n (more soluble compound)

6.6 BIBLIOGRAPHY

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2. Schwarz, C.E. and Nieuwoudt, I. 2003. *Phase Equilibrium of Propane and Alkanes: Part I: Experimental Procedures, nC32 Phase Equilibrium and EOS Modelling*. Journal of Supercritical Fluids, 27 p. 133-144.
3. Perry, R.H. and Green, D.W. 1997, *Perry's Chemical Engineers' Handbook*. 7th Edition ed. New York, USA: McGraw-Hill.

7 Pilot plant verification and evaluation of alcohol ethoxylate concentration process

This chapter entails the experimental pilot plant scale verification and a technical and economic evaluation of a supercritical fluid alcohol ethoxylate concentration process.

The aim of this chapter is to prove that it is possible to concentrate alcohol ethoxylates with supercritical propane and to obtain an order of magnitude estimation of the energy costs associated with such a process. The aim of this chapter is not to fine-tune the process in detail but to rather determine if the process is technically and economically viable. This will indicate if further investigations can be justified.

7.1 PILOT PLANT VERIFICATION OF ALCOHOL ETHOXYLATE CONCENTRATION PROCESS

As suggested in section 6.4, supercritical propane can be used to concentrate an alcohol ethoxylate. A counter-current set-up is suggested and tested on pilot plant scale.

7.1.1 PILOT PLANT SETUP

An existing pilot plant set-up, designed by Sieber-Sitec, Switzerland, and provided by SASOL, is used and modified to be suitable for use in this work. A counter-current set-up with no reflux is used.

The core of the pilot plant is a 4.3 m tall 0.017 m inner diameter extraction column with a packing height of 3.5m (0.5 m sump and 0.3 m overheads clearance). The column is constructed with 1" outer diameter medium pressure stainless steel tubing, as provided by Autoclave Engineers, and filled with Pro-Pac distillation packing (316SS from Aldrich, catalogue number Z210552). The wax feed is introduced at the top of the column with the aid of a 600 mL pressure intensifier, driven by nitrogen pressure (area ratio of 24.6). The wax is melted in the pressure intensifier and introduced as a liquid at column temperature.

The solvent cycle on the original pilot plant is used. Liquid propane is stored in the solvent storage tank (the pressure equivalent to the vapour pressure at atmospheric temperature), and after supercooling is fed to a diaphragm-metering pump, where it is pumped, in the liquid form, to the column pressure. After heating to supercritical conditions at the column temperature, the solvent is introduced at the bottom of the column. The solvent proceeds up the column and the loaded solvent then exists the column at the top and proceeds via a pressure regulating valve and heater

into the separation vessel. The separation vessel is operated at the solvent storage pressure and the wax is allowed to separate from the solvent. The solvent now proceeds through, first a water cooler and then a refrigeration system and back into the solvent storage tank - makeup solvent may be required and is added to the system at the top of the storage tank. In order to facilitate start-up a solvent recycle stream is used.

At the bottom of the column a 0.5 m long, 0.017 m inner diameter storage tank (sump) at column pressure allows for a limited quantity of bottoms product to be stored, which can be periodically removed. The overheads product is removed periodically from the bottom of the separation vessel.

A schematic representation of the pilot plant set-up is shown in Figure 7-1:

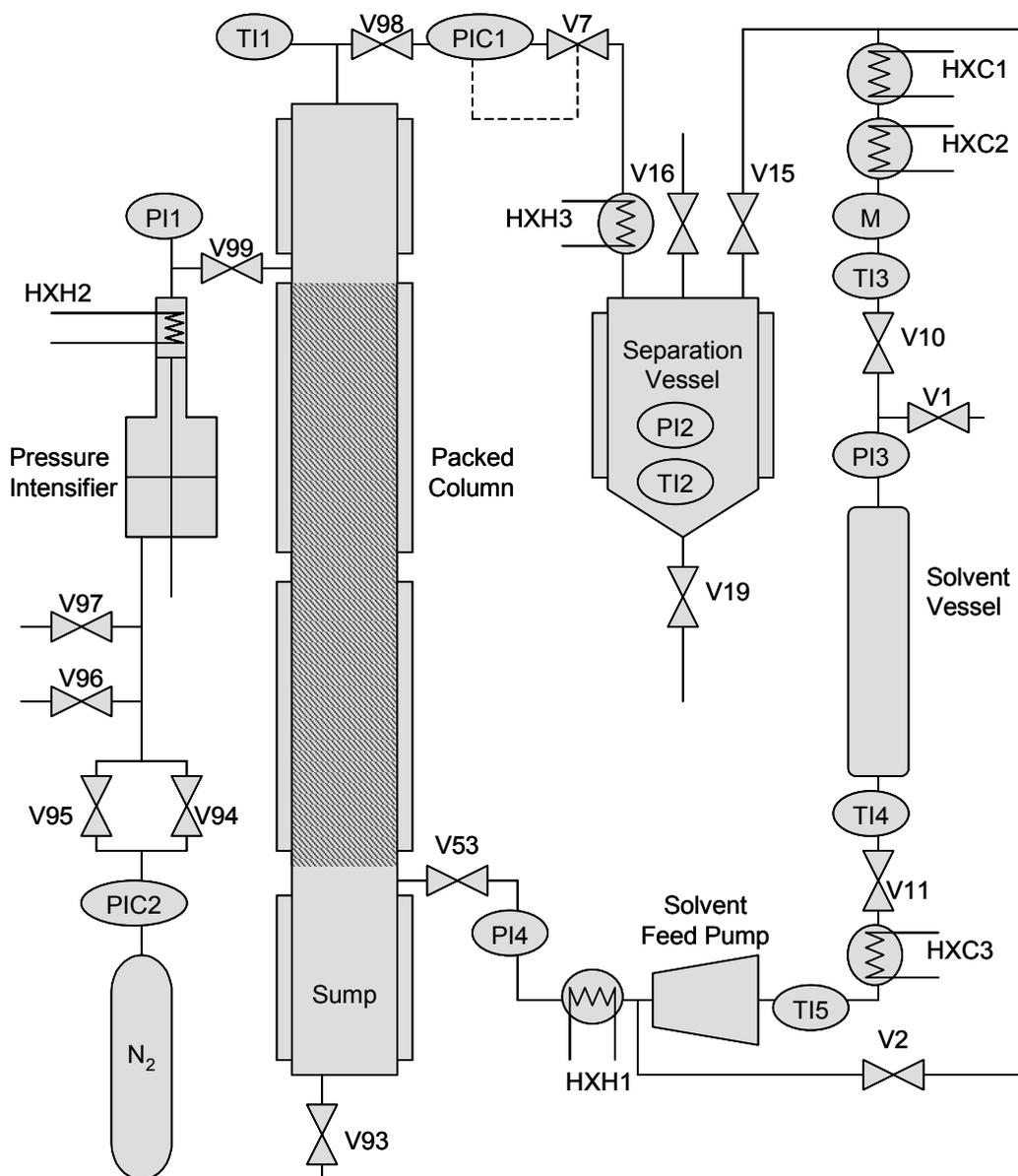


Figure 7-1: Schematic representation of pilot plant set-up

A list of the symbols used in Figure 7-1 is given in Table 7-1.

Table 7-1: Symbols used in schematic representation of pilot plant set-up (Figure 7-1)

Symbol	Description
HXC1	Solvent cooler with cooling water
HXC2	Solvent cooler from refrigeration system
HXC3	Solvent cooler from refrigeration system
HXH1	Solvent pre-heater with oil from heater 1
HXH2	Solute pre-heater with oil from heater 1
M	Solvent mass flow meter
PI1	Pressure indicator of solute feed
PI2	Pressure indicator in separator
PI3	Pressure indicator before solvent vessel
PI4	Pressure indicator on solvent feed line
PIC1	Pressure indicator on overheads product line
PIC2	Regulator and pressure indicator on nitrogen line
TI1	Temperature indicator on overheads line
TI2	Temperature indicator in separator
TI3	Temperature indicator after refrigeration cooling
TI4	Temperature indicator at solvent storage outlet
TI5	Temperature indicator at solvent feed pump inlet

A detailed description of the pilot plant operating procedures and safety procedures are given in section 10.3 in appendix B.

7.1.2 PILOT PLANT RESULTS

The aim of the pilot plant runs conducted here is to verify that separation can be achieved and to qualitatively determine the effect of pressure and temperature on the percentage feed in the overheads and the ethylene oxide content of the overheads and bottoms product streams.

The solvent feed rate is kept constant at approximately 20 kg/(s.m²) and a solvent to feed ratio at approximately 60. Where possible, a few runs at lower solvent to feed ratios were conducted, mainly between 40 and 50 and one run as low as 21. These values are high. However, the solvent pump on the existing pilot plant was designed to be used with a column with a diameter 5 times larger than the one used in this work. Although a spillback line is provided, the mass flow meter is located after the re-entry point and no measurement of the flow rate can be attained if the spillback line is used to decrease the solvent flow rate. In addition, the pressure controller is not very sensitive, even when set at the most sensitive, and at the flow rates applied here, pressure

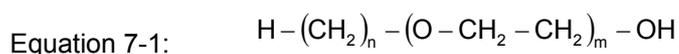
fluctuations of up to 5 bar can occur. Thus to obtain accurate results with the equipment available, relatively high solvent flow rates need to be applied. To prevent flooding, high solvent to feed ratios are thus required. It should however be remembered that the aim is not to optimise the operating conditions but rather to prove that with some fine-tuning good separation can be achieved.

The product streams are evaluated in two ways:

- Firstly the quantity of the feed extracted and present in the overheads is considered. Generally, the higher the % feed extracted into the overheads, the better. This is true up to a certain point – if the percentage feed in the overheads becomes too high, too large a percentage of the feed is removed in the overheads and the composition of the overheads becomes too close to that of the feed. Under these conditions, separation will not be of much use.
- Secondly, the oxygen content of the overheads and bottoms product streams is determined from an analysis of the carbon content. From the oxygen content, an estimation can be made as to the degree of ethoxylation of the compounds in the stream. A sharper separation is achieved for a greater difference in oxygen content of the overheads and bottoms.

These two factors often counter-balance one another and compromise between these two factors is required.

The alcohol ethoxylate has the following general formula:



Experiments are conducted using Baker-Petrolite Unithox 750. This is an alcohol ethoxylate with an average hydrocarbon backbone of molar mass 750 ($n \approx 53$) and approximately 50% ethoxylation, i.e. 50% of the average molecular weight of the alcohol ethoxylate consists of the added polyethylene oxide. Some molecules will have a hydrocarbon backbone of more than 53 carbon atoms, some with less. In the same way, for some molecules the added polyethylene oxide segment will constitute more than 50 weight percent, some less. In addition, there will be some unreacted alcohol and alkane molecules.

A total carbon analysis is conducted on the feed. Samples of both before and after removal of the lights are analysed and the carbon content is 67.0% and 69.0% respectively. Should the lights be water and this fact be incorporated into the analysis, a very similar results are attained. A 69.0% carbon content is equivalent to an alcohol ethoxylate with an average of 18 ethylene oxide units ($m = 18$) and a 51% degree of ethoxylation. Thermodynamic data on the feed wax is given in section 7.4.3.1.

In this work it is assumed that all molecules have the same hydrocarbon backbone with $n = 53$ but that a distribution of the number of ethylene oxide units, m , occurs. All results will thus give the average value of m and m thus indicates the average degree of ethoxylation of the sample.

Industrial grade propane is used as the supercritical solvent.

For the experimental runs conducted here, the extraction and separation temperatures are set the same. As counter-current extraction is used, the separation temperature has no significant effect on the extraction achieved, assuming a large enough pressure difference between the extraction and separation pressure. At 9.5barA, the solubility of the wax in the solvent at the extraction temperature can be approximated to zero and thus the use of a single temperature is justified. For an industrial process, it is however recommended to use a temperature approximately 10K higher, mainly to prevent clogging of the lines, to increase the viscosity of the liquid phase (mainly solute) and decrease the solvent solubility in the solute.

The solvent flow rate is determined by measuring the mass solvent pumped in a set time. The mass flow meter indicates the mass for a set time and also gives an indication of the instantaneous mass flow rate. The instantaneous rate is used to ensure the flow rate remains relatively constant with time.

The solute flow rate is determined by adding the total mass in the overheads and in the bottoms produced for the run time. With reference to Figure 7-1, valve V95 is closed and valve V94 is a flow-controlling valve. At the beginning of the run, a valve is set at a pre-determined setting and as the pressure drop over the valve remain constant, a steady flow of nitrogen into the pressure intensifier is assured. In addition, the piston shaft movement is monitored to ensure that the rate is constant. This method is similar to that proposed by Diez et al [8] where the degree of ethoxylation was determined by elemental analysis (CHN).

7.1.2.1 SUMMARY OF EXPERIMENTAL RESULTS

Runs were conducted between 115 and 150barA at 393.15K and at 130barA between 393.15 and 400K. An analysis of the effect of the solvent to feed ratio was conducted at 130 barA and 393.15K. A summary of the results is shown in Table 7-2. Only in runs where more than 10% of the feed is recovered in the overheads stream are analysed as facilities for carbon content measurement were readily available. Samples are analysed for total carbon content, where the total mass % carbon was determined. From the carbon content and Equation 7-1 the oxygen content and the value of m can be determined.

From the molecular formula given in Equation 7-1, it can be seen that the molar ratio of the number of carbon atoms to the number of hydrogen atoms is approximately 0.5. Using this molar ratio and the atomic weights, the mass % hydrogen in the sample is determined and using a mass balance the oxygen content is calculated. The elemental composition is now converted from mass to molar percentage. Using the molecular formula in Equation 7-1 and the mole fractions together with the assumption of $n = 53$, the value of m is calculated.

Detailed experimental data is given in section 11.3.1 in appendix C and analysis data in section 11.3.2 in appendix C.

Table 7-2: Summary of experimental data from pilot plant runs

		Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
Column temperature (°C)		119	116	120	119	122	125
Separator temperature (°C)		119	116	123	122	124	127
Column pressure (barA)		115	125	130	150	130	130
Separator pressure (barA)		8.5	8.5	8.5	8.5	8.5	8.5
Solvent to Feed Ratio		42	66	61	94	65	64
Overheads to Feed Ratio		0.052	0.209	0.243	0.361	0.231	0.174
Solute mass flow rate (kg/(m².s))		0.559	0.287	0.350	0.215	0.343	0.320
Solvent mass flow rate (kg/(m².s))		23.3	19.1	21.3	20.2	22.3	20.6
Feed composition (mass percentage)	%C	69.0	69.0	69.0	69.0	69.0	69.0
	%O	19.4	19.4	19.4	19.4	19.4	19.4
	%H	11.6	11.6	11.6	11.6	11.6	11.6
	n	53	53	53	53	53	53
	m	18.0	18.0	18.0	18.0	18.0	18.0
	Degree of Ethoxylation	51	51	51	51	51	51
Overheads composition (mass percentage)	%C	-	76.8	71.6	76.4	74.1	74.7
	%O	-	10.3	16.4	10.8	13.5	12.8
	%H	-	12.9	12.0	12.8	12.4	12.5
	n	-	53	53	53	53	53
	m	-	5.6	12.6	6.0	8.8	8.0
	Degree of Ethoxylation	-	24	42	26	34	32
Bottoms composition (mass percentage)	%C	-	65.1	65.8	66.3	62.9	66.0
	%O	-	24.0	23.2	22.6	26.5	22.9
	%H	-	10.9	11.0	11.1	10.6	11.1
	n	-	53	53	53	53	53
	m	-	31.2	28.1	26.2	44.0	27.3
	Degree of Ethoxylation	-	64	62	60	72	61
m(bottoms) / m(overheads)		-	5.6	2.2	5.0	4.4	3.4

Table 7-2 continued

		Run 7	Run 8	Run 9	Run 10	Run 11
Column temperature (°C)		126	127	122	122	127
Separator temperature (°C)		129	124	125	129	127
Column pressure (barA)		130	130	140	150	130
Separator pressure (barA)		8.5	8.5	8.5	8.5	8.5
Solvent to Feed Ratio		49	43	55	44	21
Overheads to Feed Ratio		0.191	0.157	0.279	0.273	0.151
Solute mass flow rate (kg/(m².s))		0.297	0.359	0.294	0.354	0.736
Solvent mass flow rate (kg/(m².s))		14.6	15.5	16.2	15.5	15.4
Feed composition (mass percentage)	%C	69.0	69.0	69.0	69.0	69.0
	%O	19.4	19.4	19.4	19.4	19.4
	%H	11.6	11.6	11.6	11.6	11.6
	n	53	53	53	53	53
	m	18.0	18.0	18.0	18.0	18.0
	Degree of Ethoxylation	51	51	51	51	51
Overheads composition (mass percentage)	%C	70.6	72.0	72.9	69.3	76.0
	%O	11.8	12.1	12.2	11.6	12.8
	%H	17.6	15.9	14.9	19.1	11.2
	n	53	53	53	53	53
	m	14.5	11.9	10.5	17.3	6.4
	Degree of Ethoxylation	46	41	38	50	27
Bottoms composition (mass percentage)	%C	67.0	67.0	66.2	68.2	68.6
	%O	11.2	11.2	11.1	11.4	11.5
	%H	21.8	21.8	22.7	20.4	19.9
	n	53	53	53	53	53
	m	23.7	23.7	26.6	20.1	19.0
	Degree of Ethoxylation	58	58	61	54	52
m(bottoms) / m(overheads)		1.6	2.0	2.5	1.2	3.0

In the results presented here it is assumed that no fractionation with regard to the hydrocarbon backbone occurs. Propane does have the ability to fractionate alkanes according to the number of carbon atoms in the molecule [1], [2]. There will thus be a certain amount of fractionation with

respect to the hydrocarbon backbone and in a detailed investigation and fine-tuning of the operating conditions, the extent of hydrocarbon backbone fractionation needs to be investigated. To quantify the degree of separation the selectivity is defined as the ratio of the m in the bottoms to the m on the overheads is determined, higher values indicating better separation.

7.1.2.2 GENERAL EXPERIMENTAL OBSERVATIONS

In general a low operating temperature and pressure is preferred. Lower pressures will result in a decrease in both capital and operating costs, while lower temperatures reduce the quantity of thermal degradation, increase the solubility of the solute in the solvent and reduce operating costs. It was found that separation can be achieved above approximately 120°C and 130barA. From the results above the effect of pressure, temperature and solvent to feed ratio will be investigated.

The feed contains a significant quantity of lights, approximately 10 %. These light compounds are removed in the feed pre-heater during the feed melting. It is observed that the feed is very viscous near the melting point and needs to be heated to approximately 115°C for flow to occur easily. During the evaporation of the lights, the feed also tends to foam a little – this can be attributed to the alcohol ethoxylates character: alcohol ethoxylates are surfactants and often act as foam enhancers.

The overhead product is off-white, generally brittle and has a character similar to a long chain alkane. For runs with higher m values in the overheads, the overheads are less brittle and slightly softer in character. This indicates an increase the presence of a larger quantity of higher alcohol ethoxylates. The bottoms product is also off-white but has a sticky feel to it and is not as brittle as the overheads, indicating the presence of a significant quantity of ethylene oxide groups.

The solvent pump used in this set-up was sized for a column with a cross-sectional area of 5 times the area used in this work. Control at low solvent flow rates is thus very difficult and although it is believed, and shown in the results, that the solvent flow rate used here is not too high, investigations at low solvent flow rates are not possible. The solvent flow rate as well as the solvent to feed ratio is thus at the higher end of the operational window. Comparing the flow rates and solvent to feed ratios with similar work [3], it is seen that although higher, they are of the same order of magnitude.

7.1.2.3 ACCURACY OF MEASUREMENTS

Before the effect of pressure and temperature is investigated, comment needs to be made regarding the accuracy of the experimental measurements.

The pressure measurements on the column (PIC1) and the pressure intensifier (PI1) are measured to the nearest bar with an accuracy of ± 1 bar. The pressure of the solvent feed (PI4) is measured with an accuracy of ± 2.5 bar and the pressure readings of the separator (PI2) and the solvent storage tank (PI3) with an accuracy of ± 1 bar. However, the method of pressure control in

the column needs to be taken into account: the pump pumps the solvent into the column and when the pressure on the column exceeds the set-point, valve V7 opens to release a limited quantity of overheads product. Thus in the column the pressure is not totally constant but does pulse marginally. It should also be remembered that the solvent pump is a diaphragm-metering pump, which also pumps in a pulse like manner.

The temperature in the column remains relatively constant; or rather temperature lags are longer and less steep. All temperature measurements are made to the closest degree. In the solvent cycle, faster changes do however occur and here the temperature may vary within an interval of up to 5K.

All rates are determined as the total mass flowed in a set time, usually taken for a large portion of the time of the run. The overheads and bottoms products are measured accurately to 0.1 grams, translating to an accuracy of approximately 1%. The solvent cycled in a run is measured accurately to 1 gram. The feed is determined from the sum of the overheads and bottoms products. Time is measured with a stopwatch accurate to 1s.

7.1.2.4 EFFECT OF OPERATING PRESSURE

The effect of the operating pressure is investigated up to 150barA. Above this pressure it is very difficult to keep the solvent to feed ratio constant and to maintain the same solvent flow rate without causing flooding. This can be attributed to the fact that as the pressure increases, the solubility of the solute in the solvent increases and the density difference between the co-existing phases decreases.

From the data shown in Table 7-2 above pressures of approximately 115barA a significant quantity of overheads can be achieved. If all factors are kept the same, an increase in pressure leads to an increase in the overheads to feed ratio yet at higher pressures asymptotic behaviour seems to occur. This can be explained that as the pressure is increased, the solubility of the wax increases. However at higher pressures, the lower homologue members are all dissolved while the higher members require a significantly higher pressure for solubilisation.

An increase in pressure also leads to a decrease in selectivity. As the pressure increase, the degree of ethoxylation of the bottoms and the overheads become closer to one another. This can be attributed to the increased solubility of the higher homologue at higher pressures.

7.1.2.5 EFFECT OF OPERATING TEMPERATURE

The effect of the column temperature is investigated while keeping the pressure at 130barA. From the data in Table 7-2 it is seen that an increase in temperature leads to a decrease in percentage overheads. This can be attributed to the decrease in solubility with increasing temperature. However, an increase in temperature, also leads to an increase in selectivity. This is also due to the decrease in solubility with increasing temperature.

7.1.2.6 COMBINED EFFECT OF PRESSURE AND TEMPERATURE

Consider an extraction at about 123.5°C and 130barA. An overheads to feed ratio of about 0.2 should be attained and from the analysis results, an overheads with $m = 8$ and a bottoms with $m = 28$ should be attainable thus leading to a selectivity of 3.5. Comparing this extraction to that of Run 2 with an overheads with $m = 5.6$ and a bottoms with $m = 31.2$ and a selectivity of 5.6. It can be seen that extraction at lower temperatures and pressures with the same overheads to feed ratio results in a sharper separation. Thus at a specific overheads to feed ratio, lower pressures and temperatures result in a sharper separation and should be favoured.

7.1.2.7 EFFECT OF SOLVENT TO FEED RATIO

The effect of the solvent to feed ratio was investigated while keeping the pressure at 130 barA and the temperature at 125 – 127°C. The higher temperatures allowed for easier control of the solvent feed rate.

From the data in Table 7-2 it was found that an increase in solvent to feed ratio leads to an increase in percentage overheads. This can be attributed to the fact that more solvent is cycled through the column per unit solute and thus the more solute can be dissolved.

It is found that at lower solvent to feed ratios the degree of ethoxylation of the overheads is lower while the degree of ethoxylation of the bottoms is also lower. This may sound contradictory yet it should be remembered that this observation needs to be viewed in combination with the decrease in the percentage overheads and can be explained as follows: As the solvent to feed ratio decreases less material is solubilised in the solvent. As the lower alcohol ethoxylates are more soluble, these molecules will preferentially dissolve in the solvent. Therefore the lower the solvent to feed ratio, the lower the degree of ethoxylation of the overheads. With respect to the bottoms, less material is removed as the solvent to feed ratio decreases and thus the degree of ethoxylation is closer to that of the feed.

The aim of the separation will dictate if a higher or a lower solvent to feed ratio is desired. Should the aim of the separation be to obtain a very high ethoxylated bottoms product, a high solvent to feed ratio would be desired. However, if the aim of the separation is to remove the lower alcohol ethoxylates and not significantly change the degree of ethoxylation of the bottoms, a lower solvent to feed ratio is recommended.

With specific reference to the aim of creating a narrower range alcohol ethoxylate, it can be envisaged that a narrow range product similar to the feed but with a much lower ethylene oxide distribution may be attained with the use of two columns in series: one with a low solvent to feed ratio that removes the lower homologue members and one with a high solvent to feed ratio that removes the high homologue members.

Although this analysis of the solvent to feed ratio is believed to provide an insight into the effect of the solvent, the range studied here is not wide enough and it is recommended that lower solvent to feed ratios also be investigated.

7.1.2.8 OPERATIONS PARAMETERS NOT INVESTIGATED HERE

Only the effect of pressure, temperature and solvent to feed ratio were investigated. Many other factors may play a role.

The flow rate of the solvent and the flow rate of the solute also need to be investigated. At lower flow rates, the system will have more time to attain equilibrium yet higher flow rates allow for better mixing.

A counter-current extraction set-up without the use of reflux is used in this work. The use of reflux may improve the separation that can be achieved. In supercritical processes, with behaviour as shown by the systems studied in this work, the reflux can be created insitu at the top of the column with the use of a hot finger. As the solvent, saturated with solute, comes into contact with the hot finger, the temperature of the mixture increases. With increasing temperature, the solubility decreases and thus partial 'condensation' of the solute in the solvent occurs. The reflux can be applied to both a counter-current set-up and a distillation type set-up and may increase the separation attained.

An even sharper fractionation may be achieved should the above, in conjunction with the temperature, pressure and solvent to feed ratio, be investigated.

7.1.2.9 ANALYSIS OF POSSIBILITY OF FLOODING

The solvent flow rates used here are high and thus there is a possibility of flooding. No method has been developed for testing flooding in a column with the packing used here with propane as supercritical solvent and molten wax as solute. However, Stockfleth et al. [4] studied flooding under supercritical conditions with carbon dioxide as solvent and water and olive oil deodoriser distillate as solute. The method used in the work of Stockfleth et al. will be applied to this work yet the results should be treated with caution: carbon dioxide has a higher density than propane and the wax used in this work is more viscous than the olive oil deodoriser distillate and water.

From the experimental data achieved in the runs, the flow parameter was determined. From the flow parameter, the experimental gas capacity factor was calculated as well as the gas capacity factor at flooding. The ratio of the experimental gas capacity factor divided by gas capacity factor at flooding is calculated. Flooding is expected to occur at ratios greater than 1.

The gas capacity factor at flooding is a function of the type of packing and Stockfleth et al. studied 4 types of packing: Raschig rings, Berl saddled, Sulzer CY and Sulzer EX. On the one hand the random packing correlations should approximate the behaviour better as the packing used here is random packing and is similar in shape to the Berl saddles. However, it must be remembered that the packing is usually constructed of a material other than stainless steel and that Raschig rings and Berl saddles take up a significant percentage of the column volume, unlike the packing used here. It is thus expected that these random packings may show unrealistic results. To obtain realistic results, the void fraction of small Berl Saddles (approximately 0.6) and that of the packing used here (approximately 0.96) is taken into account and flooding calculations were conducted

and are shown in Table 7-3 for all the experimental runs. Although the packing used here is random, it is also constructed from gauzelike stainless steel. The volume occupied by the packing as well as the wetting would be similar and thus the structured packing may resemble the packing used here better than the random packing. Flooding using correlations for the Sulzer CY and Sulzer EX types of structured packing will be investigated and the ratios are shown in Table 7-3 for all the experimental runs. All calculations are shown in 11.3.3 in appendix C.

Table 7-3: Ratio of experimental gas capacity factors to calculated capacity factors for the various types of packing for all experimental runs

Run	Sulzer CY	Sulzer EX	Berl Saddles with corrected void fraction
Run 1	0.74	0.81	1.77
Run 2	0.56	0.61	1.38
Run 3	0.63	0.69	1.55
Run 4	0.56	0.62	1.42
Run 5	0.65	0.72	1.62
Run 6	0.61	0.66	1.50
Run 7	0.45	0.49	1.09
Run 8	0.49	0.53	1.17
Run 9	0.49	0.53	1.19
Run 10	0.49	0.53	1.17
Run 11	0.57	0.62	1.27

The results for the structured packing show that, although sometimes close to flooding, according to this method flooding has not occurred. However, the results for the Berl Saddles show that operation was in the flooding region. Yet the limitations of the correlations should not be forgotten: The correlations were derived for a different system with a different viscosities and densities of both solvent and solute and for the Berl Saddles, the material of construction has different wetting properties. Taking all the results into account, although some entrainment may have occurred, it is believed that for most of the runs, the system was operated below flooding.

7.2 TECHNICAL EVALUATION

From the pilot plant it can be seen that it is technically possible to concentrate alcohol ethoxylates with the use of supercritical propane. To date no other method is technically viable, so no comparison can be made. With some fine-tuning it should be possible to optimise a concentration process. The optimisation would include a detailed investigation of the influence of pressure, temperature, solvent flow rate, and solvent to feed ratio as well as column set-up and

hydrodynamics and their interaction with one another. In addition, the objectives with regard to product specifications need to be made.

Two process options will now be suggested and the economic viability of these options will be investigated. Mass balances and energy considerations will be conducted on both a low and a high solvent to feed ratio.

7.3 SUGGESTED PROCESS FOR SEPARATION

From the limited information available from the experimental runs, a separation process is suggested. The process is designed to facilitate an economic evaluation via an energy balance and the experimental run at 130bar and 120°C with a solvent to feed ratio of 60 and 30 is used. These factors may affect the mass and energy balances and the column sizing, but the basic concept for a separation process could be applied at a different pressure, temperature and solvent to feed ratio.

Two alternative processes will be shown: A one stage and a two-stage decompression process. The one stage process is similar to the pilot plant set-up with the solvent storage at 9.5 barA. The two stage decompression process utilises solvent storage at 35 barA and a final solvent solute separation at 2 barA. This process does not require a refrigeration system but does require a two stage compressor. Calculations for both processes with a solvent to feed ratio of 60 and 30 will be conducted. An economic evaluation of both processes will be conducted and from the energy requirements a recommendation as to the preferred process will be made.

7.3.1 ONE STAGE DECOMPRESSION PROCESS

The set-up is similar to the pilot plant set-up with some minor changes, mainly to accommodate a larger flow rate.

7.3.1.1 FLOW DIAGRAM

Both a solvent and solute recycle streams are suggested. These recycle streams are only used during start-up and shut-down and do not influence the actual extraction. The use of an additional separator for the bottoms is required when a large quantity of product is generated due to both economic and safety considerations. In both the overheads and the bottoms line, the pressure and level controller respectively are shown as located before the heat exchanger. However, in reality these two units would have to be integrated as one unit. This is required as the reduction in pressure leads to a temperature reduction and solidification of wax in the piping may occur. Heating will ensure constant temperature operation.

A schematic representation of the process is shown in Figure 7-2 and a list of the symbols used in Figure 7-2 is given in Table 7-4:

Table 7-4: Symbols used in schematic representation of one stage decomposition process (Figure 7-2)

Symbol	Description
HXC1	Solvent cooling with cooling water
HXC2	Solvent cooling from refrigeration system
HXC3	Solvent feed pump pre-cooling from refrigeration system
HXH1	Solvent pre-heater
HXH2	Overheads product heater
HXH3	Bottoms product heater
HXH4	Solute heater
PC	Pressure controller controlling column pressure and overheads release rate

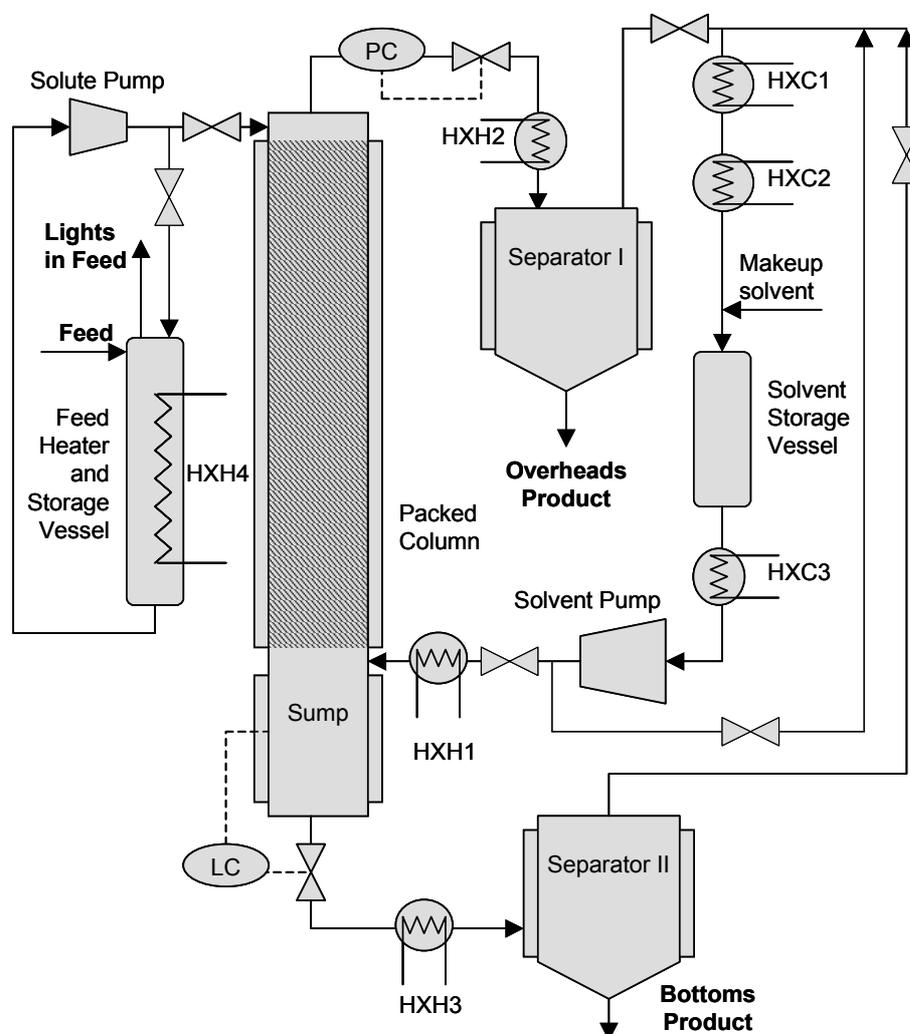


Figure 7-2: Schematic representation of the flow diagram for an alcohol ethoxylate concentration process with one stage decomposition

The process designed here, is shown for a feed similar to that provided, i.e. a cold feed containing a limited quantity of lights. Should the process be required downstream from the ethoxylation process and the feed be free of lights and at column temperature, the feed heater where the lights are removed can be replaced by a heated storage tank.

7.3.1.2 MASS BALANCE AND STREAM STATES

The following specifications and assumptions were made: These were based on the experimental results from the pilot plant test runs. For a solvent to feed ratio of 60, an overheads to feed ratio of 0.25 and a bottoms product with $m = 25$ is assumed. It is estimated that for a solvent to feed ratio of 30 at the same temperature and pressure, an overheads to feed ratio of 0.225 and a bottoms product with $m = 20.5$ is assumed.

Table 7-5: Specifications and assumptions for one stage decompression process

Solvent to feed ratio	60	30
Fraction lights in feed	0.1 g/g	0.1 g/g
Wax overheads / wax feed	0.25 g/g	0.225 g/g
Fraction wax in column bottoms	0.7 g/g	0.7 g/g
% Ethoxylation in feed	50% ($m = 17$)	50% ($m = 17$)
% Ethoxylation in overheads	24% ($m = 5.1$)	24% ($m = 4.9$)
% Ethoxylation in bottoms	60% ($m = 25$)	55% ($m = 20.5$)
Extraction temperature	393.15K	393.15K
Separator I temperature	403.15K	403.15K
Separator II temperature	403.15K	403.15K
Extraction pressure	130barA	130barA
Extraction pressure	130barA	130barA
Separator I pressure	9.5barA	9.5barA
Separator II pressure	9.5barA	9.5barA
HXC1 Exit temperature	308.15K	308.15K
HXC2 Exit temperature	293.15K	293.15K
HXC3 Exit temperature	283.15K	283.15K

A mass balance is conducted and flow rates, composition, temperature, pressure and phase for each stream is shown in section 11.4.1 in appendix C. Only the solvent pump delivery temperature was calculated from thermodynamic considerations (isentropic behaviour).

Additionally it is assumed that at 9.5 barA and 403.15K the solubility of the wax in propane can be approximated as zero and the solvent lost in the overheads and bottoms product is negligible.

7.3.2 TWO STAGE DECOMPRESSION PROCESS

The one stage decompression process uses a solvent recycle of 9.5 barA. To condense the solvent at this pressure a refrigeration system is required and as refrigeration energy is very expensive [3], it is viable to investigate a process not requiring a refrigeration system. A two-stage decompression process with decompression firstly to 35 barA and then to 2 barA can circumvent the use of a refrigeration system at the cost of a two stage compressor and is investigated here.

