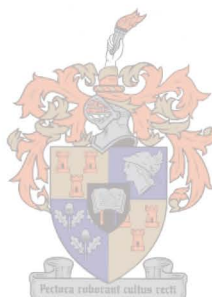


# THE SEPARATION OF ETHANOL-HEXANE MIXTURES BY PERVAPORATION

by

**J. Ferreira**



Thesis represented in partial fulfilment of the requirements for the degree of

**Master of Science (Polymer Science)**

at

**the University of Stellenbosch**

Study Leader:

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## DECLARATION

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

Date: ..... 1990 - 02 - 20 .....

I shall be telling this with a sigh  
Somewhere ages and ages hence:  
Two roads diverged in a wood, and I -  
I took the one less travelled by,  
And that has made all the difference.

From: "The Road Not Taken" by Robert Frost

## ABSTRACT

Pervaporation experiments, using polyvinyl alcohol (PVA) and modified PVA membranes cast on permeable polyether sulfone substrates, were performed with ethanol-hexane mixtures. The modified PVA membranes comprised a specially synthesized and well defined series of poly(acrylic acid-co-vinyl alcohol-co-hydroxyethyl-acrylate) terpolymers.

Experimental variables were investigated. Variation of membrane thickness showed that at least two polymer layers were necessary. The effect of changing the binary feed ratio was that selectivity increased with increasing ethanol content. Pretreatment proved to be effective in terms of both flux and selectivity.

Increasing hydrophilicity in the chemical structure of the membrane caused a decrease in the selectivity for ethanol, i.e. GFT-standard (3 300); GFT-wasserreich (270); Gantrez AN 119 (15); best synthesized terpolymer (2 200). These values were measured with a 5% ethanol mixture.

## UITTREKSEL

Pervaporasie-eksperimente, poli(viniel alkohol) (PVA) en gewysigde PVA-membrane gegiet op deurlaatbare poli-eter sulfoon substrate, is uitgevoer met etanol-heksaan-mengsels. Die gewysigde PVA-membrane behels 'n spesiaal gesintetiseerde en goed gedefinieerde reeks van poli(akrielsuur-ko-viniel alkohol-ko-hidroksietiel akrilaat) terpolimere.

Eksperimentele veranderlikes is ondersoek. Die variasie van membraandikte het getoon dat twee lae polimere voldoende is. Die invloed van veranderinge in die binêre voerverhouding was dat die selektiwiteit toeneem met 'n toenemende etanol-inhoud. Die voorbehandeling was effektief ten opsigte van die vloed en selektiwiteit.

Toenemende hidrofilisiteit in die chemiese struktuur van die membraan het 'n afname veroorsaak in die selektiwiteit ten opsigte van etanol byvoorbeeld GFT Standard (3 300); GFT-wasserreich (270); Gantrez AN 119 (15); die beste gesintetiseerde polimeer (2 200).

Dié waardes is verkry deur gebruik te maak van 'n 5%-etanolmengsel.

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*DEO GRATIA*

Dedicated to Mrs Laura du Plessis.



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# CHAPTER 1

## INTRODUCTION

### 1.1 GENERAL REVIEW

Pervaporation, a process which consists essentially of using a permselective membrane to separate compounds in a liquid mixture, was discovered in 1917<sup>(1)</sup>. Initially, little research was done on this technique. The earliest work on fractionating liquid mixtures by pervaporation techniques was conducted in the mid-1950s<sup>(2,3)</sup>. This process is potentially useful in all fields in which distillation techniques are difficult, such as fractionation of close-boiling components, azeotropic mixtures, and isomeric mixtures<sup>(3-9)</sup>. Other applications include the separation of heat-sensitive mixtures, the concentration of fruit juices<sup>(10)</sup>, the elimination of traces of impurities and the removal of water from an esterification reaction as soon as it is formed<sup>(11)</sup>.

During the past ten years pervaporation has developed from laboratory research into a large-scale industrial operation. Although today's industrial plants are concerned with the removal of water from azeotropes, dehydration of organic solvents or solvent mixtures, research and development has widened into other areas. The removal of high- and low-boiling organic substances from aqueous streams, and the separation of special compounds such as benzene from hydrocarbon mixtures, are some of the targets for the development of a new generation of membranes<sup>(12)</sup>.

While a considerable amount of research has concentrated on the separation of water/alcohol and water/hydrocarbon mixtures by the pervaporation process, little has been directed towards the separation of alcohol/hydrocarbon mixtures. Numerous papers can be consulted for a more comprehensive survey of the field<sup>(13-18)</sup>.

### 1.2 SCOPE AND OBJECTIVES

From the foregoing it can be seen that there is a need for research in the area of organic/organic separations by pervaporation. The research described in this thesis was aimed at increasing knowledge in this field. It could also be the first step towards solving an industrial problem of separating oxygenates from an organic solvent.

Since the beginning of the 1980s organic/organic separation received more attention<sup>(2,3,6,8,9,11,15-17,19-34)</sup>. However, most of the work has been aimed at the separation of azeotropes and isomers.

The purpose of this research was, therefore, to synthesize a polymer for making a membrane with which to study the separation of alcohol from the organic solvent, hexane, by pervaporation.

The objectives of this study may be specified as the following:

- (a) The design and construction of a pervaporation test apparatus.

- (b) The synthesis of polymers consisting of acrylic acid, vinyl acetate and hydroxyethyl acrylate with various monomer ratios.
- (c) Investigation of different degrees of hydrolysis and different degrees of hydrophilicity.
- (d) Characterization of synthesized polymers by means of NMR spectroscopy techniques.
- (e) Making of thin-film-composite membranes from synthesized polymers.
- (f) Testing these membranes in the pervaporation test apparatus and evaluation of the membranes and the process on the basis of GC results.



## CHAPTER 2

### HISTORY AND THEORETICAL BACKGROUND

#### 2.1 PERVAPORATION

##### 2.1.1 INTRODUCTION

In pervaporation, which comprises liquid-vapour transport, the membrane is brought into contact with the liquid mixture at atmospheric pressure, and the liquids permeate (absorb) into the membrane to vaporize on the vacuum side (downstream) of the membrane. Downstream vaporization is achieved by maintaining a low vapour pressure through a vacuum pump with or without an inert gas sweeper<sup>(35)</sup>.

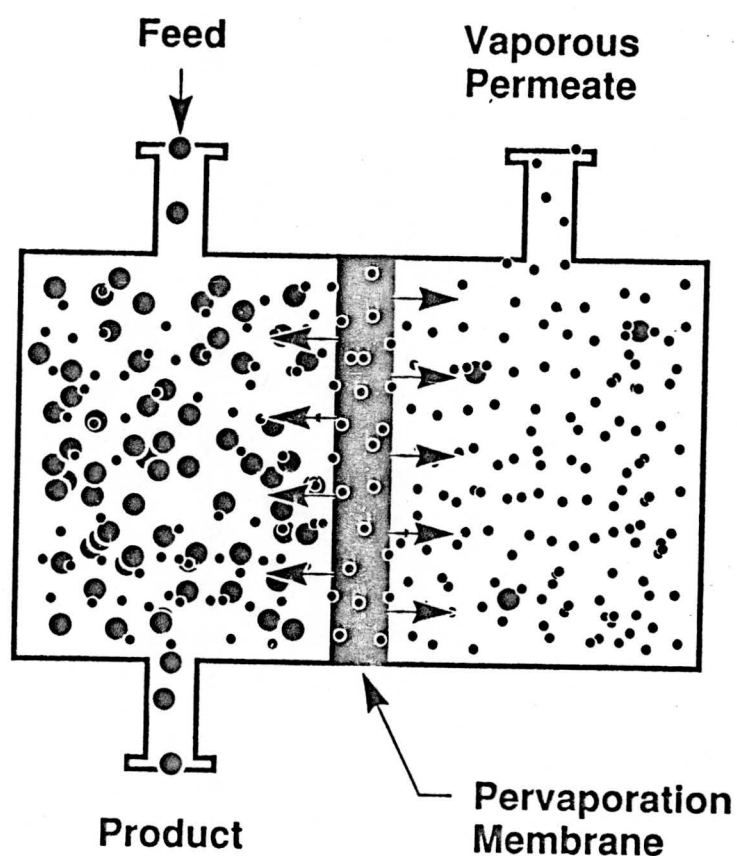


FIGURE 2.1: A SCHEMATIC REPRESENTATION OF THE PROCESS OF PERVARPORATION

## 2.2 HISTORY OF THE PROCESS

In the course of some experiments on dialysis Kober and Eberlein<sup>(1)</sup> discovered, in 1917, that water vapour passed through a collodion membrane bag suspended in still or moving air. When toluene was added to the water most of the toluene remained after the water had completely evaporated. They named this phenomenon "pervaporation". The earliest work on fractionating liquid mixtures by pervaporation techniques was developed in the mid-1950s<sup>(2,3)</sup>.

Interest was aroused in many quarters, and in the beginning of the 1960s several articles were published, of which most were directed towards the mechanism involved in the separation<sup>(36,37,38)</sup>. At Ionics Inc. work began on a small scale on the commercialization of the process. However, activity declined again, and very little happened in this area until the middle of the 1970s when the energy crisis changed the situation with respect to traditional separation methods, and the way was opened up for membrane technology<sup>(39)</sup>.

### 2.2.1 MEMBRANE MATERIALS

A literature survey done in 1976<sup>(40)</sup> showed that in the previous twenty years, many attempts had been made to separate mixtures by pervaporation. Mainly commercial membranes based on homo polymers were used<sup>(41,42)</sup>.

In a later publication in 1980, Rautenbach<sup>(43)</sup> compiled an extensive list to summarize the organic binary mixtures which had been separated by pervaporation (see Table 2.1). Rautenbach's work is of special interest to this study, namely, the separation of organic/organic mixtures.

TABLE 2.1: SEPARATION BY PERVAPORATION ON A LABORATORY SCALE<sup>(43)</sup>

Composition of Mixture	Membrane	Ref.
<b>Water:</b>		
water/alcohol		
methanol, ethanol, n, i-propanol	cellophane	44
ethanol, i-propanol	cellulose acetate	40
ethanol, n-propanol	poly(vinyl alcohol)	44
n, i-propanol, sec/tert-butanol	PTFE-PVP	40
water/hydrazine	cellophane	45
water/dimethylhydrazine	cellulose acetate	45
water/pyridine	cellophane, irradiated polyethylene	45
water/acetone	PTFE-PVP	40
	polypropylene	46
<b>Chloroform:</b>		
1. chloroform/paraffin (cyclo-, hexane, pentane)	PTFE-PVP	40
2. chloroform/naphthene (cyclohexane)	PTFE-PVP	40
3. chloroform/alcohol (ethanol)	PTFE-PVP	40
4. chloroform/aromatic hydrocarbon (benzene)	PTFE-PVP	40
<b>Mixtures of hydrocarbons:</b>		
1. mixture of isomers o, m, p-xylene	polyethylene PVDF	45 47
2. aromatic hydrocarbon/alcohol benzene/methanol, ethanol, propanol	polyethylene cellulose acetate	45 40
<b>Toluene/n-butanol</b>		
3. aromatic hydrocarbon/paraffin benzene/n-hexane toluene/n-heptane	polyethylene polyethylene	45, 48 49
4. aromatic hydrocarbon/naphthene benzene/cyclohexane toluene/cyclohexane	polyethylene polypropylene polyethylene	45, 48, 50 45 49
5. mixture of paraffins n-heptane/i-octane	cellulose acetate, polyethylene cellulose acetate, butyrate	45 45
n-hexane/n-heptane	polyethylene polyethylene	51 45
<b>Alcohol:</b>		
1. alcohol/paraffin ethanol/hexane	PTFE-PVP	40
2. alcohol/naphthene ethanol/cyclohexane	PTFE-PVP	40
3. alcohol/ketone methanol/acetone	PTFE-PVP	40

PTFE-PVP: poly (tetrafluoroethylene)-N-vinylpyrrolidone

PVDF: poly (vinylidene fluoride) modified by including Werner complexes

In 1983, Larchet *et al.*<sup>(21)</sup> studied the separation of benzene-n-heptane mixtures by pervaporation with elastomeric membranes.

In the same year Mulder<sup>(52)</sup> did a study on ethanol-water separations. As background to his study, he made a summary of the results of work on the separation of similar systems published in the literature.

Neel *et al.*<sup>(53)</sup> were interested in azeotrope separations. They studied the basic aspects of pervaporation and summarized the data on the separation of some typical positive azeotropes.

Tusel *et al.*<sup>(54)</sup> were more interested in the dehydration of binary mixtures. They studied systems in the chemical industry. Table 2.2 shows the binary mixtures which can be dehydrated by pervaporation.

**TABLE 2.2: ORGANIC COMPOUNDS MIXED WITH WATER WHICH CAN BE DEHYDRATED BY PERVAPORATION<sup>(54)</sup>**

Methanol	Ethyl-propylether	Butyric acid-methylester
Ethanol	Dioxane-1,4	Butyric acid-isobutylester
n-Propanol	Furfural	Tetrahydrofuran
iso-Propanol	Methylfurfural	Chloracetone
n-Butanol	Acetone	Trichloroethylene
iso-Butanol	Butanone	Tetrachloroethane
tert-Butanol	Methyl-ethyl-ketone	Chloroform
n-Amylol	Cyclohexanone	Dichloropropane
3-Methyl-butanol-1	2-Methylpentanone	Propionic acid-butylester
2-Methyl-butanol-1	Pentanone-2	Propionic acid-isobutylester
tert-Amylol	Pentanone-3	Propionic acid-isoamylester
Allylalcohol	Acetylacetone	N,N, Dimethylformamide
Cyclohexanol	Acetylacetone	N,N, Dimethylacetamide
Furfurylalcohol	Dimethylglyoxal	Ethanolamine
Hexanol	Diacetone-alcohol	Ethylendiamine
Glycol	Glycodiethylether	tert.-Amylamine
Propanediol-1,2	Ethylacetate	Diethylamin
Propanetriol-1,3	n-Amylacetate	Dichloropropane
Butanediol-1,4	n-Butylacetate	Isopropylamine
Pentanol-2	sec.-Butylacetate	Piperidine
Hexanediol-1,6	iso-Propylacetate	Triethanolamine
Glycerol	iso-Amylacetate	Triethylamine
Diethyleneglycol	Ethylformiate	Aniline
Tetraethyleneglycol	Benzylformiate	Hexylamine
Butanetriol	Butylformiate	Dibutylamine
Diethylether	Butyric acid-ethylester	Benzene
Diisopropylether	Butyric acid-isoamylester	Jet fuel
Dipropylether	Ethyl-tert.-butylether	

In 1986, Frennesson *et al.*<sup>(39)</sup> wrote a literature review on pervaporation and its use in ethanol upgrading. Mulder *et al.*<sup>(55)</sup> who carried out a detailed investigation in 1982 are cited in the review.

Frennesson showed that membranes with different structures were used. These structures ranged from homogeneous membranes to asymmetric membranes to composite membranes.

In the same year Laatikainen *et al.*<sup>(26)</sup> looked specifically at the separation of methanol-ethanol and ethanol-n-heptane mixtures by pervaporation. In their pervaporation experiments the separation at

different feed compositions was studied, using cellulose acetate and poly(hexamethylene adipamide) membranes. The selectivity of both membranes were found to be quite high.

In 1987 Mc Candless *et al.*<sup>(27)</sup> tested twelve polymer films, most of which were commercial membranes from Du Pont, for pervaporation.

The ethanol-water solution received attention once more in 1988. Inagaki *et al.*<sup>(56)</sup> introduced a new membrane based on plasma polymerization. The complex chemical structure of these plasma films showed that chemistry involved in the fabrication of the membranes is becoming increasingly sophisticated.

Acharya *et al.*<sup>(57)</sup> concentrated on the benzene-cyclohexane separation by pervaporation. In his article on the comparison of perstraction and pervaporation, a literature survey was included. Some of the pertinent results reported in the literature are listed in Table 2.3. (Numerical values are not rounded, but quoted from literature.)

Table 2.3 attempts to summarize all the available literature on all previously mentioned separations and membranes. The table is thorough, but not exhaustive and suffers from the need to be concise with regards to the findings of individual research papers.

The two factors which were used to evaluate the characteristic data of a pervaporation run, are:

- (i) The pervaporation flux,  $\psi$ , expressed in  $\text{kg/h.m}^2$  of membrane.
- (ii) The selectivity factor,  $\alpha$ , defined as

$$\alpha_{A/B} = \frac{Y_A/Y_B}{X_A/X_B}$$

where  $X_A$ ,  $X_B$ ,  $Y_A$  and  $Y_B$  denote the volume fraction of component A and B in the feed solution (X) and in the pervaporate (Y), respectively. A is the species which is preferentially pervaporated.