7.3.2.1 FLOW DIAGRAM

A schematic representation of a two-stage decompression process is shown in Figure 7-3 and a list of symbols used is given in Table 7-6

Table 7-6: Symbols used in schematic representation of the two stage decompression process (Figure 7-3)

Symbol	Description
HXC1	Solvent cooling with cooling water
HXC2	Compressor intermediate cooling with cooling water
HXC3	Solvent feed pump pre-cooling with cooling water
HXC4	Compressor pre-cooling with cooling water
HXH1	Solvent pre-heater
HXH2	Overheads product heater – Separator I
HXH3	Bottoms product heater
HXH4	Solute heater
HXH5	Overheads product heater – Separator II
PC1	Pressure controller for column pressure and overheads release to separator I
PC3	Pressure controller controlling pressure decrease in solvent spillback line
PC4	Pressure controller controlling separator II pressure
PC5	Pressure controller controlling separator III pressure
LC1	Level controller controlling the bottoms level and release rate
LC2	Level controller controlling separator I level and release rate
FS	Flow switch ensuring flow of solvent through the compressors

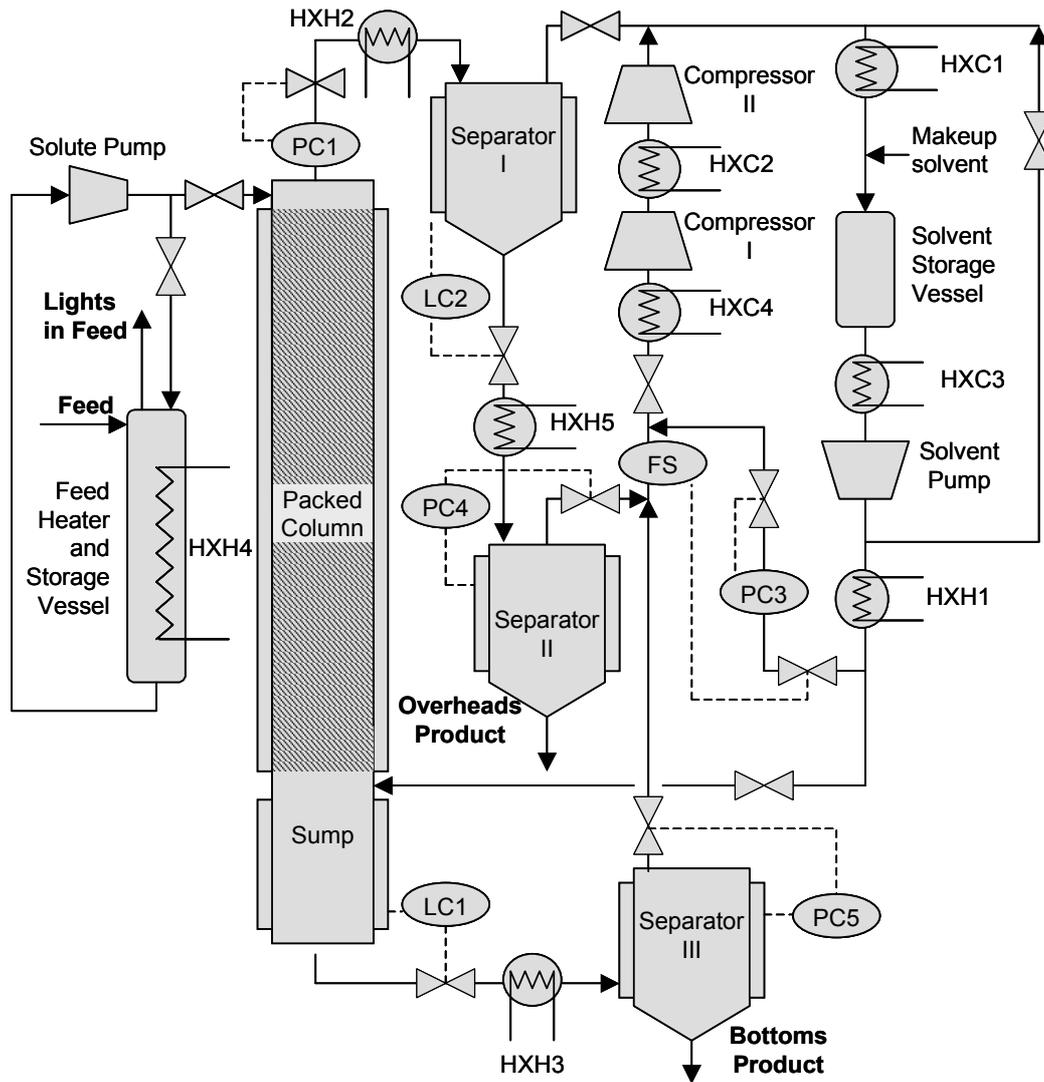


Figure 7-3: Schematic representation of the flow diagram for an alcohol ethoxylate concentration process with two-stage decompression.

7.3.2.2 MASS BALANCE AND STREAM STATES

The following specifications and assumptions were made. As in the case of the one stage process, these were based on the pilot plant test runs with an overheads to feed ratio of 25 and a bottoms product with $m = 25$ for a solvent to feed ratio of 60. For a solvent to feed ratio of 30 and an overheads to feed ratio of 0.225 and $m = 20.5$ is assumed.

A mass balance is conducted and flow rates, composition, temperature, pressure and phase for each stream is shown in 11.4.1 in appendix C. Only the solvent pump delivery temperature, compressor I outlet temperature and compressor II inlet temperature were calculated from thermodynamic considerations (assumption of isentropic behaviour). Additionally it is assumed that at 35barA and 403.15K the solubility of the wax in propane is negligible. At these conditions it is assumed that 10% propane by mass is soluble in the wax (based on the phase behaviour of the

alkane nC60 in propane – see Figure 3-29). In separator II and separator III total separation is assumed, i.e. no wax in the propane and no propane in the wax.

Table 7-7: Specifications and assumptions for mass balance of two stage decompression process

Solvent to feed ratio	60	30
Fraction lights in feed	0.1 g/g	0.1 g/g
Wax overheads / wax feed	0.25 g/g	0.225 g/g
Fraction wax in column bottoms	0.7 g/g	0.7 g/g
% Ethoxylation in feed	50% (m = 17)	50% (m = 17)
% Ethoxylation in overheads	24% (m = 5.1)	24% (m = 4.9)
% Ethoxylation in bottoms	60% (m = 25)	55% (m = 20.5)
Extraction temperature	393.15K	393.15K
Separator I temperature	403.15K	403.15K
Separator II temperature	403.15K	403.15K
Separator III temperature	403.15K	403.15K
Extraction pressure	130barA	130barA
Separator I pressure	35barA	35barA
Separator II pressure	2barA	2barA
Separator III pressure	2barA	2barA
Compressor intermediate pressure	8.4barA	8.4barA
HXC1 Exit temperature	359.14K	359.14K
HXC2 Exit temperature	338.83K	338.83K
HXC3 Exit temperature	339.14K	339.14K
HXC4 Exit temperature	308.15K	308.15K

7.4 ECONOMIC EVALUATION VIA ENERGY REQUIREMENT ANALYSIS

A detailed economic evaluation would require, besides the process conditions and the mass balances, a detailed design and sizing of equipment as well as cost information on the feed and product. The sizing of the equipment is a tedious exercise complicated by the complexity of the equipment due to the high pressures associated with a process of this type. Due to the high pressures, traditional methods for estimating capital costs cannot easily be applied. Thus, in order to obtain an indication of the economic viability of such a process, the energy requirements per unit feed will be estimated.

7.4.1 ASSUMPTIONS

The following assumptions are made in order to facilitate the calculation of the energy required:

- Pumps and compressors operate at 100% efficiency and are isentropic
- Heat losses to the environment are neglected.
- Energy available during the decompression of the overheads and bottoms is not used.
- Pressure losses in pipe and column are assumed to be negligible.
- Solvent cooling with cooling water can be achieved up to 308K.
- Solvent cooling with refrigeration system utilised to 283K.
- The quantity of solvent dissolved and lost in the overheads product stream and bottoms product stream is negligible.
- Wax feed is available at 293K.

7.4.2 ENERGY REQUIREMENTS FOR UNIT OPERATIONS

The energy requirements of each unit operation are based on an energy balance, in combination with the concept of the conservation of mass and isentropic behaviour for pumps and compressors. Additionally, the heat of mixing of the wax and the solvent is neglected. Details of the expressions for the unit energy requirements are shown in 11.4.3.1 in appendix C.

7.4.3 THERMODYNAMIC PROPERTIES OF WAX

The thermodynamic properties of the solvent can easily be obtained [5]. However, the properties of the wax are less well known and need to be estimated.

7.4.3.1 PROPERTIES OF THE WAX FEED STREAM

A DSC plot reveals the heat capacity of the feed as a function of temperature. The wax used in these experiments contains a significant quantity of volatiles, and although in the energy requirements estimations the presence of lights is included, the effect of their absence is shown:

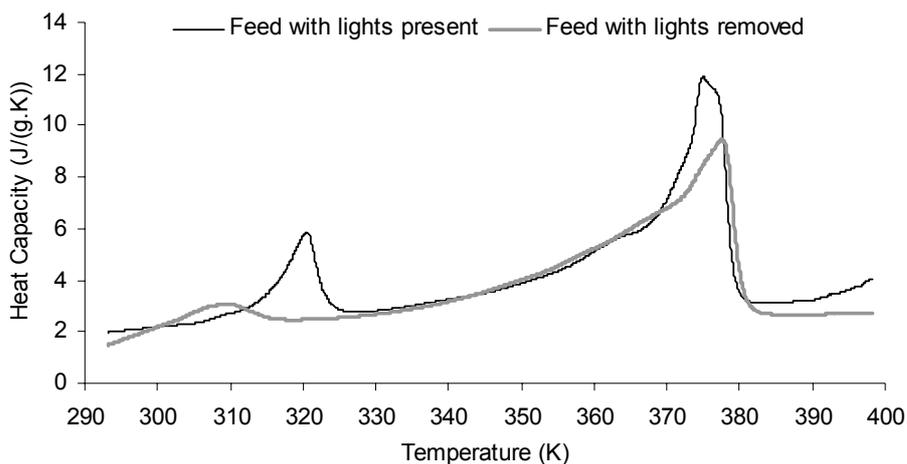


Figure 7-4: Heat capacity of feed wax with and without lights as a function of temperature

The main difference in the heat capacity curves is a peak at approximately 320K in the feed with the lights. This may either be due to thermal history in the wax or the evaporation of a solvent. Additionally, for the feed with lights, the peak between 370 and 380K (melting peak) seems wider – this may be attributed to the light component being water. During pre-heating of the feed, solvent vapours were observed but no solvent was smelt. From these observations it is postulated that the lights are water remaining from the production process and the peak at 320K is due to the thermal history.

From the heat capacity of the wax, the enthalpy required to heat the wax to the operating temperature, including the melting energy required, is calculated. The enthalpy plot is given in 11.4.2.1 in appendix C.

The quantity of lights removed is calculated by placing a known mass of wax in a vacuum oven for 2 days at 120°C. A total reduction of 9.6% of the original mass was observed and for further calculations it is assumed that 10% of the feed is removed as lights. Calculations are shown in section 11.4.2.1 in appendix C.

The density of the feed with the lights removed was calculated from the mass added and the dimensions of the pressure intensifier. A value of 808 kg/m³ was calculated. Calculations are shown in section 11.4.2.1 in appendix C.

7.4.3.2 PROPERTIES OF THE OVERHEAD AND BOTTOMS WAX

The heat capacity of the wax extracted as a function of composition in the range between the column and separator operating temperature is required. As the composition of the wax varies with run to run and no experimental values are available for the heat capacities of the wax, a method is required to estimate the heat capacities. A group contribution method, that of Ruzicka et al. [6], [7], is used. Details regarding the selection of the method and the parameters used is given in 11.4.2.2 in appendix C.

7.4.4 CALCULATED ENERGY REQUIREMENTS

The energy requirements for both above proposed systems will now be calculated, showing the difference between one and the two phase decompression and the effect of the solvent to feed ratio and heat integration. Finally, the energy requirements are compared to a similar supercritical extraction process.

7.4.4.1 ENERGY CALCULATIONS FOR THE ONE PHASE DECOMPRESSION PROCESS

The energy requirements for the one phase decompression process have been calculated and the unit requirements are shown in Table 7-8. Detailed energy calculations are shown in section 11.4.3.2 in appendix C.

Table 7-8: Energy requirements for the one phase decompression process per gram feed with a solvent to feed ratio of 60

Unit	Energy requirement (J/g feed)	Percentage of total energy requirement
Feed pump	14	0.02%
Solvent pump	743	1.15%
HXH1	16462	25.48%
HXH2	14801	22.91%
HXH3	96	0.15%
HXH4	409.6	0.63%
HXC1	10663	16.50%
HXC2	20010	30.97%
HXC3	1408	2.18%
TOTAL	64608 \equiv 64.6 kJ/g feed	

The majority of the energy required goes into the solvent preheater, the overheads heater and solvent cooling. An analysis of the type of heating required is given in Table 7-9. With energy integration it is expected that the energy required can be reduced significantly (see section 7.4.4.2)

Table 7-9: Analysis of type of energy required for the one phase decompression process with a solvent to feed ratio of 60

Unit	Energy requirement (J/g feed)	Percentage of total energy requirement
Heating energy	31770	49.2%
Cooling energy	32081	49.7%
Pumping energy	758	1.2%

It should be noted that the feed preheating energy contributes less than 1 % of the total energy requirements and thus a feed without the lights or a pre-melted feed will not significantly change the energy requirements.

Assuming saturated steam is available at 425K (5.03barA), 15 grams of steam per gram of wax is required. This is very high but it is hoped that with heat integration and possibly a lower solvent to feed ratio this value may be significantly reduced.

An analysis of the solvent to feed ratio shows that it has a significant effect on the energy requirements. Assuming all other factors remain the same, i.e. the column is modified to give the same separation, the effect of the solvent to feed ratio on the total energy required is shown in Figure 7-5:

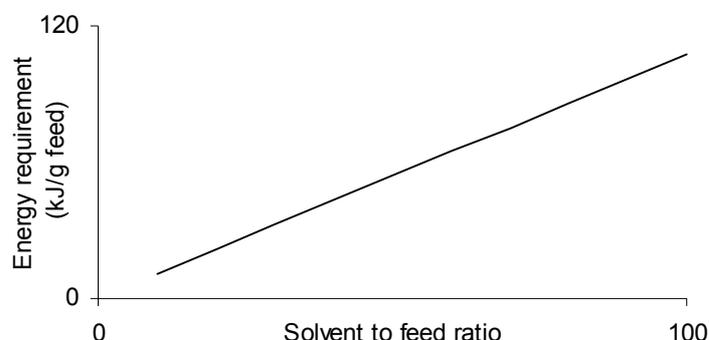


Figure 7-5: Effect of solvent to feed ratio on total energy required

It is seen that there is a relatively linear relationship between the solvent to feed ratio and the total energy requirements with the energy required increasing with increasing solvent to feed ratio. This shows that most of the energy input goes into the solvent cycle. A 50% reduction in the solvent flow rate will thus result in approximately a 50% reduction of the energy requirement. For a solvent to feed ratio of 30 the energy requirements shown in Table 7-10 and detailed calculations are shown in 11.4.3.2 in appendix C:

Table 7-10: Energy requirements for the one phase decompression process per gram feed with a solvent to feed ratio of 30

Unit	Energy requirement (J/g feed)	Percentage of total energy requirement
Feed pump	14	0.04%
Solvent pump	372	1.14%
HXH1	8231	25.31%
HXH2	7364	22.64%
HXH3	96	0.30%
HXH4	409.6	1.26%
HXC1	5331	16.39%
HXC2	10005	30.76%
HXC3	704	2.16%
TOTAL	32527 \approx 32.5 kJ/g feed	

An analysis of the type of energy required is shown in Table 7-11:

Table 7-11: Analysis of type of energy required for the one phase decompression process with a solvent to feed ratio of 30

Unit	Energy requirement (J/g feed)	Percentage of total energy requirement
Heating energy	16101	49.5%
Cooling energy	16040	49.3%
Pumping energy	386	1.2%

The ratio of the energy requirements is similar with a slight increase in pumping energy. Assuming steam is available at 425K (5.03barA), 7.7 grams of steam per gram feed is required. This is a significant reduction compared to the higher solvent to feed ratio for the same process.

7.4.4.2 ENERGY CALCULATIONS FOR THE ONE PHASE DECOMPRESSION PROCESS WITH ENERGY INTEGRATION

As seen above, the heating and cooling energy of the system constitute the majority of the energy requirements of the process. With the aid of heat integration the energy requirements can be reduced. The technique of pinch analysis is used to maximise the heat integration. Heat integration is applied to both solvent to feed ratio processes and the same modified flow diagram is suggested for both processes:

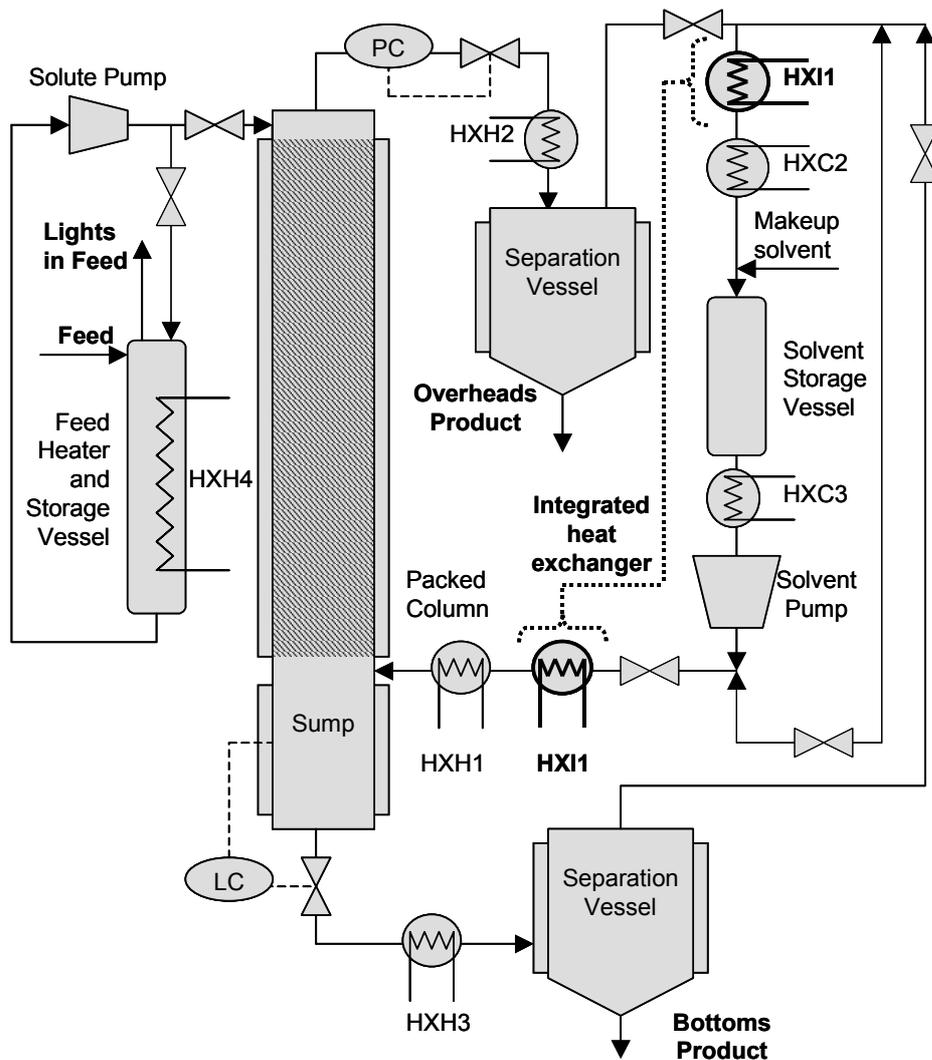


Figure 7-6: Schematic representation of one phase decompression for an alcohol ethoxylate concentration process with energy integration

The energy integration is similar for the two processes, the only difference being the numerical values. A pinch temperature of 303.15K is found, yet the energy integration was limited by the heat capacity differences. Heat exchanger HXC1 in the original process (Figure 7-2) is integrated with part of heat exchanger HXH1 to form the heat exchanger HXI1. As heat exchanger HXC1 cannot provide all the heating required in heat exchanger HXH1, a reduced heat exchanger HXH1 is still required. The operating temperatures for the integrated heat exchanger are shown in Table 7-12:

Table 7-12: Summary of heat integration heat exchanger (HXI1)

Stream	Inlet temperature (K)	Outlet temperature (K)
Solvent to be cooled	403	308
Solvent to heated	286	355

The revised energy requirements for both the high and the low solvent to feed processes are given in Table 7-13.

Table 7-13: Revised energy requirements for one stage decompression process

Unit	Solvent to feed ratio = 60		Solvent to feed ratio = 30	
	Energy requirement (J/g feed)	Percentage of total energy requirement	Energy requirement (J/g feed)	Percentage of total energy requirement
Feed pump	14	0.03%	14	0.04%
Solvent pump	743	1.72%	372	1.14%
HXH1	5800	13.40%	8231	25.31%
HXH2	14801	34.20%	7360	22.63%
HXH3	96	0.22%	100	0.31%
HXH4	410	0.95%	409.6	1.26%
HXC2	20010	46.23%	5331	16.39%
HXC3	1408	3.25%	10005	30.76%
Total	43282 J/g feed \equiv 43.3 KJ/g feed		21865 J/g feed \equiv 21.9 KJ/g feed	
% Reduction	33.0%		32.8%	

Energy integration can thus reduce the energy requirements with approximately 33%.

The process, as proposed in Figure 7-2 and improved in Figure 7-6, operates as a unit on its own. It is envisaged that such a unit may operate close to the production unit. The ethoxylation reaction is generally at temperatures higher than those used in the separation process and the ethoxylation reaction is exothermic. It may thus be possible to integrate the reactor cooling and the overheads and bottoms heating (HXH2 and HXH3) to reduce the heating energy required. This may result in an additional 30% reduction in energy requirements as the energy for HXH2 and HXH3 can be sourced from the reactor system.

7.4.4.3 ENERGY CALCULATIONS FOR THE TWO PHASE DECOMPRESSION PROCESS

The energy requirements for the two phase decompression process have been calculated and the unit requirements are shown in Table 7-14 and calculations are shown in 11.4.3.2 in appendix C.

Table 7-14: Energy requirements for the two phase decompression process per gram feed with a solvent to feed ratio of 60

Unit	Energy requirement (J/g feed)	Percentage of total energy requirement
Feed pump	14	0.03%
Solvent pump	1181	2.81%
Compressor I	24	0.06%
Compressor II	26	0.06%
HXH1	7371	17.57%
HXH2	12123	28.90%
HXH3	100	0.24%
HXH4	368.64	0.88%
HXH5	2	0.00%
HXC1	16415	39.13%
HXC2	11	0.03%
HXC3	4319	10.29%
HXC4	58	0.14%
TOTAL	41954 \equiv 42.0 kJ/g feed	

As in the case of the one phase decompression process, the majority of the energy requirements goes into the solvent pre-heater, the overheads heating and the solvent cooling. An analysis of the type of energy required is given in Table 7-15:

Table 7-15: Analysis of type of energy required for the two phase decompression process with a solvent to feed ratio of 60

Unit	Energy requirement (J/g feed)	Percentage of total energy requirement
Heating energy	19964	47.6%
Cooling energy	20803	49.6%
Pumping energy	1245	3.0%

Comparing the values in Table 7-15 with those of the one phase decompression process, it is seen that for the same solvent to feed ratio the heating and cooling energy is reduced with approximately 33% while the pumping and compression energy, although only a small percentage, is doubled. This process thus shows an improved energy requirement compared to

the one phase decompression process. Assuming saturated steam is available at 425K (5.03barA) 9.5 grams of steam per gram feed is required. This value, although still high, is less than for the one phase decompression process. As in the case of the one phase decompression process, the solvent to feed ratio has a significant effect on the energy requirements. The energy requirements for a two phase decompression process with a solvent to feed ratio of 30 is shown in Table 7-16:

Table 7-16: Energy requirements for the two phase decompression process per gram feed with a solvent to feed ratio of 30

Unit	Energy requirement (J/g feed)	Percentage of total energy requirement
Feed pump	14	0.07%
Solvent pump	590	2.78%
Compressor I	24	0.11%
Compressor II	26	0.12%
HXH1	3685	17.37%
HXH2	6032	28.43%
HXH3	100	0.47%
HXH4	368.64	1.74%
HXH5	2	0.01%
HXC1	8207	38.68%
HXC2	11	0.05%
HXC3	2160	10.18%
HXC4	58	0.27%
TOTAL	21220 \equiv 21.2 kJ/g feed	

An analysis of the type of energy required is shown in Table 7-17

Table 7-17: Analysis of type of energy required for the two phase decompression process with a solvent to feed ratio of 30

Unit	Energy requirement (J/g feed)	Percentage of total energy requirement
Heating energy	10187	48.0%
Cooling energy	10436	49.2%
Pumping energy	655	3.1%

The energy integration is similar for the two different solvent to feed processes, the only difference being the numerical values. A pinch temperature of 398.15K is found. Heat exchanger HXH1 is integrated with part of heat exchanger HXC1 and a reduced heat exchanger HXC1 is still required. Care is also required during this energy integration as HXC1 functions as both a cooler and a condenser. HXH1 is able to provide most of the cooling energy with no temperature crossover and the HXC1 will provide the remaining of the cooling and the condensation energy. The operating temperatures for the integrated heat exchanger are shown in Table 7-18:

Table 7-18: Summary of heat integration heat exchanger (HXI1)

Stream	Inlet temperature (K)	Outlet temperature (K)
Solvent to be cooled	403	362
Solvent to heated	349	393

The revised energy requirements for both the high and the low solvent to feed ratio process is given in Table 7-19:

Table 7-19: Revised energy requirements for two stage decompression process

Unit	Solvent to feed ratio = 60		Solvent to feed ratio = 30	
	Energy requirement (J/g feed)	Percentage of total energy requirement	Energy requirement (J/g feed)	Percentage of total energy requirement
Feed pump	14	0.05%	14	0.07%
Solvent pump	1181	4.34%	590	2.78%
Compressor I	24	0.09%	24	0.11%
Compressor II	26	0.10%	27	0.13%
HXH2	12123	44.55%	3685	17.37%
HXH3	100	0.37%	6029	28.41%
HXH4	369	1.35%	103	0.49%
HXH5	2	0.01%	368.64	1.74%
HXC1	9044	33.24%	1	0.01%
HXC2	11	0.04%	8207	38.67%
HXC3	4319	15.87%	11	0.05%
HXC4	58	0.21%	2160	10.18%
Total	27212 J/g feed \equiv 27.2 KJ/g feed		13849 J/g feed \equiv 13.8 KJ/g feed	
% Reduction	35.1%		34.7%	

Theoretically it is possible to integrate HXC2 and HXC4 with part of HXH4. However, this will only result in a 0.25% energy reduction and together with the fact that an additional heat exchanger is required, this integration is not justified. Energy integration can thus reduce the energy requirements with approximately 35%.

7.4.4.5 COMPARISON OF PROCESS WITH OTHER SCFE PROCESSES

Unfortunately no other alcohol ethoxylate concentration process exists so a direct comparison of the energy requirements cannot be made. The only comments that can be made in this regard involve other types of wax separation processes.

Crause [3] compared the fractionation of paraffin wax to current methods used and found for the fractionation of medium to heavy paraffin waxes, supercritical fluids is a more attractive option than crystallisation and short path distillation. From this trend, it may seem that this process may be competitive. To compare the energy costs of Crause with those in this work the same utility costs are used and the energy costs are calculated. The utility costs and calculation of the energy costs are shown in section 11.4.3.2 in appendix C and a comparison is given in Table 7-20:

Table 7-20: Energy costs associated with alcohol ethoxylate production

Process	Energy cost (R/ton)
One stage decompression process with solvent to feed ratio = 60	4507
One stage decompression process with solvent to feed ratio = 30	4213
One stage decompression process with solvent to feed ratio = 60 and heat integration	2260
One stage decompression process with solvent to feed ratio = 30 and heat integration	2113
Two stage decompression process with solvent to feed ratio = 60	726
Two stage decompression process with solvent to feed ratio = 30	510
Two stage decompression process with solvent to feed ratio = 60 and heat integration	373
Two stage decompression process with solvent to feed ratio = 30 and heat integration	265
Highest energy cost proposed by Crause [3]	202
Lowest cost proposed by Crause [3]	51

Refrigeration is very expensive. This can be seen when comparing the cost of the one phase and the two-phase decomposition process. Refrigeration costs constitute in excess of 75% of the energy costs of the one stage decompression processes. The data in Table 7-20 indicates that

the two stage decompression process at lower solvent to feed ratio costs only marginally more than the highest cost proposed by Crause [3]. The following should, however, be remembered:

- The process suggested is not fully optimised as complete optimisation is beyond the scope of this project. Should an even lower solvent to feed ratio be applied, the operating costs may be even lower. With detailed optimisation it may thus be possible to reduce the operating costs even more.
- The process proposed by Crause [3] operates at 70°C while the process designed in this work operates at 120°C. The process designed in this work thus requires more heating energy than the process suggested by Crause due to the higher operation temperature.
- The intended product is a high value product. The wax feed used in these experiments was purchased at R 72 000 per ton. The above energy costs are thus less than 0.5% of the selling price.

7.5 COMBINED TECHNICAL AND ECONOMIC VIABILITY

Technically the process is viable. This has been proven with the removal of the lower ethoxylates in the overheads to provide a concentrated product in the bottoms.

Due to the high molecular weight of the molecules, it is very difficult to determine if a narrowing in the alcohol ethoxylate distribution has occurred. However, the results do show that fractionation according to the number of ethylene oxide units added has occurred and thus it can be implied that the distribution has been narrowed, resulting in a superior product.

Economically, the separation process running costs compare well other processes. A clear-cut answer regarding the economic viability can not be made at this point as the economic viability depends on a number of factors, including but not limited to:

- The capital cost of the separation process.
- The contribution of the post-production separation costs to the final product cost.
- The price at which the concentrated alcohol ethoxylate can be sold.
- The degree to which fine-tuning of the process can further reduce the economic viability.

Another aspect that may influence the economic viability in a positive way is the fact that the fractions removed from the feed can be recycled for reprocessing or possibly even marketed as a stand-alone product.

There are still a number of technical and economic aspects that need investigation. However, from the analysis shown above, it can be seen that further investigation is definitively worthwhile.

7.6 NOMENCLATURE

Symbol	Description
m	Average number of ethylene oxide units per alcohol ethoxylate molecule
n	Average number of carbon atoms in the hydrocarbon backbone of an alcohol ethoxylate molecule

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8 Conclusions and future work

Synthetic waxes have an enormous potential yet due to their virtual insolubility, their use is limited. By grafting the hydrocarbon backbone of the synthetic wax with a polyethylene glycol segment to form an alcohol ethoxylate, the solubility of the wax in many solvents can be increased without significantly changing the characteristics of the molecule. These wax-like alcohol ethoxylates have an enormous potential application, yet production problems still hamper its implementation. By concentrating the alcohol ethoxylates, a superior product may be attained that could be marketed for numerous uses.

This chapter will summarise the findings of the investigation of the use of supercritical fluid extraction as a post-production separation process to concentrate alcohol ethoxylates. It also indicates what further work may be required.

8.1 CONCLUSIONS

The starting point of this work was a detailed study of the production of alcohol ethoxylates. The working of the catalysts highlighted the origins of the wide distribution of ethylene oxide addition products and the large residual alcohol content: The reaction path way is controlled by the acidity of the catalyst and traditional base catalysts, which do not produce unwanted by-products, favour a wide ethylene oxide distribution and a high residual alcohol content.

The aim of this work is to improve the alcohol ethoxylate produced. It was found that this could be achieved by either re-evaluating the addition reaction or implementing a post-production separation process. A large amount of work has already been conducted regarding the addition reaction and this work thus concentrated on a post-production separation process. Traditional separation methods such as distillation and liquid-liquid extraction were briefly investigated yet due to the nature of the alcohol ethoxylate molecule, these methods cannot be applied. Supercritical fluid extraction was suggested as an alternative separation method.

The system investigated here was modelled to contain three pseudo-components: an alkane, an alcohol and an alcohol ethoxylate. To design a supercritical fluid extraction process, knowledge of the phase behaviour of each of these pseudo-components with the supercritical solvent is required. Carbon dioxide and propane were investigated as suitable solvents for a supercritical extraction process. Propane was selected as solvent of choice due to the larger difference in the solubility difference between the alkane and polyethylene glycol, a higher alkane loading and a more suitable operational region.

A literature study revealed that the propane-alkane data is complete enough at low molecular weights [1] but the possibility of extrapolation needed further investigation. At higher molecular weights the large size of the molecule compared to that of the solvent starts to influence the

system and the molecular conformation of the alkane in supercritical. This in turn may influence the phase behaviour. The molecular conformation behaviour of long chain molecules thus needed to be investigated.

It is well known fact that crystalline linear polyethylene [2], [3], [4], [5], [6] and high molecular weight normal alkanes [7] molecules take on a folded configuration. This folded configuration is found to be a function of supercooling [8]. The dependence of molecular folding in the alkane and in the polyethylene on the supercooling was superimposed and the same relationship was found. The phenomena resulting in molecular folding in crystalline alkanes and that of crystalline polyethylene is thus the same. However, information on molecular folding in the liquid phase and in solution was found to be inconclusive. A model was proposed for molecular folding in supercritical solution: If an alkanes of n carbon atoms folds while in (supercritical) solution, then it will no longer behave as one alkane molecule of n carbon atoms but rather as two alkane molecules of $n/2$ carbon atoms. This model needed to be tested experimentally.

Pure alkanes are commercially available up to nC_{60} and higher molecular weight alkanes needed to be synthesised. Various methods for the synthesis of long chain alkanes were investigated and the method of Carothers et al. [9] and Heitz et al. [10] was selected. The product synthesised was an alkane mixture with alkanes in increments of 12 carbon atoms and an average of 102 carbon atoms per molecule.

To compare the results of a mixture of alkanes with a pure alkane, the application of the principle of congruency needed to be proven. A low molecular weight alkane mixture was used to prove that the principle of congruence can be applied to the high-pressure phase equilibria of high molecular weight alkanes in supercritical solution. Phase equilibrium measurements of the synthesised alkane mixture in supercritical propane were conducted and it was found that:

- In the high wax mass fraction region the data measured was below the extrapolated value. The data points were between the no folding and single fold relationship. This may either be due to the polydisperse nature of the sample or that a limited quantity of alkane underwent molecular folding.
- In the mixture critical region the data measured was very similar to extrapolated value and it is expected that molecular folding did not occur.
- In the low wax mass fraction region the data measured was either slightly above or slightly below the extrapolated value and it is expected that the molecular folding did not occur.

It was proposed that two factors influence molecular folding in normal alkanes:

- The concentration of the solvent in the wax: At high wax mass fractions the molecules no longer behave independently of one another and thus start to influence each other.
- The molar concentration of the molecules undergoing molecular folding: At low mass fractions molecular folding may occur but the effect is sufficiently diluted by non-folding molecules and solvent that no noticeable change in the phase transition pressure is found.

The alkane-propane phase behaviour was now described sufficiently well and the propane-alcohol and propane alcohol-ethoxylate phase behaviour needed to be investigated. No propane-alcohol and propane-alcohol ethoxylate data was available and thus needed to be measured.

Phase equilibrium measurements of propane with a high molecular weight alcohol mixture with an average hydrocarbon backbone of 39 carbon atoms were conducted between 378 and 408K. Total solubility was achieved below 140barA and type V phase behaviour suggested.

Phase equilibrium measurement of propane with an alcohol ethoxylate mixture was measured. The alcohol ethoxylate mixture had an average hydrocarbon backbone of 39 carbon atoms and an average of 12.5 ethylene oxide groups. The measurements were conducted between 378 and 408K with pressures up to of 275barA. At very low alcohol ethoxylate mass fractions (less than 0.025) and at high alcohol ethoxylate mass fractions (greater than 0.5) solubility was achieved. The gradients were, however, very steep. Between an alcohol ethoxylate mass fraction of 0.025 and 0.5 the solubility pressure exceeded 275barA. At low mass fractions a temperature inversion occurred and type IV phase behaviour suggested.

When the phase equilibrium of the alkane, the alcohol and the alcohol ethoxylate was compared, it was seen that the alkane is the most soluble, followed by the alcohol. The alcohol ethoxylate is the least soluble. It was suggested that the alcohol ethoxylate is concentrated with the use of a counter-current supercritical extraction process operating at 120 – 130°C and marginally above the mixture critical pressure of the propane-alkane system.

A counter-current supercritical fluid extraction pilot plant was modified to test the ability of supercritical propane to concentrate the alcohol ethoxylate. Pilot plant test runs were conducted between 115 and 150barA and 120 and 130°C. All runs showed an increase in the degree of ethoxylation in the bottoms stream and a decrease in the degree of ethoxylation in the overheads stream. Separation according to the degree of ethoxylation thus occurred.

An increase in temperature lead to a decrease in percentage feed in the overheads while an increase in pressure lead to an increase in percentage feed in the overheads. For an increased temperature and pressure while maintaining the same percentage feed in the overheads, the degree of separation is not as sharp. It was concluded that a process should thus run at as low temperature and pressure as possible to obtain as sharp as possible separation.

A process flow diagram for an intended separation process was set-up and together with a mass balance, an estimation of the energy required per unit feed was determined. A DSC plot and a group contribution method was used to describe the alcohol ethoxylate thermal characteristics. The majority of the energy requirements were found to go into heating and cooling. It was found that the solvent to feed ratio had a significant effect on the energy requirements and the energy requirements could be reduced by approximately 33 % with heat integration.

The proposed flow diagram with heat integration required an energy cost of R 4213 per ton. Although high, it is less than 10 % of the purchase price of the unconcentrated alcohol ethoxylate.

However, the process needs to be optimised. With a detailed optimisation it is believed that the utility costs can be reduced.

From the analysis done in this work it is shown that the process is both technically and economically viable and further investigation is definitively recommended.

8.2 CONTRIBUTIONS MADE IN THIS WORK

The major contribution of this work is two-fold:

- Firstly, an investigation of the phase behaviour of long chain alkanes of more than 60 carbon atoms in supercritical propane was conducted. This work is the first to investigate and comment, with experimental backing, on the presence of molecular folding in alkanes in supercritical solution and showed that at low mass fractions, the phase behaviour is similar to the expected behaviour extrapolated from normal alkanes.
- Secondly, it was proven that alcohol ethoxylates can be concentrated with the use of supercritical propane. This was tested on pilot plant scale and showed both technical and economic viability.

However, in achieving the above-mentioned contributions, other contributions were also made:

- For the first time the fold period of the alkane and polyethylene as a function of supercooling are superimposed and show good agreement (See Figure 4-17). This provides a good bridge between the molecular behaviour of alkanes and polyethylene.
- This work is the first to apply principles of congruency to link pure alkane and alkane mixture phase behaviour in supercritical fluids.
- For the first time phase equilibrium measurements of propane with high molecular weight alcohols and propane with high molecular weight alcohol ethoxylates were conducted.

8.3 FURTHER INVESTIGATIONS

This work shows that the use of supercritical fluid extraction for concentrating wax-like alcohol ethoxylates is both technically and economically viable. However, a number of issues still need to be addressed:

- The alcohol ethoxylate process suggested here needs to be optimised. Optimisation would include parameters such as temperature, pressure, solvent to feed flow rate, solvent flow rate and feed flow rate. Additionally the column performance needs to be investigated so that the optimum column geometry for a set feed and solvent rate can be determined.
- The use of LPG instead of propane needs to be investigated. LPG is considerably cheaper and as it contains some normal and iso-butanenes, the pressures required will thus be lower.

- The possibility of separating alcohols from alkanes with the use of supercritical fluids needs to be investigated.
- In this analysis it is assumed that all separation occurs only according to the ethylene oxide content. However, it is known [1] that propane is able to fractionate hydrocarbon molecules according to their molecular weight. The effect of hydrocarbon fractionation during the alcohol ethoxylate concentration process needs to be investigated.

This work also highlighted a number of additional issues that also warrant further investigation:

- Phase equilibrium of an alkane mixture with a lower polydispersity together with propane needs to be conducted to investigate the effect of polydispersity.
- Should the alcohol ethoxylates overheads be characterised sufficiently well enough i.e. both average molecular weight and oxygen content, phase equilibrium measurements of these fractions with propane can be conducted to investigate the phase equilibria as a function of the degree of ethoxylation and the hydrocarbon backbone length.
- Various proposals can be made to improve the ethoxylation set-up. These possible improvements step away from investigating the behaviour of the catalysts and concentrate on alternative ethoxylation set-ups. Ethoxylation may be more successful in a counter current type set-up, as proposed in Figure 2-18. This may be combined with a reactive distillation type set-up to prove a better distribution of the final product.
- No single study has been conducted to compare a large number of the ethoxylation catalysts. Various studies have been conducted but as the reaction conditions are not the same, direct comparisons cannot be made. Such a study may include parameters such as temperature, pressure, residence time, alcohol molecular weight and the quantity of ethylene oxide added.
- To date, no equation of state exists that can successfully predict the phase behaviour of the alcohol ethoxylate in supercritical propane. An equation of state needs to be developed to describe this type of phase behaviour. As a starting point, a model such as the statistical associating fluid theory (SAFT) equation of state [11], [12] or the model proposed by du Rand [13] is suggested.