TABLE 2.3: SUMMARY OF THE LITERATURE ON PERVAPORATION

Feed Mixture		Pervaporation					Remarks	Ref.
Compounds	Compo- sition (WT% of A)	Temp (°C)	$\alpha$ A/B	$\psi$ (kg/hm <sup>2</sup> )	Membrane	Thick- ness ( m)		
A / B								
<b>Organic/Organic Separations:</b>								
Benzene/Methanol	60,5	60	7,2	2,1	Polyethylene	-	Azeotrope separation	2
Methanol/Benzene	39,5	60	5,1	3,1	CA	-	Azeotrope separation	2
Benzene/Cyclohexane	50(v)	80	2,7	3	Organophosphored cellulose ester	-	Elastomeric membrane	58
	50(v)	80	5,2	3,8	Modified cellulose ester	-	Elastomeric membrane	59
Benzene/Methanol	60,5	42	11,9	0,3	Polyethylene	-	Azeotrope separation	7
Benzene/Cyclohexane	55	25	2,37	0,26	Polypropylene	40	Doubly oriented PP	60
	55	74	2,19	1,32	Polypropylene	40	Doubly oriented PP	60
	55	25	1,32	0,4	Polypropylene	40	Oriented PP	60
	55	74	1,25	1,57	Polypropylene	40	Oriented PP	60
	55	25	1,1	1,73	Polypropylene	20	Unoriented PP	60
	55	74	1,1	13,51	Polypropylene	20	Unoriented PP	60
	50	60	2,6	1,0	Polypropylene	40	Unoriented PP	60
	50	25	2,19	0,316	Polyisoprene	40	Oriented PI	60
	50	74	2,37	1,61	Polyisoprene	40	Oriented PI	60
	50	25	1,6	0,43	Polyethylene	25	Low-density PE	48
	50	45	1,5	2,54	Polyethylene	25	Low-density PE	48
Benzene/n-Hexane	50	25	1,63	0,43	Polyethylene	16	Low-density PE	48
	50	45	1,44	2,4	Polyethylene	16	Low-density PE	48
	50	25	1,5	0,7	Polyethylene	16	Low-density PE	48

	50	45	1,5	2,7	Polyethylene	16	Low-density PE	48
Benzene/n-Hexane	50	30	1,7	0,0045	Polyethylene-styrene	16	Graft copolymer	8
	50	30	1,6	1,0	Polyethylene-styrene	24	Graft copolymer	8
Benzene/n-Heptane	50	30	1,5	0,0027	Polyethylene-styrene	16	Graft polymer	8
Benzene/n-Heptane	50	2,5	1,4	1,6	Polyethylene	-	Azeotrope separation	61
Toluene/Heptane	60	30	1,4	0,27	Polyethylene	51	Azeotrope separation	49
Toluene/Cyclohexane	20(v)	25	2,2	-	Polyethylene	16	Azeotrope separation	62
	80(v)	25	1,2	-	Polyethylene	16	Azeotrope separation	62
Benzene/Cyclohexane	50(v)	56	5,45	0,093	PVDF + 3-methyl-sulfolane	16	23% 3-methylsulfolane added	62
	50	56	5,5	0,1	PVDF + 3-methyl-sulfolane	100	23% 3-methylsulfolane added	62
Toluene/Methyl-cyclohexane	50(v)	72	3,6	0,151	PVDF + 3-methyl-sulfolane	16	23% 3-methylsulfolane added	62
Benzene/Cyclohexane	50	60	11	0,32	Polyphosphonate + acetyl cellulose	20	Polymeric alloys; azeotrope separation	63
1,3 Butadiene/trans-2-Butene	0,8	-	4,9	0,02	Aromatic imide polymer	25	Azeotrope separation; positive azeotrope	66
1,3 Butadiene/Isobutene	0,38	22	3,1	0,3	1,3-Butadiene-acrylo-nitrile copolymer	20	Azeotrope separation; positive azeotrope	67
Benzene/Cyclohexane	50(v)	60	6,2	0,1	PVDF	16	5% DMSO added in feed	64
	50	78	10	0,8	Polyphosphonate + acetyl cellulose	100	50%:50%	65
Chloroform/n-Hexane	72	25	3,9	2,65	PVDF + PVP	12	Azeotrope separation; positive azeotrope	40
Ethanol/Cyclohexane	30,5	25	16,8	1,10	PTFE + PVP	-	Azeotrope separation; positive azeotrope	40
n-Butanol/Cyclohexane	10	25	23,5	0,30	PTFE + PVP	-	Azeotrope separation; positive azeotrope	40
Ethanol/Ethylacetate	31	25	2,4	0,95	PTFE + PVP	-	Azeotrope separation; positive azeotrope	40
Methanol/Acetone	12	25	2,9	0,65	PTFE + PVP	-	Azeotrope separation; positive azeotrope	40
Ethanol/Benzene	32,4	25	1,3	2,90	PTFE + PVP	-	Azeotrope separation; positive azeotrope	40
Chloroform/Ethanol	93	25	1,2	5,30	PTFE + PVP	-	Azeotrope separation; positive azeotrope	40

Ethanol/Hexane	21	25	8,0	1,10	PTFE + PVP	- Azeotrope separation; positive azeotrope	40
Propanol/Cyclohexane	20	25	24	0,50	PTFE + PVP	- Azeotrope separation; positive azeotrope	40
Isopropanol/Cyclohexane	33	25	13	0,4	PTFE + PVP	- Azeotrope separation; positive azeotrope	40
Methanol/Methyl acetate	18,7	25	2,9	1,50	PTFE + PVP	- Azeotrope separation; positive azeotrope	40
Methanol/Ethyl acetate	48,6	25	3,3	1,75	PTFE + PVP	- Azeotrope separation; positive azeotrope	40
Ethanol/Ethyl acetate	31,0	25	2,4	0,95	PTFE + PVP	- Azeotrope separation; positive azeotrope	40
Isopropanol/Ethyl acetate	23,0	25	3,3	0,50	PTFE + PVP	- Azeotrope separation; positive azeotrope	40
Methanol/Methyl acrylate	54,0	25	1,9	1,50	PTFE + PVP	- Azeotrope separation; positive azeotrope	40
Ethanol/Ethyl acrylate	72,7	25	1,0	0,80	PTFE + PVP	- Azeotrope separation; positive azeotrope	40
Propanol/Diethyl ketone	57	25	1,5	0,55	PTFE + PVP	- Azeotrope separation; positive azeotrope	40
Ethanol/Triethylamine	51	25	5,9	0,25	PTFE + PVP	- Azeotrope separation; positive azeotrope	40
Methanol/Benzene	39,5	25	2,0	5,80	PTFE + PVP	- Azeotrope separation; positive azeotrope	40
Ethanol/Benzene	32,4	25	1,3	2,90	PTFE + PVP	- Azeotrope separation; positive azeotrope	40
Ethanol/Toluene	68,0	25	1,0	2,60	PTFE + PVP	- Azeotrope separation; positive azeotrope	40
Propanol/Benzene	32,4	25	1,3	2,90	PTFE + PVP	- Azeotrope separation; positive azeotrope	40
Chloroform/Acetone	80,0	25	1,8	0,85	PTFE + PVP	- Azeotrope separation; negative azeotrope	40
Chloroform/Methyl ethyl ketone	17,0	25	1,0	1,50	PTFE + PVP	- Azeotrope separation; negative azeotrope	40
Butanol/Pyridine	71,0	25	1,4	1,25	PTFE + PVP	- Azeotrope separation; negative azeotrope	40
Acetic Acid/Dioxane	77,0	25	2,7	0,27	PTFE + PVP	- Azeotrope separation; negative azeotrope	40
Acetic Acid/N,N-Dimethyl formamide	26,0	25	1,2	0,04	PTFE + PVP	- Azeotrope separation; negative azeotrope	40
Formic Acid/Pyridine	63,5	25	2,8	0,22	PTFE + PVP	- Azeotrope separation; negative azeotrope	40
Acetic Acid/Pyridine	35,0	25	1,0	0,09	PTFE + PVP	- Azeotrope separation; negative azeotrope	40
Propionic Acid/Pyridine	74,0	25	1,7	0,13	PTFE + PVP	- Azeotrope separation; negative azeotrope	40
Hexane/Heptane	77(m)	30	1,2	0,00013	Polyethylene	254 Elastomeric membrane	51



Benzene/Cyclohexane	75	50	1,42	6,12	Surlyn A	45	Membrane no 1652	68
Methanol/Hexane	8	25	0,0446	0,63	Polyphenylene oxide	-		69
Toluene/Benzene	-	25	1,10	0,075	SBR	100	Elastomeric membrane	70
Benzene/Cyclohexane	10	35	2,5	1,0	Polyethylene	30		43
	90	35	1,1	2,0	Polyethylene	30		43
	50	25		2,08	2-Hydroxy-3-(diethyl- amino) propyl methacrylate-styrene	40	Copolymer	71
	50	25		0,25	2-Hydroxyethyl methacrylate-methyl acrylate	30	Graft copolymer	72
Xylene/Isoamyl alcohol	28(m)	43	30,98	0,07	Polyethylene	41		73
Benzene/Toluene	60	40	-	-	PETF	3,5		19
Benzene/Cyclohexane	40	-	8	-	Poly( $\gamma$ -methyl L-glutamate)	43		20
o-Xylene/p-Xylene	50	20	1,30	-	CTP	-		28
	50	20	1,36	-	CAB 272	-		28
	50	20	1,34	-	CAB 171	-		28
Benzene/n-Heptane	50	60	5,7	1,73	NBR 83	100	Elastomeric membrane	21
	20	60	8,1	0,2	NBR 83	100	Elastomeric membrane	21
	50	60	5,8	-	NBR 61	343		21
	10	50	2,2	-	SBR 30	-		21
Benzene/Cyclohexane	55	77,8	19	0,024	CA	20		74
	55	77,8	12	1,0	PPN-I + CA	20	Alloy with 6,1% PPN	74
	55	77,8	40	1,21	PPN-I + CA	20	Alloy with 10,5% PPN	74
	55	77,8	13,3	0,048	PPOPh + CA	20	Alloy	74
Methanol/Hexane	6	25	40	0,5	PPN-III + CA	40		74
	6	25	0,0446	0,63	QPPO	40		74
	20	40	25	0,25	Nafion 125	40		74
Styrene/Ethylbenzene	50	25	1,7	<0,005	Nafion 125	40		74
	50	25	1,35	-	PPN-III + CA	40		74
	50	25	2,1	-	QPPO	40		74

Benzene/Cyclohexane	28	-	-	0,18	PPN-I + CA	20		74	
	40	50	1,2	35,6	Polyethylene	53		23	
	40	50	1,2	26,7	Polypropylene	39		23	
Benzene/Methanol	40	50	2,7	-	Polyethylene	53		23	
	40	50	6,0	-	Polypropylene	40		23	
	40	50	5,3	-	Polypropylene	39		23	
	50	-	-	5,2	PVA/PVP	-		75	
	50	-	-	5,2	PVP/PVA	-		75	
	50	-	-	0,6	PVA/PVP	-		75	
	50	-	-	0,6	PVP/PVA	-		75	
	50	-	-	1,2	PDMS	-		75	
	Benzene/n-Heptane	50	60	3,4	-	NBR 61	343		22
-		-	-	-	NBR	-		76	
1,3-Butadiene/ Isobutene	-	60	-	-	NBR	-		76	
Benzene/Cyclohexane	55	30	13,3	0,04	PSP + CA	20	Alloy		
	55	77,8	9,0	0,81	PSP + CA	20	Alloy	53	
	40	30	1,5	-	PE	36		77	
Methanol/Ethanol	86,7	25	6,9	$1,2 \times 10^{-6}$	CA	10		26	
	68,9	25	3,8	$1,3 \times 10^{-6}$	CA	10		26	
	50	25	4,5	$1,2 \times 10^{-6}$	CA	10		26	
	49,8	25	4,3	$2,0 \times 10^{-6}$	CA	10		26	
	231	25	4,5	$4,0 \times 10^{-6}$	CA	10		26	
	7,6	25	2,4	$6,9 \times 10^{-6}$	CA	10		26	
Ethanol/n-Heptane	88,4	25	76,6	$2,9 \times 10^{-6}$	CA	10		26	
	69,2	25	68,3	$3,6 \times 10^{-7}$	CA	10		26	
	50	25	80	-	CA	10		26	
	47,8	25	82,1	$4,3 \times 10^{-7}$	CA	10		26	
	27,4	25	78,5	$6,2 \times 10^{-7}$	CA	10		26	
	8,6	25	80,8	$9,5 \times 10^{-7}$	CA	10		26	
	Methanol/Ethanol	85,8	25	4,4	$8,1 \times 10^{-7}$	PA	10		26
		63,5	25	3,5	$1,1 \times 10^{-6}$	PA	10		26
50		25	2,2	$1,69 \times 10^{-6}$	PA	10		26	
49,6		25	3,2	$1,5 \times 10^{-6}$	PA	10		26	

	38,6	25	3,0	$1,8 \times 10^{-6}$	PA	10		26
	13,8	25	1,9	$2,8 \times 10^{-6}$	PA	10		26
Ethanol/n-Heptane	72,9	25	54,3	$2,5 \times 10^{-7}$	PA	10		26
	50	25	75	-	PA	10		26
	46,9	25	54,1	$3,4 \times 10^{-7}$	PA	10		26
	28,9	25	59,5	$3,9 \times 10^{-7}$	PA	10		26
	4,1	25	43,4	$5,8 \times 10^{-7}$	PA	10		26
Methanol/Benzene	50	20	400	0,04	Cellophane	-		25
Ethanol/Benzene	50	30	124	0,031	Cellophane			25
Methanol/Ethanol	-	40	-	-	Poly( $\gamma$ -methyl L-glutamate)	-		78
p-Xylene/Ethylbenzene	-	23	1,20	0,06	PE	30	Membrane: 125A101; Du Pont	27
p-Xylene/m-Xylene	-	23	1,21	0,05	PE	30	Membrane: 125A101; Du Pont	27
	-	55	1,11	1,67	PE	30	Membrane: 125A101; Du Pont	27
p-Xylene/o-Xylene	-	31	1,37	0,13	PE	30	Membrane: 125A101; Du Pont	27
p-Xylene Ethylbenzene	-	20	1,22	-	PP	20	Membrane: Clysar 350P-1A 3; Du Pont	27
p-Xylene/m-Xylene	-	25	1,16	0,19	PP	20	Membrane: Clysar 350P-1A 3; Du Pont	27
	-	75	1,21	0,31	PP	20	Membrane: Clysar 350P-1A 3; Du Pont	27
p-Xylene/o-Xylene	-	26	1,30	0,15	PP	20	Membrane: Clysar 350P-1A 3; Du Pont	27
	-	67	1,25	1,30	PP	20	Membrane: Clysar 350P-1A 3; Du Pont	27
p-Xylene/Ethylbenzene	-	60	1,14	0,15	Saran Wrap	20	Purchased in USA	27
p-Xylene/m-Xylene	-	49	1,25	0,05	Saran Wrap	20	Purchased in USA	27
p-Xylene/o-Xylene	-	49	1,26	0,08	Saran Wrap	20	Purchased in USA	27
p-Xylene/Ethylbenzene	-	225	1,15	-	Teflon	50	Membrane: FEP, 200A; Du Pont	27
p-Xylene/m-Xylene	-	132	1,25	0,01	Teflon	50	FEP, 200A; Du Pont	27
	-	150	1,08	0,09	Teflon	50	FEP, 200A; Du Pont	27
p-Xylene/Ethylbenzene	-	163	1,80	-	Polyimide	25	Kapton, 100H; Du Pont	27
	-	225	1,66	0,02	Polyimide	25	Kapton, 100H; Du Pont	27
p-Xylene/m-Xylene	-	213	1,69	0,01	Polyimide	25	Kapton, 100H; Du Pont	27
	-	260	1,43	0,02	Polyimide	25	Kapton, 100H; Du Pont	27
	-	274	1,64	0,04	Polyimide	25	Kapton, 100H; Du Pont	27
p-Xylene/o-Xylene	-	132	2,18	-	Polyimide	25	Kapton, 100H; Du Pont	27
p-Xylene/Ethylbenzene	-	72	1,31	0,01	Poly(vinyl fluoride)	25	Tedlar, 100AG3 OUT; Du Pont	27

p-Xylene/m-Xylene	-	81	1,61	0,01	Poly(vinyl fluoride)	25	Tedlar, 100AG3 OUT; Du Pont	27
	-	101	1,13	0,03	Poly(vinyl fluoride)	25	Tedlar, 100AG3 OUT; Du Pont	27
p-Xylene/o-Xylene	-	43	1,39	0,01	Poly(vinyl fluoride)	25	Tedlar, 100AG3 OUT; Du Pont	27
	-	72	1,33	0,02	Poly(vinyl fluoride)	25	Tedlar, 100AG3 OUT; Du Pont	27
p-Xylene/Ethylbenzene	-	66	1,22	0,01	Parylene C	10	Union Carbide	27
	-	95	1,33	0,04	Parylene C	10	Union Carbide	27
p-Xylene/m-Xylene	-	53	1,42	0,01	Parylene C	10	Union Carbide	27
	-	86	1,32	0,02	Parylene C	10	Union Carbide	27
	-	127	1,23	0,01	Parylene C	10	Union Carbide	27
p-Xylene/o-Xylene	-	132	1,56	-	Parylene C	10	Union Carbide	27
p-Xylene/Ethylbenzene	-	106	1,35	0,02	Parylene N	10	Union Carbide	27
p-Xylene/m-Xylene	-	94	1,15	0,01	Parylene N	10	Union Carbide	27
	-	131	1,24	0,07	Parylene N	10	Union Carbide	27
p-Xylene/Ethylbenzene	-	118	1,23	0,02	CA	25	100 CA-43; Du Pont	27
p-Xylene/m-Xylene	-	98	1,45	0,02	CA	25	100 CA-43; Du Pont	27
	-	118	1,48	0,02	CA	25	100 CA-43; Du Pont	27
	-	133	1,43	0,02	CA	25	100 CA-43; Du Pont	27
	-	150	1,42	0,03	CA	25	100 CA-43; Du Pont	27
p-Xylene/o-Xylene	-	81	1,56	0,01	CA	25	100 CA-43; Du Pont	27
	-	134	1,52	-	CA	25	100 CA-43; Du Pont	27
p-Xylene/Ethylbenzene	-	108	1,19	0,02	CA	40	Membrane with matt finish	27
p-Xylene/m-Xylene	-	100	1,34	0,03	CA	40	Membrane with matt finish	27
	-	154	1,22	0,04	CA	40	Membrane with matt finish	27
p-Xylene/Ethylbenzene	-	120	1,26	0,01	Nylon	25	Allied Chemical; Capron 77C	27
p-Xylene/m-Xylene	-	120	1,22	0,01	Nylon	25	Allied Chemical; Capron 77C	27
p-Xylene/o-Xylene	-	128	1,42	0,01	Nylon	25	Allied Chemical; Capron 77C	27
p-Xylene/Ethylbenzene	-	77	1,21	0,06	PVDF	50	Kynar, Pennwalt; Cast from DMF	27
	-	137	1,15	0,50	PVDF	50	Kynar, Pennwalt; Cast from DMF	27
p-Xylene/m-Xylene	-	98	1,14	0,01	PVDF	50	Kynar, Pennwalt; Cast from DMF	27
	-	135	1,10	0,18	PVDF	50	Kynar, Pennwalt; Cast from DMF	27