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9 Appendix A: Literature information and data

9.1 DATA CONCERNING ALCOHOL ETHOXYLATES

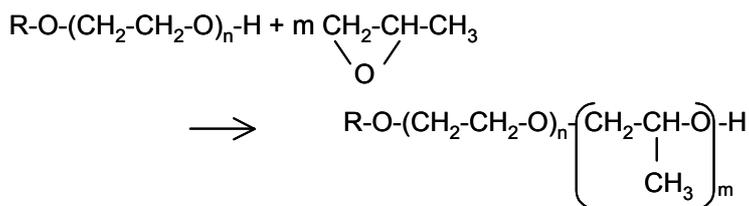
9.1.1 ALCOHOL ETHOXYLATES AS STARTING MATERIALS FOR OTHER SURFACTANTS

9.1.1.1 ALKYL AND ARYL TERMINALLY BLOCKED ALCOHOL ETHOXYLATES

By substituting the hydrogen atom of the terminal hydroxyl group of an ethoxylate by hydrophobic residues such as benzyl, butyl or methyl groups, terminally blocked alcohol ethoxylates are obtained that are chemically more resistant, especially in alkali media, than the corresponding ethoxylates with free hydroxyl groups. Blocked ethoxylates also foam less in aqueous solutions than their starting ethoxylates and thus they have a certain value in alkaline cleaning products involving strong mechanical action. However, due to the terminal blocking of the hydroxyl groups by hydrophobic residues, such ethoxylates lose their surfactant character to some extent and become less water-soluble and less amphiphilic.

9.1.1.2 CO-POLYMERISATION OF ALCOHOL ETHOXYLATES

Co-polymerisation of the alcohol ethoxylate, especially with propylene oxide, may be conducted and the process is illustrated according to the following reaction scheme:



Equation 9-1:

9.1.1.3 PRODUCTION OF ALCOHOL ETHOXYLSULPHATES AND ALCOHOL ETHOXYLSULPHATE SALTS

Alcohol ethoxysulphate salts are used as detergents and hair and body care products with high foam, high cleaning power and low sensitivity to hardness and fats. Alcohol ethoxysulphate salts are expressed according to the following formula:



Alcohol ethoxysulphate can be produced by sulphation of alcohol ethoxylates with gaseous sulphur trioxide or chlorosulphonic acid [1], [2]. Sulphation of alcohol ethoxylates can also be achieved by reacting the alcohol ethoxylate with 96 – 100% sulphuric acid [3], [3].

9.1.1.4 PRODUCTION OF CARBOXY METHYLATED ALCOHOL ETHOXYLATES

Alcohol carboxymethylated ethoxylates are used in detergent compositions in conjunction with an electrolyte and water. Alcohol carboxymethylated ethoxylates are expressed according to the following formula:



Carboxymethylation of alcohol ethoxylate can be achieved by converting the alcohol ethoxylates into an alkali metal ethoxylated alcoholate (by using alkali hydroxide, especially sodium hydroxide) and then reacting the alkali metal ethoxylated alcoholate with a haloacetic acid salt [4].

9.1.1.5 PRODUCTION OF CARBOXYLIC ACID ALCOHOL ETHOXYLATES

Alcohol ethoxycarboxylates can be produced in various manners. Firstly the same method shown in Paragraph 9.1.1.4 can be applied to produce alcohol ethoxycarboxylates from alcohol ethoxylates, the only change being the additional step of converting the carboxylate into a carboxylic acid in the presence of an acid such as hydrochloric acid [5]. Alternatively, the alcohol ethoxylate can be converted directly to an alcohol ethoxylate via oxidation. [5], [6], [7]. Fried et al. [8] used a free radical nitroxide compound to convert alcohol ethoxylates to carboxylic acid alcohol ethoxylates.

9.1.1.6 PRODUCTION OF KETONE DERIVATIVES OF ALCOHOL ETHOXYLATES

Ketone derivatives of alcohol ethoxylates can be produced by contacting the alcohol ethoxylate with dioxane and sodium hydroxide, followed by a 1% aqueous solution of sulphuric acid in dioxane [9].

9.1.1.7 PRODUCTION OF ALCOHOL ETHOXYLATED DERIVED DIOLS

Alcohol ethoxylates can be used to produce $R-O-(CH_2-CH_2-O)_n-CH_2-CH(OH)-CH_2-OH$, which is used together with the alcohol ethoxylate from which it, is derived as a surfactant [10].

9.1.1.8 PRODUCTION OF TERMINAL NITROGEN DERIVATES OF ALCOHOL ETHOXYLATES

Terminal amides can be produced from alcohol ethoxylates by converting the alcohol ethoxylate into a carboxymethylated alcohol ethoxylate and converting the carboxymethylated alcohol ethoxylate into tertiary amide. [11]. Amide oxime derivatives and hydroxamic acids can also be produced from alcohol ethoxylates [12], [13].

9.1.2 PRODUCTION OF ALCOHOL

9.1.2.1 ZIEGLER PROCESS

In this process, ethylene is allowed to react with triethyl aluminium to yield a high molecular weight trialkyl aluminium which, in turn, is allowed to oxidise with air to form the corresponding aluminium alcoholate. The resultant alcoholate is hydrolysed to yield the corresponding normal alcohol. The process is illustrated in Figure 9-1 [14], [15]:

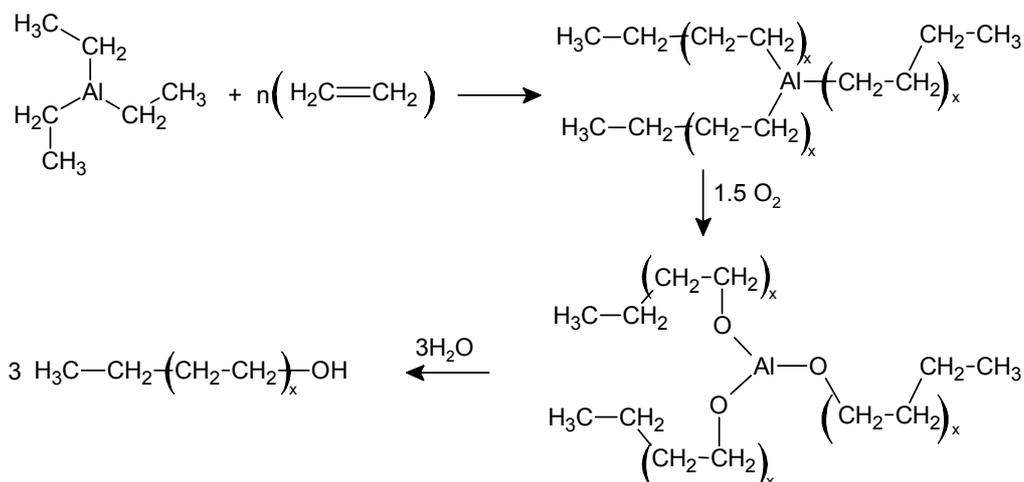


Figure 9-1: Schematic representation of production of long chain primary alcohols via the Ziegler process [14]

9.1.2.2 OXO PROCESS VIA HYDROFORMYLATION

In the oxo process, carbon monoxide and hydrogen are allowed to add to an olefin, to yield an aldehyde that contains one more carbon than the starting unsaturated hydrocarbon. This reaction, referred to as hydroformylation, yields the two structural isomers, one resulting in a primary alcohol with no additional branching, the other leading to a primary alcohol with the formation of an additional methyl side group [14], [16]. The ratio of the products formed depends on the reaction conditions, especially on the $\text{H}_2:\text{CO}_2$ ratio. The process is illustrated in Figure 9-2:

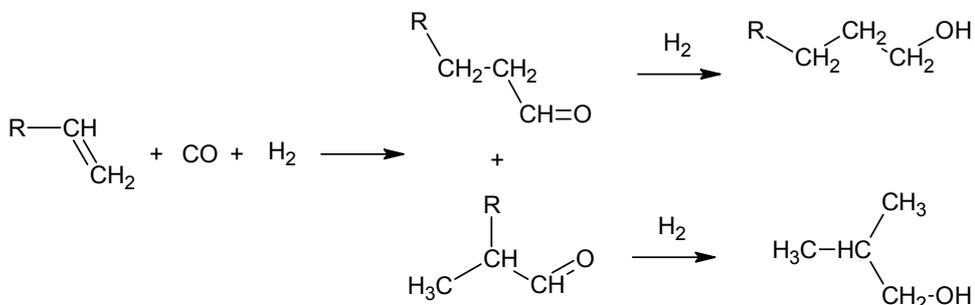


Figure 9-2: Schematic representation of production of long chain primary alcohols via the Oxo process [14]

9.1.2.3 PARAFFIN OXIDATION

Air or oxygen enriched air oxidation of linear paraffins, in the presence of boric acid, leads to a random mixture of secondary alcohol structure isomers. The hydroxyl groups added are distributed statistically along the hydroxyl chain. A small portion of the alcohol may be further oxidised to the corresponding ketone during the reaction sequence. Any ketones formed are, in turn, reduced to alcohols by standard procedures. Schematically the reactions involved are given in Figure 9-3 [14]:

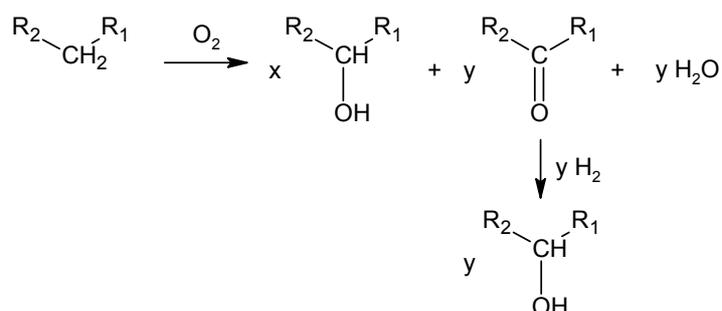


Figure 9-3: Schematic representation of production of long chain primary alcohols by oxidising paraffins [14]

9.1.2.4 NATURAL SOURCES

Surfactant range primary alcohols may be recovered from naturally occurring vegetable and animal sources, most notably coconut and palm kernel oil and animal fats. These natural triglycerides are usually transesterified with methyl alcohol and the resultant methyl esters reduced to the corresponding alcohols by hydrogenation according to Figure 9-4 [14]:

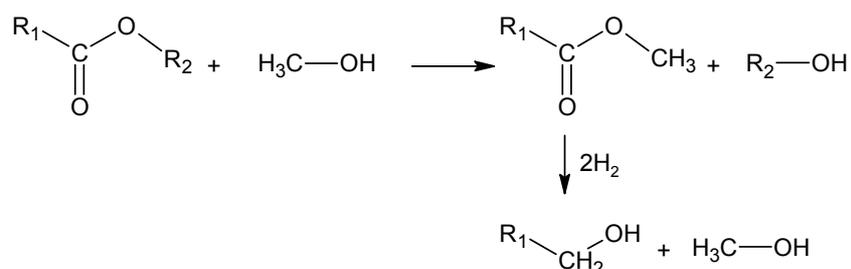


Figure 9-4: Schematic representation of production of long chain primary alcohols from natural sources [14]

9.1.2.5 HYDROGENATION OF ALDEHYDES, CARBOXYLIC ACIDS AND ESTERS

Aldehydes, carboxylic acids and esters can be hydrogenated to form alcohols [17].

9.1.3 CATALYSTS FOR ALCOHOL ETHOXYLATE PRODUCTION

Table 9-1: Details literature data available for production of alcohol ethoxylate with basic catalysts

Catalyst	Temperature and pressure	Notes	Reference
Alkali or alkaline earth metal catalysts e.g. KOH, NaOH	Temperature: 90 – 200°C Pressure: 11-35 bar A		[18]
Barium catalyst promoted by phenol / alkylate phenols e.g. phenol, o-cresol, p-cresol, m-cresol, 2,4 dialkyl phenol, 2,5 dialkyl phenol etc. An increase in phenol leads to a shorter induction period and a decrease in byproducts formed. Effective from 0.1% based on weight of alcohol, usually 0.1 – 2%, preferably 0.15 – 1.5%, most preferred 0.3 – 0.8% Examples: Barium oxide, hydrated barium oxides, barium metal, barium hydroxide, hydrated barium hydroxides, other barium bases Usually 0.1 – 0.5%. An increase in quantity leads to an increase in rate but does not affect distribution.	Temperature: 90 – 260°C, preferably 120 – 160°C Pressure: Atm to 8 barA, preferably 1.6 – 5 barA		[19], [20]
Strontium catalyst promoted by phenol / alkylate phenols e.g. phenol, o-cresol, p-cresol, m-cresol, 2,4 dialkyl phenol, 2,5 dialkyl phenol etc. An increase in phenol leads to a shorter induction period and a decrease in by-products formed. Effective from 0.1% based on weight of alcohol, usually 0.1 – 2%, preferably 0.15 – 1.5%, most preferred 0.3 – 0.8% Examples: strontium oxide, hydrated strontium hydroxide, strontium hydroxide. Usually 0.1 – 0.5%. An increase in quantity leads to an increase in rate but does not affect distribution.	Temperature: 90 – 260°C, preferably 120 – 160°C Pressure: Atm to 8 barA, preferably 1.6 – 5 barA	Continuous contact with barium should be avoided. Process leads to narrow ethylene oxide distribution, low levels of free alcohols and reduces induction period	[21], [22]

Table 9-1 continued

Catalyst	Temperature and pressure	Notes	Reference
<p>Basic salt of an alkaline earth metal e.g. calcium, strontium and barium alkoxides, amides, phenoxides etc. Preferably metal alkoxides and phenoxides where alcohol and phenol are same or similar to reaction product. Also calcium chloride, calcium sulphate, calcium cyanide, barium bromide can be used</p>	<p>Temperature: T = 50 – 270°C, preferably 100 – 200°C Pressure: Not critical</p>	<p>Advantage: Provide narrow molecular distribution</p>	<p>[23]</p>
<p>Strontium or Barium baring catalyst and promoters such as CaOH, Mg, Mg(OH)₂, Zn(OH)₂, AL. Quantity: > 0.1% based on weight of alcohol, preferably 0.1 – 5.0%, most preferred 0.1 – 0.2% Examples: Sr, Ba, SrH₂, BaH₂, SrO, BaO, Sr(OH)₂, Ba(OH)₂, HSrOH, HBa(OH). Quantity: > 0.1% based on weight of alcohol, preferably 0.1 – 5.0%, most preferred 0.1 – 0.2%</p>	<p>Temperature: 120 – 260°C, preferably 150 – 200°C, most preferred 160 – 190°C.</p>		<p>[24]</p>
<p>Basic salt of an alkaline earth metal e.g. calcium, strontium and barium alkoxides, amides, phenoxides etc. Preferably metal alkoxides and phenoxides where alcohol and phenol are same or similar to reaction product. Also calcium chloride, calcium sulphate, calcium cyanide, barium bromide can be used</p>	<p>Temperature: T = 50 – 270°C, preferably 100 – 200°C Pressure: Not critical</p>	<p>Advantage: Provide narrow molecular distribution</p>	<p>[23]</p>
<p>Combined barium and strontium compounds Barium compounds: Ba, Ba(OH)₂, BaO, BaH₂, HBaOH Strontium compounds: Sr, Sr(OH)₂, SrO, SrH₂, HSrOH</p>	<p>Temperature: 120 – 260°C</p>	<p>A promoter with boiling points above 100°C: e.g. Phenols with 6 –30 carbon atoms, Polyols with 2 to 30 carbon atoms, Primary, secondary and tertiary amines with 1 – 30 carbon atoms, Organic acids with 1 – 30 carbon atoms</p>	<p>[25]</p>

Table 9-1 continued

Catalyst	Temperature and pressure	Notes	Reference
<p>Soluble compounds of calcium. Catalyst is soluble if quantity required for catalysation can be dissolved.</p> <p>Examples: Calcium oxides (preferred), calcium phenoxides, calcium ammoniate, calcium amides, calcium thiolates, calcium thiophenoxides, calcium nitrides.</p>	<p>Temperature: 90 – 250°C, preferably 130 – 210°C, more preferred 145 – 190°C, most preferred 155 – 175°C</p> <p>Pressure: Not critical but atm – 11 barA</p>	<p>Allows for a high selectivity and thus leads to a narrow range product and low levels of unreacted alcohol.</p> <p>Neutralisation is required to ensure chemical stability. Neutralisation by using acid from the group of propanoic and benzoic acids.</p>	<p>[26]</p>
<p>Alcohol soluble basic magnesium catalyst and reaction activator. Catalyst must be soluble to promote the desired reaction.</p> <p>Quantity: > 0.1 mol%, preferably 0.2 – 20%, more preferred 0.5 – 15%, most preferred 1.5 – 10%. An increase in catalyst concentration leads to an increase in reaction rate.</p> <p>Examples: alcholates, alkoxides, phenoxides, ammoniates, amides, thiolates, thiophenoxides, nitrides.</p> <p>Preferred are alcholates, alkoxides, and phenoxides. Most preferred are alkoxides especially with R = C1 – C30, more especially R = C1 – R6, most especially with R = C1 – C3.</p> <p>Activator: one or more alkoxylation products of alcohols C7 – C22, preferably C8 – C18, most preferred C10 – C16. Important: Should contain the same number of carbon atoms as alcohol reactant.</p>	<p>Temperature: 90 – 250°C, preferably 130 – 210°C, more preferred 150 – 190°C, most preferred 165 – 175°C.</p>	<p>Dilute reactant with inert compound e.g. N₂ to prevent explosions</p>	<p>[27]</p>

Table 9-1 continued

Catalyst	Temperature and pressure	Notes	Reference
<p>Basic salt of calcium and/or strontium (alkoxides, preferably C8 and lower, and/or phenoxides). Catalyst must be soluble in reactants and reaction products. Quantity: 0.05 – 5%.</p> <p>Catalytic amount of acid as alkoxylation promoter and salts thereof: super phosphoric acid, phosphoric acid, diphosphoric acid, triphosphoric acid, phosphoric acid, dihydrogen phosphate compounds, P₂O₅, P₂O₃, sulphuric acid, carbon dioxide, oxalic acid, etc. Quantity: 0.001 – 1%.</p>	<p>Temperature: 50 – 400°C, preferably 100 – 200°C.</p> <p>Pressure: 1.7 – 7 BarA</p>	<p>Use an acid which will convert the catalyst to a neutral salt for neutralisation</p>	<p>[28]</p>
<p>Basic salt of barium (alkoxides, preferably C8 and lower, and/or phenoxides). Catalyst must be soluble in reactants and reaction products. Quantity: 0.05 – 5%.</p> <p>Catalytic amount of acid as alkoxylation promoter and salts thereof: superphosphoric acid, phosphoric acid, diphosphoric acid, triphosphoric acid, phosphoric acid, dihydrogen phosphate compounds, P₂O₅, P₂O₃, sulphuric acid, carbon dioxide, oxalic acid, etc. Quantity: 0.001 – 1%.</p>	<p>Temperature: 50 – 400°C, preferably 100 – 200°C.</p> <p>Pressure: 1.7 – 7 BarA</p>	<p>Use an acid which will convert the catalyst to a neutral salt for neutralisation</p>	<p>[29]</p>
<p>Soluble basic magnesium compound, e.g. alkoxides, phenoxides, ammoniate, amide, thiolate, thiophenoxide, nitride. Preferred are alkoxides and phenoxides, most preferred are alkoxides such as MeOCH₃, MeOCH₂CH₃. Quantity: Min 0.1 mol%, preferably 0.2 – 20%, more preferred 0.5 – 15%, most preferred 1.5 – 10%</p> <p>Process is activated by an alkolate of the type prepared in the process. Quantity: min 2 mol% based on mole of alcohol, preferably 3%, more preferred 5%, most preferred 7%</p>	<p>Temperature: 90 – 250°C, preferably 130 – 210°C, more preferred 150 – 190°C, most preferred 165 – 175°C</p> <p>Pressure: 1 – 11 BarA</p>	<p>Reaction conditions so that alcohol and activator are liquid, alkoxylation are vapour.</p>	<p>[30]</p>

Table 9-1 continued

Catalyst	Temperature and pressure	Notes	Reference
<p>Calcium containing catalyst: $\text{Ca}(\text{XRH})_p$ where $P = 1$ or 2; XRH = organic containing residue having an active carbon; X = Oxygen, nitrogen, sulphur or phosphorus; R = organic residue which may contain a double bonded oxygen, heteroatoms such as oxygen, sulphur, nitrogen, phosphorus etc and usually has $1 - 20$ atoms</p> <p>The catalyst is partially neutralised by a strong, preferably oxy acid leading to an essentially solid composition which is catalytically active. Quantity $0.2 - 0.9$, preferably $0.45 - 0.7$ amount required to neutralise catalyst composition</p>	<p>Temperature: $50 - 270^\circ\text{C}$, preferably $100 - 200^\circ\text{C}$.</p>	<p>Narrow but balanced distribution of alcohol ethoxylates can be obtained for higher ethoxylation moieties i.e. 4 or more ethylene oxide adduct units</p>	<p>[31]</p>
<p>Alkaline or alkaline earth metal hydroxide e.g. NaOH or KOH</p>	<p>Temperature: $120 - 200^\circ\text{C}$, preferably $140 - 160^\circ\text{C}$</p> <p>Pressure: $P_{\text{Tot}} = 4 - 9 \text{ BarA}$, preferably $4.5 - 8.5 \text{ BarA}$ EO PP 2 – 5 barA, preferably $2.5 - 4.5 \text{ barA}$</p>		<p>[32]</p>
<p>Sodium / potassium alkoxyated / methylate / ethylate</p>		<p>Improvement the neutralisation process: Neutralised salts have limited solubility in reaction product and limited quantity of catalyst used. Here quantity of catalyst is increased beyond solubility level of neutralised salt, leading to better product. Achieved by conducting neutralisation in presence of finely divided solids, preventing precipitation of solids on inner parts of equipment and improving filterability</p>	<p>[33]</p>

Table 9-1 continued

Catalyst	Temperature and pressure	Notes	Reference
NaCH ₃ OH, NaOH, Na, NaCH ₃ CH ₂ OH, KOH	Temperature: 135 – 150 °C (batch); 250 – 350 °C (continuous) Pressure: 50 – 70 atm	Reaction product neutralised with acetic anhydride, phosphoric acid or CO ₂	[34], [35]
Alkaline metal or alkaline earth metal hydroxide: 0.1 – 0.6%, preferably 0.1 – 0.4%	Temperature: 120 – 220 °C, preferably 140 – 160 °C Pressures: P _{Tot} = 2.76 – 7.58 barA, preferred 3.45 – 6.21 barA EO PP = 1.03 – 4.14 barA, preferred 1.34 – 3.45 barA	Pressure achieved by vapour pressure of ethylene oxide. For safety reasons: Keep EO PP below about 4 BarA and dilute with inert gas. Can also be conducted at higher pressures and concentrations if required but safety precautions are required.	[36] [37]
Basic aluminates e.g. alkaline or alkaline earth metal aluminates e.g. NaAlO ₂ , Na ₂ O·Al ₂ O ₃ Quantity: 0.1 – 1.0%, preferably 0.1 – 0.3%	Temperature: 100 – 160 °C, preferably 135 °C for ethoxylation Pressure: 6 – 8 bar	Advantage: Selective catalysis and improved space-time yields. Basicity comparable with KOH and NaOH. May be conducted in the presence of an inert solvent e.g. xylene	[38]
NaOH, KOH Quantity: 0.05- 5%, preferably 0.1 – 0.5%	Temperature: 90 – 150 °C, preferably 120 – 140 °C		[39]

Table 9-2: Details literature data available for production of alcohol ethoxylate with acid catalysts and salts thereof

Catalyst	Temperature and pressure	Notes	Reference
<p>Salt of triflic acid (trifluoromethanesulphonic acid) e.g. alkali metals, alkali earth metals, group II metals</p> <p>Quantity 1 – 100 ppm by weight of reaction mixture</p>	<p>Temperature: 40 – 250°C, preferably 60 – 200°C, most preferred 80 – 150°C.</p>	<p>The salt is soluble in the reaction medium, has a high level of selectivity, a high level of activity, no risk of explosion and not corrosive on usual metals.</p>	[40]
<p>Perfluorosulphonic acid: $X[(SO_3)_wM(SO_3R)_{z-w}]_y$ where: M = Multivalent metal ion e.g. Al, Zn, Se, Cu, Sn, Cr, Co, Hg, Mg, Ni, B, preferably Al^{3+}, Zn^{2+}, R = C1 – C8 fluorinated alkyl group, z = valence of M, w = integer having a value between 1 and z-1, X = perfluorosulphonic acid polymer backbone with average molecular weight > 2000, sulphonic acid groups molecular weight 500 – 20000, preferably 900 – 2000. Allow minimum 10% of available sulphonic acid groups on polymer to be substituted with metal fluorosulphonic acid salt, Y = integer</p> <p>Quantity: 1 – 10000 ppm</p>	<p>Temperature: 20 – 140°C</p> <p>Pressure: 1 – 20 barA</p>		[41]
<p>One or more phosphorus containing acid with an aluminium alkolate or phenolate. Examples: Phosphoric acid, oxides of phosphorus, alkyl phosphonic acid, aryl phosphonic acid, alkyl phosphinic acid, aryl phosphinic acid, super phosphoric acid, alkali metal dihydrogen phosphates, alkali earth metal dihydrogen phosphates, dihydrogen diphosphates.</p> <p>Ratio acid to aluminium compound: 0.1 : 1 to 2.5 : 1</p>		<p>In comparison to traditional acid catalysts a higher quality product, a narrower distribution of alkylene oxide adduct product and a reduced level of residual alcohol is achieved.</p>	[42]

Table 9-2 continued

Catalyst	Temperature and pressure	Notes	Reference
<p>Tribariumorthophosphate or barium triorthophosphate – NOT Dibarium diorthophosphate</p> <p>Quantity: 0.1 wt% based on free hydroxyl mass, preferably 0.2 – 5%, most preferred 0.5 – 2%</p>	<p>Temperature: 90 – 250 °C, preferably, 120 – 210 °C, most preferred 130 – 190 °C</p> <p>Pressure: 1.7 – 12 barA – need to maintain active hydrogen compound in liquid state</p>	<p>Neutralisation of H₃PO₄ with BaOH</p>	<p>[43]</p>
<p>KBaPO₄, NaBaPO₄: Quantity: Based on mole of active hydrogen. Per mole active hydrogen: > 0.1%, preferably 0.2-5%, most preferred 0.5 – 2%. Generally, the higher the desired average alkylene oxide adduct number of the alkoxyate product and the higher the desired rate of reaction, the greater the quantity of catalyst required</p>	<p>Temperature: 90 – 250 °C, preferably, 120 – 210 °C, most preferred 130 – 190 °C</p> <p>Pressure: 1.7 – 12 barA</p>	<p>Neutralise catalyst with BaOH, followed by NaOH. Reaction time depends on degree of alkoxylation and rate of reaction, usually 1 – 24 hours. Post treatment to remove catalysts and by products: Treatment with strong acids, alkali metal carbonates and bicarbonates, solid organic acids, zeolites and clays followed by filtration. Advantage: relatively low residual active hydrogen compound</p>	<p>[44]</p>
<p>B([phi])₃ or HB([phi])₄ where phi = phenol moiety with substituents: 1 – 5 F atoms OR 1 – 5 CF₃ groups OR 1 – 5 O-CF₃ groups OR 1 – 5 S-CF₃ groups OR O-R where R = H, alkyl/aryl with 1 – 22 carbon atoms</p> <p>e.g. tri(pentafluorophenyl)borane, tris(3,5 di(trifluoromethyl)phenyl borane</p>	<p>Temperature: 20 – 200°C</p>	<p>Process for production of alkoxyates with narrow molecular weight distribution. Yields product with narrower molecular weight distribution than produced by conventional base catalysts and lower residual content of active hydrogen organic starting material (alcohol). Process requires 10% of catalyst compared to conventional process.</p>	<p>[45]</p>

Table 9-3: Details literature data available for production of alcohol ethoxylate with acid-base and combined catalysts

Catalyst	Temperature and pressure	Notes	Reference
<p>Bismuth compounds e.g. BiOX, BiX₃, X₂BiOBiOX₂ where X is a weakly coordinated anion e.g. CF₃SO₃⁻, ClO₄⁻, B(C₆H₆)⁴⁺, B(C₆F₆)⁴⁺ and thereof.</p> <p>Quantity: Usually 5 – 500 ppm, preferably 50 – 100 ppm</p>	<p>Temperature: 80 – 180 °C, preferably 100 – 120 °C</p>		[46]
<p>2 Stage process:</p> <p>1st Stage: React alcohol and ethylene oxide in presence of an acidic catalyst e.g. fluorides and chlorides of B, Al, Sn, Fe, Ti and complexes of such halides with ethyl ether. Sulphuric and phosphonic acid can also be used.</p> <p>Quantity: 0.02- 0.05%</p> <p>2nd Stage: Remove acidic catalyst and unreacted alcohol. React mixture with ethylene oxide in presence of alkali metal alcoholate of initial alcohol or corresponding alcoholate of mono- or polyethylene glycol.</p>	<p>Temperature: 1st Stage: 0 – 80°C, preferably 50°C 2nd Stage: 80°C – 200°C, preferably 125°C</p> <p>Pressure: 1st Stage: 1 – 4.5 BarA</p>	<p>Production of polyethers of higher saturated aliphatic monohydric alcohol.</p> <p>Process: 1st Stage Use acid catalyst as larger portion of ethylene oxide reacts with alcohol.</p> <p>Between stages: Neutralised mixture and remove all unreacted alcohol.</p> <p>Process 2nd Stage: Base catalyst process</p>	[47]
<p>Tertiary oxonium: (R₁R₂R₃Y)⁺X⁻ or HC(OR₄)(OR₅)⁺X⁻ where: Y = oxygen atom or C=O group; X = unpolarisable or only slightly polarisable halogen complex ion e.g. BF₄⁻, FeCl₄⁻, AlCl₄⁻, SbCl₆⁻, SnCl₆²⁻; R₁ = C1 – C4 or phenyl; R₂ and R₃ = C1 – C24, aromatic, alicyclic or heterocyclic ring systems with 3 to 14 ring atoms. R₂ and R₃ can also be combined into one ring having 4 – 14 ring atoms</p> <p>R₄ and R₅ = C1 – C24, aromatic, alicyclic or heterocyclic ring systems with 5 to 20 ring atoms.</p> <p>Examples: trimethyloxonium fluoroborate; triethyloxonium fluoroborate; triethyloxonium hexachloroantimonate; trimethyloxonium tetrachloroferrate; triphenyl oxonium fluoroborate</p> <p>Quantity: 0.05 – 5% preferably, 0.1 – 1.5%</p>	<p>Temperature: 0 – 200°C, preferably 40 – 160°C</p> <p>Pressure: 1 atm up to 500 bar, with an increase in pressure leading to a decrease in reaction time</p>	<p>Batch or Continuous process</p>	[48]

Table 9-3 continued

Catalyst	Temperature and pressure	Notes	Reference
<p>Neutral organic salts: Fluoroborates & perchlorates</p> <p>Examples: Sodium fluoroborate; nickel, magnesium, calcium, manganese and zinc perchlorate. Preferred: zinc perchlorate</p> <p>Quantity: > 0.001%, preferably < 10%, more preferred 0.1 – 1%. For R > C7, preferably 0.5 – 5%</p>	<p>Temperature: 80 – 200°C, preferably 100 – 150°C.</p>	<p>Neutral salts catalyse the reaction, remain neutral, accelerate the reaction rate and favour narrow molecular weight distribution. Solvent can be used but can also use an excess of organic compound</p>	[49]
<p>HF + metal alkoxides or mixed metal alkoxides: $M(OC_nH_{2n+1})_q$ where: q = valence of M (usually 3 or 4); n = 1 – 22, preferably 1 – 14; M = Al, Ga, In, Tl, Ti, Zr, Hf, preferably Al, Ti. HF and the metal oxides only work in combination, they do not work when used alone.</p> <p>Molar ratio HF:metal oxide 1:10 – 10:1, preferably 1:1 -3:1</p>	<p>Temperature: 20 – 260 °C, preferably 90 – 200 °C, most preferred 100 – 200°C</p> <p>Pressure: <7 bar, preferably <2.5 bar</p>		[50] [51]
<p>BF_3 or SiF_4 + metal alkoxides or mixed metal alkoxides: $M(OC_nH_{2n+1})_q$ where : q = valence of M (usually 3 or 4); n = 1 – 22, preferably 1 – 14; M = Al, Ga, In, Tl, Ti, Zr, Hf, preferably Al, Ti. BF_3 or SiF_4 and the metal oxides only work in combination, they do not work when used alone</p> <p>Molar ratio BF_3 or SiF_4: metal oxide 1:10 – 10:1, preferably 1:5 to 2:1</p>	<p>Temperature: 20 – 260 °C, preferably 90 – 200 °C, most preferred 100 – 200°C</p> <p>Pressure: Not critical but < 7 barA, preferably < 2.5 barA</p>	<p>An inert solvent is used such as hexane, heptane, octane, nonane, decane or low polynuclear aromatic compounds</p>	[52]
<p>$(RO)_n-M-O-M'-O-M-(OR)_n$ where R = optionally substituted organic moiety, usually with 1 – 6 carbon atoms; M' = divalent metal from groups Va, VIa, VIIa, e.g. Al, Ti, B, Va, Sc, Ge, Yt, Zr, La, Hf, Tn, Pd, Sb etc.; M = trivalent or tetravalent metal e.g. Mo, Va, V etc.; n = 2 if M is trivalent, 3 if M is tetravalent</p> <p>Quantity: > 0.01%, preferably > 0.1%, most preferred 0.2 – 1%</p>	<p>Temperature: 130–200°C, preferably 150–190°C, most preferred 165–175°C</p> <p>Pressure: P_{TOT} = 1.7–11barA, preferably 4–9barA, most preferred 4.5–7.5barA. EO PP: 2–5barA, preferably 2.5–4.5barA</p>	<p>Bimetallic oxo catalyst resulting in an exceptionally narrow range ethylene oxide adduct product relatively free of by-products</p>	[53], [54]

Table 9-3 continued

Catalyst	Temperature and pressure	Notes	Reference
<p>1. One or more sulphur containing acid: sulphur trioxide, sulphuric acid, alkyl sulphuric acids and organic and inorganic sulphuric acids.</p> <p>2. One or more soluble aluminium compound: alcoholates or phenolates, formed in situ with alcohols used.</p> <p>Quantities: Ratio acid : Al compound (mole) 0.1:1 to 2:1, preferably 0.3:1 to 1:1, most preferred 0.4:1 to 0.6: Concentration: > 0.1%, preferably > 0.5%, most preferred 0.1 – 1%</p>	<p>Temperature: 70 – 200°C, most preferred 100 – 170°C</p> <p>Pressure: P_{TOT} > 1barA , preferably 1.7 – 12 barA, most preferred 4.5 – 7.5 barA. EO PP: maximum 5 barA, most preferred 2.5 – 4.5 barA</p>	<p>Narrow range alcohol ethoxylates produced</p> <p>Residence time between 1 and 30 hours</p>	<p>[55]</p>
<p>Anion based zirconium oxides and other anion bound metal oxides.</p> <p>Anions: SO₄²⁻, BF₄⁻, CO₃²⁻, BO₃³⁻, MoO₄²⁻, B₄O₇²⁻ etc.</p> <p>Metal oxides: ZrO₂, NiO, Al₂O₃, SnO₂, Mg₂O₃, Rb₂O, TiO₂, ThO₂, HfO₂ etc.</p> <p>Quantity: 0.5 – 50% based on total weight of ethylene oxide</p>	<p>Temperature: 80 – 180°C</p> <p>Pressure: 2.4 – 7.8 barA</p>	<p>Advantage: Narrow molecular weight range and minimal undesirable high molecular weight co-products or by-products</p> <p>Operated as fixed-bed or fluidised bed reactor</p>	<p>[56]</p>
<p>Calcium based catalyst consisting of calcium containing compound, alkoxyated alcohol, inorganic acid and aluminium alkoxide. Components heated to allow partial exchange of alkoxide groups and hydroxyl group.</p> <p>Calcium containing catalyst: At least partially dispersible in alkoxyated alcohol, e.g. calcium hydride, oacetate, oxylate, nitrate, oxide, hydroxide.</p> <p>Alkoxyated alcohol: where R = C1 – C30, preferably C8 – C14, most preferred C10 – C12 and n = 1 – 20, preferably 1- 12, most preferred 1 - 4</p> <p>Inorganic acid: acids and acid salts including sulphuric acid, hydrochloric acids, hydrofluoric acid, phosphoric acid, pyrophosphoric acid, ammonium bifluoride, ammonium sulphate etc.</p> <p>Aluminium alkoxide: AlR₁R₂R₃ where R₁, R₂ and R₃ are C1 – C30, preferably C8 – C14, most preferred C10 – C12.</p>			<p>[57]</p>

Table 9-3 continued

Catalyst	Temperature and pressure	Notes	Reference
<p>Composition:</p> <ol style="list-style-type: none"> 1. Calcium containing compound at least partially dispersible in the alkoxyated alcohol e.g. CaH_2, $\text{Ca}(\text{OH})_2$, CaO, CaNO_2. 2. Inorganic acids or acid salts such as H_2SO_4, HCl, HF, H_3PO_4 (NH_4)SO_4 etc. 3. Aluminium trialkoxide with alkyl residue C1 – C30. <p>Quantities:</p> <p>Ca compound:Al-Oxide 1:1 to 10:1 Acid : Al-oxide is 0.25:1 to 4:1</p>			[58], [59]
<p>Three part catalyst:</p> <ol style="list-style-type: none"> 1. Sulphuric acid; 2. One or more soluble aluminium compound consisting alcoholates or phenolates; 3. Water <p>Quantities:</p> <p>Acid:Al compound (mole) 0.2:1 – 0.7:1, most preferred 0.3:1 – 0.5:1; Water : Al compound (mole) 0.1:1 – 1.5:1, most preferred 0.3:1 – 0.5:1 Concentration: >0.1%, preferably > 0.5%, most preferred 0.1 – 1%</p>			[60]
<p>Magnesium aryloxides</p> <p>Reaction product of magnesium aryloxides or high molecular weight magnesium alkoxides with phosphorus containing acids or esters</p> <p>Catalyst can be generated insitu</p>	<p>Temperature: Usually 80 – 260 °C, preferably 120 – 200 °C</p> <p>Pressure: 2.35 – 14.8 bar</p>	<p>Narrow molecular range alcohol ethoxylates produced. A solvent may be used but is not required. Batch or continuous process</p>	[61]
<p>L_pX_q where L = Rare earth elements 21, 39 and 57 – 71; may also be mixtures; X = organic or inorganic metal free anion; p, q = number satisfying the valency requirements, e.g. LaCl_3, Ce_2O_3, $\text{Y}(\text{OH})_3$, $\text{Sm}_2(\text{CO}_3)_3$ etc.</p> <p>Quantity: > 0.01, preferably 0.02 – 5%, most preferred 0.5 – 2%</p> <p>General rule: The higher the desired average ethylene oxide adduct number and the higher the desired reaction rate, the greater the quantity catalyst required.</p>	<p>Temperature: 90 – 250°C, most preferred 130 – 190°C</p> <p>Pressure: $P_{\text{TOT}} = 1.7 – 11.5\text{barA}$, most preferred 4.4 – 7.4barA EO PP: 2 – 5.2barA, preferably 2.4 – 4.4barA</p>	<p>Rare earth or mixtures thereof simple metal salt compound resulting in a narrow distribution and enhanced catalyst activity.</p> <p>Preferably conducted in presence of oxo acid of sulphur or phosphorus.</p>	[62], [63]

Table 9-3 continued

Catalyst	Temperature and pressure	Notes	Reference
<p>Structure: $(R_1-X_1-M_1)_f-(Y_1-(M_3-Y_2)_j)-(M_2-X_2-R_2)_g$ where: R_1 and R_2 are independently H and residue of an organic compound with at least one active H; X_1 and X_2 are independently -O-, -S- or -N-; Y_1 and Y_2 a divalent oxyacid anion of valency 2 – 6, -O-, -S- or -N- with either Y_1 or Y_2 being a divalent oxy anion; M_1, M_2 and M_3 are independently a divalent or polyvalent metal - at least one of these is a Group IIA metal and at least one is any other metal; j is an integer from 0 to 100, f and g are integers to satisfy valency</p>	<p>Temperature: 50 – 270°C, preferably, 100 – 200°C</p>	<p>Group IIA containing bimetallic and polymetallic catalyst</p>	<p>[64], [65]</p>
<p>Tribarium orthophosphate also known as barium triorthophosphate - $Ba_3(PO_4)_2$ – Other barium containing compounds may be added but the catalyst should be essentially $Ba_3(PO_4)_2$ Quantity: minimum 1%, preferably 0.2 – 5%, most preferred 0.5 – 2%.</p>	<p>Temperature: 90 – 250°C, preferably 130 – 190°C Pressure: P_{TOT} 1.7 – 12 barA, most preferred 4.5 – 7.5barA, EO PP 2–5 barA, most preferred 2.5 – 4.5 barA</p>	<p>Process should be substantially free of water, maximum 500 ppm, preferably less than 200 ppm, most preferred less than 100 ppm.</p>	<p>[66]</p>
<p>Antimony pentahalogenes</p>	<p>Temperature: Step 1: < 60°C, preferably 20–60°C; Step 2: 20–80°C; Step 3: 40–16°C, preferably 60–140°C Pressure: Step 3: > 1barA, preferably 2 – 6 barA</p>	<p>Three step process for narrow distribution alcohol ethoxylates: 1. Premixing of catalyst with some alcohol. 2. Mixing of remaining alcohol 3. Alkoxylation Step.</p>	<p>[67]</p>
<p>Catalytic amount of silver impregnated on an inert refractory solid support essentially free of fluoride anions and efficiency enhancing cation of Li^+, Na^+, K^+, Rb^+, Cs^+ and Ba^+ and anion comprising of SO_4^-, F^- and one member of the group of oxyanionis of element 21 to 74 periodic table of elements. Quantities: Silver in catalyst: 2–45%, preferably 2–40, most preferred 6–35.</p>	<p>Temperature: 200 – 300°C Pressure: 5 – 30 BarA</p>		<p>[68]</p>

Table 9-3 continued

Catalyst	Temperature and pressure	Notes	Reference
<p>$[M(II)_{1-x}M(III)_x(OH)_{x/n}] \cdot mL$ and $[LiAl_2(OH)_6]A_{1/n} \cdot mL$ where: M(II) = a divalent metal ion e.g. Zn^{2+}; M(III) = a trivalent metal ion e.g. Mn^{3+}; A = Inorganic anion or mixtures thereof e.g. HCO_3^-; L = Organic solvent e.g. methanol, ethanol, iso-propanol or water; n = (average) Valence state of A; x = 0.1 - 0.5; m = 0 - 10</p>		Polycation mixed hydroxide with improved filterability	[69]
<p>Basic catalyst + formic acid or a salt of formic acid or a combination thereof</p> <p>Basic catalyst: Alkali metal hydroxides (NaOH, LiOH, KOH, CeOH), alkali metal alkoxides ($Na-O-CH_3$, $K-O-CH_3$, $K-O-CH_2-CH_3$ etc). Quantity: 0.1–20, most preferred 2–5 mol% based on OH groups</p> <p>Formic acid or salt thereof or combination thereof. Preferred are Alkali metal formates (Li, Na, K formates) and ammonium formates. Particular preference: Na and K formate. Quantity: 0.1 – 10, preferably 0.5 – 8, more preferred 1 – 6, most preferred 2 – 5 mol% based on number of OH groups</p>	<p>Temperature: One step process: 80 to 170 °C, preferably 100 – 160 °C Two step process: Step 1: 80 –130 °C Step 2: 130 –170 °C, preferably 130 – 145 °C Pressure: Two step process: Step 1: 1 – 20 bar Step2: 1 – 20 bar, preferably 2 – 10 bar</p>	<p>One or two-step process. One step process: When reaction mixture is free of water, i.e. < 1000 ppm, preferably < 500 ppm. Time 4–20 hours, preferably 8–12 hours. Two step method: When an aqueous solution is used in the first step and when amines are used 1. Reaction time 2–12 hours, preferably 4–8 hours. 2. Reaction time 2–25 hours, preferably 5–12 hours. Post reaction processing: Remove volatiles at 40–140°C and 0.1–100 mBar for 5 minutes to 5 hours.</p>	[70]
<p>Composition: 1. Calcium salts of low molecular carboxylic and/or hydroxycarboxylic acids and/or hydrates of the former; 2. Strong oxy acid, preferably sulphuric acid; 3. Alcohol and/or ester</p>		Ethoxylation catalyst and preparation method of catalyst	[71]
<p>$B(\Phi)^3$ or $HB(\Phi)^4$ where Φ is a phenyl moiety with 1 to 5 fluorine substituents, 1 to 5 $-CF_3$ moieties, 1 to 5 $-SCF_3$ moieties etc. Example: Tris(pentafluorophenyl)borane etc.</p>	<p>Temperature: 20 – 200°C</p>	Boron containing catalyst with the advantage of narrower range products than base catalysed products, lower residual alcohol, lower operating temperatures and approximately 10^{th} of quantity of catalyst	[72]

Table 9-3 continued

Catalyst	Temperature and pressure	Notes	Reference
<p>$R^1R^2R^3X$ where: X = lanthanide e.g. Nd, Yb, Gd, La, Ce, Pr, Sm, Eu, Tb, Dy, Er, Tm, Lu, preferred are Nd, Yb and Gd; R^1, R^2, and R^3 triflimide group of the formula $-N(SO_2Z)_2$ where Z = C_nF_{2n+1} and n = 1 – 15, preferably Z = $-CF_3$ Example: $Nd[N(SO_2CF_3)_2]_3$</p> <p>Quantity: 10^{-5} M to 10^{-1}M</p>	<p>Temperature: 20 – 200°C</p>	<p>Rare earth triflimide catalyst with advantage narrower range product than base catalysts product, lower residual alcohols, lower operating temperatures and about 10^{th} of quantity of catalyst</p>	[73]
<p>Composition:</p> <p>Metal component: metal ions of group Ia, IIa, IIIa, IVa to VIIIa, Ib and IIb. Preferred are Zn, Cu, Ni, Pd, Pt and Co</p> <p>Bidentate organic compound esp. substituted or unsubstituted mono or polynuclear aromatic di, tri and tetracarboxylic acids</p> <p>Framework material: monodentate ligands</p>		<p>Porous Metallo-organic framework, especially micro and mesopores, i.e. < 50nm</p> <p>Surface area: > $5m^2/g$, preferably > $50m^2/g$, more preferred > $500m^2/g$, most preferred > $2000m^2/g$</p>	[74], [75]
<p>Combination of HF and dimetallic cyanide catalyst with a co-catalyst (element from group IIIA, IVa, IVb). A hydroxyl containing initiator, e.g. H_2O is required. HF: 0.0005 – 10%, preferably 0.001 – 5%, most preferred 0.002 – 1%; Dimetallic cyanide: > 25 ppm</p>	<p>Temperature: 10 – 150°C, most preferred 80 – 130°C</p> <p>Pressure: < 21barA, preferably 2 – 6 barA</p>	<p>Catalyst is very active and displays high polymerisation reaction rate. Reaction rate varies between a few minutes to a few days, preferably a few hours.</p>	[76]
<p>Trimetal oxide containing Mg, Al and one metal from groups VIa, VIIa and VIII e.g. Cr, Mo, Mg, Fe, Te, Co, Ni, Ru etc or combinations thereof (Preferably Cr, Mg or Fe) Ratio 3rd metal / total metal: 0.05 – 0.4, preferably 0.1 – 0.25</p> <p>Quantity: 0.01 – 20%, preferably 0.05 – 5%</p>	<p>Temperature: 80 – 230°C, most preferred 160 – 180°C</p> <p>Pressure 1- 21.2 barA, preferably 3.0 – 9.1 barA</p>	<p>Trimetal oxide where the third metal acts to inhibit the formation of high molecular weight PEG</p>	[77]
<p>$SbFX_mY_{4-m}$ or complex thereof, $RSbFX_mY_{4-m}$ where X = anionic moiety e.g. F^-, Cl^-, Br^-, I^- sulphates etc.; Y = anion or anion resulting from deprotonation of an active hydrogen containing compound; R = active hydrogen compounds acting as molecules of solvation</p> <p>Quantity: 0.01–50 000ppm, preferably 0.01–500ppm, most preferred 100 ppm</p>	<p>Temperature: 60 – 240°C, preferably 100 – 200°C</p>	<p>Antimony catalyst with advantage of high production rate, excellent selectivity and remarkably low unwanted by-product formation</p>	[78]

9.2 EXTENDED CHAIN MELTING POINT DATA FOR ALKANES AND POLYETHYLENE

Table 9-4: Data used in fitting model in section 4.6.2

Carbon Number	Melting Point (K)	References
44	359.6	[79], [80], [81]
44	360.0	[82]
46	361.2	[80], [81]
50	365.0	[82]
50	365.3	[79], [80], [81]
50	366.2	[79]
52	367.2	[79], [80], [81]
54	368.2	[79], [80], [81]
60	372.1	[79]
60	372.4	[80], [81], [82]
60	373.0	[82]
60	374.2	[83]
62	373.7	[79], [80], [81]
64	375.2	[79]
64	375.3	[80], [81], [84]
66	376.8	[80], [81], [84]
67	377.3	[80], [81], [84]
70	378.0	[82]
70	378.4	[79]
70	378.5	[80], [81], [84]
75.4 *	380.5	[84]
80	382.8	[85]
82	383.0	[82]
82	383.5	[80], [81], [82] [84]
84.8 *	383.4	[84]
94	387.0	[82], [80], [81], [84]
100	388.4	[80], [81], [82], [84]
100	389.0	[82]
102	388.3	[85]
102	388.9	[85]
120	390.0	[83]
120	392.2	[84]
120	392.4	[85]
140	394.2	[84]

Table 9-4 continued

Carbon Number	Melting Point (K)	References
144	393.0	[83]
159 *	399.2	[86]
160	397.5	[85]
168	397.5	[83], [87]
198	399.8	[87], [88]
216	401.5	[83], [87]
246	401.8	[87]
269 *	405.2	[86]
288	402.0	[83], [87]
294	403.6	[87], [88]
335 *	408.1	[84]
377.8 *	409.3	[84]
384	404.5	[83], [87]
390	405.2	[87], [88]
400 *	407.4	[86]
515.3 *	409.2	[84]
912.3 *	411.2	[84]
3863.2 *	412.6	[84]
6001.4 *	413.6	[84]

* Refers to polyethylene samples

9.3 METHODS FOR SYNTHESIS OF LONG CHAIN ALKANES

9.3.1 STARTING MATERIALS

The following are considered as possible starting materials in the synthesis of normal alkanes.

Table 9-5: Availability and suitability of alkanes with two different active end groups

Type	Chemical formula	Highest available	Used for synthesis	Used for testing
ω -Bromo-carboxylic acids	$\text{HOOC}-(\text{CH}_2)_n\text{-Br}$	n = 15	n = 11	n = 11
Methyl ω -Chloro- ω -oxyalkanoate	$\text{CH}_3\text{OCO}-(\text{CH}_2)_{n-2}\text{-CO-Cl}$	n = 10	n = 10	n = 15
ω -Hydroxy carboxylic acids	$\text{HO}-(\text{CH}_2)_{n-1}\text{-COOH}$	n = 16	n = 12	n = 12

Table 9-6: Availability and suitability of alkanes with two identical active end groups

Type	Chemical formula	Highest available	Used for synthesis	Used for testing
Dibasic alcohols	HO-(CH ₂) _n -OH	n = 16	n = 12	n = 12
Dicarboxylic acids	HOOC(CH ₂) _{n-2} -COOH	n = 22	n = 14	n = 14
Dimethyl esters of dicarboxylic acids	CH ₃ OOC-(CH ₂) _{n-2} -COOCH ₃	n = 11	n = 10	n = 10
Dibromoalkanes	Br-(CH ₂) _n -Br	n = 18	n = 12	n = 10
Di-Iodoalkanes	I-(CH ₂) _n -I	n = 10	n = 10	n = 10
Dichloro-dicarboxylic acids	ClCO-(CH ₂) _{n-2} -CO-Cl	n = 10	n = 9	n = 6

Table 9-7: Availability and suitability of alkanes with one active end group

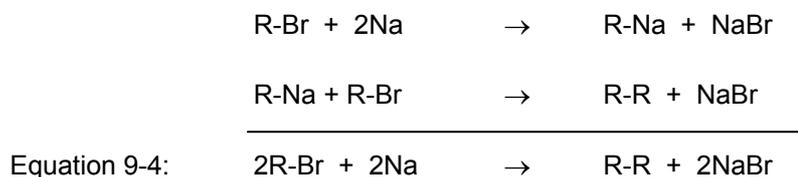
Type	Chemical formula	Highest available	Used for synthesis	Used for testing
Alcohols	H(CH ₂) _n -OH	n = 30	n = 22	n = 12
Monocarboxylic acid	H(CH ₂) _{n-1} -COOH	n = 30	n = 22	n = 12
Methyl esters of monocarboxylic acids	H(CH ₂) _{n-1} -COOCH ₃	n = 31	n = 18	n = 16
Chloroalkanes	H(CH ₂) _n -Cl	n = 18	n = 18	n = 16
Bromoalkanes	H(CH ₂) _n -Br	n = 22	n = 22	n = 16
Iodo-alkanes	H(CH ₂) _n -I	n = 18	n = 16	n = 12
1-Alkenes	CH ₃ -(CH ₂) _{n-3} -CH=CH ₂	n = 20	n = 16	n = 10

9.3.2 SYNTHESIS ACCORDING TO ROBINSON AND CO-WORKERS

Robinson and co-workers [89], [90], [91], [92] proposed a synthesis method in which carboxylic acids, R•COOH, are converted to γ -keto-acids, R•CO•CH₂•CH₂•COOH. In turn, the acid is converted to a chloride, condensed with a sodium ethyl aceto ester and the product hydrolysed with a dilute potassium hydroxide solution. For the reaction of dodecanoic acid with sodium ethyl acetosuccinate a conversion of 72 % is given. Alternatively, carboxylic acids are reacted with higher ω -bromo-n-fatty acids, thus increasing the number of methylene groups being added in each reaction. The resultant keto acid can be converted into an acid by the Wolff-Kishener reduction [93].

9.3.4 SYNTHESIS ACCORDING TO DOOLITTLE ET AL.

Doolittle et al. [95] prepared hexatriacontane and tetrahexacontane by the Wurtz reaction [96] of 1-bromo-octadecane and 1-bromodotriacontane respectively according to the following reaction scheme:

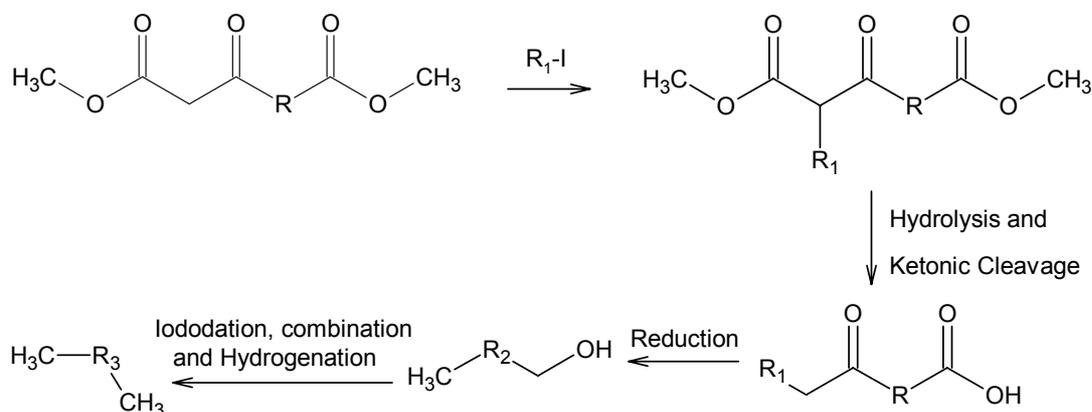


Advantages: The method is simple. The reaction, even with the high molecular weight molecules occurs readily. A single product is formed and as the molecular weight of the reactant and the product differs significantly, any remaining reactant can easily be removed.

Disadvantages: A 1-bromoalkane is required for this process. Commercially, the highest alkane with an active terminal group available is methylhentriacontanoate. When bromated and reacted according to this method, the product, dohexacontane, has a mere two carbon atoms more than hexacontane, the highest commercially available n-alkane. For this method to be applied, high molecular weight bromides would have to be synthesised.

9.3.5 SYNTHESIS ACCORDING TO STÄLLBERG ET AL.

Ställberg et al [97] suggested a method where the chain lengthening involves the use of long chain β -keto di-esters, according to the reaction scheme described in Figure 9-6:



where

- R = Alkane chain with a $-\text{CH}_2-$ groups
- R_1 = Alkane chain with b $-\text{CH}_2-$ groups, terminated with a H atom
- R_2 = Alkane chain with c $-\text{CH}_2-$ groups where $c = a + b + 2$
- R_3 = Alkane chain with d $-\text{CH}_2-$ groups where $d = 2c + 2$

Figure 9-6: Representation of reaction scheme according to Ställberg et al.. [97]

In this method, the long chain β -keto esters react with a 1-iodoalkane, which, after hydrolysis and ketonic cleavage, forms a keto acid. The keto acid can be reduced to a primary alcohol and from

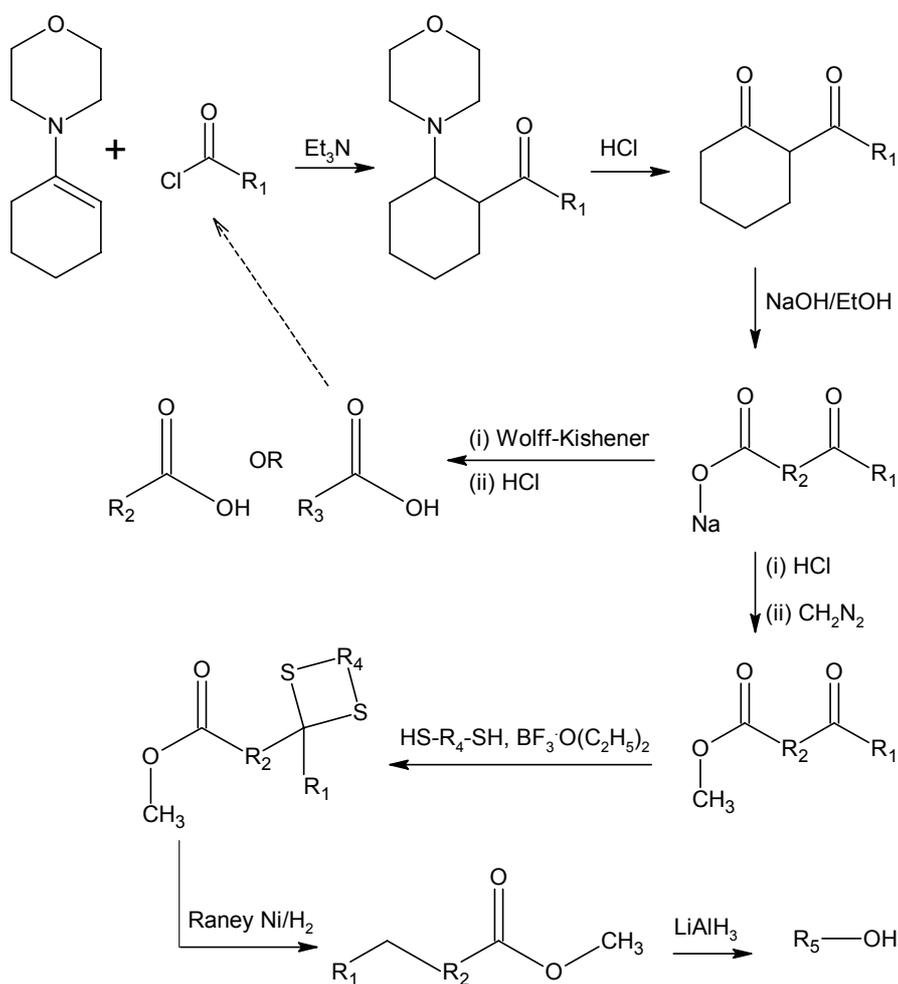
the alcohol, an iodide is formed and the Wurtz synthesis was used to combine two iodide molecules. A total conversion of between 32 and 40 % can be obtained.

Advantages: This synthesis method results in a single product.

Disadvantages: Although high molecular weight 1-iodo alkanes are commercially available, significantly large enough β -keto diesters are hard to come by and are excessively expensive. The process does not lend itself to easy repetition.

9.3.6 SYNTHESIS ACCORDING TO RAMA RAO ET AL.

Rama Rao et al. [98] proposed a method for the synthesis of 1-triacontanol without the use of unstable organo-metallic reagents:



where R_1 = Alkane chain with a $-\text{CH}_2-$ groups, terminated with a H atom
 R_2 = Alkane chain with 5 $-\text{CH}_2-$ groups
 R_3 = Alkane chain with b $-\text{CH}_2-$ groups where $b = a + 6$, terminated with a H atom
 R_4 = Alkane chain with 2 or 3 $-\text{CH}_2-$ groups
 R_5 = Alkane chain with c $-\text{CH}_2-$ groups where $c = a + 7$, terminated with a H atom

Figure 9-7: Representation of reaction scheme according to Rama Rao et al. [98]

In this method an aliphatic acid chloride is reacted with 1-morpholino-1-cyclohexene so as to increase the chain length with 6 carbon atoms per cycle. After the coupling reaction, well known chemistry is used to convert the reaction product into an acid or an alcohol. Rama Rao conducted the experiments starting with $a = 17$ and during the first cycle used the Wolff-Kishner method of reduction. During the second cycle the HCl method was used and yielded 1-triacontanol as product. For the process a total conversion of about 28 % was achieved. It is important to note that for the addition reaction of 1-morpholino-1-cyclohexene to stearyl chloride ($a = 17$) a conversion of 95 % is achieved while for the addition to tetracosanoyl chloride ($a = 23$) a conversion of only 51 % was achieved.

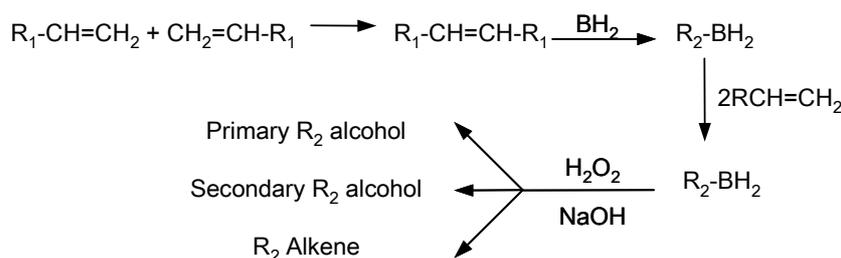
Commercially 1-morpholino-1-cyclohexene as well as 1-morpholino-1-dodecene is available. By using the latter, the increase in carbon atoms per cycle can be increased from 6 to 12, thus halving the number of cycles that need to be repeated.

Advantages: This process achieves chain lengthening without the use of water sensitive unstable organo-metallic compounds. Repeated addition of 6 carbon atoms can be achieved, 12 if 1-morpholino-1-dodecene is used. A single product is formed.

Disadvantages: The difference in the yield from the coupling reaction between the acid chloride and 1-morpholino-1-hexene for $a = 17$ and $a = 23$ is significant. A decrease of nearly 50 % in conversion is found for an increase in 6 carbon atoms in the hydrocarbon chain of the acid chloride. This indicates that at even higher molecular weights the reaction may occur at an even lower conversion, or may not occur at all.

9.3.7 SYNTHESIS ACCORDING TO MARUYAMA ET AL. AND SINGH ET AL.

Maruyama et al. [99] and Singh et al. [100] proposed similar methods for the synthesis of a terminal alcohol from two terminal alkenes through hydroboration:



where R = Alkane chain with a $-CH_2-$ groups, terminated with a H atom
 R_1 = Alkane chain with b $-CH_2-$ groups, terminated with a H atom
 R_2 = Alkane chain with c $-CH_2-$ groups where $c = 2b + 2$, terminated with a H atom

Figure 9-8: Representation of reaction scheme according to Murayama et al. [99]

An overall yield of 47 % per cycle is attained. However, a mixture of three or more products is formed. Table 9-8 shows the product distribution attained by Maruyama et al. [99]:

Table 9-8: Product distribution for synthesis of triacontanol with a = 14 and a = 6 (two cycles), b = 14 [99]:

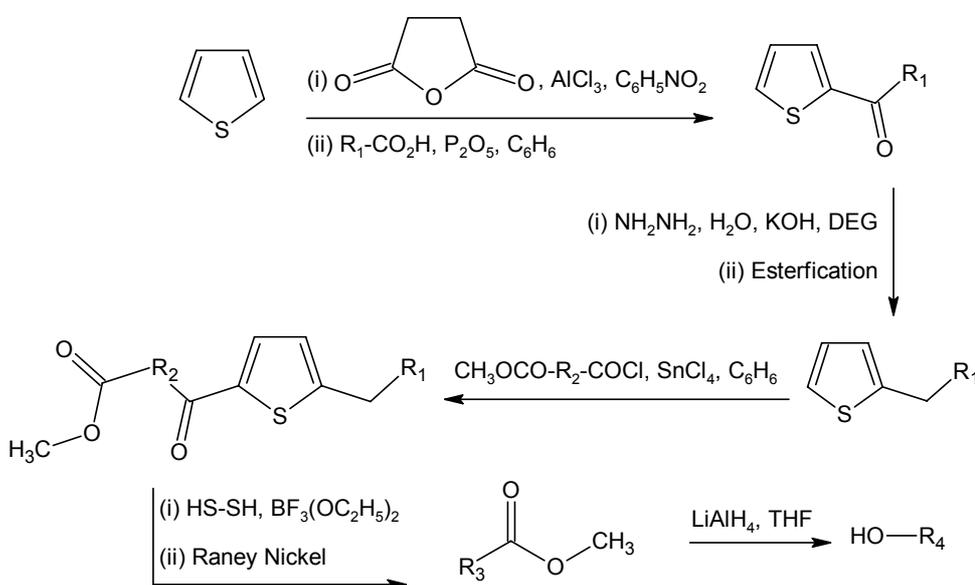
	a = 14	a = 6
Primary C ₃₀ alcohol	66 %	63 %
Secondary C ₃₀ alcohol	13 %	27 %
C ₃₀ alkene	21 %	7 %

Although the desired product is formed in the largest quantity, the by-products are formed in a significant quantity.

Advantages: This process creates a terminal molecule from a non-terminal alkene. The primary alcohol can be converted into a terminal alkene and the process can be repeated. A cyclic process can thus be developed from this method.

Disadvantages: By products are formed in a significant quantity. With current technology, it is excessively difficult, if not impossible, to separate the by-products from the main product due to the high molecular weight of the hydrocarbon backbone.

9.3.8 SYNTHESIS ACCORDING TO MILLER ET AL. AND BHALERAO ET AL.



where R_1 = Alkane chain with a $-\text{CH}_2-$ groups, terminated with a H atom
 R_2 = Alkane chain with b $-\text{CH}_2-$ groups, terminated with a H atom
 R_3 = Alkane chain with c $-\text{CH}_2-$ groups where $c = a + b + 6$, terminated with a H atom
 R_4 = Alkane chain with d $-\text{CH}_2-$ groups where $d = c + 1$, terminated with a H atom

Figure 9-9: Representation of reaction scheme according to Bhalerao et al.. [102]

Miller et al. [101] proposed a method for the synthesis of long chain monocarboxylic acids using thiophene as a coupling agent based on the high reactivity of the 2 and 5 positions for the stepwise additions of an acid and a half ester acid chloride. Bhalerao et al. [102] improved the methods and this method can be represented according to Figure 9-9.

Figure 9-9 represents the method where the acid is first added. However, the half-ester acid chloride can also be added first, resulting in the same product with similar conversions. The conversions attained by Miller et al. [101] are given in Table 9-9.

Table 9-9: Conversion data for synthesis method according to Miller et al. [101]

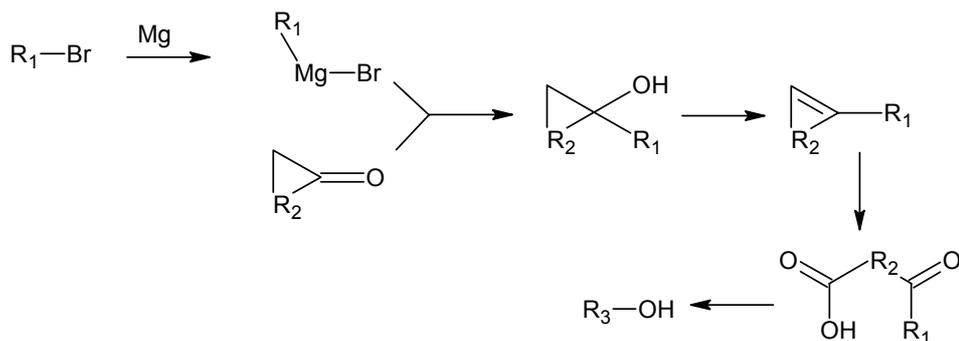
a	b	d	Conversion
15	4	26	63.9 %
15	2	24	68.0 %
17	8	32	75.0 %
11	8	26	74.7 %

Advantages: This process utilises simple chemical procedures that are well known and documented. The process can be terminated before the reduction of the ester to the alcohol and by converting the ester to an acid the process can be repeated. The conversion attained for a single cycle in this process is good.

Disadvantages: In the first addition step the acid or half methyl ester acid chloride is added to one of two active sites and thus the possibility of double addition to some thiophene molecules and no addition to other molecules cannot be excluded. A difficult, if not impossible separation process may thus be required. No information is given regarding the influence of the molecular weight of the reactants on the conversion.

9.3.9 SYNTHESIS ACCORDING TO VILLEMIN

Villemin [103] proposed a method for the synthesis of long chain molecules with the aid of a Grignard type coupling. The Grignard is coupled to a cyclic ketone and processed according to the scheme as set out in Figure 9-10:



where R_1 = Alkane chain with a $-CH_2-$ groups, terminated with a H atom
 R_2 = Alkane chain with b $-CH_2-$ groups
 R_3 = Alkane chain with c $-CH_2-$ groups, terminated with a H atom where $c = a + b + 2$

Figure 9-10: Schematic representation of synthesis according to Villemin

Villeman synthesised 1-triacontanol with an overall yield of 33 to 45 %, depending on method of pyrolysis and oxidation.

Advantages: The chemistry involved in this process is known and well documented. The process can easily be repeated to form a cyclic process.

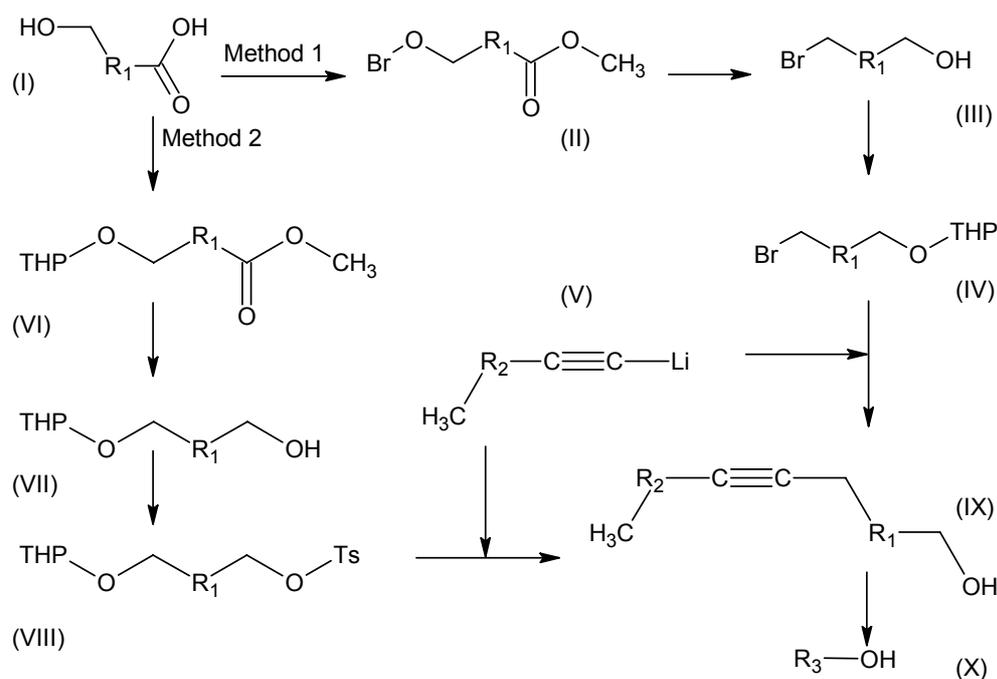
Disadvantages: Grignard components are excessively sensitive to water, even trace amounts of water. Only a single molecular weight has been investigated and the yield reported. An increase in the molecular weight may result in a decrease in reaction rate, or the reaction may not occur at all.

9.3.10 SYNTHESIS ACCORDING TO IYER ET AL.

Iyer et al. [104] synthesised n-triacontanol by using 16-hydroxy-9-dexadecenoic acid. The double bond in the 16-hydroxy-9-dexadecenoic acid formed does not play a role in the synthesis and it is assumed that the double bond significantly far removed from the terminal functional groups so as not to influence the reaction. Figure 9-11 gives a schematic representation of the method including both methods for the preparation of the reagents for the coupling reaction.

In method 1, the hydroxy acid (I) is converted to a hydroxy bromide (III) via an ω -bromo-methyl carboxylic acid (II). The hydroxy group is now protected as its THP ether (IV). In method 2, the hydroxy acid (I) the hydroxy group is firstly protected as its THP ether (VI), followed by converting the acid group to alcohol (VII). The reagent for the coupling reaction is prepared by reacting the pyranloxy alcohol (VII) with tosyl chloride to form the corresponding tosylate (VIII).

The coupling reaction is conducted by coupling either the bromide (IV) or the tosylate (VIII) with a lithium-alkyne (V), which after depyranylation yields the α -hydroxy internal alkyne (IX). The hydroxy-alkyne can be catalytically hydrogenated with H_2 in Pd to yield the terminal alcohol (X).



where R_1 = Alkane chain with a $-CH_2-$ groups
 R_2 = Alkane chain with b $-CH_2-$ groups
 R_3 = Alkane chain with c $-CH_2-$ groups, $c = a + b + 5$, terminated with H-atom

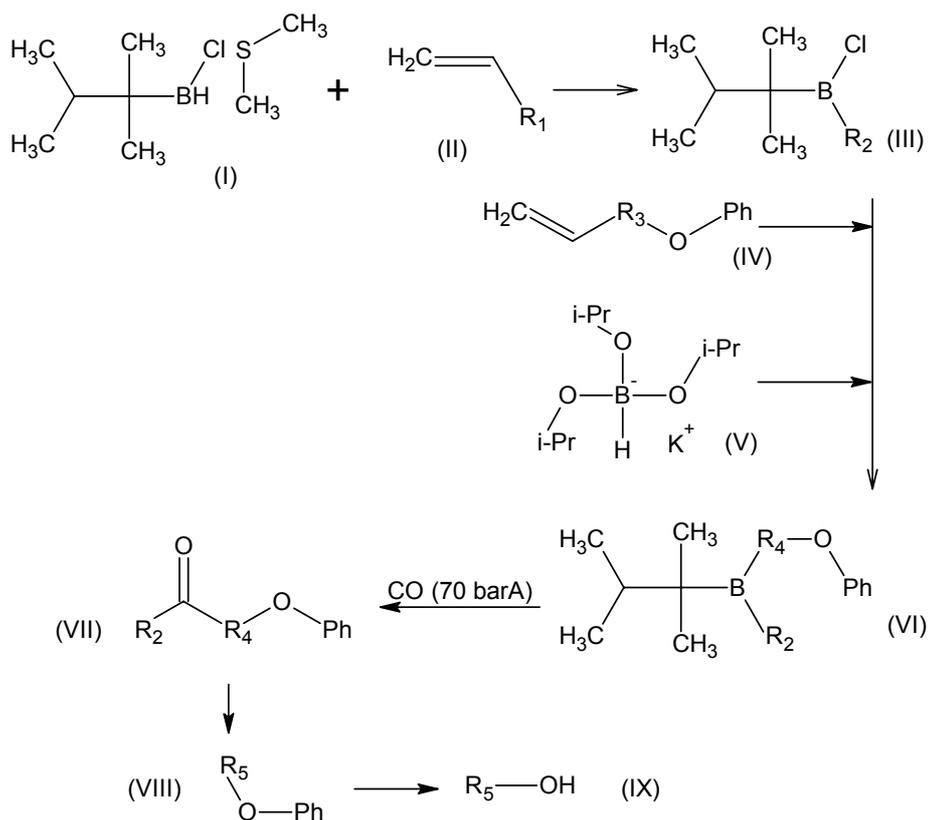
Figure 9-11: Schematic representation of reaction scheme according to Iyer et al. [104]

Advantages: A single product is attained with one terminal functional group.

Disadvantages: The process cannot easily be repeated.