m-Xylene/o-Xylene	50	30	2,82	0,063	HEMA/HEA	70	3,4 DNP	30
m-Xylene/p-Xylene	50	30	2,39	0,047	HEMA/HEA	70	3,4 DNP	30
o-Xylene/p-Xylene	50	30	1,71	0,079	HEMA/HEA	70	3,4 DNP	30
m-Xylene/o-Xylene	50	30	1,37	0,059	HEMA/HEA	70	3,5 DNP	30
m-Xylene/p-Xylene	50	30	1,95	0,025	HEMA/HEA	70	3,5 DNP	30
o-Xylene/p-Xylene	50	30	1,82	0,049	HEMA/HEA	70	3,5 DNP	30
Ethanol/Heptane	-	23	-	-	Cellulose	-	-	34
Pentane/Methanol	50	20	6857,4	0,12	Nylon 6/PAA	75	-	33
Methanol/Pentane	10	-	44	-	Nafion 117	-	-	79
	10	-	60	-	PVA	-	-	79
	1	-	467	-	Nafion 117	-	-	79
	1	-	-	-	PVA	-	-	79
Benzene/Cyclohexane	40	70	4,5	0,36	PPQ	27	-	80
Toluene/Ethanol	40	70	7	0,46	PPQ	27	-	80

#### Water/Organic Separations:

Water/Ethanol	50	25	0,9	-	Cellophane	-	Azeotrope separation	81
	50	45	2,0	4,6	Cellophane	-	Azeotrope separation; homogeneous membrane	81
	45	80	85	1,95	CA	-	Azeotrope separation; homogeneous membrane	2
Water/Isopropanol	12	60	15,6	0,7	Cellophane	-	Azeotrope separation; homogeneous membrane	82
	12	80	20	3,7	Modified CA	140	Azeotrope separation; asymmetric membrane	83
Water Ethanol	50	30	9,0	1,3	Cellophane	-	Azeotrope separation; homogeneous membrane	44
	4	60	6,6	0,8	PTFE-PVP	-	Azeotrope separation; asymmetric membrane	35
	4	20	6,2	0,1	Cellulose	-	Azeotrope separation; asymmetric membrane	35
	4	20	5,9	0,2	CA	-	Azeotrope separation; asymmetric membrane	35
Water/t-Butanol	11,8	25	41	0,35	PVDF + PVP	-	Exceptional azeotrope separation	40
	11,8	2,5	41	0,35	PTFE + PVP	-	Exceptional azeotrope separation	40
Water/Ethanol	4	25	2,9	2,2	PTFE + PVP	-	Azeotrope separation; asymmetric membrane positive azeotrope	82
Water/THF	57	25	19,1	0,94	PTFE + PVP	-	Azeotrope separation; asymmetric membrane positive azeotrope	40
Water/Dioxane	18,4	25	18,1	1,33	PTFE + PVP	-	Azeotrope separation; asymmetric membrane positive azeotrope	40

Water/Propanol	28,2	25	6,4	1,70	PTFE + PVP	- Azeotrope separation; positive azeotrope	40
	12,2	25	8,9	0,58	PTFE + PVP	- Azeotrope separation; positive azeotrope	40
Water/sec-Butanol	32	25	13	1,15	PTFE + PVP	- Azeotrope separation; positive azeotrope	40
Water/t-Butanol	11,8	25	41	0,35	PTFE + PVP	- Azeotrope separation; positive azeotrope	40
Water/Diacetone alcohol	87,0	25	7,1	0,40	PTFE + PVP	- Azeotrope separation; positive azeotrope	40
Water/Pyridine	57	25	5,6	0,60	PTFE + PVP	- Azeotrope separation; positive azeotrope	40
Water/Hexylamine	51	25	31	1,80	PTFE + PVP	- Azeotrope separation; positive azeotrope	40
Water/Formic acid	22,5	25	1,0	2,74	PTFE + PVP	- Azeotrope separation; negative azeotrope	40
Water/Ethanol	4	60	11	0,5	CA	- Homogeneous membrane	84
	9,9	60	8	3,0	Cellophane	- Homogeneous membrane	84
	50	25	5,0	1,9	PTFE + PS	- Homogeneous membrane	85
	99,99	25	1,67	<0,1	PE	- Homogeneous membrane	86
	99,99	25	-	-	PETF	- Homogeneous membrane	86
	99,99	25	2,5	<0,5	PVA	- Homogeneous membrane	86
	99,99	25	0,14	<0,1	PDMS	- Homogeneous membrane	86
	50	25	0,22	-	PDMS	- Homogeneous membrane	87
	50	25	0,22	0,005	Silicone	- Homogeneous membrane	87
	4,5	78	4,50	4,0	PVA/PS polyester	- Composite membrane	88
	50	20	2,0	1,13	CA 383	- Homogeneous membrane	55
	50	20	4,2	0,68	CA 398	- Homogeneous membrane	55
	50	20	2,7	0,23	CTA	- Homogeneous membrane	55
	50	20	2,6	0,55	CTP	- Homogeneous membrane	55
	50	20	4,0	0,29	CAB 17	- Homogeneous membrane	55
	50	20	4,1	0,3	CAB 27	- Homogeneous membrane	55
	50	20	3,2	0,23	CAB 38	- Homogeneous membrane	55
	50	20	70	0,015	PAN	- Homogeneous membrane	55
	50	20	1,0	0,45	PVDF	- Homogeneous membrane	55
	50	20	332	0,004	PS	- Homogeneous membrane	55
50	20	0,3	0,17	PDMS	- Homogeneous membrane	55	
50	20	19,0	0,05	PS/PVDF	- Composite membrane	55	
50	20	9,0	0,20	PAN/Nylon 6	- Composite membrane	55	
50	20	12,3	0,27	CA	- Asymmetric membrane	55	
50	20	3,0	0,14	PS	- Asymmetric membrane	55	

	50	20	9,3	0,02	PPO	-	Asymmetric membrane	55
Ethanol/Water	10	22	20	-	Silicone	458	Homogeneous membrane	89
	5	25	0,11	0,025	Silicone	-	Homogeneous membrane	90
Benzene/Water	50	30	20 000	0,0017	NBR 51	100	Elastomeric membrane	21
	(ppm)							
Ethanol/Water	50	20	2,0	-	CA 383	10		523
	50	20	4,2	-	CA 398	20		523
	50	20	2,7	-	CTA	10		523
	50	20	2,6	-	CTP	20		523
	50	20	4,0	-	CAB 171	30		523
	50	20	4,1	-	CAB 272	20		523
Ethanol/Water	50	20	3,2	-	CAB 381	30		523
	50	20	70	-	PAN	25		523
	50	20	1,0	-	PVDF	20		523
	50	20	332	-	PSF	20		523
	50	20	0,3	-	PDMS	10		523
	50	20	19	-	PSF-PVDF	-		523
	50	20	9	-	PAN-Nylon 6	-		523
	50	20	1,0	-	PVDF support	-		523
	50	20	1,0	-	Nylon 6 support	-		523
Methanol/Water	-	-	-	-	Poly( $\gamma$ -methyl L-glutamate)	-		91
Isopropanol/Water	-	60	-	-	Cellulose hydrate	30		92
Ethanol/Water	4	15	350	0,005	PMA	-	Homogeneous membrane	93
	92	15	32	0,082	PMA	-	Homogeneous membrane	93
	6,5	43	14,8	0,6	PEU/PS polyester	-	Composite membrane	94
Water/Ethanol	51	40	7,5	0,11	PMA	25		95
	15	15	33,41	0,008	PMA	25		95
Water/1-Propanol	15	15	3 722	0,007	PMA	25		95
Water/2-Propanol	15	15	11 330	0,005	PMA	25		95
Water/1-Butanol	15	15	770,6	0,009	PMA	25		95
Water/2-Butanol	15	15	112,1	0,008	PMA	25		95
Water/Ethanol	18	40	491,6	-	Poly(acrylate-co-acrylonitrile)	20	Copolymer	96