9.3.11 SYNTHESIS ACCORDING TO BROWN ET AL.

Brown et al. [105] proposed three methods for the synthesis of long chain alcohols and carboxylic acids by using organoboranes. Only the carbonylation method, where a α -alkene and a α -benzyloxy- ω -alkene are coupled resulting in a terminal alcohol is applicable. In this method the α -alkene (II) is hydroborated with thexylchloroborane-methylsulfide(I). The product (III) is hydrated by KIPBH (potassium triisopropoxyborohidride, V) in the presence of the α -benzyloxy- ω -alkene (IV) resulting in the corresponding trialkylborane (VI). The trialkylborane is carbonylated with high-pressure carbon monoxide, resulting in the corresponding benzyloxy ketone (VI). The benzyloxy ketone is reduced to the benzyloxyalkane, which in turn is converted to the corresponding alcohol. According to Brown et al., an overall yield of 84 % is attained when $a = 16$ and $c = 9$.



where

- R_1 = Alkane chain with a $-\text{CH}_2-$ groups, terminated with a H atom
- R_2 = Alkane chain with b $-\text{CH}_2-$ groups where $b = a + 2$, terminated with a H atom
- R_3 = Alkane chain with c $-\text{CH}_2-$ groups
- R_4 = Alkane chain with d $-\text{CH}_2-$ groups where $d = c + 2$
- R_5 = Alkane chain with e $-\text{CH}_2-$ groups where $e = b + d + 1 = a + c + 5$, terminated with a H atom

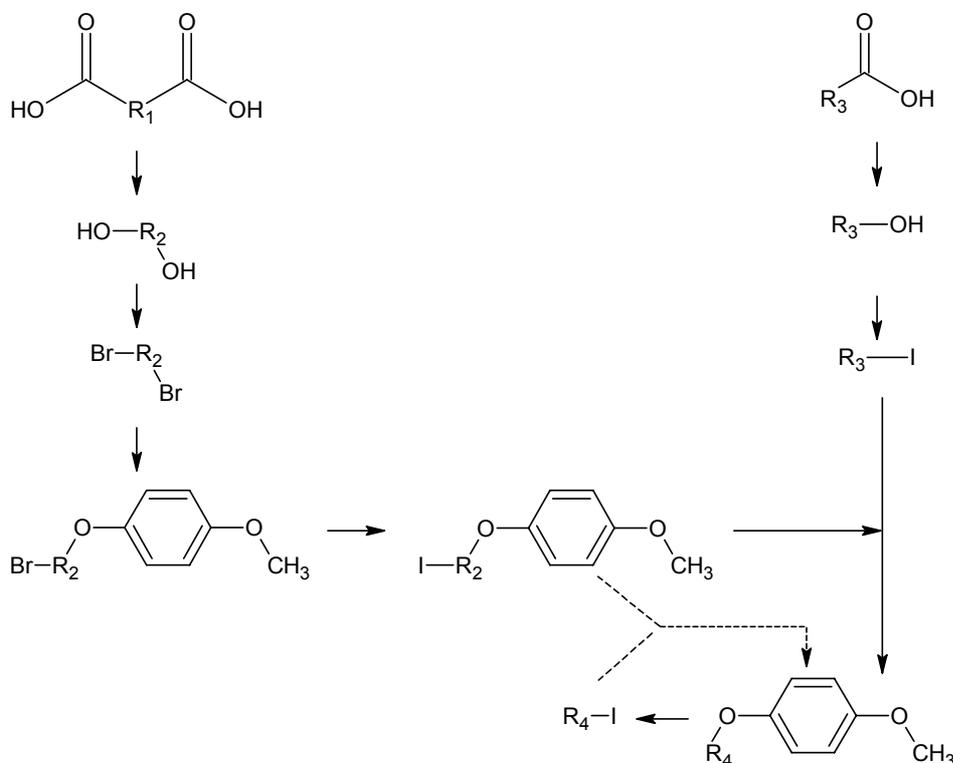
Figure 9-12: Representation of reaction scheme according to Brown et al. [105]

Advantages: The overall yield obtained here, in comparison to the many other processes is excellent and according to Brown et al. [105], the process yields a single product.

Disadvantages: In some of the steps in this process quite extreme reaction conditions are required. The reaction of the α -alkene (I) with hexylchloroborane-methylsulfide(II), as well as the addition of the α -benzyloxy- ω -alkene, is to be conducted at 0°C and as the carbonylation reaction is conducted at about 70 barA. Very little information regarding the kinetics of the system at molecular weights other than those published by Brown et al. is available. The α -benzyloxy- ω -alkenes are not readily available and for this process to work, the α -benzyloxy- ω -alkenes would have to be synthesised.

9.3.12 SYNTHESIS ACCORDING TO URABE ET AL.

Urabe et al. [85] synthesised long chain molecules by using Wurtz condensation of iodides as the chain lengthening technique. The method uses a mono and a dibasic carboxylic acid as starting reactants and proceeds according to the reaction scheme set out in Figure 9-13:



where

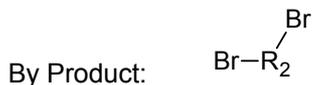
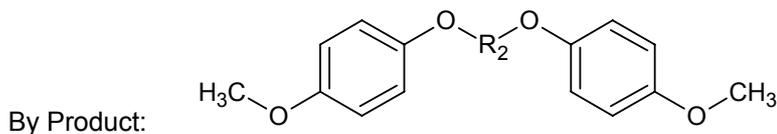
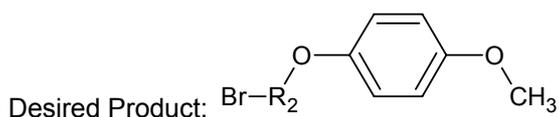
- R_1 = Alkane chain with a $-CH_2-$ groups
- R_2 = Alkane chain with b $-CH_2-$ groups where $b = a + 2$
- R_3 = Alkane chain with c $-CH_2-$ groups, terminated with a H atom
- R_4 = Alkane chain with d $-CH_2-$ groups where $d = b + c$, terminated with a H atom

Figure 9-13: Schematic representation of reaction scheme according to Urabe et al. [85]

From the method set out in Figure 9-13, it can be seen that instead of a dibasic acid, a dibasic alcohol or bromide can be used and instead of a mono carboxylic acid, an alcohol or iodide can be used. As illustrated, the process could be repeated. No indication of the conversion is given.

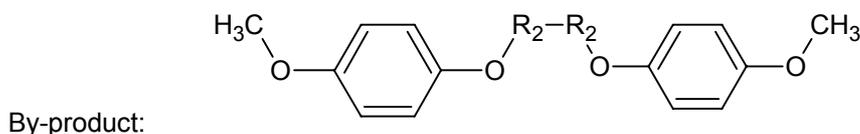
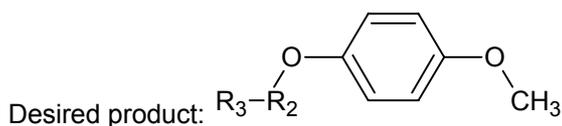
Advantages: The method is simple and the reaction, even with the high molecular weight molecules occurs readily. Relatively high molecular weight starting products can be purchased. The final product can be formed by combining two R_3-I molecules, thus doubling the size of alkane chain.

Disadvantages: During the step where the one side of the dibromide is protected with a methoxyphenoxy group, by-products may occur:



Heitz et al. [106] illustrated that similar type of molecules can be separated when the p-methoxyphenoxy group is replaced by a cyclo-hexanoate group on a molecule where $b = 10$. The desired product can be vacuum distilled at about 1.3 Pa between 120 and 130 °C. In the case of the by-products of this reaction the separation will probably have to occur at an even lower pressure due to the presence of the aromatic ring instead of the saturated ring.

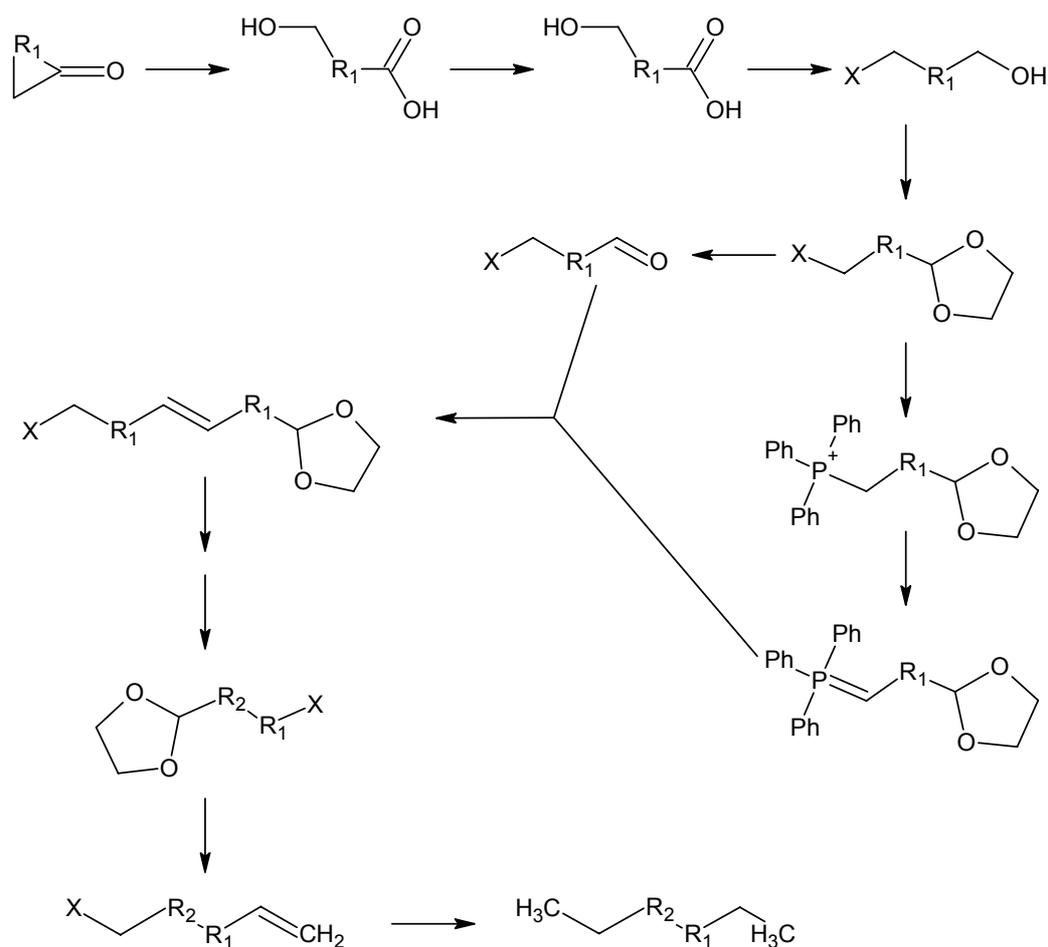
During the coupling of the iodides, any two iodide molecules can combine:



No comment is made as to which products mentioned above are preferentially formed. A separation method is thus required, and as is the case for the formation of the α -iodo- ω -(p-methoxyphenoxy)-alkane, separation is excessively difficult with traditional methods.

9.3.13 SYNTHESIS ACCORDING TO WHITING AND CO-WORKERS

During the last 20 years, Whiting and co-workers [107], [108], [109], [110], [111], [112] have developed a method for the synthesis of very long chain n-alkanes. Their approach is based on the repeated doubling of the chain of a completely homogenous building block, cyclododecanone, and thus results in a homogenous series a geometrical rather than arithmetic progression. The method can be summarised as shown in Figure 9-14:



where

- R₁ = Alkane chain with a -CH₂- groups
- R₂ = (R₁-CH=CH)_n
- n = 2^m - 1
- m = Number repetitions of the process
- X = Halogen atom

Figure 9-14: Schematic representation of reaction scheme according to Whiting and co-workers [107], [108], [109], [110], [111], [112]

The coupling reaction, known as the Wittig reaction, of an ylide (phosphonium salt) with an aldehyde or ketone results in an alkene with a double bond forming between the carbonyl carbon of the aldehyde or ketone and the negatively charged carbon of the ylide. The compound is hydrogenated to remove all double bonds and the halide. Theoretically X may be a fluorine, chlorine, bromine or iodine atoms. A compromise needs to be made between the ease of formation of the halide (fluoride > chloride > bromide > iodide) and the reactivity of the halide (iodide > bromide > chloride > fluoride), and thus usually bromides or chlorides are usually used. Brooke et al. [112] used chlorides above bromides for the lower molecular weight combinations as the chlorides are much less reactive towards the nucleophiles than the corresponding bromides. However, the reaction rate of the chloroacetals with triphenyl phosphine is very slow. The C12 chloroacetal needs to be reacted for 20 days while the C24 chloroacetals needs to be reacted for

28 days, and the reaction of the C48 chloroacetal was incomplete after 60 days. By using bromoacetals the reaction time was reduced to 3 ½ days. No reference was given to reaction times of any of the larger bromoacetals.

As an alternative, a large amount of C12 ylide can be made and be repeatedly added to an ever-increasing chloroacetal. This will however result in a decrease in the overall conversion of the reaction and will require considerably more work as the hydrocarbon chain can only be extended with 12 carbon atoms at a stage. A base is required for the formation of the ylide. Lithium diisopropyl pylamide is a suitable base (avoids the formation of unwanted by-products), however the reaction takes place at -25°C to -10°C .

The conversion for this method only shows a slight dependence on the length of the carbon chain:

Table 9-10: Conversion for Wittig reaction for formation of various members of a homologous series [112]

Aldehyde	Ylide	Product	Conversion
C12 chloroaldehyde	C12 ylide	C24 chloroacetal	86 %
C24 chloroaldehyde	C24 ylide	C48 chloroacetal	80 %
C48 chloroaldehyde	C48 ylide	C96 chloroacetal	77 %
C96 bromoaldehyde	C96 ylide	C192 bromoacetal	77 %

Advantages: The reaction is carried out in an alkaline medium and very mild conditions. The synthesis can be carried out with the knowledge that it is exactly known which carbon atoms bond during the combination reaction.

Disadvantages: The reaction is water sensitive and contamination with water may lead to poisoning of the reaction or the formation of unwanted by-products. The major drawback of this process is the long reaction times required for the formation of the ylide. Lithium diisopropyl pylamide requires reaction temperatures of -25°C to -10°C , which will require a refrigeration system that can provide refrigeration liquid between -20°C and -35°C .

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10 Appendix B: Experimental procedures and safety regulations

10.1 WAX SYNTHESIS EXPERIMENTS

10.1.1 EXPERIMENTAL PROCEDURE

10.1.1.1 PREPARATION OF SODIUM DISPERSION IN DIETHYL ETHER

Sodium dispersion in diethyl ether from sodium dispersion in toluene

The sodium in toluene is placed in the reaction flask according to the following method:

- The argon is switched on and allowed to flow for about 1 hour. Argon is heavier than air and will thus replace the lighter air as the only opening of the system is at the top of the condenser.
- 100 mL Xylene is added to the reaction flask.
- 100 grams of a 30 weight % sodium dispersion in toluene is carefully transferred into the reaction flask. For the purpose of adding the sodium, the dropping funnel is replaced with a normal funnel and xylene in a wash bottle is used to aid the flow of the sodium into the reaction flask, to prevent contact with air and to clean the funnel of sodium. Usually a total of 350 to 450 mL of xylene is required for the sodium addition, resulting in a total of about 500 to 600 mL liquid in the reaction flask.

The aromatics need to be replaced by diethyl ether. However, due to the fine nature of the sodium particles, the sodium takes a long time to settle. The following procedure must be followed:

- The system is allowed to settle overnight. The liquid phase is sucked up with a pipette. Ideally enough liquid is sucked up so that about 200 mL remains in the flask. It is important that enough liquid remains in the flask so cover the sodium. 250 mL of diethyl ether is added to the reaction flask with the aid of a wash bottle so as to aid mixing with the remaining fluid.
- The mixture is left to settle for about 4 hours after which 250 mL of fluid is removed and replaced with 250 mL diethylether, as described above.
- The mixture is left for another 4 hours to settle, where 250 mL of the liquid is removed and replaced with 350 mL of diethyl ether. The additional diethyl ether is required as the system is now left to settle overnight and significant evaporation may occur.

- The system is allowed to settle overnight, after which 250 mL of fluid is removed and replaced with 250 mL of diethyl ether.

The system is now ready for the polymerisation reaction. According to this method the system now has a maximum of 4% aromatics in the diethyl ether, and after the dibromide addition less than 3%. As neither the diethyl ether nor the xylene is totally water free, it has been estimated that with a maximum water content of 0.1 % in both a total of 2.5 grams of water entered the system. The sodium will neutralize the water, producing sodium hydroxide. About 3.2 grams of sodium is used to neutralise the water and thus the total sodium content is now about 26.5 grams.

Sodium dispersion in diethyl ether from sodium dispersion in low molecular weight paraffin wax

The sodium in paraffin is placed in the flask according to the following method:

- The sodium dispersion in paraffin wax is a solid and is purchased as chunks of sodium dispersion. As these chunks are relatively large and should be handled as little as possible, the chunks should be inserted through the neck of the flask. The reflux cooler is thus removed for the sodium addition.
- 100 mL cyclohexane is added to the flask
- Argon is switched on and allowed to flow for ½ hour to replace the air in the flask.
- The sodium dispersion chunks are added to the reaction flask. During the sodium addition enough cyclohexane is added to ensure that the sodium dispersion chunks are always covered in liquid, usually a total of about 500 mL of cyclohexane is required.

The paraffin wax and cyclohexane needs to be replaced by diethyl ether. As the melting point of the paraffin wax is above the boiling point of the diethyl ether and the solubility of the solid wax in ether is quite low, the paraffin wax is replaced with cyclohexane and the cyclohexane then replaced by diethyl ether. The following method is used to replace the paraffin wax with cyclohexane:

- It needs to be insured that the sodium dispersion in paraffin wax is mixed with a minimum of 500 mL cyclohexane so as to extract as much of the paraffin wax as possible.
- The reaction flask is left for about ½ hour to allow the sodium to neutralise any trace water and alcohols in the cyclohexane.
- The cyclohexane, paraffin wax and sodium mixture is heated up to boiling point. This allows for the paraffin wax to melt and the formation of a liquid phase of cyclohexane saturated with paraffin wax.
- The mixture is allowed to cool down for about 1 hour. This allows enough time for the sodium to settle while ensuring that the mixture is still warm. It is essential that the mixture

is still warm when the cyclohexane is drawn off, so as to remove as much paraffin wax as possible.

- As much of the cyclohexane as possible is drawn off, leaving about 150 mL of fluid in the reaction flask.
- 400 mL of cyclohexane is added to the reaction flask, the mixture is heated until boiling point and allowed to cool down for 1 hour. 400 mL of fluid is drawn off. The process is repeated once more.
- 400 mL of cyclohexane is added to the reaction flask. The mixture is not heated but allowed to cool down to room temperature in preparation of replacing the cyclohexane with diethyl ether.

As the particle size of the sodium from the sodium in paraffin wax is considerably larger than from the sodium in toluene, the particles settle much faster and usually within about 10 minutes the liquid is clear. The following method is used to replace the cyclohexane with diethyl ether:

- 400 mL of fluid is drawn from the reaction flask and replaced with 250 mL of diethyl ether. The sodium is allowed to settle for about 20 minutes.
- The above process is repeated two more times, after which the sodium is ready for the polymerisation process.

10.1.1.2 POLYMERISATION REACTION OF ALPHA-OMEGA DIBROMIDE WITH SODIUM

The alpha-omega dibromide is polymerised to a high molecular weight wax according to the following experimental procedure. The method is set out for sodium from a sodium suspension in toluene. The difference in the method for sodium from a sodium dispersion in paraffin wax is set out at the end of the description of the method.

- About 65-70 grams of 1-12 dibromo dodecane is dissolved in diethyl ether so that the total volume of the solution is about 200 mL. It is recommended that the solution be prepared a few hours before the polymerisation reaction as the dibromide exhibits a strongly negative heat of solution and the resultant decrease in the temperature of the solution results in a decrease of the solubility of the dibromide. If the solution is made a few hours before the start of the reaction, the solution has enough time to heat up to room temperature and dissolve all the dibromide.
- The polymerisation reaction of the dibromide with sodium is exothermic and thus the dibromide needs to be added stepwise to prevent over boiling. About 50 mL of the dibromide solution is carefully added to the sodium dispersion. The reaction of the dibromide has a lag time and usually after about 10 min the solution starts to boil. The reaction is allowed to proceed until the boiling has slowed down to a gentle simmer and no

reflux is being generated. This usually takes about 20 minutes from the first dibromide addition.

- The remaining dibromide is added to the reaction flask in 50 mL portions. Between each addition the system is allowed to react, come to boiling point and cool down to a gentle simmer before the next dibromide addition. However, if after 20 minutes, no boiling occurs the following portion can be added. During the dibromide addition the colour of the system changes from grey-pink colour of the sodium dispersion through deep purple to dark blue. The dark blue colour may not necessarily be attained during the addition process and may only appear once the system is heated up.
- After all the dibromide is added to the solution the system is left until all boiling ceases. The heating mantle is placed around the flask and the system is now ready for heating.
- The system must be heated very carefully as a small heat addition may be enough to trigger further polymerisation reactions. A 500 W 2000 mL Electrothermal heating mantle is used. The heating mantle has no temperature regulator and thus manual on-off control is required. Initial heating of 15, 15, 10 and then 5 seconds with 6 minute intervals is applied.
- The system is left for about 20 min and if boiling has not commenced, the system can be heated further. Should the system start to boil, no additional heating is applied until the system cools down to a gentle simmer.
- Further heating is applied at 5, 5, 10, 10 and then 15 seconds with 6 minute intervals, after which the system is heated for 15 seconds with 6 minute intervals until the completion of the heating process. Heating is continued until 6 hours 40 minutes after the first dibromide addition.
- The system is left to cool down before the heating mantle is removed and any excess sodium neutralised. Methanol is used to neutralise any excess sodium according to the following reaction:

Equation 10-1:
$$\text{Na} + \text{CH}_3\text{OH} \rightarrow \text{Na}^+ \text{CH}_3\text{O}^- + \frac{1}{2} \text{H}_2$$
- The neutralization reaction is highly exothermic and hydrogen gas is liberated. Extreme care must be taken during this step and the methanol must be added very slowly and very carefully.
- As it is not known exactly how much sodium is left, the maximum theoretical amount of sodium required is calculated according to the initial amount of sodium in the system. To neutralise all the sodium about 50 mL of methanol is required. However, sodium methanoate has a high heat of dissolution in methanol and thus extra methanol is required. An excess of methanol is used and a total of about 400 mL of methanol is added during neutralization.
- Neutralisation is started 7 hours after the 1st dibromide addition.

- Initially methanol is added drop wise to the reaction flask and as the neutralization process continues, the rate of methanol addition can be increased. The methanol is added at such a rate that the system boils with a gentle reflux. During the methanol addition, the colour of the system changes. Once most of the sodium has been neutralised and the methanol starts to dissolve the sodium methanoate, the colour of the solution starts to lighten slightly, and once most of the methanol is added the solution has taken on a light blue colour, which will turn white when left overnight. Neutralization usually takes 1 ½ to 2 ½ hours.

During the entire reaction time the ether in the reaction flask decreases. This can be attributed to two factors: Firstly, ether is used up in the reaction process. Secondly, ether is lost to the environment. In the condenser, ether can only be condensed as far as the partial pressure of the ether at the cooling water temperature. Ether boils at 35°C and has a vapour pressure of 47.9kPa at 15°C (estimated maximum temperature of the cooling water) [1]. This, in addition with the slow yet constant flow of argon through the system results in a significant loss of ether to the environment. The liquid level in the system must thus be monitored constantly during the entire reaction process and if required, additional diethyl ether should be added.

Due to the slight difference in nature of the sodium used, particularly with regard to the particle size and the different trace amounts of original solvent, the process, when using sodium from sodium dispersion in paraffin wax differs as follows:

- The sodium from a dispersion in paraffin wax is not as reactive as the sodium from a dispersion in toluene. The reaction thus takes longer to start. 30 minutes is therefore required between each dibromide addition.
- Additional care is required during the neutralization process as the sodium particles are larger and the sodium tends to settle at the bottom of the flask.

As the sodium is less reactive, these experiments could be conducted at double quantity. Except in the cases listed below, all quantities and sizes are doubled:

- The same experimental set-up, with a 2L flask, is used.
- Initially about 700 mL of cyclohexane is required and after each boiling and settling 500 mL is removed and added.
- For the replacement of the cyclohexane with diethyl ether 350 mL of diethyl ether is removed and added.
- The dibromide is dissolved in about 300 mL of diethyl ether.
- 700 mL of methanol is used during the neutralization process, and this process takes between 2 and 3 hours.

10.1.1.3 ISOLATION OF POLYMER FROM REACTION MIXTURE

For each individual run the following procedure is followed to obtain a dry reaction product. This procedure includes the solid-liquid separation and the cold water washing:

- The reaction mixture is left to stand overnight after which it takes on a yellow upper layer and a light blue lower layer.
- The reaction mixture is mixed well.
- 500 mL of distilled water is added. Although no more sodium should be present in the reaction mixture, it is advisable that the addition is done carefully.
- The mixture is placed in a 2L-separating funnel where the aqueous and organic layers are allowed to separate.
- The lower aqueous layer is drawn off and filtered. The filtration is conducted so that any solid waxy parts are not lost. The aqueous filtrate can be discarded.
- 500 mL of water is added to the organic layer, still in the separating funnel. The purpose of adding water is to remove as much of the water soluble salts as possible.
- The aqueous layer is once again drawn off and filtered, the aqueous layer being discarded.
- The organic layer, containing the polymer compound, is drawn off and is usually ~ 600 mL.
- To aid filtration, the organic layer is filtered in three parts and a suction flask is used to draw the liquid through. Each part is filtered until a dry solid remains on the filter.
- The solids on the filter are collected and suspended in 200 mL of water, to remove any remaining ether and water-soluble salts.
- The suspension is filtered and the dry polymer is placed in a wide neck beaker and allowed to dry for about 48 hours in a vacuum cupboard. Before drying the vacuum cupboard, the polymer may contain about twice its weight in liquid.

Before the following procedure is followed, the product from a number of the runs is collected. The polymer is now washed in melted form with pressurised water. As a relatively large autoclave (2L Parr autoclave) is available for the pressurised washing, larger quantities of wax can be washed at once. The wax is washed in quantities of about 100 grams at a time according to the following procedure:

- 100 grams of dry wax is placed in the autoclave.
- About 750 mL of distilled water is added to the autoclave.
- The autoclave is closed and sealed and the stirrer is switched on. The stirring speed is set high enough to allow movement in the autoclave and contact between the polymer and the water, however not too high so as to prevent the formation of an emulsion.

- The autoclave is equipped with electrical heaters and thus the temperature is increased slowly to prevent overheating and thermal degradation. The temperature of the autoclave is set at 75°C and left for 45 minutes allowing the system to reach thermal equilibrium.
- The autoclave temperature is now set to 100°C and once again left for 45 minutes to allow the system to reach thermal equilibrium.
- The autoclave temperature is now set to 115°C and once again left for 45 minutes to allow the system to reach thermal equilibrium.
- The autoclave temperature is now set to 130°C and left for about an hour to allow the system to reach thermal equilibrium and to allow as much of the organic and inorganic salts to dissolve in the water.
- The autoclave is now switched off and allowed to cool down to room temperature.
- The water and the polymer are separated, the polymer is washed with cold water and the washing procedure is once again repeated.
- The procedure is repeated twice more, so that the product is washed a total of four times.
- The resultant product is melted to remove any residual water.

10.1.1.4 HYDROGENATION PROCEDURE

Preparation of sodium dispersion in dibutyl ether

The sodium dispersion in dibutyl ether is prepared from a sodium dispersion in low molecular weight paraffin wax. The same method as described above for the preparation of a sodium dispersion in diethyl ether is used with the exception that instead of diethyl ether, dibutyl ether is used.

Hydrogenation of polymer with sodium

The hydrogenation reaction of the polymer with the aid of sodium is conducted in the same way as the polymerisation reaction of the dibromide with sodium from a dispersion in paraffin wax, as set out above, with the following exceptions:

- The ratio of the mass of polymer to the mass of sodium is considerably higher than the ratio of the mass of dibromide to the mass of sodium. Consequently only one unit of sodium is used 33 grams and is reacted with about 125 grams of polymer.
- The polymer is not readily soluble in solvent and as it is best to add the reagents at room temperature, it is recommended that the polymer be broken into small pieces and about 25 grams at a time added through the neck of the flask.

- Due to a much higher boiling point of the solvent and less energy liberation from the reaction, more heating is required during the hydrogenation process than during polymerisation. As in the polymerisation experiment, heating is conducted at 6 min intervals. Initially heating is applied at 2 minutes per 6 minutes until boiling point is reached after which the mixture is allowed to cool down to just below boiling point where after heating is applied at 55 sec per 6 minutes.
- The reaction mixture should only be heated for 6 hours until after the first addition of the polymer and be left for a full hour before the reaction mixture is neutralised.
- As the boiling point of methanol is considerably lower than that of boiling dibutyl ether, methanol is added at such a rate that the reaction flask remains warm to the hand.
- Although dibutyl ether is used in the reaction, the quantity used and the losses to the environment is substantially less than in the case of the diethyl ether and thus only a small quantity of dibutyl should be required to be replaced.

Isolation of polymer mixture from reaction mixture

The same method is used as described above for the isolation of the polymer mixture after the polymerisation reaction.

10.1.2 SAFETY PRECAUTIONS REQUIRED

Firstly the general safety precautions will be discussed, followed by precautions specific when working with certain chemicals. The information below is obtained from the MSDS as published by the suppliers.

General safety

During the entire experiment, suitable protective clothing should be worn, with particular reference to gloves and eye/face protection. As many of the chemicals are volatile, the experiments should be conducted in a fume cupboard, else, if not possible, in a well ventilated area. As many of the chemicals are flammable, the set-up should be placed so that in the event of a fire, a safe exit passage exists. Fire extinguishing media should also be readily available.

The following precautions apply to many of the chemicals used and should be implemented during the entire experiment:

- Skin contact and inhalation should be avoided. Protective clothing, eyewear and rubber gloves are required.
- As static discharges and sparks may cause ignition of many liquids used here, the work area should be well ventilated and static discharges should be limited, if not avoided.

- The vapour of the liquids used here may travel a considerable distance to the source of ignition and if ignited, the flame may flash back, experiments should thus be conducted within a bund wall and a well ventilated area.
- With the exception of sodium, a normal ABC fire extinguisher can be used for all other chemicals. However, if these chemicals are in contact with sodium, a type D fire extinguisher, dry soda ash, dry salt or dry sand must be used as an ABC fire extinguisher is incompatible with sodium.

Cyclohexane

Cyclohexane is highly flammable, harmful to eyes, the respiratory systems and the skin and is incompatible with strong oxidising agents. All precautions required are mentioned under the general precautions.

1,10-dibromodecane and 1,12-dibromododecane

As 1,10-dibromodecane and 1,12-dibromododecane are chemically similar with only the length of the hydrocarbon backbone differing, the precaution required are the same. Dibromides are incompatible with strong oxidising agents and strong bases. Contact with these types of chemicals must be avoided. Care should be taken when reacting the dibromide with sodium and the dibromide should be added to the sodium suspension slowly to prevent boiling over, explosion and fire.

Diethyl ether

The following hazards associated with diethyl ether need to be taken into account:

- High flammable
- May form explosive peroxides
- Vapours may cause drowsiness and dizziness
- Harmful to eyes, respiratory system and skin
- Diethyl ether has a high vapour pressure at room temperature and considerable evaporation may occur.
- Incompatible with oxidizing agents and strong acids

The following precautions should be taken:

- Where possible, experiments should be conducted in a fume cupboard and the work area should be well ventilated. This will decrease the quantity of diethyl ether in the atmosphere aiding in the prevention of personal harm and reducing the flammability level. Diethyl ether should not be transported or used in a small confined area without sufficient ventilation.

- Diethyl ether may cause drowsiness and dizziness. Experiments should not be conducted alone and sufficient ventilation is required to ensure the operator remains conscious during the entire experiments. Diethyl ether is heavier than air and should the operator feel dizzy or drowsy, he/she should stand up to reduce the concentration of diethyl ether in the air being breathed in and call for help.
- To minimise the formation of explosive peroxides diethyl ether is purchased in glass bottles in small quantities (2.5 L) and the diethyl ether has been stabilised with 2,6-di-butyl-4-methylphenol (5 mg/L).

Methanol

The following hazards associated with methanol need to be taken into account:

- Highly flammable
- Toxic with the danger of very serious irreversible effects if inhaled, swallowed or in contact with the skin.
- Methanol is incompatible with acids, acid chlorides, acid anhydrides, oxidizing agents, alkali metals and reducing agents.

The following precautions should be taken:

- Where possible, experiments should be conducted in a fume cupboard and the work area should be well ventilated. This will decrease the quantity of methanol in the atmosphere aiding in the prevention of personal harm and reducing the flammability level. Methanol should not be transported or used in a small confined area without sufficient ventilation.
- Methanol reacts highly exothermically with sodium. Extreme care should be taken during the neutralization of sodium with methanol and the methanol should be added drop wise to prevent excessive boiling during neutralization.

Sodium

Sodium metal dispersion is used in this synthesis. The following needs to be taken into account during the formulation of the experimental procedure and while conducting the experiment.

- Sodium reacts violently with water, liberating highly flammable hydrogen gas.
- Sodium is incompatible with oxygen and may ignite spontaneously in moist air or in oxygen.
- Sodium is incompatible with carbon dioxide and a normal ABC fire extinguisher can not be used in the event of a fire. A type D fire extinguisher or dry soda ash, dry salt or dry sand must be used.

To ensure that the experiment runs safely, the following precautions have been implemented:

- At all times the sodium is kept under a compatible material, such as xylene, toluene, diethyl ether, cyclohexane etc.
- Until the sodium neutralization is complete, the experiment is conducted under an argon atmosphere. Argon is selected above nitrogen as argon is heavier than air and will thus remain in the system.
- Although ultra high purity argon is used, it contains about 1 ppm moisture. To remove as much of this water as possible, a water trap consisting of a combination of blue silica gel and molecular sieve is used.
- A bucket with dry sand is kept nearby that in the event that a fire or sodium spillage, the fire may be extinguished and the sodium covered as soon as possible.

In the event of excessive boiling the following procedure should be followed:

- Firstly, additional diethyl ether should be added to the system to quench the liquid, and although quenching the liquid, the experiment is still saved.
- Should the addition of diethyl ether not be successful in quenching the system, xylene should be added. Xylene is fully compatible with sodium and has a boiling point in excess of 140°C. The addition of a small amount of xylene will thus result in a significant increase in the boiling point, thus hopefully succeeding in quenching the system. For this purpose, a wash bottle with ± 500 mL of Xylene is kept close to the experimental set-up.

In the event of the liquid boiling over, the following procedure should be followed, providing the safety of the operator is not endangered:

- Any boiled over liquid should be covered with sand as soon as possible.
- Should the heating mantel be on, it must be switched off immediately and the plug removed from the wall socket.
- For the clean-up operations the standard accidental release measures, as set out in the MSDS should be followed.

Tetrahydrofuran (THF)

The following hazards associated with THF need to be taken into account during the experiment:

- Flammable
- May form explosive peroxides
- Harmful to eyes, respiratory system and skin
- THF is incompatible with oxidizing agents and oxygen
- Exposure to high airborne concentrations may lead to anaesthetic effects.

The following precautions should be taken:

- To prevent high concentrations of THF, which may cause anaesthetic effects, the working area should be well ventilated and, if possible, the experiment should be conducted in a fume cupboard.
- To minimise the formation of explosive peroxides THF is purchased in glass bottles in small quantities (max 2.5 L) and the THF has been stabilised with 2,6-di-butyl-4-methylphenol (0.025%)

Toluene

Toluene is flammable, harmful to eyes, the respiratory system and the skin and is incompatible with strong oxidising agent. All precautions required are mentioned under the general precautions.

Xylene

Xylene is flammable, harmful to eyes, the respiratory system and the skin and is incompatible with strong oxidising agent. All precautions required are mentioned under the general precautions.

10.2 HIGH PRESSURE PHASE EQUILIBRIUM EXPERIMENTS

For the detailed design methodology, mechanical drawings, operating procedures etc the reader is referred to Schwarz [2] and Schwarz et al. [3]. A brief description of the operating procedures and safety requirements:

10.2.1 OPERATING PROCEDURES

10.2.1.1 LOADING PROCEDURE

The following process was used to load the cell with solvent and wax.

- The piston is removed from the cell so that wax can be loaded.
- The cell is loaded with a known amount of wax. The amount of wax required is calculated from the mass fraction desired and the expected density. The wax is weighed of in grams accurate to 0.01g. In cases where less than one and a half grams of wax is required, the wax is weighed off accurate to 0.001g.
- The cell, containing the wax and a magnetic stirrer bar, is closed and securely fastened.
- As much air as possible is removed from the cell. A vacuum pump is used and the cell is evacuated to at least 1mBar (100 Pa).
- The cell is now flushed 4 to 6 times with the solvent. The solvent is introduced into the cell and bled through the valve on the gas cylinder, the gas cylinder being attached to the

vacuum pump set-up in such a manner that no air can enter the set-up. On completion of the flushing process, the inlet valve to the cylinder is closed and the gas cylinder is removed.

- The gas cylinder, containing the liquefied solvent, is now weighed accurate to 0.01g.
- The cylinder is re-attached to the cell and the section between the cell valve and the gas cylinder is evacuated to 1mBar again.
- On completion of the evacuation process, the cell valve is opened for the loading of the solvent.
- The gas cylinder is opened and the solvent is allowed to flow into the cell.
- Once all the solvent is loaded the gas cylinder is closed off from the equilibrium cell.
- Before the valve can be closed, the section between the cell valve and the gas cylinder is heated up to allow any solvent in this section to evaporate, therefore minimizing the error in the calculation of the amount of solvent added.
- The cell is now completely loaded and ready for heating and experimental measurements.

In some runs, the wax from the previous run will be left in the cell and only solvent will be loaded. Should this method be followed, the first three steps are omitted and from there the process is repeated.

10.2.1.2 DATA ACQUISITION PROCEDURE

The following process was followed to obtain the experimental data:

- After the cell is loaded, the heating oil is set to T_1 , usually 110°C.
- Once all the wax has melted the magnetic stirrer is switched on and the pressure can be increased. While the cell reaches thermal equilibrium, the pressure inside the cell is kept high enough that the fluid is in the one phase region. This will ensure that in the event of a small leak, the composition in the cell remains constant and the pressure data from the run can still be used.
- Once it has been established that the cell is at thermal equilibrium the phase transition point can be determined.
- To determine the phase transition point the pressure in the cell is adjusted. The pressure in the cell is adjusted by adjusting the pressure of the nitrogen gas in the head end of the cell. The pressure, temperature, piston position and number of phases present are logged. This is repeated at various points and with the aid of a bisection method, the transition point is measured. The transition point is measured accurate to 0.2bar and the highest pressure where two phases occur is taken as the transition pressure.

- Once the transition pressure is determined at a heating oil temperature of T_1 , the temperature of the heating oil is adjusted to T_2 (usually 125°C) and the process is repeated. The process is once again repeated at a heating oil temperature of T_3 (usually 140°C). When the set point of the heating oil is changed, the pressure in the cell needs to be increased by about 30bar therefore ensuring that the contents is in the single phase while thermal equilibrium is attained.

10.2.1.3 UNLOADING PROCEDURE

Two unloading procedures are required. The procedure selected depends on if the wax and the solvent are removed from the cell or if only the solvent is removed and the wax is left behind to be used again.

Removing Solvent and Wax

The following process was followed to unload both the wax and solvent from the cell and to clean the cell from all possible wax. To unload the solvent as well as the wax from the cell, the wax in the cell needs to be a liquid. The temperature inside the cell as well as in the nozzle should therefore be above the melting point of the wax. However, for safety reasons the unloading temperature and pressure should be kept as low as possible. To take both these factors into account, the cell will therefore be unloaded with the heating oil set at about 25 to 30°C above the melting temperature of the wax. For systems where the wax is of lower molecular weight, the cell may be needed to be cooled down.

- The pressure on the piston needs to be released. This will allow the cell to be unloaded at the lowest possible pressure.
- Before unloading the contents of the cell, the cell is turned upside down. This allows the liquid phase to be unloaded first therefore unloading the most of the wax before the solvent is unloaded.
- The valve is opened very slowly in small increments to allow the wax and the solvent to escape into an Erlenmeyer glass flask. The cell should not be unloaded too slowly as this allows the wax to solidify in the nozzle resulting in a blockage and a loss of wax. For safety reasons, the cell should also not be unloaded at too fast a rate.
- Once all the wax and solvent are removed, the cell is positioned upright and the head is removed with care. The unloading procedure is now complete and the cell is now ready to be cleaned.

Removing Solvent Only

The following steps are used when only the solvent is removed:

- To ensure only the solvent is unloaded, the wax needs to be in a solid form. To ensure that the wax is not entrained with the solvent, it should be in as large crystals as possible. On completion of the run the cell is allowed to cool down. In addition the, the magnetic stirrer is turned off. The cell is positioned in the normal operating position to prevent the solid wax from clogging the inlet valve.
- Once the cell is at about 25 °C, the solvent can be removed.
- The solvent is removed slowly to prevent any loose wax from escaping.
- Once all the solvent is removed, the cell should be left open for about 15 to 30 minutes to allow any free solvent in the wax to escape. The cell is now ready to be loaded with solvent again.

10.2.1.4 CLEANING PROCEDURE

The cleaning procedure is only required if the wax is removed.

- The first washing cycle is done with xylene at about 110°C. Xylene is a solvent that, at temperatures close to its boiling point, dissolves the wax fairly well. The cell is first washed with xylene until the xylene is relatively free of wax.
- Once most of the wax is removed the cell is positioned upright and the valve is closed. The cell is filled with xylene and the magnetic stirrer is switched on to allow the xylene to move as freely as possible and to obtain the highest temperature possible. The cell, with the magnetic stirrer on, is left standing for about 30 minutes to allow the wax in the crevices to dissolve in the xylene.
- The xylene is removed and the process is repeated, but the xylene is left stirring for an hour.
- The cell is now rinsed with xylene until the xylene is relatively free of wax.
- On completion of the xylene washing process, the cell is cooled down to about 50°C where the cell is washed with methanol. Methanol is used to remove the xylene from the cell.
- The process is repeated until the methanol that exits the cylinder is free of xylene. Any remaining methanol can be removed by blowing air into the cell.
- The final step in the process is to remove any methanol or other substances in the cell. This can be done by rinsing the cell with pentane once the cell is below 30°C and using paper to wipe the inside of the cell. On completion of this step the remaining pentane can once again be removed by drying the cell with air.

10.2.2 SAFETY PROCEDURES

It is of utmost importance that the operator is safe when using the equipment. The following were taken into account to ensure safety:

- The chemicals used in operation and for cleaning.
- The pressure of the system.
- The temperature of the system.

10.2.2.1 SAFETY IN DESIGN

The equipment is designed so that the cell can withstand the high pressures required. Large safety factors were included in the design and the system was tested well above the operation pressures envisaged. In addition, the pressure regulator used on this cell has been chosen so that the maximum pressure applied by the regulator can not exceed the maximum pressure of the cell.

10.2.2.2 CHEMICALS USED

Wax

The waxes used here do not pose a serious hazard to the operator or the environment.

Supercritical solvent

The solvents are highly flammable and therefore no open flames, sparks or smoking is permitted near the equipment, both during set-up and during the run. In addition, the laboratory needs to be well ventilated to prevent a build-up of the solvents. Propane and LP gas are heavier than air and may travel along the ground. Precaution should be taken due to the fact that the gas can travel and distant ignition may occur.

Nitrogen

Although nitrogen is not combustible and occurs freely in air, the inhalation of excess nitrogen may result in weakness and unconsciousness due to the lowering of the concentration of oxygen in the air. Should loss of containment occur, the room should be evacuated.

Cleaning solvent

Xylene, methanol and pentane are used to clean the cell after operation. The following precautions are required for safe operation:

- All the solvents are highly flammable and thus no open flames, sparks or smoking is allowed. In addition, no strong oxidants are permitted when using solvents as these may result in fire and explosion hazard.

- Explosive vapour/air mixtures can be formed for all components. The laboratory should thus be well ventilated.
- The solvents may cause the skin to dry out and methanol can be absorbed through the skin. Protective clothing is thus required. Long-term exposure results in defatting of the skin and dermatitis.
- All the components are hazardous when inhaled and thus the solvents should only be used below their boiling temperature. In addition, special care should be taken when working with methanol and pentane because these substances are volatile at room temperature.
- Safety goggles are required during the cleaning process to protect the eyes.
- Vapours produced by the liquids are heavier than air and may travel along the ground. Precaution should be taken as the gas can travel and distant ignition may occur.

10.2.2.3 TEMPERATURE

Although the temperatures used here are not excessively high, they are still able to cause injury. All equipment around the cell and the heating bath needs to be treated as if it is hot. During the unloading process, the solvent wax mixture needs to be unloaded while hot. To protect the operator, safety goggles and thermal gloves need to be worn. During cleaning with xylene and toluene, the operator is also required to treat the entire equipment as if hot and safety goggles are required.

10.2.2.4 PRESSURE

The cell contains fluids at high pressures. The hazard associated with the high pressures is the possible rupture of the cell. This was taken into account in the design of the cell. In addition, the operator is not allowed to look directly into the cell and the camera system must be used.

To prevent the cell from containing so much of the wax-solvent mixture that the pressure of the cell at the maximum piston position is excessively high, the operator needs to log loadings made and with the aid of these loadings and the phase transition piston positions ensure that not too much wax or solvent is loaded. Additionally, before heating up the cell, the mass of the contents needs to be determined and the resultant pressure estimated. As an additional precaution, the cell pressure increase needs to be monitored at regular intervals while the cell is heating up. The last two requirements are especially important during the first few runs and when a new system will be studied.

10.3 PILOT PLANT EXPERIMENTS

10.3.1 OPERATING PROCEDURES

The following should be done when starting the pilot plant:

- Switch on the main power supply to the pilot plant.
- Check that the compressed air is working.
- Switch on heaters 1 and 2 and allow the unit to reach thermal equilibrium. This must be done the previous day to allow sufficient time for the pilot plant to heat up thoroughly. Heater H1 should be set approximately 20°C above the desired extraction temperature and heater H2 approximately 20°C above the separator temperature.
- Place wax in the pressure intensifier and allow sufficient time to melt.
- Set the required temperature of the separator on the control panel and press the corresponding start button. This must be done the day beforehand as well.
- Switch on the cooling water.
- Switch on the refrigeration unit. Ensure the settings correspond to the required settings for the solvent to be used. The refrigeration unit should be run for a while before the system is started.

The extraction process set-up is now started:

- Close the pressure intensifier.
- Set the extraction temperature to 0°C.
- Set the required extraction pressure to approximately 20barG on the control panel. Push the black confirmation/reset button.
- Check the following valves are in the fully open position: V1, V11, V2, V10, V98, V94.
- Check the following valves are in the fully closed position: V53, V15, V16, V20, V19, V99, V97, V96, V95, V93.
- If a new cylinder is used, close V1. Open the connection from the solvent gas cylinder to the pilot plant unit slowly, especially if carbon dioxide is used. Now open V1 slowly.
- If a new type of solvent is used, vent the column and the separator of trapped air by opening V16 briefly. Also vent the solvent storage tank.
- Start the solvent pump with the dial in position 10.00 mm. If the pump does not start, press the reset button on the pressure controller. Monitor the gas feed pressure – if the pressure increases significantly above the gas bottle pressure, switch the pump off immediately.
- Allow the solvent to recycle in the system until a sufficient liquid level is achieved in the solvent storage vessel.
- Open V53.
- Open V15.

- Allow the system to cycle for two to three minutes.
- With the hand wheel the solvent feed pump capacity can be adjusted directly at the pump. Release the safety lever, set the required capacity by means of the pump stroke and lock the safety lever.
- Slowly close V2. Important: Ensure that no major pressure build-up beyond the extraction pressure occurs in the column and in the gas feed line as well as in the separator. In the event that this occurs, switch off the pump immediately and open V2 immediately. Also ensure that no pressure build-up occurs in the separator.
- Increase the column pressure slowly to the required extraction pressure.
- Pressure control may be optimised with the adjusting knob.
- Increase the set extraction temperature at the temperature controller to the required extraction temperature.
- Allow the solvent to continue cycling for approximately 10 minutes to allow the flow rate to attain equilibrium.

The column is now ready to start the extraction process:

- Open V99. Allow the pressure to build up in the pressure intensifier, usually about 10bar above the extraction pressure.
- Open the nitrogen cylinder. The extraction is now started.
- Depending on the quantity of wax to be fractionated and the split achieved, the bottoms and the overheads may have to be discharged periodically.

The following procedure should be followed upon completion of an extraction run:

- Close V99.
- Close the nitrogen cylinder and open V97 to discharge the nitrogen used in the pressure intensifier to the atmosphere.
- Allow the pump to cycle solvent for an additional 20 minutes to remove any product in the overheads line into the separator.
- Stop the solvent feed pump.
- Reopen V99 to allow any wax remaining in the feed line to be pushed back into the pressure intensifier.
- Once the piston in the pressure intensifier has reached its maximum position, close V99.
- Reduce the set pressure slowly to approximately 10bar above the solvent tank pressure.

- Empty the column bottom by slowly discharging through V96
- Empty the separator bottom by slowly discharging through V19
- Open V2.
- Close V53 and V15.
- Depressurise the column and the separator to remove any remaining product.
- Stop the thermostatic circulator H2.
- Switch thermostatic regulator H1 off.
- Stop the temperature control in the column and the separator by pressing the start buttons.
- Allow the refrigeration system and the cooling water to run a few more minutes and then switch off.
- Switch the mains of the pilot plant off.

10.3.2 SAFETY REQUIREMENTS

The main safety precautions centre around the following three concepts:

- The high operating pressure of the process.
- The high temperature of the process.
- The flammability and other properties of the solvent.

10.3.2.1 HIGH PRESSURE

The experimental set-up consists of a high-pressure fractionation unit constructed by Sieber-Sitec, Switzerland, with modifications of an additional thinner, higher column and a pressure intensifier as a feed pump.

Safety during design

The part of the system designed by Sieber-Sitec was tested by them. All tubing and fitting on the high-pressure side has been rated well above the operating pressure. Both the solvent pump is explosion proof.

The modifications made on the high-pressure side were constructed from standard 1/8" stainless steel tubing, thick walled 1/4" stainless steel tubing or 1" medium pressure stainless steel tubing as supplied by Autoclave Engineers. For 1/8" tubing Swagelok stainless steel double ferrule fittings were used. For 1/4" tubing, a combination of Swagelok stainless steel double ferrule fittings, Autoclave Engineers medium pressure stainless steel fittings and high-pressure Sitec fittings were used. The column is constructed from a 1" outer diameter (17mm inner diameter)

medium pressure tube, as supplied by Autoclave Engineers, filled with Pro-Pac distillation packing (316SS from Aldrich, catalogue number Z210552). All fittings are standard 1" medium pressure stainless steel fittings from Autoclave Engineers.

A pressure intensifier was designed to operate as a pump. The pressure intensifier was constructed from steel and designed to withstand 250barA with a safety factor of 2. The department of Mechanical Engineering at the University of Stellenbosch assisted in the strength calculations and the specification of the screw threads etc of the parts under pressure. In addition, they checked the entire design. The pressure intensifier was pressure tested up to 215barA.

All parts of the modified design were tested with a dead weight tester with water as pressurisation medium. A pressure of 270barA was applied and the system was able to hold this pressure for an excess of 100 hours without any liquid loss.

The entire system has thus been designed and tested for pressures exceeding the working pressures. The individual units are rated as follows:

- Column: Maximum 220barA
- Separator: Maximum 320barA
- Solvent gas tank: Maximum 100barA
- Solvent diaphragm metering pump: Maximum 320barA
- Solute diaphragm metering pump: Maximum 320barA
- Pre-condenser/Cooler: Maximum 100barA
- Mass flow meter: Maximum 100barA
- Pressure intensifier: Maximum 200barA

Safety during operation

While operating the pilot plant it is imperative that the individual units operate within their specifications. To ensure this, the following needs to be implemented:

The pressure within the system needs to be monitored constantly. There is no automatic shut down or control procedure in the unit so the unit may not be left unattended. The gas feed pressure, the column pressure and the separator pressure need to be monitored continuously. The gas feed pressure should not rise significantly above the extraction pressure and the separator pressure should only be marginally above the gas bottle pressure.

In the event of a pressure build-up the pump should be switched off immediately. The excess pressure should be vented carefully and the reason for the pressure build-up should be investigated.

As the column, the line from the column through the pressure control valve to the separator and the separator contains wax with a high melting point, it needs to be ensured that these parts are heated well above the melting point, it needs to be ensured that these parts are always well above the melting temperature of the wax to prevent blockages. Additionally, in the event of a blockage, care needs to be taken when unblocking these lines as a pressure build-up may have occurred.

10.3.2.2 HIGH TEMPERATURE

The wax used in this process has a melting point in excess of 100°C. As it is required that the process is conducted with the wax in the liquid form, the operating temperature of the column is approximately 120°C with the separator about 10°C higher.

Although these temperatures are not extreme, precautions are still required when operating the process. All equipment that may be hot should not be touched as contact may result in severe burns.

10.3.2.3 FLAMMABILITY AND OTHER PROPERTIES OF SOLVENT

Propane is used for the experiments while carbon dioxide is used while troubleshooting the pilot plant.

Propane

Propane is selected as the solvent for this process. Propane is highly flammable and it should be noted that although the propane should run in a closed circuit, small leaks may occur and precautions need to be taken in the event of a loss of containment:

- Fans in the lab need to be on – air in at the top, out at the bottom. The big door should be kept closed to prevent the fans from shortcutting. The smaller side door should be marginally open.
- The large roll door to the workshop should be kept closed while the experiment is being conducted.
- No welding in the big lab during the experiments and for approximately an hour and a half after the experiments.
- The use of any electric hand held equipment such as grinder, electric drills etc may not be used on the ground floor of the lab during the experiment and for an hour and a half afterwards.
- No cars may be parked in the big lab.
- Experiments will be scheduled so that they do not run concurrently with scheduled practicals on the ground floor near the set-up, i.e. the distillation practical and the evaporator practical.

- In the event that the fans trip and the experiment has already started, both the big door and the side door of the lab will be opened.
- A small fire extinguisher is placed near the experimental set-up.

A copy of these requirements will be attached to the control panel of the equipment together with emergency shut down procedures.

Carbon dioxide

Carbon dioxide is used as solvent medium for the test runs as it is safer and cheaper than propane. The flammability considerations required for propane need not be taken into account, yet the following need to be taken into account:

- Fans in the lab need to be on – air in at the top, out at the bottom. The big door should be kept closed to prevent the fans from shortcutting. The smaller side door should be marginally open.
- In the event that the fans trip and the experiment has already started, both the big door and the side door of the lab will be opened.
- Carbon dioxide causes suffocation when inhaled in too high concentrations. However, carbon dioxide is heavy and will thus tend towards the ground. The room should thus be well ventilated and extreme care should be taken should a leak occur or be suspected.
- When carbon dioxide is expanded at a high rate, it may undergo sufficient cooling to cause solidification and the formation of dry ice. Small pieces of solid carbon dioxide may block valves etc and upon sublimation may cause problems. When expanding carbon dioxide, extreme care needs to be taken to do so slowly so as to prevent solidification and the problems associated therewith.

General safety precautions

The following general precautions need to be taken while conducting experiments:

- The experiments should not be conducted alone or after hours.
- A description of the pilot plant operating and emergency procedures has been circulated to the entire department and brought to the attention of the workshop manager and the person in charge of the laboratory.

10.3.3 EMERGENCY SHUT DOWN PROCEDURES

The following procedures need to be followed in the event of any of the following emergencies:

10.3.3.1 PRESSURE BUILDUP

In the event of a pressure build-up the solvent pump and the pressure intensifier should immediately be switched off.

10.3.3.2 LOSS OF CONTAINMENT

In the event of a loss of containment of solvent, the following should be done:

- Close the solvent container.
- Switch off both the pumps.
- Close V11.
- Switch off the heaters.
- Leave the cooling water and the refrigeration unit on.
- Open both roll doors to provide maximum airflow.
- If carbon dioxide is used as solvent, move to the first floor of the big lab or move out of the big lab until sufficient time is allowed for the carbon dioxide to disperse.

10.3.3.3 FIRE

The following actions should be taken in the event of a fire. These actions should only be taken if it is safe to do so:

- Switch off the main power supply – if this is not possible, switch off the solvent pump and the heaters.
- Close the solvent bottle
- Use an ABC fire extinguisher to extinguish the fire.
- If possible, leave the cooling water on to remove heat from the system.

10.3.3.4 IN THE EVENT OF A POWER FAILURE

The equipment has been designed in such a manner that in the event of a sudden power loss, no major safety related problems should occur. However, the following precautions need to be taken, mainly to prevent problems centred around the return of power:

- Switch off the heaters.
- Depressurise the column until bottle pressure and close V53.
- Remove additional pressure from the column.

- Open V2.
- Release some pressure from the separator.
- Switch the mains of the pilot plant off so that in the event of a return of power, no major problems can occur.

10.3.3.5 IN THE EVENT OF COOLING WATER FAILURE

Follow the shut down procedures immediately as if the run was complete.

10.3.3.6 IN THE EVENT OF A CONTROL AIR FAILURE

Follow the shut down procedures immediately as if a power failure has occurred.

10.4 BIBLIOGRAPHY

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11 Appendix C: Experimental data and calculations

11.1 PHASE EQUILIBRIUM DATA

11.1.1 PROPANE – COMMERCIAL ALKANE MIXTURES

11.1.1.1 EXPERIMENTAL MEASUREMENTS

Table 11-1: Phase equilibrium data for the system propane-Parafint C80

Solute				Parafint C80					
Solvent				Propane					
Mass Solute (g)	Mass Solvent (g)	Total Mass (g)	Fraction Solute (g/g)	Pressure		Temperature		Piston Position (mm)	Density (kg/m ³)
				Reading (BarG)	Corrected (BarA)	Reading (°C)	Corrected (K)		
6.02	4.33	10.35	0.582	45.2	41.8	103.8	377.0	24.1	593.7
				55.4	51.4	117.8	391.2	24.9	580.5
				69.8	65.5	132.0	405.6	25.6	569.4
6.02	5.29	11.31	0.532	46.2	42.8	103.5	376.7	28.7	573.7
				64.0	60.0	117.9	391.3	29.2	566.5
				79.8	75.4	132.1	405.7	30.1	554.2
6.02	6.91	12.93	0.466	47.8	44.4	103.4	376.6	42.5	486.8
				66.3	62.3	117.1	390.4	43.8	475.3
				85.5	81.2	131.2	404.7	45.4	461.8
6.02	8.35	14.37	0.419	51.1	47.7	103.0	376.2	50.4	471.5
				71.0	67.0	116.9	390.2	52.0	459.5
				89.1	84.8	130.7	404.2	53.8	446.8
6.02	9.65	15.67	0.384	55.1	51.7	103.9	377.1	56.9	465.0
				75.0	70.9	117.8	391.2	58.7	453.0
				93.8	89.4	131.8	405.3	60.8	439.7
6.02	10.70	16.72	0.360	54.6	51.2	104.1	377.3	64.6	445.6
				76.2	72.2	118.1	391.5	66.7	433.6
				95.5	91.2	132.2	405.8	69.1	420.6

Table 11-1 continued

Solute				Parafint C80					
Solvent				Propane					
Mass Solute (g)	Mass Solvent (g)	Total Mass (g)	Fraction Solute (g/g)	Pressure		Temperature		Piston Position (mm)	Density (kg/m ³)
				Reading (BarG)	Corrected (BarA)	Reading (°C)	Corrected (K)		
2.55	5.75	8.30	0.307	54.6	51.3	102.1	375.3	22.3	501.8
				76.0	72.0	117.0	390.3	23.4	485.8
				95.7	91.4	131.3	404.8	24.6	469.4
2.55	7.67	10.22	0.250	55.7	52.3	104.2	377.4	37.7	422.7
				76.7	72.7	117.8	391.2	39.3	409.2
				96.4	92.1	131.8	405.3	40.9	396.6
2.55	11.03	13.58	0.188	56.1	52.7	104.6	377.8	58.2	395.4
				77.0	73.0	118.5	391.9	60.8	381.1
				95.7	91.4	132.7	406.3	63.3	368.3
2.55	14.01	16.56	0.154	55.1	51.7	103.9	377.1	86.9	340.9
				75.6	71.6	118.2	391.6	91.0	327.2
				84.1	80.0	124.3	397.7	92.6	322.1
1.124	9.20	10.32	0.109	56.6	53.2	104.4	377.6	46.6	361.1
				77.2	73.2	118.4	391.8	48.7	348.4
				96.9	92.5	132.5	406.1	50.8	336.5
0.619	10.15	10.77	0.057	51.6	48.2	102.8	376.0	53.7	335.3
				72.8	68.8	117.3	390.7	56.1	323.3
				89.3	85.0	131.1	404.6	59.8	306.5
0.326	10.15	10.48	0.031	52.5	49.1	104.2	377.4	56.7	311.8
				71.7	67.7	117.3	390.7	59.0	301.5
				89.6	85.2	133.6	407.2	61.9	289.5
0.180	10.13	10.31	0.017	51.5	48.1	104.6	377.8	59.5	294.6
				69.1	65.0	118.3	391.7	61.9	284.9
				85.2	80.8	132.4	406.0	64.8	274.1

11.1.1.2 TEMPERATURE CORRECTED DATA

Table 11-2: Table with temperature corrected pressure data at phase equilibrium for propane – Paraflint C80

Solute				Paraflint C80		
Solvent				Propane		
Mass Fraction Solute (g/g)	Parameters for temperature correction of pressure $P = A * T + B$			Temperature		
	A	B	R ²	378.1 K Pressure (BarA)	393.1 K Pressure (BarA)	408.1 K Pressure (BarA)
0.582	0.829	-271.5	0.9890	42.0	54.4	66.8
0.532	1.124	-380.5	0.9992	44.6	61.5	78.4
0.466	1.310	-448.9	1.0000	46.3	66.0	85.6
0.419	1.325	-450.5	0.9995	50.5	70.3	90.2
0.384	1.337	-452.3	0.9999	53.2	73.2	93.3
0.360	1.403	-478.0	0.9990	52.7	73.7	94.8
0.307	1.359	-458.8	0.9999	55.2	75.6	96.0
0.250	1.426	-485.8	0.9996	53.5	74.9	96.3
0.188	1.358	-459.9	0.9988	53.5	73.8	94.2
0.154	1.374	-466.3	1.0000	53.1	73.7	94.3
0.109	1.379	-467.3	0.9998	54.0	74.7	95.4
0.0575	1.288	-435.5	0.9972	51.4	70.8	90.1
0.0311	1.206	-404.9	0.9937	50.9	69.0	87.0
0.0175	1.159	-398.6	0.9992	39.7	57.1	74.5

Table 11-3: Table with temperature corrected density data at phase equilibrium for propane – Parafint C80

Solute				Parafint C80		
Solvent				Propane		
Mass Fraction Solute (g/g)	Parameters for temperature correction of density $\rho = A * T + B$			Temperature		
	A	B	R ²	378.1 K Density (kg/m ³)	393.1 K Density (kg/m ³)	408.1 K Density (kg/m ³)
0.582	-0.8494	913.5	0.9970	592.4	579.6	566.9
0.532	-0.6726	827.9	0.9751	573.6	563.5	553.4
0.466	-0.8904	822.4	0.9988	485.7	472.4	459.0
0.419	-0.8828	803.7	0.9997	470.0	456.7	443.5
0.384	-0.8950	802.7	0.9992	464.3	450.8	437.4
0.360	-0.8779	777.0	0.9996	445.1	431.9	418.7
0.307	-1.0973	913.8	0.9998	498.9	482.4	465.9
0.250	-0.9331	774.6	0.9994	421.8	407.8	393.8
0.188	-0.9514	754.5	0.9986	394.8	380.5	366.2
0.154	-0.9162	686.3	0.9992	339.9	326.1	312.4
0.109	-0.8603	685.7	0.9995	360.5	347.6	334.7
0.0575	-1.0076	715.1	0.9871	334.1	319.0	303.9
0.0311	-0.7450	592.8	0.9997	311.1	299.9	288.7
0.0175	-0.7302	570.7	0.9994	294.6	283.6	272.7

11.1.2 PROPANE – SYNTHESISED ALKANE MIXTURE

11.1.2.1 EXPERIMENTAL MEASUREMENTS

Table 11-4: Phase equilibrium data for the system propane-synthesised wax

Solute				Synthesised wax					
Solvent				Propane					
Mass Solute (g)	Mass Solvent (g)	Total Mass (g)	Fraction Solute (g/g)	Pressure		Temperature		Piston Position (mm)	Density (kg/m ³)
				Reading (BarG)	Corrected (BarA)	Reading (°C)	Corrected (K)		
10.12	3.32	13.44	0.753	64.4	60.1	134.3	407.9	34.7	592.3
				68.5	64.0	138.9	412.5	34.8	591.0
				73.5	68.8	143.6	417.3	35.1	587.2
8.60	3.60	12.20	0.705	75.6	71.2	135.1	408.7	29.6	605.1
				82.2	77.8	139.2	412.8	29.7	604.4
				89.2	84.6	143.8	417.5	29.7	603.6
5.19	5.38	10.57	0.491	180.2	176.4	133.6	407.2	29.1	530.8
				185.7	182.3	138.2	411.8	29.2	259.6
				191.4	187.6	143.1	416.7	29.3	528.2
5.19	9.14	14.33	0.362	199.3	196.5	124.4	397.9	50.5	469.4
				213.2	210.7	133.7	407.4	50.7	467.9
				218.6	216.1	138.5	412.1	50.8	467.1
				225.7	222.9	413.3	417.0	50.9	466.4
3.30	6.71	10.01	0.330	210.8	207.6	134.7	408.3	22.8	596.2
				217.1	214.1	139.3	412.9	23.4	585.8
				222.6	219.3	143.9	417.6	24.3	570.9
0.288	10.20	10.49	0.0275	179.5	176.1	124.5	397.9	47.2	363.0
				189.0	185.7	133.9	407.5	48.7	353.9
				201.8	198.4	143.4	417.1	49.8	347.5
0.254	10.76	11.01	0.0231	130.2	126.8	124.3	397.7	56.7	327.8
				144.4	140.6	132.8	406.4	57.6	323.5
				155.9	152.0	142.5	416.2	59.2	316.1

11.1.2.2 TEMPERATURE CORRECTED DATA

Table 11-5: Table with temperature corrected pressure data at phase equilibrium for propane – synthesised wax

Solute				Synthesised wax			
Solvent				Propane			
Mass Fraction Solute	Parameters for temperature correction of pressure $P = A * T + B$			Temperature			
	(g/g)	A	B	R ²	378.1 K Pressure (BarA)	393.1 K Pressure (BarA)	408.1 K Pressure (BarA)
0.753	0.926	-317.8	0.9978		32.4	46.2	60.1
0.705	1.521	-550.3	0.9991		24.8	47.6	70.4
0.491	1.1779	-303.1	0.9976		412.3	160.0	177.6
0.362	1.3710	-348.6	0.9975		169.8	190.3	210.9
0.330	1.258	-305.6	0.9951		169.9	188.7	207.6
0.0275	1.162	-286.6	0.9936		152.6	170.0	187.4
0.0231	1.358	-412.6	0.9921		100.9	121.2	141.6

Table 11-6: Table with temperature corrected density data at phase equilibrium for propane – synthesised wax

Solute				Synthesised Wax			
Solvent				Propane			
Mass Fraction Solute	Parameters for temperature correction of density $\rho = A * T + B$			Temperature			
	(g/g)	A	(kg/m ³)	(kg/m ³)	378.1 K Density (kg/m ³)	393.1 K Density (kg/m ³)	408.1 K Density (kg/m ³)
0.753	-0.5480	816.2	0.9304		609	601	593
0.705	-0.1685	674.0	0.9984		610	608	605
0.491	-0.2769	643.5	0.9996		539	535	350
0.362	-0.1583	532.5	0.9999		473	470	468
0.0275	-0.8079	684.0	0.9899		379	366	354
0.0231	-0.6331	580.0	0.9865		341	331	322

11.1.3 PROPANE – ALCOHOLS

11.1.3.1 EXPERIMENTAL MEASUREMENTS

Table 11-7: Phase equilibrium data for the system propane-unilin 550

Solute				Unilin 550 (Alcohol)					
Solvent				Propane					
Mass Solute (g)	Mass Solvent (g)	Total Mass (g)	Fraction Solute (g/g)	Pressure		Temperature		Piston Position (mm)	Density (kg/m ³)
				Reading (BarG)	Corrected (BarA)	Reading (°C)	Corrected (K)		
10.04	2.56	12.60	0.797	36.6	35.6	106.4	379.6	27.9	681
				43.9	42.5	120.6	394.0	28.7	670
				52.1	50.4	134.8	408.4	29.9	654
10.04	4.65	14.69	0.683	50.8	49.7	106.1	379.3	39.5	640
				60.6	59.1	121.1	394.5	40.6	628
				74.2	72.5	134.1	407.7	41.5	619
10.04	6.77	16.81	0.597	60.4	59.4	106.6	379.8	50.6	617
				74.7	73.2	120.6	394.0	51.9	606
				92.1	90.4	134.6	408.2	53.3	594
10.04	10.08	20.12	0.499	76.9	75.9	105.2	378.4	71.6	569
				97.0	95.6	119.0	392.4	73.6	557
				115.5	114.0	132.7	406.3	75.2	548
4.34	5.52	9.86	0.440	85.7	84.7	106.0	379.2	26.2	553
				106.9	105.5	118.9	392.3	27.0	543
				124.4	122.8	133.6	407.2	27.6	537
4.34	8.19	12.53	0.346	97.6	96.6	105.3	378.5	42.7	518
				116.9	115.5	119.5	392.9	44.3	505
				135.6	134.1	133.5	407.1	45.9	493
4.34	10.27	14.61	0.297	98.7	97.7	105.5	378.7	57.0	492
				120.0	118.6	119.3	392.7	59.0	479
				138.0	136.5	133.1	406.7	61.0	468
4.34	13.15	17.49	0.248	98.9	97.9	106.8	380.0	79.0	458
				118.8	117.4	120.8	394.2	81.6	446
				137.2	135.7	134.4	408.0	84.0	436
1.63	6.32	7.95	0.205	97.5	96.5	105.9	379.1	21.6	495
				118.3	116.9	119.7	393.1	22.3	487
				134.9	133.4	132.7	406.3	23.5	473

Table 11-7 continued

Solute				Unilin 550 (Alcohol)					
Solvent				Propane					
Mass Solute (g)	Mass Solvent (g)	Total Mass (g)	Fraction Solute (g/g)	Pressure		Temperature		Piston Position (mm)	Density (kg/m ³)
				Reading (BarG)	Corrected (BarA)	Reading (°C)	Corrected (K)		
1.63	9.22	10.85	0.150	99.0	98.0	105.8	379.0	41.8	455
				119.7	118.3	119.9	393.3	43.2	445
				137.2	135.7	133.8	407.4	45.3	431
1.001	9.15	10.15	0.0986	97.3	96.3	107.0	380.2	42.9	418
				117.3	115.9	121.3	394.7	45.1	404
				135.3	133.8	135.4	409.0	47.2	391
0.611	9.78	10.39	0.0588	92.6	91.6	106.6	379.8	46.7	404
				112.0	110.6	121.0	394.4	48.8	391
				127.4	125.9	135.2	408.8	51.0	379
0.420	10.17	10.59	0.0397	86.3	85.3	106.1	379.3	51.1	386
				103.7	102.3	120.2	393.6	54.5	368
				118.8	117.3	134.6	408.2	57.8	353
0.236	9.73	9.97	0.0237	80.6	79.6	106.8	380.0	48.2	379
				97.4	96.0	120.7	394.1	50.9	364
				116.7	115.1	134.8	408.4	52.6	356
0.146	9.57	9.72	0.0150	75.2	74.2	106.5	379.7	46.9	376
				94.6	93.1	120.8	394.2	48.9	365
				111.2	109.7	135.1	408.7	50.8	356

11.1.3.2 TEMPERATURE CORRECTED DATA

Table 11-8: Table with temperature corrected pressure data at phase equilibrium for propane – unilin 550

Solute				Unilin 550 (Alcohol)		
Solvent				Propane		
Mass Fraction Solute (g/g)	Parameters for temperature correction of pressure $P = A * T + B$			Temperature		
	A	B	R^2	378.1 K	393.1 K	408.1 K
				Pressure (BarA)	Pressure (BarA)	Pressure (BarA)
0.797	0.5139	-159.6	0.9985	34.7	42.4	50.1
0.683	0.7982	-253.9	0.9801	47.9	59.9	71.8
0.597	1.092	-355.7	0.9960	57.0	73.3	89.7
0.499	1.366	-440.7	0.9997	75.7	96.1	116.6
0.440	1.356	-428.5	0.9919	84.3	104.6	125.0
0.346	1.311	-399.7	1.0000	96.1	115.8	135.4
0.297	1.386	-426.6	0.9980	97.4	118.1	138.9
0.248	1.350	-415.0	0.9999	95.4	115.7	135.9
0.205	1.358	-417.7	0.9981	95.6	116.0	136.3
0.150	1.328	-404.8	0.9984	97.2	117.2	137.1
0.0986	1.302	-398.6	0.9995	93.8	113.3	132.9
0.0588	1.183	-357.1	0.9966	90.2	107.9	125.6
0.0397	1.107	-334.2	0.9982	84.4	101.0	117.6
0.0237	1.250	-395.9	0.9984	76.8	95.6	114.3
0.0150	1.224	-390.2	0.9986	72.6	91.0	109.3

Table 11-9: Table with temperature corrected density data at phase equilibrium for propane – unilin 550

Solute		Unilin 550 (Alcohol)				
Solvent		Propane				
Mass Fraction Solute (g/g)	Parameters for temperature correction of density $\rho = A * T + B$			Temperature		
	A	B	R ²	378.1 K	393.1 K	408.1 K
				Density (kg/m ³)	Density (kg/m ³)	Density (kg/m ³)
0.797	-0.9464	1041.4	0.9893	684	669	655
0.683	-0.7322	917.3	0.9993	640	629	619
0.597	-0.7994	920.8	0.9999	619	607	595
0.499	-0.7712	860.9	0.9947	569	558	546
0.440	-0.5767	770.8	0.9838	553	544	535
0.346	-0.8780	850.1	0.9999	518	505	492
0.297	-0.8664	819.8	0.9998	492	479	466
0.248	-0.7860	856.6	0.9992	559	548	536
0.205	-0.7908	795.6	0.9759	497	485	473
0.150	-0.8570	780.5	0.9892	456	444	431
0.0986	-0.9280	770.8	0.9992	420	406	392
0.0588	-0.8420	723.6	1.0000	405	393	380
0.0397	-1.1487	821.3	0.9984	387	370	353
0.0237	-0.8066	684.2	0.9773	379	367	355
0.0150	-0.7140	647.3	0.9990	377	367	356

11.1.4 PROPANE – ALCOHOL ETHOXYLATES

11.1.4.1 EXPERIMENTAL MEASUREMENTS

Table 11-10: Phase equilibrium data for the system propane-unithox 550

Solute				Unithox 550 (Alcohol ethoxylate)					
Solvent				Propane					
Mass Solute (g)	Mass Solvent (g)	Total Mass (g)	Fraction Solute (g/g)	Pressure		Temperature		Piston Position (mm)	Density (kg/m ³)
				Reading (BarG)	Corrected (BarA)	Reading (°C)	Corrected (K)		
12.96	2.97	15.93	0.814	59.7	58.3	116.0	389.3	35.1	752.7
				68.9	67.3	125.4	398.9	35.6	745.9
				77.2	75.5	134.9	408.5	36.3	736.6
12.76	3.44	16.20	0.788	61.2	60.2	106.4	379.6	-	-
				78.1	76.6	120.6	394.0	-	-
				91.9	90.2	134.8	408.4	-	-
12.96	3.64	16.60	0.781	52.0	50.9	107.0	380.2	33.6	806.3
				62.9	61.4	121.4	394.8	35.3	781.5
				92.4	90.7	135.3	408.9	35.4	780.1
12.96	4.28	17.24	0.752	70.5	69.4	107.4	380.6	39.9	749.1
				86.4	84.9	121.6	395.0	40.9	736.8
				104.7	103.1	135.3	408.9	41.6	728.4
12.96	4.79	17.75	0.730	90.1	89.1	106.2	379.4	42.7	736.7
				103.5	102.1	120.5	393.9	43.7	725.1
				120.0	118.4	134.7	408.3	44.6	715.0
11.09	5.34	16.43	0.675	146.4	145.4	106.0	379.2	42.8	680.8
				162.1	160.8	120.1	393.5	43.7	671.2
				175.4	174.1	134.0	407.6	44.8	659.8
12.76	6.40	19.16	0.666	157.7	156.8	106.4	379.6	-	-
				162.9	161.6	120.8	394.2	-	-
				174.3	173.0	135.0	408.6	-	-
11.09	6.53	17.62	0.629	182.4	181.5	106.1	379.3	49.0	664.4
				195.3	194.1	120.1	393.5	50.2	653.0
				206.7	205.4	134.0	407.6	51.3	642.9
11.09	6.83	17.92	0.619	187.1	186.2	106.4	379.6	49.7	668.9
				199.5	198.3	120.2	393.6	50.9	657.5
				210.2	208.9	134.0	407.6	52.0	647.5
12.96	8.46	21.42	0.605	176.9	176.1	104.4	377.6	59.9	697.3
				187.0	185.7	118.9	392.3	61.3	685.2
				198.1	196.8	133.1	406.7	62.6	674.4