Ethanol/Water	-	20	-	-	CA	20		97
Water/i-Propnaol	40	35	-	0,6	CA	60		98
Water/Ethanol	-	25	-	-	PAN	-		53
	60	25	-	0,01	PAN	25		53
	40	60	-	2	GFT-membrane	-	Commercial membrane	53
Ethanol Water	65	17	9,8	-	CA	500		99
Water/Ethanol	-	20	-	-	CA	20		100
	-	20	-	-	PAN	20		100
	-	20	-	-	PSF	20		101
	-	30	2,4	-	SBR 27	305		101
Water/Acetone	-	30	16	-	NBR-51	194		101
	-	30	32	-	SVR-27	305		101
Water/Chloroform	-	30	25 000	-	NBR-51	194		101
	-	30	20 000	-	SBR-27	305		101
Water/Benzene	-	30	20 000	-	NBR-51	194		101
	-	30	40 000	-	SBR-27	305		101
Water/Ethanol	60	15	19,3	0,004	Poly(N-phenylmale- imide-co-styrene)	24		102
	14,6	26	725	0,15	Modified PE	40	PE is sulphonated	103
Water/i-Propanol	10,4	26	>28 709	0,2	Modified PE	40	PE is sulphonated	103
Water/Ethanol	-	-	-	-	CMV	150		104
	3	60	70	0,08	AMV	140	Counterions : SO <sub>4</sub> <sup>2-</sup>	104
	7	60	53	0,38	AMV	140	Counterions : OH <sup>-</sup>	104
	15	60	38	0,47	AMV	140	Counterions : SCN <sup>-</sup>	104
	20	60	27	0,83	AMV	140	Counterions : Cl <sup>-</sup>	104
	13	60	14	0,92	CTA	140		104
Water/i-Propanol	94,8	29	11,4	1,64	Nafion-811	-	Counterions : Li <sup>+</sup>	105
	94,8	29	11,6	1,44	Nafion-811	-	Counterions : H <sup>+</sup>	105
	94,8	11,6	14,8	1,26	Nafion-811	-	Counterions : Na <sup>+</sup>	105
	94,8	11,6	36,5	0,99	Nafion-811	-	Counterions : K <sup>+</sup>	105
	94,8	11,6	19,5	1,04	Nafion-811	-	Counterions : Ca <sup>2+</sup>	105
	94,8	11,6	3,6	0,32	Nafion-811	-	Counterions : Al <sup>3+</sup>	105
Water/Ethanol	21,7	29	10,4	0,18	Nafion	-	Counterions : Cs <sup>+</sup>	105
	21,7	29	8,4	0,26	Nafion	-	Counterions : K <sup>+</sup>	105



	5	30	13,2	1,35	IPC/PEI	-	106
	5	30	18,6	0,94	TMC/PEI	-	106
	5	30	171	0,33	CSIPC/PEI	-	106
Ethanol/Water	7	-	11,2	1,1-2,7 $\times 10^{-4}$	Styrene-dimethyl- siloxane)	- Copolymer	107
	10	-	11,2	$1,15 \times 10^{-3}$	Poly[1-(trimethyl- 1-propyne]	-	108
Water/Methanol	-	2-	-	-	N-Methoxymethyla- ted Nylon 3	97	109
Water/Ethanol	-	2-	-	-	N-Methoxymethyla- ted Nylon 3	97	109
Water/i-Propanol	12	30	10,2	0,74	Nafion	103 Counterions : Li <sup>+</sup>	110
	12	30	19,8	0,25	Nafion	103 Counterions : Na <sup>+</sup>	110
	12	30	31,0	0,072	Nafion	103 Counterions : K <sup>+</sup>	110
	12	30	36,0	0,046	Nafion	103 Counterions : Cs <sup>+</sup>	110
Ethanol/Water	8	-	16,3 - 45	0,6 - $1,1 \times 10^{-3}$	Styrene-fluoroalkyl acrylate	- Graft copolymer	111
	10	-	5,7 - 9,4	1,1 - $5,6 \times 10^{-6}$	PDMS	- Block copolymer	112
	5 -	--	14,9 - 16,5	3,6 - $5,1 \times 10^{-2}$	Silicone rubber	- Zeolite-filled polymer	113
	8	-	3 - 5,5	3,3 - 8,1	Gore Tex	-	114
	-	-	-	-	Silicone	335	115
Dichloromethane/Water	-	-	-	-	Silicone	335	115
Chloroform/Water	-	-	-	-	Silicone	335	115
Bromoethane/Water	-	-	-	-	Silicone	335	115
Acetone/Water	-	-	-	-	Silicone	335	115
Water/Ethanol	20	25	-	-	CMC	- DS = 0,34	116
	20	25	-	-	CMC	- DS = 0,70	116
	20	25	-	-	CMC	- DS = 0,77	116
	20	25	-	-	CMC	- DS = 0,87	116
	20	25	-	-	CMC	- DS = 1,26	116
	20	25	-	-	CMC/Poly(sodium vinyl solphonate)	-	116

	20	25	-	-	CMC/Sodium poly-	-		116
					acrylate)			
	20	25	-	-	CMC/Sodium poly-	-		116
					acrylic acid)			
	80	25	-	-	CA	150		29
	80	25	-	-	Silicone rubber	300		29
Water/i-Propanol	80	25	-	-	CA	150		29
	80	25	-	-	Silicone rubber	300		29
Water/THF	29,6	20	-	-	Cuprophan	18		117
Water/i-Propanol	27	20	-	-	Cuprophan	30		117
Water/Ethanol	13	20	-	-	Cuprophan	30		117
Methanol/Water	-	-	-	-	PTFE	-		114
Ethanol/Water	-	-	-	-	PTFE	-		114
Propanol/Water	-	-	-	-	PTFE	-		114
Water/Ethanol	50	35	-	0,7	PE/AA	-	Graft copolymer; counterions : H <sup>+</sup>	118
	50	35	-	0,5	PE/AA	-	Graft copolymer; counterions : Li <sup>+</sup>	118
	50	35	-	0,9	PE/AA	-	Graft copolymer; counterions : Na <sup>+</sup>	118
	50	35	-	2,6	PE/AA	-	Graft copolymer; counterions : K <sup>+</sup>	118
	50	35	-	4,5	PE/AA	-	Graft copolymer; counterions : Rb <sup>+</sup>	118
Water/Ethanol	20	70	18	0,066	Polyamide	24		119
	20	70	26	0,278	Polyamide	8		119
	20	70	105	0,111	Polyamideimide	11		119
	20	70	62	0,029	Polyimideimide	16		119
	20	70	36	0,188	Polyimide	10		119
	20	70	96	0,025	Polyimide	14		119
Methanol/Water		22,5	-	-	PDMS	150		113
Ethanol/Water		22,5	-	-	PDMS	150		113
1-Propanol/Water		22,5	-	-	PDMS	150		113
2-Propanol/Water		22,5	-	-	PDMS	150		113
Ethanol/Water		20	-	-	PVAc/PSf	-		120
		20	-	-	CA/CTA	-		120
		20	-	-	PSf 3	-		120
	50	60	-	4,3	Chitosan	-		121
	50	60	-	7,6	Alginate acid	-		121

Ethanol/Water	5	30	-	1,04	Silicone	-	122
	5	30	-	12,5	PP	-	122
	-	30	-	-	PTMSP/PPP	- Copolymer	123
	-	-	28	0,001	PTMSP/PDMS	- Copolymer	123
	7	-	40	-	PPP/PDMS	- Copolymer	123
	76	20	-	-	Cuprophan	-	124
	50	25	-	-	PE	-	125
	-	-	-	-	GFT	- Composite membrane	126
i-Propanol/Water	-	-	-	-	GFT	- Composite membrane	126
Water/i-Propanol	-	25	-	-	PVA	-	126
	20	70	-	1,0	PVA/PAN	- Mo 1085	126
	20	70	-	0,5	PVA/PAN	- Mo 1108	126
Ethanol/Water	50	25	25	0,02	Polyacrylic acid/ Nylon 6	25	127
	4	-	4,5	0,46	HMDSO	- Plasma films	56
	20	-	1,4	1,5	Nucleopore / HMDSO	27 000 HDMSO plasma	56
	15	-	1,0	3,5	Nucleopore / HMDSO	34 000 HDMSO plasma	56
	15	-	1,0	0,2	Nucleopore / HMDSO	41 000 HDMSO plasma	56
	4	-	4,5	0,46	HMDSO	- Plasma films	56
i-Propanol/Water	-	50	-	-	CA	-	128
Methanol/Water	-	-	-	-	Poly(tetramethylene glycol)/Nylon 12	-	128
Ethanol/Water	-	-	-	-	Poly(tetramethylene glycol)/Nylon 6	-	128
i-Propanol/Water	-	-	-	-	Poly(tetramethylene glycol)/Nylon 6	-	128
Ethanol/Water	-	-	-	-	PTFE	-	129
	-	-	-	-	PP	-	129
	-	-	-	-	Silicone	- Zeolite-filled	130
Water/Ethanol	40	60	-	0,5	GFT-PVA	-	131
Water/Methanol	20	6-	-	2,5	GFT-PVA	-	131