Table 11-10 continued

Solute				Unithox 550 (Alcohol ethoxylate)					
Solvent				Propane					
Mass Solute (g)	Mass Solvent (g)	Total Mass (g)	Fraction Solute (g/g)	Pressure		Temperature		Piston Position (mm)	Density (kg/m ³)
				Reading (BarG)	Corrected (BarA)	Reading (°C)	Corrected (K)		
6.92	6.08	13.00	0.532	223.0	222.1	106.6	379.8	0.0	0.0
				231.2	230.1	115.9	389.2	0.0	0.0
8.05	5.84	13.89	0.580	194.3	193.4	107.2	380.4	0.0	0.0
				205.5	204.3	121.4	394.8	0.0	0.0
				214.1	212.7	134.5	408.1	0.0	0.0
0.261	10.28	10.54	0.0248	258.9	257.8	115.8	389.1	37.3	476.6
				252.8	251.8	125.2	398.7	39.1	462.2
				241.8	241.2	134.4	408.0	41.6	443.4
0.243	9.96	10.20	0.0238	232.9	232.0	105.7	378.9	37.7	458.2
				231.4	230.4	112.3	385.6	38.5	451.9
				229.6	228.4	119.8	393.2	39.7	442.8
				227.4	226.3	126.4	399.9	40.8	434.8
				220.8	220.0	133.9	407.5	42.6	422.4
0.231	11.08	11.31	0.0204	210.4	209.5	105.7	378.9	45.0	451.0
				215.6	214.6	115.0	388.4	46.1	443.5
				217.7	216.8	124.3	397.7	47.4	434.9
				220.3	219.6	133.5	407.1	48.4	428.6
0.165	9.94	10.10	0.0163	195.8	194.9	105.0	378.2	38.8	445.3
				206.8	205.6	119.1	392.5	39.0	443.8
				210.6	209.3	132.9	406.5	40.9	430.0
0.153	10.57	10.72	0.0143	175.4	174.5	105.9	379.1	43.3	439.0
				195.0	193.8	119.9	393.3	44.7	429.5
				200.5	199.4	133.6	407.2	47.3	412.9
0.129	9.44	9.57	0.0135	189.7	188.8	106.4	379.6	34.3	456.6
				197.8	196.6	115.7	389.0	35.5	446.7
				206.0	204.7	125.1	398.6	36.6	438.0
0.128	9.67	9.80	0.0131	186.6	185.7	106.1	379.3	38.4	434.7
				195.5	194.3	120.4	393.8	40.3	421.0
				206.6	205.3	133.9	407.5	42.4	406.9
				213.6	212.2	134.7	408.3	38.1	426.7
0.123	10.89	11.01	0.0112	181.3	180.4	107.1	380.3	36.5	505.0
				191.3	190.0	121.1	394.5	37.7	494.5
				200.7	199.6	135.1	408.7	39.2	482.0

11.1.4.2 TEMPERATURE CORRECTED DATA

Table 11-11: Table with temperature corrected pressure data at phase equilibrium for propane – unithox 550

Solute				Unithox 550 (Alcohol ethoxylate)		
Solvent				Propane		
Mass Fraction Solute (g/g)	Parameters for temperature correction of pressure $P = A * T + B$			Temperature		
	A	B	R ²	378.0 K	393.0 K	408.0 K
				Pressure (BarA)	Pressure (BarA)	Pressure (BarA)
0.814	0.8958	-290.3	0.9993	48.3	61.7	75.2
0.788	1.0417	-334.8	0.9971	59.0	74.6	90.3
0.781	1.3828	-478.0	0.9256	44.7	65.4	86.1
0.752	1.1901	-384.1	0.9968	65.8	83.6	101.5
0.730	1.0137	-296.1	0.9955	87.1	102.3	117.5
0.675	1.0107	-237.6	0.9985	144.5	159.7	174.8
0.666	0.5581	-56.16	0.9458	154.8	163.2	171.5
0.629	0.8446	-138.6	0.9991	180.6	193.3	206.0
0.619	0.8107	-121.3	0.9985	185.1	197.3	209.5
0.605	0.7111	-92.71	0.9977	176.1	186.8	197.4
0.532	0.8511	-101.1	-	220.6	233.4	246.1
0.580	0.6976	-71.68	0.9973	192.0	202.5	212.9
0.0248	-0.8769	599.8	0.9721	268.4	255.2	242.0
0.0238	-0.3945	382.5	0.9134	233.3	227.4	221.5
0.0204	0.3464	79.00	0.9660	209.9	215.1	220.3
0.0163	0.5097	3.26	0.9301	195.9	203.6	211.2
0.0143	0.8878	-159.9	0.9119	175.7	189.0	202.4
0.0135	0.8181	-121.7	0.9996	187.6	199.9	212.1
0.0131	0.6940	-78.03	0.9925	184.3	194.7	205.1
0.0112	0.6761	-76.70	1.0000	178.9	189.0	199.1

Table 11-12: Table with temperature corrected density data at phase equilibrium for propane – unithox 550

Solute				Unithox 550 (Alcohol ethoxylate)		
Solvent				Propane		
Mass Fraction Solute (g/g)	Parameters for temperature correction of density $\rho = A * T + B$			Temperature		
	A	B	R ²	378.0 K	393.0 K	408.0 K
				Density (kg/m ³)	Density (kg/m ³)	Density (kg/m ³)
0.814	-0.8381	1079.3	0.9912	762.5	749.9	737.4
0.752	-0.7332	1027.6	0.9902	750.5	739.5	728.5
0.730	-0.7518	1021.7	0.9986	737.5	726.2	715.0
0.675	-0.7417	962.4	0.9972	682.0	670.9	659.8
0.629	-0.7592	952.1	0.9989	665.2	653.8	642.4
0.619	-0.7694	959.1	0.9988	668.2	656.7	645.1
0.605	-0.7849	993.5	0.9994	696.8	685.0	673.2
0.0248	-1.7564	1160.8	0.9932	496.9	470.5	444.2
0.0238	-1.1202	883.2	0.9970	459.7	442.9	426.1
0.0204	-0.8061	756.3	0.9969	451.6	439.5	427.4
0.0163	-0.5402	651.7	0.8182	447.5	439.4	431.2
0.0143	-0.9263	791.4	0.9740	441.2	427.3	413.4
0.0135	-1.0252	845.8	0.9978	458.3	442.9	427.5
0.0131	-0.9862	809.0	0.9993	436.2	421.4	406.6

11.2 DATA FOR SUPERPOSITION GRAPHS

Table 11-13: Data used in superposition graph at x = 0.0231

Alkane	Data Point 1		Data Point 2		Interpolated	No folding	Single fold
	x	P (barA)	x	P (barA)	x = 0.0231	relationship	relationship
nC32	0.0286	79.7	0.0200	77.3	78.2	77.6	57.7
nC36	0.0255	84.1	0.0151	81.9	83.6	82.5	60.2
nC38	0.0322	87.4	0.0149	82.3	84.7	85.0	61.4
nC40	0.0249	86.5	0.0217	87.2	86.9	87.5	62.7
nC44	0.0255	94.3	0.0146	87.1	92.7	92.5	65.1
nC46	0.0383	97.7	0.0210	92.4	93.1	95.0	66.4
nC54	0.0244	106.2	0.0147	96.1	104.9	104.9	71.4
nC60	0.0249	115.2	0.0143	104.0	113.3	112.3	75.1
nC100	-	-	-	-	-	162.0	99.9
nC160	-	-	-	-	-	236.5	137.2

Table 11-14: Data used in superposition graph at x = 0.0275

Alkane	Data Point 1		Data Point 2		Interpolated	No folding	Single fold
	x	P (barA)	x	P (barA)	x = 0.0275	relationship	relationship
nC32	0.0286	79.7	0.0200	77.3	79.4	78.4	57.5
nC36	0.0425	89.8	0.0255	84.1	84.7	83.7	60.1
nC38	0.0322	87.4	0.0149	82.3	86.0	86.3	61.4
nC40	0.0373	92.2	0.0249	86.5	87.7	88.9	62.7
nC44	0.0420	96.6	0.0255	94.3	94.6	94.1	65.3
nC46	0.0383	97.7	0.0210	92.4	94.4	96.8	66.6
nC54	0.0440	114.4	0.0244	106.2	107.5	107.2	71.9
nC60	0.0295	116.8	0.0249	115.2	116.1	115.1	75.8
nC100	-	-	-	-	-	167.5	102.0
nC160	-	-	-	-	-	246.1	141.3

Table 11-15: Data used in superposition graph at x = 0.330

Alkane	Data Point 1		Data Point 2		Interpolated	No folding	Single fold
	x	P (barA)	x	P (barA)	x = 0.330	relationship	relationship
nC32	0.381	88.0	0.316	90.5	89.9	89.9	60.3
nC36	0.378	95.8	0.269	99.1	97.3	97.3	64.0
nC38	0.388	97.6	0.322	99.8	99.5	101.0	65.8
nC40	0.336	107.2	0.309	107.9	107.4	104.7	67.7
nC44	0.354	113.6	0.312	111.6	112.5	112.1	71.4
nC46	0.362	112.0	0.305	113.8	113.0	115.8	73.2
nC54	0.382	127.9	0.324	133.0	132.5	130.6	80.6
nC60	0.364	139.6	0.304	142.1	141.0	141.7	86.2
nC100	-	-	-	-	-	215.7	123.2
nC160	-	-	-	-	-	326.7	178.7

Table 11-16: Data used in superposition graph at x = 0.363

Alkane	Data Point 1		Data Point 2		Interpolated	No folding	Single fold
	x	P (barA)	x	P (barA)	x = 0.330	relationship	relationship
nC32	0.381	88.0	0.3160	90.5	88.7	89.9	60.3
nC36	0.378	95.8	0.269	99.1	96.3	97.3	64.0
nC38	0.388	97.6	0.322	99.8	98.4	101.0	65.8
nC40	0.336	107.2	0.376	105.4	106.0	104.7	67.7
nC44	0.354	113.6	0.371	112.8	113.2	112.1	71.4
nC46	0.362	112.0	-	-	112.0	115.8	73.2
nC54	0.382	127.9	0.324	133.0	129.7	130.6	80.6
nC60	0.364	139.6	0.304	142.1	139.7	141.7	86.2
nC100	-	-	-	-	-	215.7	123.2
nC160	-	-	-	-	-	326.7	178.7

Table 11-17: Data used in superposition graph at x = 0.491

Alkane	Data Point 1		Data Point 2		Interpolated	No folding	Single fold
	x	P (barA)	x	P (barA)	x = 0.330	relationship	relationship
nC32	0.4510	80.9	0.511	77.2	78.4	46.5	34.4
nC36	0.576	66.7	0.472	84.4	81.2	49.6	35.9
nC38	0.506	83.0	0.451	91.6	85.3	51.1	36.7
nC40	0.499	92.8	0.439	100.7	93.9	52.6	37.4
nC44	0.542	88.4	0.481	96.4	95.1	55.7	38.9
nC46	0.484	95.4	0.556	92.8	95.1	57.2	39.7
nC54	0.453	117.5	1.000	0.0	109.4	63.3	42.7
nC60	0.452	127.1	1.000	0.0	118.1	67.8	45.0
nC100	-	-	-	-	-	98.2	60.2
nC160	-	-	-	-	-	143.9	83.0

Table 11-18: Data used in superposition graph at x = 0.705

Alkane	Data Point 1		Data Point 2		Interpolated	No folding	Single fold
	x	P (barA)	x	P (barA)	x = 0.705	relationship	relationship
nC32	0.566	69.6	1.000	0.0	47.3	46.5	34.4
nC36	0.472	88.2	1.000	0.0	49.3	49.6	35.9
nC38	0.567	73.4	1.000	0.0	50.0	51.1	36.7
nC40	0.551	82.1	1.000	0.0	54.0	52.6	37.4
nC44	0.542	88.4	1.000	0.0	56.9	55.7	38.9
nC46	0.484	95.4	1.000	0.0	54.5	57.2	39.7
nC54	0.453	117.5	1.000	0.0	63.4	63.3	42.7
nC60	0.452	127.1	1.000	0.0	68.4	67.8	45.0
nC100	-	-	-	-	-	98.2	60.2
nC160	-	-	-	-	-	143.9	83.0

Table 11-19: Data used in superposition graph at x = 0.753

Alkane	Data Point 1		Data Point 2		Interpolated	No folding	Single fold
	x	P (barA)	x	P (barA)	x = 0.753	relationship	relationship
nC32	0.566	69.6	1.000	0.0	39.6	39.0	28.8
nC36	0.472	88.2	1.000	0.0	41.3	41.5	30.1
nC38	0.567	73.4	1.000	0.0	41.9	42.8	30.7
nC40	0.551	82.1	1.000	0.0	45.2	44.1	31.3
nC44	0.542	88.4	1.000	0.0	47.7	46.6	32.6
nC46	0.484	95.4	1.000	0.0	45.7	47.9	33.2
nC54	0.453	117.5	1.000	0.0	53.1	53.0	35.8
nC60	0.452	127.1	1.000	0.0	57.3	56.8	37.7
nC100	-	-	-	-	-	82.3	50.4
nC160	-	-	-	-	-	120.4	69.5

11.3 ALCOHOL ETHOXYLATE PILOT PLANT CONCENTRATION DATA

11.3.1 EXPERIMENTAL DATA

Table 11-20: Experimental pilot plant data – part 1

			Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
Temperatures	TH1Set	°C	140	140	140	140	145	150
	TH2Set	°C	140	145	140	140	145	150
	TI1	°C	119	116	120	119	122	125
	TI2	°C	119	116	123	122	124	127
	TI3	°C	18	14	11	15	14	16
	TI4	°C	17	17	15	13	16	15
	TI5	°C	13	10	16	8	13	11
Pressures	PIC1	barA	115	125	130	150	130	130
	PIC2	barA	7.5	8.0	8.0	8.0	8.0	8.0
	PI1	barA	126	136	140	160	140	140
	PI2	barA	8.5	8.5	8.5	8.5	8.5	8.5
	PI3	barA	8.5	8.5	8.5	8.5	8.5	8.5
	PI4	barA	125	135	140	160	140	140
Solvent	Time	s	2040	5584	5038	5580	6250	5710
	Mass	kg	10.8	24.2	24.4	25.5	31.7	26.7
	Rate	kg/m ² .s	23.3	19.1	21.3	20.2	22.3	20.6
Solute	Time	s	2219	5525	5100	5548	6308	5541
	Mass	g	281.5	360.0	404.6	271.1	491.0	402.4
	Rate	kg/m ² .s	0.559	0.287	0.350	0.215	0.343	0.320
Solvent/Feed		-	41.8	66.5	61.0	93.6	65.1	64.5
Overheads/Feed		-	0.052	0.209	0.243	0.361	0.231	0.174
Overheads	Mass	g	14.6	75.3	98.4	97.9	113.2	70.2
	Carbon	Mass %	-	76.8	71.6	76.4	74.1	74.7
	Hydrogen	Mass %	-	12.9	12.0	12.8	12.4	12.5
	Oxygen	Mass %	-	10.3	16.4	10.8	13.5	12.8
	m		-	5.6	12.6	6.0	8.8	8.0
	n		-	53	53	53	53	53
Bottoms	Mass	g	266.9	284.7	306.2	173.2	306.2	377.8
	Carbon	Mass %	-	65.1	65.8	66.3	62.9	66.0
	Hydrogen	Mass %	-	10.9	11.0	11.1	10.6	11.1
	Oxygen	Mass %	-	24.0	23.2	22.6	26.5	22.9
	m		-	31.2	28.1	26.2	44.0	27.3
	n		-	53	53	53	53	53

Table 11-20: Experimental pilot plant data – part 2

			Run 7	Run 8	Run 9	Run 10	Run 11
Temperatures	TH1Set	°C	150	150	140	140	150
	TH2Set	°C	150	150	140	140	150
	TI1	°C	126	127	122	122	127
	TI2	°C	129	124	125	129	127
	TI3	°C	13	8	12	8	6
	TI4	°C	18	17	15	15	15
	TI5	°C	5	7	5	4	6
Pressures	PIC1	barA	130	130	140	150	130
	PIC2	barA	8.0	8.0	8.0	8.0	8.0
	PI1	barA	140	140	150	160	140
	PI2	barA	8.5	8.5	8.5	8.5	8.5
	PI3	barA	8.5	8.5	8.5	8.5	8.5
	PI4	barA	140	140	150	160	140
Solvent	Time	s	6605	5710	6675	6705	3210
	Mass	kg	21.9	20.1	24.6	23.6	11.2
	Rate	kg/m ² .s	14.6	15.5	16.2	15.5	15.4
Solute	Time	s	6515	5830	6660	5955	3190
	Mass	g	438.5	474.7	443.9	478.1	532.7
	Rate	kg/m ² .s	0.297	0.359	0.294	0.354	0.736
Solvent/Feed	-	49.3	43.2	55.2	43.8	20.9	
Overheads/Feed	-	0.191	0.157	0.279	0.273	0.151	
Overheads	Mass	g	83.6	74.6	123.9	130.5	80.7
	Carbon	Mass %	70.6	72.0	72.9	69.3	76.0
	Hydrogen	Mass %	11.8	12.1	12.2	11.6	12.8
	Oxygen	Mass %	17.6	15.9	14.9	19.1	11.2
	m		14.5	11.9	10.5	17.3	6.4
	n		53	53	53	53	53
Bottoms	Mass	g	354.9	400.1	320.0	347.6	452.0
	Carbon	Mass %	67.0	67.0	66.2	68.2	68.6
	Hydrogen	Mass %	11.2	11.2	11.1	11.4	11.5
	Oxygen	Mass %	21.8	21.8	22.7	20.4	19.9
	m		23.7	23.7	26.6	20.1	19.0
	n		53	53	53	53	53

11.3.2 ANALYSIS DATA

Table 11-21: Analysis results for overheads and bottoms product streams

		Mass %			Mole %			n	m
		C	H	O	C	H	O		
Run 2	Overheads	76.8	12.9	10.3	32.2	64.5	3.3	53	5.6
	Bottoms	65.1	10.9	24.0	30.5	61.0	8.4	53	31.2
Run 3	Overheads	71.6	12.0	16.4	31.5	63.1	5.4	53	12.6
	Bottoms	65.8	11.0	23.2	30.6	61.3	8.1	53	28.1
Run 4	Overheads	74.1	12.4	13.5	31.9	63.8	4.3	53	8.8
	Bottoms	62.9	10.6	26.5	30.1	60.3	9.6	53	44.0
Run 5	Overheads	74.7	12.5	12.8	32.0	63.9	4.1	53	8.0
	Bottoms	66.0	11.1	22.9	30.7	61.3	8.0	53	27.3
Run 6	Overheads	76.4	12.8	10.8	32.2	64.4	3.4	53	6.0
	Bottoms	66.3	11.1	22.6	30.7	61.4	7.9	53	26.2
Run 7	Overheads	70.6	11.8	17.6	31.4	62.8	5.9	53	14.5
	Bottoms	67.0	11.2	21.8	30.8	61.7	7.5	53	23.7
Run 8	Overheads	72.0	12.1	15.9	31.6	63.2	5.2	53	11.9
	Bottoms	67.0	11.2	21.8	30.8	61.7	7.5	53	23.7
Run 9	Overheads	72.9	12.2	14.9	31.7	63.4	4.9	53	10.5
	Bottoms	66.2	11.1	22.7	30.7	61.4	7.9	53	26.6
Run 10	Overheads	69.3	11.6	19.1	31.2	62.4	6.4	53	17.3
	Bottoms	68.2	11.4	20.4	31.0	62.0	6.9	53	20.1
Run 11	Overheads	76.0	12.8	11.2	32.1	64.3	3.6	53	6.4
	Bottoms	68.6	11.5	19.9	31.1	62.2	6.8	53	19.0
Feed with lights		69.0	11.6	19.4	31.1	62.3	6.6	53	18.0
Feed without lights		67.0	11.2	21.8	30.8	61.7	7.5	53	23.7

11.3.3 FLOODING CALCULATIONS

Table 11-22: Flooding calculations for Sulzer EX packing

Flooding calculations		Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
Feed pressure	bar	125	135	140	160	140	140
Feed temperature	K	392	389	393	392	395	398
Propane density	kg/m ³	379	391	389	402	385	379
Wax density	kg/m ³	800	800	800	800	800	800
Propane mass flow	kg/m ² .s	23.3	19.1	21.3	20.2	22.3	20.6
Wax mass flow	kg/m ² .s	0.559	0.287	0.350	0.215	0.343	0.320
Flow parameter	-	0.0165	0.0105	0.0114	0.0076	0.0107	0.0107
Gas capacity at flooding							
K3	m/s	0.109	0.109	0.109	0.109	0.109	0.109
K4	-	1.77	1.77	1.77	1.77	1.77	1.77
Gas capacity factor	m/s	0.0724	0.0781	0.0771	0.0818	0.0779	0.0779
Gas capacity at operation							
Gas velocity	m/s	0.0617	0.0488	0.0548	0.0501	0.0580	0.0544
Gas capacity factor	m/s	0.0585	0.0477	0.0533	0.0504	0.0558	0.0516
Operation/Flooding	-	0.81	0.61	0.69	0.62	0.72	0.66

Table 11-22 continued

Flooding calculations		Run 7	Run 8	Run 9	Run 10	Run 11
Feed pressure	bar	140	140	150	160	140
Feed temperature	K	399	400	395	395	400
Propane density	kg/m ³	377	376	391	397	373
Wax density	kg/m ³	800	800	800	800	800
Propane mass flow	kg/m ² .s	14.6	15.5	16.2	15.5	15.4
Wax mass flow	kg/m ² .s	0.297	0.359	0.294	0.354	0.736
Flow parameter	-	0.0139	0.0159	0.0127	0.0161	0.0326
Gas capacity at flooding						
K3	m/s	0.109	0.109	0.109	0.109	0.109
K4	-	1.77	1.77	1.77	1.77	1.77
Gas capacity factor	m/s	0.0746	0.0729	0.0758	0.0727	0.0626
Gas capacity at operation						
Gas velocity	m/s	0.0387	0.0412	0.0414	0.0391	0.0412
Gas capacity factor	m/s	0.0366	0.0388	0.0405	0.0387	0.0386
Operation/Flooding	-	0.49	0.53	0.53	0.53	0.62

Table 11-23: Flooding calculations for Sulzer CY packing

Flooding calculations		Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
Feed pressure	bar	125	135	140	160	140	140
Feed temperature	K	392	389	393	392	395	398
Propane density	kg/m ³	379	391	389	402	385	379
Wax density	kg/m ³	800	800	800	800	800	800
Propane mass flow	kg/m ² .s	23.3	19.1	21.3	20.2	22.3	20.6
Wax mass flow	kg/m ² .s	0.559	0.287	0.350	0.215	0.343	0.320
Flow parameter	-	0.0165	0.0105	0.0114	0.0076	0.0107	0.0107
Gas capacity at flooding							
K3	m/s	0.123	0.123	0.123	0.123	0.123	0.123
K4	-	1.95	1.95	1.95	1.95	1.95	1.95
Gas capacity factor	m/s	0.0787	0.0854	0.0842	0.0899	0.0852	0.0852
Gas capacity at operation							
Gas velocity	m/s	0.0617	0.0488	0.0548	0.0501	0.0580	0.0544
Gas capacity factor	m/s	0.0585	0.0477	0.0533	0.0504	0.0558	0.0516
Operation/Flooding	-	0.74	0.56	0.63	0.56	0.65	0.61

Table 11-23 continued

Flooding calculations		Run 7	Run 8	Run 9	Run 10	Run 11
Feed pressure	bar	140	140	150	160	140
Feed temperature	K	399	400	395	395	400
Propane density	kg/m ³	377	376	391	397	373
Wax density	kg/m ³	800	800	800	800	800
Propane mass flow	kg/m ² .s	14.6	15.5	16.2	15.5	15.4
Wax mass flow	kg/m ² .s	0.297	0.359	0.294	0.354	0.736
Flow parameter	-	0.0139	0.0159	0.0127	0.0161	0.0326
Gas capacity at flooding						
K3	m/s	0.123	0.123	0.123	0.123	0.123
K4	-	1.95	1.95	1.95	1.95	1.95
Gas capacity factor	m/s	0.0813	0.0793	0.0827	0.0791	0.0673
Gas capacity at operation						
Gas velocity	m/s	0.0387	0.0412	0.0414	0.0391	0.0412
Gas capacity factor	m/s	0.0366	0.0388	0.0405	0.0387	0.0386
Operation/Flooding	-	0.45	0.49	0.49	0.49	0.57

Table 11-24: Flooding calculations for Berl Saddles with corrected void fractions

Flooding calculations		Run 1	Run 2	Run 3	Run 4	Run 5	Run 6
Feed pressure	bar	125	135	140	160	140	140
Feed temperature	K	119	116	120	119	122	125
Propane density	kg/m ³	392	389	393	392	395	398
Wax density	kg/m ³	379	391	389	402	385	379
Propane mass flow	kg/m ² .s	800	800	800	800	800	800
Wax mass flow	kg/m ² .s	23.3	19.1	21.3	20.2	22.3	20.6
Flow parameter	-	0.559	0.287	0.350	0.215	0.343	0.320
Gas capacity at flooding							
K3	m/s	0.026	0.026	0.026	0.026	0.026	0.026
K4	-	0.95	0.95	0.95	0.95	0.95	0.95
Gas capacity factor	m/s	0.0207	0.0216	0.0214	0.0222	0.0216	0.0216
Gas capacity at operation							
Gas velocity	m/s	0.0617	0.0488	0.0548	0.0501	0.0580	0.0544
Gas capacity factor	m/s	0.0585	0.0477	0.0533	0.0504	0.0558	0.0516
Corrected gas capacity	m/s	0.0365	0.0298	0.0333	0.0315	0.0349	0.0323
Operation/Flooding	-	0.0365	0.0298	0.0333	0.0315	0.0349	0.0323

Table 11-24 continued

Flooding calculations		Run 7	Run 8	Run 9	Run 10	Run 11
Feed pressure	bar	140	140	150	160	140
Feed temperature	K	126	127	122	122	127
Propane density	kg/m ³	399	400	395	395	400
Wax density	kg/m ³	377	376	391	397	373
Propane mass flow	kg/m ² .s	800	800	800	800	800
Wax mass flow	kg/m ² .s	14.6	15.5	16.2	15.5	15.4
Flow parameter	-	0.297	0.359	0.294	0.354	0.736
Gas capacity at flooding						
K3	m/s	0.026	0.026	0.026	0.026	0.026
K4	-	0.95	0.95	0.95	0.95	0.95
Gas capacity factor	m/s	0.0210	0.0207	0.0212	0.0207	0.0189
Gas capacity at operation						
Gas velocity	m/s	0.0387	0.0412	0.0414	0.0391	0.0412
Gas capacity factor	m/s	0.0366	0.0388	0.0405	0.0387	0.0386
Corrected gas capacity	m/s	0.0229	0.0243	0.0253	0.0242	0.0241
Operation/Flooding	-	1.09	1.17	1.19	1.17	1.27

11.4 ALCOHOL ETHOXYLATE CONCENTRATION MASS AND ENERGY BALANCE DATA

11.4.1 MASS BALANCE

Table 11-25: Mass balance and stream specifications of streams for one phase decompression process and solvent to feed ratio of 60

Stream	Flow rate	Composition (g/g)		Temperature (K)	Pressure (barA)	Phase
		Propane	Wax			
Feed	1.00	0.00	1.00	298.15	0.0	Liquid
Lights from feed	0.10	0.00	0.10	393.15	0.0	Vapour
Solute pump suction side	0.90	0.00	0.90	393.15	0.0	Liquid
Solute pump delivery side	0.90	0.00	0.90	393.15	130.0	Liquid
Solute feed to column	0.90	0.00	0.90	393.15	130.0	Liquid
Solvent entering storage tank	54.00	54.00	0.00	293.15	9.5	Liquid
Solvent exiting storage tank	54.00	54.00	0.00	293.15	9.5	Liquid
Solvent pump suction side	54.00	54.00	0.00	283.15	9.5	Liquid
Solvent pump delivery side	54.00	54.00	0.00	286.20	130.0	Liquid
Solvent pre-heater inlet	54.00	54.00	0.00	0.00	130.0	Liquid
Solvent entering column	54.00	54.00	0.00	393.15	130.0	SC Fluid
Overheads exiting column	53.94	53.71	0.23	393.15	130.0	SC Fluid
Reduced pressure overheads	53.94	53.71	0.23	-	9.5	Mixed
Overheads entering separator	53.94	53.71	0.23	403.15	9.5	Mixed
Overheads product	0.23	0.00	0.23	403.15	9.5	Liquid
Overheads solvent recycle	53.71	53.71	0.00	403.15	9.5	SC Fluid
Combined solvent recycle	54.00	54.00	0.00	403.15	9.5	Vapour
Cooled solvent recycle	54.00	54.00	0.00	308.15	9.5	Vapour
Chilled solvent recycle	54.00	54.00	0.00	293.15	9.5	Liquid
Bottoms exiting column	0.96	0.29	0.68	393.15	130.0	Liquid
Reduced pressure bottoms	0.96	0.29	0.68	-	9.5	Mixed
Bottoms entering separator	0.96	0.29	0.68	403.15	9.5	Mixed
Bottoms product stream	0.68	0.00	0.68	403.15	9.5	Liquid
Bottoms solvent recycle	0.29	0.29	0.00	403.15	9.5	SC Fluid

Table 11-26: Mass balance and stream specifications of streams for one phase decompression process and solvent to feed ratio of 30

Stream	Flow rate	Composition (g/g)		Temperature (K)	Pressure (barA)	Phase
		Propane	Wax			
Feed	1.00	0.00	1.00	298.15	0.0	Liquid
Lights from feed	0.10	0.00	0.10	393.15	0.0	Vapour
Solute pump suction side	0.90	0.00	0.90	393.15	0.0	Liquid
Solute pump delivery side	0.90	0.00	0.90	393.15	130.0	Liquid
Solute feed to column	0.00	-	-	393.15	130.0	Liquid
Solvent entering storage tank	0.90	0.00	0.90	293.15	9.5	Liquid
Solvent exiting storage tank	0.00	-	-	293.15	9.5	Liquid
Solvent pump suction side	27.00	27.00	0.00	283.15	9.5	Liquid
Solvent pump delivery side	27.00	27.00	0.00	286.20	130.0	Liquid
Solvent pre-heater inlet	27.00	27.00	0.00	0.00	130.0	Liquid
Solvent entering column	27.00	27.00	0.00	393.15	130.0	SC Fluid
Overheads exiting column	27.00	27.00	0.00	393.15	130.0	SC Fluid
Reduced pressure overheads	27.00	27.00	0.00	-	9.5	Mixed
Overheads entering separator	0.00	-	-	403.15	9.5	Mixed
Overheads product	26.90	26.70	0.20	403.15	9.5	Liquid
Overheads solvent recycle	26.90	26.70	0.20	403.15	9.5	SC Fluid
Combined solvent recycle	26.90	26.70	0.20	403.15	9.5	Vapour
Cooled solvent recycle	0.20	0.00	0.20	308.15	9.5	Vapour
Chilled solvent recycle	26.70	26.70	0.00	293.15	9.5	Liquid
Bottoms exiting column	27.00	27.00	0.00	393.15	130.0	Liquid
Reduced pressure bottoms	27.00	27.00	0.00	-	9.5	Mixed
Bottoms entering separator	27.00	27.00	0.00	403.15	9.5	Mixed
Bottoms product stream	1.00	0.30	0.70	403.15	9.5	Liquid
Bottoms solvent recycle	1.00	0.30	0.70	403.15	9.5	SC Fluid

Table 11-27: Mass balance and stream specifications of streams for two phase decompression process and solvent to feed ratio of 60

Stream	Flow rate	Composition (g/g)		Temperature (K)	Pressure (barA)	Phase
		Propane	Wax			
Feed	1.00	0.00	1.00	298.15	1.0	Liquid
Lights from feed	0.10	0.00	0.00	393.15	1.0	Liquid
Solute pump suction side	0.90	0.00	0.90	393.15	1.0	Liquid
Solute pump delivery side	0.90	0.00	0.90	393.15	130.0	Liquid
Start-up solute recycle	0.00	0.00	0.00	393.15	130.0	Liquid
Solute feed to column	0.90	0.00	0.90	393.15	130.0	Liquid
Make-up solvent from cylinder	0.00	0.00	0.00	-	-	Liquid
Solvent entering solvent storage tank	54.00	54.00	0.00	359.14	35.0	Liquid
Solvent exiting solvent storage tank	54.00	54.00	0.00	359.14	35.0	Liquid
Solvent pump suction side	54.00	54.00	0.00	339.14	35.0	Liquid
Solvent pump delivery side	54.00	54.00	0.00	349.33	130.0	Liquid
Solvent pre-heater inlet	54.00	54.00	0.00	349.33	130.0	Liquid
Solvent entering column	54.00	54.00	0.00	393.15	130.0	SC Fluid
Start-up solvent recycle	0.00	0.00	0.00	-	-	Liquid
Overheads exiting column	53.94	53.71	0.23	393.15	130.0	SC Fluid
Reduced pressure overheads	53.94	53.71	0.23	-	35.0	Mixed
Overheads entering separator I	53.94	53.71	0.23	403.15	35.0	Mixed
Overheads product	0.23	0.00	0.23	403.15	2.0	Liquid
Vapour exiting separator I	53.69	53.69	0.00	403.15	35.0	Vapour
Total solvent recycle	54.00	54.00	0.00	403.15	35.0	Vapour
Cooled solvent recycle	54.00	54.00	0.00	359.14	35.0	Liquid
Bottoms exiting column	0.96	0.29	0.68	393.15	130.0	Liquid
Reduced pressure bottoms	0.96	0.29	0.68	-	2.0	Mixed
Bottoms entering separator III	0.96	0.29	0.68	403.15	2.0	Mixed
Bottoms product stream	0.68	0.00	0.68	403.15	2.0	Liquid
Bottoms solvent recycle	0.29	0.29	0.00	403.15	2.0	Vapour
Liquid stream exiting separator I	0.25	0.03	0.23	403.15	35.0	Liquid
Reduced pressure from Separator I	0.25	0.03	0.23	-	2.0	Mixed
Steam entering separator II	0.25	0.03	0.23	403.15	2.0	Mixed
Vapour stream from separator II	0.03	0.03	0.00	403.15	2.0	Vapour
Combined low pressure solvent recycle	0.31	0.31	0.00	403.15	2.0	Vapour

Table 11-27 continued

Compressor recycle stream	0.00	0.00	0.00	-	-	SC Fluid
Flow controlled compressor recycle	0.00	0.00	0.00	-	-	SC Fluid
Reduced pressure compressor recycle	0.00	0.00	0.00	-	-	SC Fluid
Stream entering compressor pre-cooler	0.31	0.31	0.00	403.15	2.0	Vapour
Compressor I inlet	0.31	0.31	0.00	308.15	2.0	Vapour
Compressor I outlet	0.31	0.31	0.00	361.21	8.4	Vapour
Compressor II inlet	0.31	0.31	0.00	338.83	8.4	Vapour
Compressor II outlet	0.31	0.31	0.00	403.15	35.0	Vapour
Combined solvent recycle	54.00	54.00	0.00	403.15	35.0	Vapour

Table 11-28: Mass balance and stream specifications of streams for two phase decompression process and solvent to feed ratio of 30

Stream	Flow rate	Composition (g/g)		Temperature (K)	Pressure (barA)	Phase
		Propane	Wax			
Feed	1.00	0.00	1.00	298.15	1.0	Liquid
Lights from feed	0.10	0.00	0.00	393.15	1.0	Liquid
Solute pump suction side	0.90	0.00	0.90	393.15	1.0	Liquid
Solute pump delivery side	0.90	0.00	0.90	393.15	130.0	Liquid
Start-up solute recycle	0.00	0.00	0.00	393.15	130.0	Liquid
Solute feed to column	0.90	0.00	0.90	393.15	130.0	Liquid
Make-up solvent from cylinder	0.00	0.00	0.00	-	-	Liquid
Solvent entering solvent storage tank	27.00	27.00	0.00	359.14	35.0	Liquid
Solvent exiting solvent storage tank	27.00	27.00	0.00	359.14	35.0	Liquid
Solvent pump suction side	27.00	27.00	0.00	339.14	35.0	Liquid
Solvent pump delivery side	27.00	27.00	0.00	349.33	130.0	Liquid
Solvent pre-heater inlet	27.00	27.00	0.00	349.33	130.0	Liquid
Solvent entering column	27.00	27.00	0.00	393.15	130.0	SC Fluid
Start-up solvent recycle	0.00	0.00	0.00	-	-	Liquid
Overheads exiting column	26.90	26.70	0.20	393.15	130.0	SC Fluid
Reduced pressure overheads	26.90	26.70	0.20	-	35.0	Mixed
Overheads entering separator I	26.90	26.70	0.20	403.15	35.0	Mixed
Overheads product	0.20	0.00	0.20	403.15	2.0	Liquid

Table 11-28 continued

Vapour exiting separator I	26.69	26.69	0.00	403.15	35.0	Vapour
Total solvent recycle	27.00	27.00	0.00	403.15	35.0	Vapour
Cooled solvent recycle	27.00	27.00	0.00	359.14	35.0	Liquid
Bottoms exiting column	1.00	0.30	0.70	393.15	130.0	Liquid
Reduced pressure bottoms	1.00	0.30	0.70	-	2.0	Mixed
Bottoms entering separator III	1.00	0.30	0.70	403.15	2.0	Mixed
Bottoms product stream	0.70	0.00	0.70	403.15	2.0	Liquid
Bottoms solvent recycle	0.30	0.30	0.00	403.15	2.0	Vapour
Liquid stream exiting separator I	0.23	0.02	0.20	403.15	35.0	Liquid
Reduced pressure from Separator I	0.23	0.02	0.20	-	2.0	Mixed
Steam entering separator II	0.23	0.02	0.20	403.15	2.0	Mixed
Vapour stream from separator II	0.02	0.02	0.00	403.15	2.0	Vapour
Combined low pressure solvent recycle	0.32	0.32	0.00	403.15	2.0	Vapour
Compressor recycle stream	0.00	0.00	0.00	-	-	SC Fluid
Flow controlled compressor recycle	0.00	0.00	0.00	-	-	SC Fluid
Reduced pressure compressor recycle	0.00	0.00	0.00	-	-	SC Fluid
Stream entering compressor pre-cooler	0.32	0.32	0.00	403.15	2.0	Vapour
Compressor I inlet	0.32	0.32	0.00	308.15	2.0	Vapour
Compressor I outlet	0.32	0.32	0.00	361.21	8.4	Vapour
Compressor II inlet	0.32	0.32	0.00	338.83	8.4	Vapour
Compressor II outlet	0.32	0.32	0.00	403.15	35.0	Vapour
Combined solvent recycle	27.00	27.00	0.00	403.15	35.0	Vapour

11.4.2 ALCOHOL ETHOXYLATE PROPERTIES

11.4.2.1 FEED PROPERTIES

Table 11-29: Calculation of percentage volatiles in feed

Glass Empty	69.37
Glass with wax	109.51
After heat to 120	105.64
Total wax in	40.14
Total wax out	36.27
% Volatiles in feed	0.096413

Table 11-30: Calculation of density of wax feed

Mass raw feed	560.1g
Volatiles	54.00g
Mass feed total	506.1g
	0.5061kg
Length	319mm
	0.319m
Diameter	50mm
	0.05m
Volume	0.000626m ³
Density	808kg/m ³

Enthalpy plot for wax feed:

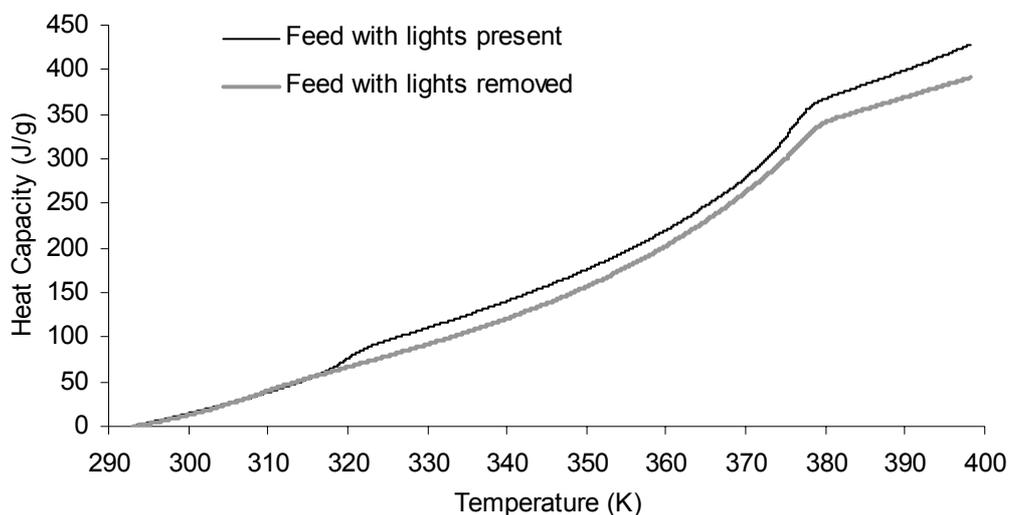


Figure 11-1: Enthalpy requirement for heating and melting of feed wax with and without lights to operating temperature as a function of temperature

11.4.2.2 PROPERTIES OF THE OVERHEADS AND BOTTOMS WAX

Various methods exist for estimating unknown thermodynamic properties including empirical correlations and theoretical approaches. A theoretical approach, the group contribution method [1] is based on the assumption that various groups in a molecule contribute a specific value to the total molar heat capacity and this value is independent of other groups present. Group contribution methods and possibly empirical correlations are the best starting point in developing a method for estimating the enthalpy of alcohol ethoxylates. Two methods will be evaluated to assess their suitability:

- Ruzicka et al. [2], [3] proposed a second order group contribution method for the heat capacity as a function of temperature.
- Guilyazetdinov [4] proposed an empirical method for estimating the heat capacity based on the fit of an empirical equation on petroleum and tar fractions.

In order to test the ability of these methods to predict the alcohol ethoxylate enthalpy, firstly the long chain alkane enthalpies will be estimated followed by the heat capacity of polyethylene glycol.

When the experimental liquid specific heat capacity is plotted as a function of temperature in the mass based unit, i.e. J/(g.K), it is found that for nC10 and higher the heat capacity is generally independent of molecular weight:

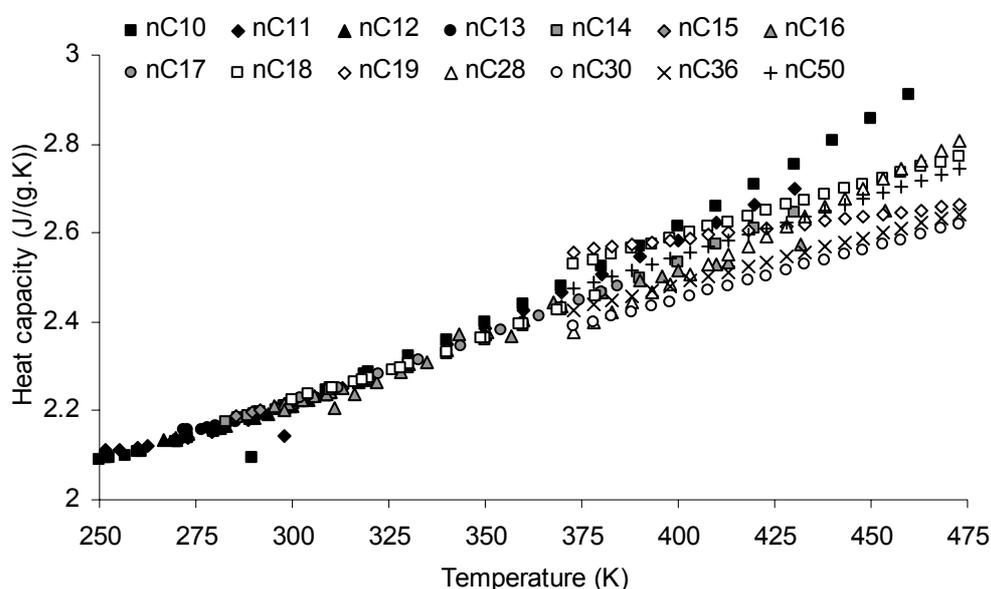


Figure 11-2: Plot of specific experimental heat capacity as a function of temperature for various normal alkanes [5], [6], [7], [2], [8]

Figure 11-2 shows that for higher alkanes the effect of the $-\text{CH}_3$ group's contribution is overshadowed by the $-\text{CH}_2-$ group's contribution. There is however, some scatter in the above-mentioned data yet it should be noted that no clear trend with molecular weight is noted and the data be regarded as independent of molecular weight. The heat capacity for nC40 is calculated with the method of Ruzicka et al. [2] and that of Guilyazetdinov [4] and plotted together with the upper and lower limit of the experimental values from 370 to 450 K:

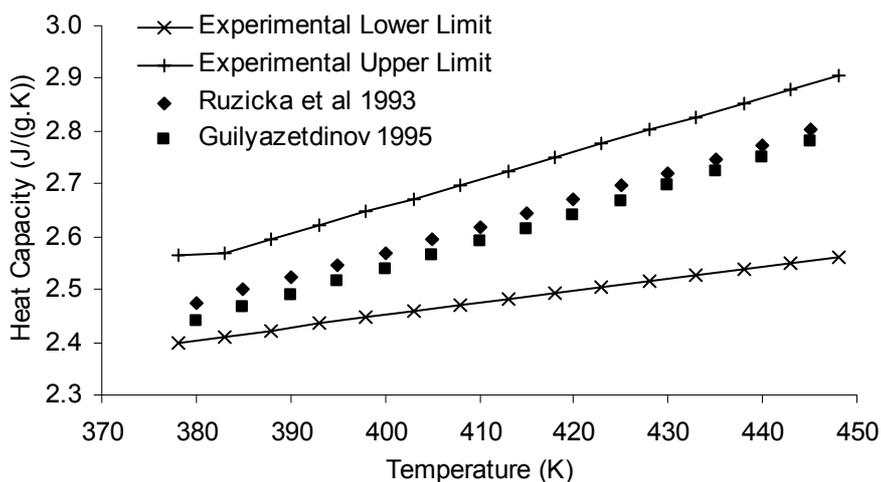


Figure 11-3: Comparison of alkane heat capacity predictions for nC40 with method of Ruzicka et al. [2] and Guilyazetdinov [4] with upper and lower limit of experimental data from 375 to 450K [5], [6], [7], [2], [8]

Both methods predict the data well and investigation of both methods with regard to their ability to predict polyethylene oxide (PEO) heat capacity is now conducted:

The group contribution method of Ruzicka et al. [2], [3] is used to predict the polyethylene oxide heat capacity. In the work of Ruzicka [3] the temperature range of application for the ether group is from 150 to 350K. The temperature range in this work, as well as the temperature range of the polyethylene oxide data exceeds this range. The d parameter, the coefficient of temperature squared in the group contribution method, has been refitted to the polyethylene oxide data ($d_{\text{refitted}} = 0.284041$). The error in prediction of the specific heat capacity with this method for both the original and refitted parameters for three polyethylene oxide fractions is shown in Figure 11-4 as a function of temperature:

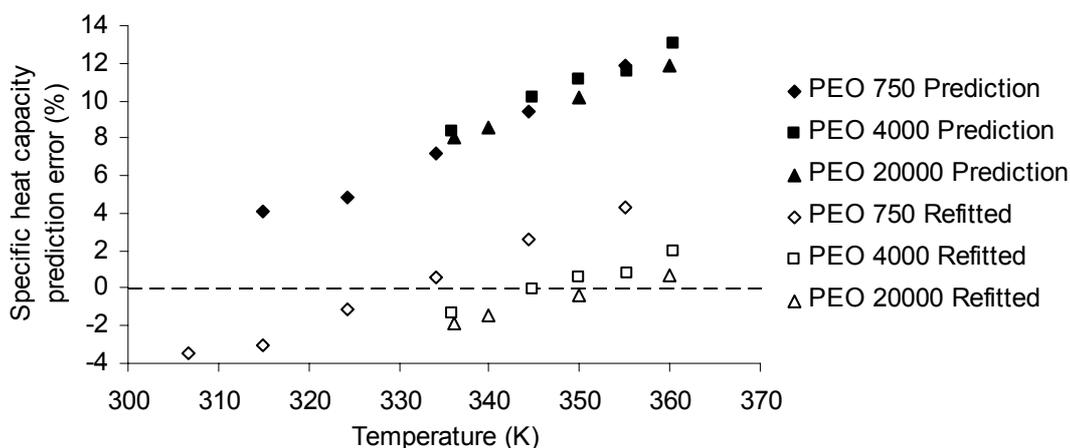


Figure 11-4: Plot of the percentage specific heat capacity error as a function of temperature for the method of Ruzicka [2],[3] for both the original parameters and the refitted parameters

The method of Guilyazetdinov has no direct parameter for hydroxy and ether groups and the parameters for phenoxy and cyclic ethers are used to incorporate hydroxy and ether groups. The error in the prediction of the specific heat capacity as a function of temperature for various polyethylene oxide fractions is shown in Figure 11-5:

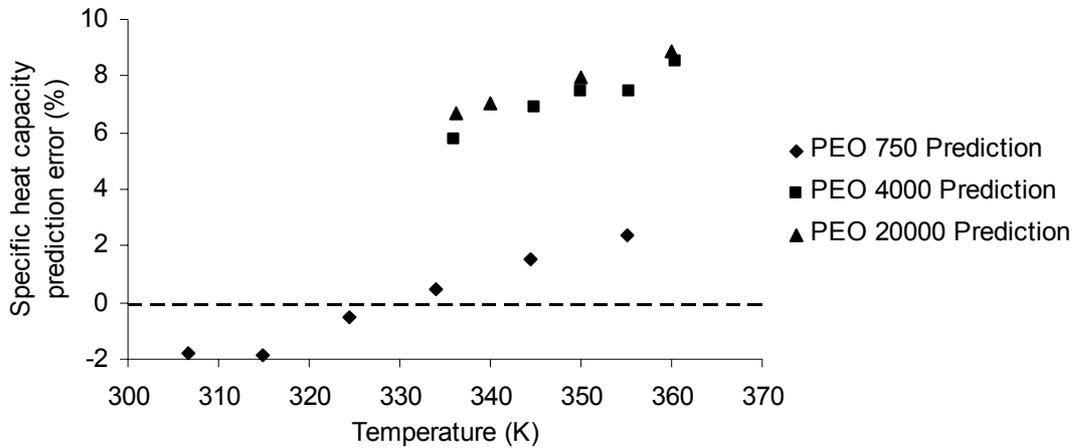


Figure 11-5: Plot of the percentage specific heat capacity error as a function of temperature for the method of Guilyazetdinov [4]

The prediction of the PEO 750 with the method of Guilyazetdinov is better than that of Ruzicka et al., however the higher molecular weight predictions of Ruzicka et al. is better and the method of Ruzicka et al. is less dependent on molecular weight. The method of Ruzicka et al. with the refitted parameters will this be used to estimate the enthalpy of the alcohol ethoxylate.

11.4.3 ENERGY BALANCE DATA

11.4.3.1 UNIT OPERATIONS

The unit operations calculations shown below are for the one step process. The same principles are used for the two-step process.

Pump energy to compress wax feed

Assuming incompressible, frictionless flow with negligible changes in potential and kinetic energy, the work done by the wax can be calculated as follows [9]:

$$\text{Equation 11-1: } \dot{W} = \frac{m_{\text{feed}}}{\rho_{\text{feed}}} (P_{\text{col}} - P_{\text{atm}})$$

In Equation 11-1 the specific volume of the wax is calculated from the density and as the pressures are known, the pumping energy requirement can be calculated.

Isentropic solvent pumping from 9.5barA to column pressure

It is assumed that the solvent pump operates isentropically. The pump outlet temperature and enthalpy are calculated by determining the point on the constant entropy line from the pump inlet temperature and pressure to the pump outlet pressure. The work required can then be calculated:

$$\text{Equation 11-2: } \dot{W} = m_{\text{sol}} (h_{\text{sol},T_{\text{pump}},P_{\text{col}}} - h_{\text{sol},283\text{K},9.5\text{barA}})$$

The entropy and enthalpy values required can be obtained from literature data or an equation of state. In this work, the enthalpy and entropy data for the solvent is obtained from data published by ASHRAE (American Society of Heating, Refrigeration and Air-Conditioning Engineers) [10].

HXH1: Solvent heating from pump outlet temperature to column temperature

The heating required is estimated from an enthalpy change and can be calculated as follows:

$$\text{Equation 11-3: } \Delta\dot{Q} = m_{\text{sol}} (h_{\text{sol},T_{\text{col}},P_{\text{col}}} - h_{\text{sol},T_{\text{pump}},P_{\text{col}}})$$

The enthalpy values are obtained from ASHRAE [10].

HXH2: Heating of overheads product from column temperature and pressure to separator temperature and pressure

The column pressure indicator controller (PIC) and heat exchanger (HXH2) are shown as two units. However, in practice these two units would be integrated. As the stream is expanded through the valve severe cooling would occur. The heat exchanger thus functions, in addition to heating the overheads from the column temperature to the separator temperature, as a counter measure against the severe cooling occurring during expansion. To calculate the energy required, the difference in enthalpy between the overheads stream exiting the column and that entering the separator needs to be estimated. Assuming two pseudo components (i.e. solvent and solute) the heat required can be estimated according to the following equation:

$$\text{Equation 11-4: } \Delta\dot{Q} = m_{\text{osol}} (h_{\text{sol},T_{\text{osep}},P_{\text{osep}}} - h_{\text{sol},T_{\text{col}},P_{\text{col}}}) + m_{\text{ovhds}} \int_{T_{\text{col}}}^{T_{\text{osep}}} C_{\text{powax}} dT + (m_{\text{osol}} + m_{\text{ovhds}}) (\Delta h_{\text{mix},T_{\text{osep}},P_{\text{osep}}} + \Delta h_{\text{mix},T_{\text{col}},P_{\text{col}}})$$

In Equation 11-4 the heat of mixing in the separator is approximated to be zero as total separation is assumed. The mixing enthalpy at the column conditions is assumed also to be zero. The heating required can thus be calculated as follows:

$$\text{Equation 11-5: } \Delta\dot{Q} = m_{\text{osol}} (h_{\text{sol},T_{\text{osep}},P_{\text{osep}}} - h_{\text{sol},T_{\text{col}},P_{\text{col}}}) + m_{\text{ovhds}} \int_{T_{\text{col}}}^{T_{\text{osep}}} C_{\text{powax}} dT$$

In Equation 11-5 the enthalpies of the solvent can be determined from ASHRAE [10] and the heat capacity of the wax is determined by a group contribution method.

HXH3: Heating of bottoms product from column temperature and pressure to separator temperature and pressure

The identical methodology as used in the overheads stream can be applied to the bottoms stream and the heat required in the heat exchanger is calculated in a similar manner:

$$\text{Equation 11-6: } \Delta \dot{Q} = m_{\text{bsol}} (h_{\text{sol}, T_{\text{bsep}}, P_{\text{bsep}}} - h_{\text{sol}, T_{\text{col}}, P_{\text{col}}}) + m_{\text{btms}} \int_{T_{\text{col}}}^{T_{\text{bsep}}} C_{\text{pbwax}} dT$$

In Equation 11-6 the enthalpies of the solvent can be determined from ASHRAE [10] and the heat capacity of the wax is determined by a group contribution method.

HXH4: Heating of wax to column temperature

The heating is equivalent to the enthalpy change and is calculated as follows:

$$\text{Equation 11-7: } \Delta \dot{Q} = m_{\text{feed}} \int_{293\text{K}}^{T_m} C_{\text{psolid, feed}} dT + m_{\text{feed}} \Delta h_{\text{fus}} + m_{\text{feed}} \int_{T_m}^{T_{\text{col}}} C_{\text{pliquid, feed}} dT$$

This information will be obtained from a DSC plot.

HXC1: Cooling of solvent from separator temperature to 308K (cooling water)

The cooling required is equivalent to the enthalpy change and is calculated as follows:

$$\text{Equation 11-8: } \Delta \dot{Q} = m_{\text{osol}} h_{\text{sol}, T_{\text{osep}}, P_{\text{osep}}} + m_{\text{bsol}} h_{\text{sol}, T_{\text{bsep}}, P_{\text{bsep}}} - m_{\text{sol}} h_{\text{sol}, 308\text{K}, 9.5\text{barA}}$$

The enthalpy values are obtained from ASHRAE [10].

HXC2: Cooling of solvent from 308K to 293K (refrigeration unit)

The cooling required is equivalent to the enthalpy change and is calculated as follows:

$$\text{Equation 11-9: } \Delta \dot{Q} = m_{\text{sol}} (h_{\text{sol}, 308\text{K}, 9.5\text{barA}} - h_{\text{sol}, 293\text{K}, 9.5\text{barA}})$$

The enthalpy values are obtained from ASHRAE [10].

HXC3: Supercooling solvent from 293K to 283K (refrigeration unit)

The cooling required is equivalent to the enthalpy change and is calculated as follows:

$$\text{Equation 11-10: } \Delta \dot{Q} = m_{\text{sol}} (h_{\text{sol}, 293\text{K}, 9.5\text{barA}} - h_{\text{sol}, 283\text{K}, 9.5\text{barA}})$$

The enthalpy values are obtained from ASHRAE [10].

11.4.3.2 ENERGY CALCULATIONS

Energy calculations for one step decompression with solvent to feed ratio of 60

Isentropic solvent pumping from 9.5 barA to column pressure

Mass flow rate	54	g
Inlet enthalpy	548.3	J/g
Inlet entropy	4.333	J/(g.K)
Entropy at 280K, 130 barA	4.280	J/(g.K)
Entropy at 290K, 130 barA	4.366	J/(g.K)
Outlet entropy	4.333	J/(g.K)
Temperature	286.2	K
Outlet enthalpy	562.0	J/g
Work required	743	J/g feed

Pump energy to compress was feed

Mass flow rate	0.9	g/m ³
Density	808000	g/m ³
Column Pressure	13000000	Pa
Atmospheric Pressure	101000	Pa
Work required:	14.4	J/g feed

HXH1: Solvent heating from pump outlet temperature to column temperature

Mass flow rate	54	g
Enthalpy at pump outlet	562.0	J/g
Enthalpy at column entry	866.9	J/g
Heating energy required	16462	J/g feed

HXH2: Heating of overheads product from column to separator conditions

Overheads solvent mass flow rate	53.71	g
Solvent enthalpy - column conditions	866.9	J/g
Solvent enthalpy - overheads separator conditions	1142	J/g
Overheads wax mass flow rate	0.225	g
Integral evaluated	26.5	J/g
Heating energy required	14801	J/g feed

HXH3: Heating of bottoms product from column to separator conditions

Bottoms solvent flow rate	0.2893	g
Solvent enthalpy - column conditions	866.9	J/g
Solvent enthalpy - bottoms separator conditions	1142	J/g
Bottoms wax mass flow rate	0.675	g
Integral evaluated	24.9	J/g
Heating energy required	96	J/g feed

HXH4: Heating of wax to column temperature

Mass flow rate	1	g
Enthalpy from 293K to Tcol	409.6	J/g
Heating required	409.6	J/g feed

HXC1: Cooling of solvent from separator temperature to 308K

Overheads solvent flow rate	53.71	g
Overheads solvent separator exit enthalpy	1142	J/g
Bottoms solvent flow rate	0.2893	g
Bottoms solvent separator exit enthalpy	1142	J/g
Solvent recycle flow rate	54	g
HX outlet enthalpy	944.9	J/g
Cooling required	10663	J/g feed

HXC2: Cooling of solvent from 308K to 293K

Solvent flow rate	54	g
HX inlet enthalpy	944.9	J/g
HX outlet enthalpy	574.3	J/g
Cooling required	20010	J/g feed

HXC3: Supercooling from 293K to 283K

Solvent flow rate	54	g
HX inlet enthalpy	574.3	J/g
HX outlet enthalpy	548.3	J/g
Cooling required	1408	J/g feed

Summary

Feed pump	14	0.02%
Solvent pump	743	1.15%
HXH1	16462	25.48%
HXH2	14801	22.91%
HXH3	96	0.15%
HXH4	409.6	0.63%
HXC1	10663	16.50%
HXC2	20010	30.97%
HXC3	1408	2.18%
TOTAL	64608	J/g feed
	64.6	kJ/g feed

Energy calculations for one step decompression with solvent to feed ratio of 30

Pump energy to compress was feed

Mass flow rate	0.9	g/m ³
Density	808000	g/m ³
Column Pressure	13000000	Pa
Atmospheric Pressure	101000	Pa
<hr/>		
Work required:	14.4	J/g feed

Isentropic solvent pumping from 9.5 barA to column pressure

Mass flow rate	27	g
Inlet enthalpy	548.3	J/g
Inlet entropy	4.333	J/(g.K)
Entropy at 280K, 130 barA	4.280	J/(g.K)
Entropy at 290K, 130 barA	4.366	J/(g.K)
Outlet entropy	4.333	J/(g.K)
Temperature	286.2	K
Outlet enthalpy	562.0	J/g
<hr/>		
Work required	372	J/g feed

HXH1: Solvent heating from pump outlet temperature to column temperature

Mass flow rate	27	g
Enthalpy at pump outlet	562.0	J/g
Enthalpy at column entry	866.9	J/g
<hr/>		
Heating energy required	8231	J/g feed

HXH2: Heating of overheads product from column to separator conditions

Overheads solvent mass flow rate	26.70	g
Solvent enthalpy - column conditions	866.9	J/g
Solvent enthalpy - overheads separator conditions	1142	J/g
Overheads wax mass flow rate	0.225	g
Integral evaluated	26.4	J/g
<hr/>		
Heating energy required	7360	J/g feed

HXH3: Heating of bottoms product from column to separator conditions

Bottoms solvent flow rate	0.2989	g
Solvent enthalpy - column conditions	866.9	J/g
Solvent enthalpy - bottoms separator conditions	1142	J/g
Bottoms wax mass flow rate	0.6975	g
Integral evaluated	25.1	J/g
<hr/>		
Heating energy required	100	J/g feed

HXH4: Heating of wax to column temperature

Mass flow rate	1	g
Enthalpy from 293K to Tcol	409.6	J/g
<hr/>		
Heating required	409.6	J/g feed

HXC1: Cooling of solvent from separator temperature to 308K

Overheads solvent flow rate	26.71	g
Overheads solvent separator exit enthalpy	1142	J/g
Bottoms solvent flow rate	0.2893	g
Bottoms solvent separator exit enthalpy	1142	J/g
Solvent recycle flow rate	27	g
HX outlet enthalpy	944.9	J/g
<hr/>		
Cooling required	5331	J/g feed

HXC2: Cooling of solvent from 308K to 293K

Solvent flow rate	27	g
HX inlet enthalpy	944.9	J/g
HX outlet enthalpy	574.3	J/g
<hr/>		
Cooling required	10005	J/g feed

HXC3: Supercooling from 293K to 283K

Solvent flow rate	27	g
HX inlet enthalpy	574.3	J/g
HX outlet enthalpy	548.3	J/g
<hr/>		
Cooling required	704	J/g feed

Summary

Feed pump	14	0.04%
Solvent pump	372	1.14%
HXH1	8231	25.31%
HXH2	7360	22.63%
HXH3	100	0.31%
HXH4	409.6	1.26%
HXC1	5331	16.39%
HXC2	10005	30.76%
HXC3	704	2.16%
<hr/>		
TOTAL	32527	J/g feed
	32.5	kJ/g feed

Energy calculations for two step decompression with solvent to feed ratio of 60**Pump energy to compress was feed**

Mass flow rate	0.90	g/m ³
Density	808000	g/m ³
Column Pressure	13000000	Pa
Atmospheric Pressure	101000	Pa
Work required:	14.4	J/g feed

Isentropic solvent pumping from 35 barA to column pressure

Mass flow rate	54.00	g
Inlet enthalpy	708.5	J/g
Outlet enthalpy	730.4	J/g
Work required	1181	J/g feed

Isentropic compression from 2 to 8.4 barA (Compressor I)

Mass flow rate	0.31	
Inlet enthalpy	969	
Outlet enthalpy	1044	
Work required	23.6	J/g feed

Isentropic compression from 8.4 to 35 barA (Compressor II)

Mass flow rate	0.31	
Inlet enthalpy	1009	
Outlet enthalpy	1092	
Work required	26.2	J/g feed

HXH1: Solvent heating from pump outlet temperature to column temperature

Mass flow rate	54.00	g
Enthalpy at pump outlet	730.4	J/g
Enthalpy at column entry	866.9	J/g
Heating energy required	7371	J/g feed

HXH2: Heating of overheads product from column temperature and pressure to separator I temperature and pressure

Overheads solvent mass flow rate	53.71	g
Solvent enthalpy - column conditions	866.9	J/g
Solvent enthalpy - overheads separator conditions	1092	J/g
Overheads wax mass flow rate	0.23	g
Integral evaluated	26.5	J/g
Heating energy required	12123	J/g feed

HXH3: Heating of bottoms product from column temperature and pressure to separator III temperature and pressure

Bottoms solvent flow rate	0.2893	g
Solvent enthalpy - column conditions	866.9	J/g
Solvent enthalpy - bottoms separator conditions	1154	J/g
Bottoms wax mass flow rate	0.68	g
Integral evaluated	24.9	J/g
Heating energy required	100	J/g feed

HXH4: Heating of wax to column temperature

Mass flow rate	0.90	g
Enthalpy from 293K to Tcol	409.6	J/g
<hr/>		
Heating required	368.64	J/g feed

HXH5: Heating of bottoms product from separator I to separator II temperature and pressure

Bottoms solvent flow rate	0.0250	g
Solvent enthalpy - column conditions	1092.5	J/g
Solvent enthalpy - bottoms separator conditions	1154	J/g
Bottoms wax mass flow rate	0.23	g
Integral evaluated (Zero due to same temperature)	0.0	J/g
<hr/>		
Heating energy required	2	J/g feed

HXC1: Cooling and condensing of solvent from separator I temperature to 359.14K

Solvent flow rate	54.00	g
HX inlet enthalpy	1092.48	g
HX outlet enthalpy	788.5	J/g
<hr/>		
Cooling required	16415	J/g feed

HXC2: Intermediate cooling between compressors

Solvent flow rate	0.31	g
HX inlet enthalpy	1043.7	J/g
HX outlet enthalpy	1009.1	J/g
<hr/>		
Cooling required	11	J/g feed

HXC3: Supercooling from 359.14K to 339.15K

Solvent flow rate	54.00	g
HX inlet enthalpy	788.5	J/g
HX outlet enthalpy	708.5	J/g
<hr/>		
Cooling required	4319	J/g feed

HXC4: Precooling before compressor

Solvent flow rate	0.31	g
HX inlet enthalpy	1154.2	J/g
HX outlet enthalpy	968.5	J/g
<hr/>		
Cooling required	58	J/g feed

Summary

Feed pump	14	0.03%
Solvent pump	1181	2.81%
Compressor I	24	0.06%
Compressor II	26	0.06%
HXH1	7371	17.57%
HXH2	12123	28.90%
HXH3	100	0.24%
HXH4	368.64	0.88%
HXH5	2	0.00%
HXC1	16415	39.13%
HXC2	11	0.03%
HXC3	4319	10.29%
HXC4	58	0.14%
<hr/>		
TOTAL	41954	J/g feed
	42.0	kJ/g feed

Energy calculations for two step decompression with solvent to feed ratio of 30

Pump energy to compress was feed

Mass flow rate	0.90	g/m ³
Density	808000	g/m ³
Column Pressure	13000000	Pa
Atmospheric Pressure	101000	Pa
Work required:	14.4	J/g feed

Isentropic solvent pumping from 35 barA to column pressure

Mass flow rate	27.00	g
Inlet enthalpy	708.5	J/g
Outlet enthalpy	730.4	J/g
<hr/>		
Work required	590	J/g feed

Isentropic compression from 2 to 8.4 barA (Compressor I)

Mass flow rate	0.32	
Inlet enthalpy	969	
Outlet enthalpy	1044	
<hr/>		
Work required	24.1	J/g feed

Isentropic compression from 8.4 to 35 barA (Compressor II)

Mass flow rate	0.32	
Inlet enthalpy	1009	
Outlet enthalpy	1092	
<hr/>		
Work required	26.8	J/g feed

HXH1: Solvent heating from pump outlet temperature to column temperature

Mass flow rate	27.00	g
Enthalpy at pump outlet	730.4	J/g
Enthalpy at column entry	866.9	J/g
<hr/>		
Heating energy required	3685	J/g feed

HXH2: Heating of overheads product from column temperature and pressure to separator I temperature and pressure

Overheads solvent mass flow rate	26.70	g
Solvent enthalpy - column conditions	866.9	J/g
Solvent enthalpy - overheads separator conditions	1092	J/g
Overheads wax mass flow rate	0.20	g
Integral evaluated	26.4	J/g
<hr/>		
Heating energy required	6029	J/g feed

HXH3: Heating of bottoms product from column temperature and pressure to separator III temperature and pressure

Bottoms solvent flow rate	0.2989	g
Solvent enthalpy - column conditions	866.9	J/g
Solvent enthalpy - bottoms separator conditions	1154	J/g
Bottoms wax mass flow rate	0.70	g
Integral evaluated	25.0	J/g
<hr/>		
Heating energy required	103	J/g feed

HXH4: Heating of wax to column temperature

Mass flow rate	0.90	g
Enthalpy from 293K to Tcol	409.6	J/g
<hr/>		
Heating required	368.64	J/g feed

HXC1: Cooling and condensing of solvent from separator I temperature to 359.14K

Solvent flow rate	27.00	g
HX inlet enthalpy	1092.48	g
HX outlet enthalpy	788.5	J/g
<hr/>		
Cooling required	8207	J/g feed

HXH5: Heating of bottoms product from separator I to separator II temperature and pressure

Bottoms solvent flow rate	0.0225	g
Solvent enthalpy - column conditions	1092.5	J/g
Solvent enthalpy - bottoms separator conditions	1154	J/g
Bottoms wax mass flow rate	0.20	g
Integral evaluated (Zero due to same temperature)	0.0	J/g
<hr/>		
Heating energy required	1	J/g feed

HXC2: Intermediate cooling between compressors

Solvent flow rate	0.32	g
HX inlet enthalpy	1043.7	J/g
HX outlet enthalpy	1009.1	J/g
<hr/>		
Cooling required	11	J/g feed

HXC3: Supercooling from 359.14K to 339.15K

Solvent flow rate	27.00	g
HX inlet enthalpy	788.5	J/g
HX outlet enthalpy	708.5	J/g
<hr/>		
Cooling required	2160	J/g feed

HXC4: Precooling before compressor

Solvent flow rate	0.32	g
HX inlet enthalpy	1154.2	J/g
HX outlet enthalpy	968.5	J/g
<hr/>		
Cooling required	60	J/g feed

Summary

Feed pump	14	0.07%
Solvent pump	590	2.78%
Compressor I	24	0.11%
Compressor II	27	0.13%
HXH1	3685	17.37%
HXH2	6029	28.41%
HXH3	103	0.49%
HXH4	369	1.74%
HXH5	1	0.01%
HXC1	8207	38.68%
HXC2	11	0.05%
HXC3	2160	10.18%
HXC4	60	0.28%
<hr/>		
TOTAL	21222	J/g feed
	21.2	kJ/g feed

11.4.3.3 ENERGY INTEGRATION CALCULATIONS

One step decompression

Table 11-31: Stream data for energy integration via Pinch analysis

Stream	Type	Temperature			Interval temperatures		Energy	Heat
		Inlet	Outlet	Difference	Inlet	Outlet	Required	Capacity
		K	K	K	K	K	J	J/K
HXH1	Cold	286.20	393.15	106.95	291.20	398.15	8231	76.96
HXH2	Cold	393.15	403.15	10.00	398.15	408.15	7360	736.04
HXH3	Cold	393.15	403.15	10.00	398.15	408.15	100	9.98
HXH4	Cold	298.15	393.15	95.00	303.15	398.15	410	4.31
HXC1	Hot	403.15	308.15	95.00	398.15	303.15	5331	56.12
HXC2	Hot	308.15	293.15	15.00	303.15	288.15	10005	667.01
HXC3	Hot	293.15	283.15	10.00	288.15	278.15	704	70.38

Table 11-31 continued

	HXH1	HXH2	HXH3	HXH4	HXC1	HXC2	HXC3
408.15		Heating	Heating				
398.15	Heating	Heating	Heating				
303.15	Heating			Heating	Cooling		
291.20	Heating			Heating	Cooling	Cooling	
288.15						Cooling	Cooling
278.15						Cooling	Cooling

Table 11-31 continued

Temperature	Temperature Change	CP Change	Enthalpy Change	Sum of Energy	Corrected
(K)	(K)	(J/K)	(J)	(J)	(J)
408.15				0	9850.09
	10	-746.03	-7460.27		
398.15				-7460.27	2389.8
	95	-25.16	-2389.82		
303.15				-9850.09	0
	11.95	590.05	7049.80		
291.2				-2800.29	7049.8
	3.05	667.01	2035.85		
288.15				-764.441	9085.6
	10	70.38	703.76		
278.15				-60.69	9789.4

One step decompression

Table 11-32: Stream data for energy integration via Pinch analysis

Stream	Type	Temperature			Interval temperatures		Energy	Heat
		Inlet	Outlet	Difference	Inlet	Outlet	Required	Capacity
		K	K	K	K	K	J	J/K
HXH1	Cold	349.33	393.15	43.82	354.33	398.15	3685	84.1
HXH2	Cold	393.15	403.15	10.00	398.15	408.15	6029	602.9
HXH3	Cold	393.15	403.15	10.00	398.15	408.15	103	10.3
HXH4	Cold	298.15	393.15	95.00	303.15	398.15	369	3.9
HXH5	Cold	403.15	403.15	0.00	408.15	408.15	1	
HXC1	Hot	403.15	359.14	44.01	398.15	354.14	8207	186.5
HXC2	Hot	361.21	338.83	22.39	356.21	333.83	11	0.5
HXC3	Hot	359.14	339.14	20.00	354.14	334.14	2160	108.0
HXC4	Hot	403.15	308.15	95.00	398.15	303.15	60	0.6

Table 11-32 continued

	HXH1	HXH2	HXH3	HXH4	HXH5	HXC1	HXC2	HXC3	HXC4
408.15		Heating	Heating						
398.15	Heating	Heating	Heating	Heating		Cooling			Cooling
356.21	Heating			Heating		Cooling	Cooling		Cooling
354.33	Heating			Heating		Cooling	Cooling		Cooling
354.14				Heating		Cooling	Cooling	Cooling	Cooling
334.14				Heating			Cooling	Cooling	Cooling
333.83				Heating			Cooling		Cooling
303.15				Heating					Cooling

Table 11-32 continued

Temperature	Temperature Change	CP Change	Enthalpy Change	Sum of Energy	Corrected
(K)	(K)	(J/K)	(J)	(J)	(J)
408.15				0	6132.5
	10	-613.25	-6132.52		
398.15				-6132.52	0
	41.94	99.13	4156.97		
356.21				-1975.55	4157.0
	1.89	99.63	187.87		
354.33				-1787.68	4344.8
	0.19	291.07	55.74		
354.14				-1731.94	4400.6
	20	105.22	2104.40		
334.14				372.46	6505.0
	0.31	-2.76	-0.85		
333.83				371.61	6504.1
	30.68	-3.25	-99.77		
303.15					

11.4.3.4 UTILITY COSTS

Table 11-33: Utility costs [11]

Utility	Cost (R/GJ)
Saturated steam (160°C)	26.29
Electricity	139.33
Cooling Water	1.33
Refrigeration (5°C)	165.86

Table 11-34: Utility costs for one stage decompression processes

	Process	Solvent to feed ratio = 60	Solvent to feed ratio = 30	Solvent to feed ratio = 60 with energy integration	Solvent to feed ratio = 30 with energy integration
Energy cost	R/ton	4507	4213	2260	2113
Energy required (J/g feed)	Steam	4507	21107	16101	10770
	Electricity	758	758	386	386
	Cooling W	10663	0	5331	0
	Refrig	21418	21418	10709	10709
Costs (R/ton)	Steam	835	555	423	283
	Electricity	106	106	54	54
	Cooling W	14	-	7	-
	Refrig	3552	3552	1776	1776

Table 11-35: Utility costs for two stage decompression processes

	Process	Solvent to feed ratio = 60	Solvent to feed ratio = 30	Solvent to feed ratio = 60 with energy integration	Solvent to feed ratio = 30 with energy integration
Energy cost	R/ton	R/ton	726	510	373
Energy required (J/g feed)	Steam	Steam	19964	12593	10187
	Electricity	Electricity	1245	1245	655
	Cooling W	Cooling W	20803	4388	10436
	Refrig	Refrig	-	-	-
Costs (R/ton)	Steam	Steam	525	331	268
	Electricity	Electricity	173	173	91
	Cooling W	Cooling W	28	6	14
	Refrig	Refrig	-	-	-

11.5 NOMENCLATURE

Symbol	Description
$C_{p, \text{liquid, wax}}$	Specific heat capacity of wax liquid in solid phase (J/g.K)
$C_{p, \text{solid, wax}}$	Specific heat capacity of wax feed in solid phase (J/g.K)
C_{pbwax}	Specific heat capacity of bottoms product stream wax (J/g.K)
C_{powax}	Specific heat capacity of overheads product stream wax (J/g.K)
Δh_{fus}	Specific enthalpy of fusion of feed wax (J/g)
$\Delta h_{mix, T_{osep}, P_{osep}}$	Specific enthalpy of mixing at overheads separator conditions (J/g)
$\Delta h_{mix, T_{col}, P_{col}}$	Specific enthalpy of mixing at column conditions (J/g)
$h_{sol, 283K, 9.5barA}$	Specific enthalpy of solvent at 283K and 9.5barA (J/g)
$h_{sol, 293K, 9.5barA}$	Specific enthalpy of solvent at 293K and 9.5barA (J/g)
$h_{sol, 308K, 9.5barA}$	Specific enthalpy of solvent at 308K and 9.5barA (J/g)
$h_{sol, T_{bsep}, P_{bsep}}$	Specific enthalpy of solvent at bottoms separator conditions (J/g)
$h_{sol, T_{col}, P_{col}}$	Specific enthalpy of solvent at column conditions (J/g)
$h_{sol, T_{osep}, P_{osep}}$	Specific enthalpy of solvent at overheads separator conditions (J/g)
$h_{sol, T_{pump}, P_{col}}$	Specific enthalpy of solvent at solvent pump outlet (J/g)
m_{bsol}	Mass flow rate of solvent from bottoms separator (g/s)
m_{btms}	Mass flow rate of bottoms product stream (g/s)
m_{feed}	Mass flow rate of wax feed (g/s)
m_{osol}	Mass flow rate of solvent from overheads separator (g/s)

m_{ovhds}	Mass flow rate of overheads product stream (g/s)
m_{sol}	Mass flow rate of solvent entering the column (g/s)
P_{atm}	Atmospheric pressure (Pa)
P_{col}	Column pressure (Pa)
$\Delta \dot{Q}$	Rate of heat required (J/s)
T_{bsep}	Bottoms separator temperature (K)
T_{col}	Column temperature (K)
T_{osep}	Overheads separator temperature (K)
T_{m}	Melting temperature of feed wax (K)
\dot{W}	Work rate (J/g)
ρ_{feed}	Density of wax feed (g/m^3)

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*“The world is round and the place that may seem like the end
may also be only the beginning.”*

Ivy Baker Priest