Water/i-Propanol	40	60	-	1,4	GFT-PVA	-	131
Water/Dioxane	70	60	-	1,5	GFT-PVA	-	131
Ethanol/Water	5	25	-	-	SR (Silicalite)	210	132
Propanol/Water	8,5	25	-	-	SR (Silicalite)	210	132
Methanol/Water	-	-	-	-	Poly(tetramethylene glycol) / Nylon 12	- Copolymer membrane	133
Ethanol/Water	-	-	-	-	Poly(tetramethylene glycol) / Nylon 12	- Copolymer membrane	133
i-Propanol/Water	-	-	-	-	Poly(tetramethylene glycol) / Nylon 12	-	134
Ethanol/Water	-	-	-	-	Poly(tetramethylene glycol) / Nylon 12	-	135
Methanol/Water	-	-	-	-	Silicone rubber	-	135
Ethanol/Water	90	40	114	18x10 <sup>3</sup>	Chitosan	-	135
i-Propanol/Water	-	-	-	-	Chitosan	-	135
Methanol/Water	-	-	-	-	PS	-	135
Ethanol/Water	-	-	-	-	PS	-	135
i-Propanol/Water	-	-	-	-	PS	-	135
Methanol/Water	-	-	-	-	PDMS	-	135
Ethanol/Water	-	-	-	-	PDMS	-	135
i-Propanol/Water	-	-	-	-	PDMS	-	135
Water/Ethanol	-	-	7,2	-	PVA-2	10	136
	5	70	920	0,22	PAA	- Composite; counterions : K <sup>+</sup>	137
	5	70	220	0,83	PAA/Polyethylene-imine	-	137
	5	70	750	0,51	PAA/Polyallylamine	-	137
	5	70	1 710	0,79	PAA/PCA	- PCA synthesized by the Menshutkin reaction	137
	5	70	830	0,34	PAA/PAL	- PAL supplied by Nippon Senka Chem. Ind.	137
	5	70	380	0,22	PAA/PCQ	- PCQ supplied by Nippon Senka Chem. Ind.	137
	5	70	170	0,23	PAA/Polyethylene glycol	-	
Phenol/Water	-	-	-	2	Polyetheramide	170	
Ethanol/Water	35	29,2	2,4	180	CA	10 DMSO solvent	139
	35	46,2	4,0	-	CA	5 DMSO solvent	139

	80	67	69	-	PVA	8	Water solvent	139
	80	66	107	-	PVA	15	Water solvent	139
Chlorobenzene/ Water	-	30	31,8	-	Polybenzimidazole	-		140
Toluene/Water	-	30	11,8	-	Polybenzimidazole	-		140
Xylene/Water	-	10,5	10,5	-	Polybenzimidazole	-		140
Carbon disulfide/Water	-	30	10,8	-	Polybenzimidazole	-		140
Ethanol/Water	-	30	1,87	-	Polybenzimidazole	-		140
i-Propanol/Water	-	30	1,89	-	Polybenzimidazole	-		140
Water/Ethanol	-	40	-	-	PP/HEMA	-	Graft copolymer	141
	-	-	-	-	Nafion 117	-		142
Water/i-Propanol	-	-	-	-	PE - Styrene sulphonate	-	Graft copolymer	142
i-Propanol/Water	-	-	-	-	CA	40		143
Ethanol/Water	-	25	2 000	0,01	PAN	-		144
	-	-	-	-	Poly(L-leucine-L- lysine)	-		145
Ethylbenzene/Water	-	30	13,7	-	Polybenzimidazole	-		140
Dichlorobenzene/Water	-	30	6,47	-	Polybenzimidazole	-		140
Methyl butyl ketone/ Water	-	30	2,44	-	Polybenzimidazole	-		140
Ethyl Ether/Water	-	30	1,95	-	Polybenzimidazole	-		140
Propanol/Water	-	30	1,88	-	Polybenzimidazole	-		140
i-Butanol/Water	-	30	1,88	-	Polybenzimidazole	-		140
Methanol/Water	-	30	1,83	-	Polybenzimidazole	-		140
Acetonitrile/Water	-	30	1,82	-	Polybenzimidazole	-		140
Acetaldehyde/Water	-	30	1,78	-	Polybenzimidazole	-		140
Ethyl Acetate/Water	-	30	1,77	-	Polybenzimidazole	-		140
Ethylene Glycol/Water	-	30	1,76	-	Polybenzimidazole	-		140
Butanol/Water	-	30	1,72	-	Polybenzimidazole	-		140
Phenol/Water	-	30	1,70	-	Polybenzimidazole	-		140
Glycol/Water	-	30	1,70	-	Polybenzimidazole	-		140
Dioxane/Water	-	30	1,59	-	Polybenzimidazole	-		140
Acetone/Water	-	30	1,56	-	Polybenzimidazole	-		140

Cyclohexane/Water	-	30	1,39	-	Polybenzimidazole	-	140
Methyl Ethyl Ketone/ Water	-	30	1,30	-	Polybenzimidazole	-	140
Water/Ethanol	-	30	2,1	-	Polybenzimidazole	-	140
Water/i-Propanol	-	30	4,6	-	Polybenzimidazole	-	140
Ethanol/Water	90	40	9 161	16 000	CAS	-	135
	90	40	2 557	25 000	GAC	-	135
	10	40	0,8	0,85	PDMS	-	135
Water/Ethanol	20	70	5	0,205	PPQ	27	80
Water/i-Propanol	60	70	30	0,35	PPQ	27	80
i-Propanol/Water	-	25	-	-	CA	-	134
Ethanol/Water	90	70	10 000	0,01	PAN	40	144
Water/i-Propanol	10	90	-	1,4	GFT	-	146
Water/Ethanol	-	-	-	-	PVA/PAN	-	147
Water/Methanol	70	25	-	0,004	Polyimide	25	148
	70	25	-	0,014	Polyamide	50	148
Water/Methanol	70	25	-	0,004	PSF	76	148
	70	25	-	0,025	CTA	50	148
	70	25	-	0,060	PAN	45	148
	70	25	-	0,047	Ethylcellulose	130	148
	70	25	-	0,110	Cuprophane	8	148
	70	25	-	0,031	Silicone	150	148
	70	25	-	0,126	PP	25	148
Ethanol/Water	-	-	-	0,210	PEBA-40	46	138
n-Butanol/Water	-	-	-	0,240	PEBA-40	46	138
sec-Butanol/Water	-	-	-	0,240	PEBA-40	46	138
Acetic Acid/Water	-	-	-	0,180	PEBA-40	46	138
Ethanol/Water	-	-	-	0,480	Silicone rubber	-	138
Acetic Acid/Water	-	-	-	0,390	Silicone rubber	-	138

## ABBREVIATIONS

WT%	- Weight percent	n	- Normal	i	- Iso
°C	- Degrees Celsius	sec	- Secondary	m	- meta
v	- Volume	(m)	- Mole	o	- ortho
t	- Tertiary	p.p.m.	- Parts per million	p	- para
CA	- Cellulose acetate	PAN	- Polyacrylonitrile	PA	- Poly(hexamethylene adipamide)
PP	- Polypropylene	PSf	- Polysulphone	DMF	- Dimethylformamide
PI	- Polyisoprene	PPN-I	- Poly[styrene(diethyl phosphonate)] [65]	CMC	- Carboxymethylcellulose
PE	- Polyethylene	PPN-III	- Poly[bromophenylene oxide (dimethyl)phosphonate]	AA	- Acrylic acid
PTFE	- Polytetrafluoroethylene	QPPO	- Quarternary Poly(phenylene oxide)	PVAc	- Polyvinyl acetate
PVP	- Polyvinylpyrrolidone	PPO	- Poly(phenylene oxide)	HEMA	- 2-Hydroxyethyl methylacrylate
PVDF	- Polyvinylidene fluoride	PMA	- Poly(maleimide-co-acrylonitrile)	HEA	- 2-Hydroxyethyl acrylate
DMSO	- Dimethylsulphoxide-	PEU	- Polyetherurea [RC 100; UOP Inc.]	PTMSP	- Poly(1-trimethylsilyl-1-propyne)
THF	- Tetrahydrofuran	PSP	- Poly(phenylene oxide hydroquinone dimethylphosphonate)	PPP	- 1-Phenyl-1-propyne
SBR	- Polybutadiene-styrene	CMV	- Cation exchange membrane	HMDSO	- Hexamethyldisiloxane
PS	- Polystyrene	AMV	- Anion exchange membrane	PAA	- Polyacrylic acid
PETF	- Polyethyleneterephthalate	IPC	- Isophthaloyl chloride	PPQ	- Polyphenylquinoxaline
PVA	- Polyvinylalcohol	PEI	- Polyethylene-imine	CAS	- Chitosan acetate salt
PDMS	- Polydimethylsiloxane	TMC	- Trimesoyl chloride	GAC	- Gultaraldehyde/chitosan
CTP	- Cellulose tripropionate	CSIPC	- 5-Chlorosulfonyl isophthaloyl chloride	PEBA	- Polyether block polyamide
CAB	- Cellulose acetate butyrate				
NBR	- Polybutadiene-acrylonitrile				
CTA	- Cellulose triacetate				
GFT	- Gesellschaft für Trenntechnik				

All the previous literature surveys show that no work has been done on the separation of ethanol and hexane by pervaporation.

### 2.2.2 TRANSPORT MECHANISMS<sup>(39)</sup>

The studies on pervaporation carried on in the 1960s resulted in a number of explanations of the mechanisms of selectivity and transport in the operation.

Schrodt *et al.*<sup>(38)</sup> suggested that hydrogen bonds between polymer and solvent components played an important role. Binning *et al.*<sup>(149)</sup> were of the opinion that selectivity took place in a boundary layer between the liquid zone and the gas zone in the membrane. Michaels *et al.*<sup>(37)</sup> interpreted the selectivity as a result of sieving in the polymer crystals, and Long<sup>(36)</sup> suggested that diffusion and concentration gradients in the different solvent components were the governing factors.

In the construction of mathematical models for the description of pervaporation the process is divided into three steps: selective adsorption of a liquid mixture, diffusion through the membrane, and desorption on the permeate side. When a binary mixture comes into contact with a membrane, the equilibrium between the liquid and vapour phases is changed. If it is assumed that the polymer has different affinities for the different components in the mixture, the component which requires the least solvation energy will be transported most rapidly<sup>(63,65,82)</sup>. Polymer materials swell in contact with liquids, and the distribution of the components in the membrane will be different from that in the solution, and the diffusivity will also be improved.

In their investigations, Eustache and Histi<sup>(85)</sup> showed that in an inelastic membrane material with strong crosslinking, the rate of separation is determined by the diffusivity within the membrane, whereas in an elastic polymer (e.g. rubber), in which the chains are more flexible, the rate of separation is controlled mainly by adsorption at the liquid-membrane surface. In a sufficiently dense membrane the molecular chains will be in constant motion and this will affect the diffusion of the components of the mixture. Diffusion is dependent on several physical and chemical factors such as the size and shape of the molecules in the solution (functionality), the interaction between the components of the solution and the polymer, and the interaction between the components of the solution. The fact that the transport of a certain component through the membrane is affected by the presence of another component in the liquid means that this type of separation is different from gas separation where the concentrations in the membrane are much lower<sup>(55)</sup>.

Vaporization on the permeate side of the membrane is generally considered to be a fast, non-selective step as the partial pressure is kept low<sup>(40,55,74,82,150)</sup>. When the pressure approaches the partial vapour pressure of the liquid component, the permeate flux remains unaltered but then suddenly decreases and becomes dependent on the rate of vaporization. This is an important factor in the working of asymmetric membranes in which the capillaries in the porous support constitute the surface where the vaporization takes place<sup>(151)</sup>.

When capillaries are narrow, the pressure-drop profile inside them can be such that only a small fraction of the total pore length can be used for vaporization, and the "active" capillary surface area therefore becomes very sensitive to variations in the pore diameter.



Compared with the traditional membrane processes, ultrafiltration and reverse osmosis, the fluxes obtained in pervaporation studies to date have been very low. It is thus clear that normally this process is of interest only where traditional techniques are costly, for example, in azeotropic distillation.

With new technology, such as hollow fine fibre membranes which are becoming available for pervaporation, the low fluxes ought not to be limiting in the expanding commercialization of the process in future.

### 2.2.3 MATHEMATICAL MODELS

Much work is in progress on mathematical modelling of the mass transport in pervaporation, and to relate it to variables such as the pressure on the permeate side, and the temperature and the composition of the feed. As with all other membrane processes, the pervaporation process must be investigated experimentally for each individual case. Several groups are working on this on a laboratory scale.

Huang and Lin<sup>(48)</sup> investigated the dependence of the rate of permeation of a liquid through a polymer membrane on the solubility of the liquid and its diffusivity in the polymer. A form of Fick's Law was used to describe the steady-state permeation process. The values of diffusivity depend strongly on the concentration of liquid in the polymer membrane. Many expressions have been proposed to relate the diffusivity to the solubility of liquid in the membrane and to a diffusivity obtained at zero concentration of liquid.

Polymer morphology has a strong effect on permeation characteristics. The degree of crystallinity and the size of crystallites within the polymer affect both the rate of transport and the efficiency of separation. Since only amorphous regions in the polymer take part in the transport process, in highly crystalline polymers any factor which disrupts the order of these regions can have an effect on the liquid permeation process.

Fels and Huang<sup>(61)</sup> developed a theoretical model for the interpretation of permeabilities of binary liquid mixtures through polymer membranes, which is in reasonable agreement with experimental data. Further accuracy could be achieved by obtaining actual experimental data to avoid the necessity for some of the assumptions used in the model. Although it is impractical to predict binary permeabilities through novel membranes because of the difficulties of obtaining the diffusion coefficients, insights into the way in which the permeation of each individual component in a binary mixture is affected by the presence of the other component may be obtained.

Rhim and Huang *et al.*<sup>(152)</sup> modified this model of Fels and Huang for the prediction of the separation factors and the permeabilities for the binary mixture. Their model is based on the extension of the free-volume theory and the introduction of the Flory-Huggins thermodynamics for the calculations of the binary interaction parameter and the diffusion coefficients. This model considers the coupling effect of the presence of a component on the rate of transfer of the other.

This model is demonstrated for the n-hexane-benzene binary mixture and polyethylene system. The calculated permeabilities of each component are much closer to the experimental values than are those from the previous Fels and Huang<sup>(61)</sup> model.

Aptel *et al.*<sup>(40,153)</sup> investigated the effect of the composition of the feed on the values of  $\alpha$  and  $\psi$  (selectivity and flux respectively), and it was found that when the concentration of A (the more easily pervaporated component) was reduced the membrane flux decreased while the selectivity increased. This could be explained by changes in the driving force and in the characteristics of the membrane. With decreasing concentration of A in the feed, the concentration gradient of A in the membrane decreases, thereby reducing the flux. The membrane's solvation also changes, so that the increase in the concentration of B in the feed does not necessarily lead to an increase in the adsorption of this component.

Aptel *et al.*<sup>(154)</sup> also studied the extraction of trace organics from water by pervaporation, both theoretically and experimentally. A model derived from the film theory was developed. Experiments were performed using various silicone hollow fibrous membranes and chlorinated hydrocarbons as solutes. The experimental data agreed with the model. This indicated that for very dilute solutions, the concentration polarization at the liquid-membrane interface controls the mass transfer of the solute. The model has also been used to design industrial units for the removal of micropollutants from water.

Neel *et al.*<sup>(82,155)</sup> continued this work and formulated equations which describe a process in which an azeotropic mixture of water and dioxane is continuously separated by passing it through several parallel membrane units, without treating the mass transport through the membranes in detail. The production capacity and energy consumption in the separation of azeotropic solution using PTFE membranes were calculated.

Neel *et al.* divided the energy into two parts:

- (i) heat of evaporation; dependent on the selectivity and the required separation;  
and
- (ii) the compression energy; the conversion of vapour phase to a liquid at 20°C.

They also presented the results of tests on a one-stage pervaporation module with 1 m<sup>2</sup> membrane area without recirculation. Procedures for testing the equipment were described.

Hoover and Hwang<sup>(87)</sup> worked on a continuous membrane column, in which medical silicone-rubber tubes of different thicknesses were used. They studied the permeability over the whole composition range; this is described by a parabolic curve. No attempt was made to describe the process mathematically, but the effects of interactions between the membrane and the liquid, and between the liquid components themselves were discussed, on the basis of the activity coefficients. An "effective permeability coefficient" includes the effects of solvation, concentration, pressure and membrane swelling.

The model has been used for computer simulations, and the results gives a reasonable picture of the process.

In 1974 Rautenbach and Albrecht<sup>(43)</sup> presented a mathematical model which describes the mass transport of a binary mixture through a membrane. They started with Fick's Law and studied concentration dependence and the coupled-diffusion coefficient, i.e. the diffusion coefficient for one component is linearly dependent on the concentrations of both liquid components in the membrane. The partition coefficients were determined with sorption experiments, and were assumed to be

independent of the concentration. The effects of the temperature fall on the permeate side of the membrane due to vaporization were also discussed.

The model was experimentally tested with different benzene-cyclohexane mixtures in a flat module with a homogeneous polyethylene film, but it should be pointed out that it can be used generally in other pervaporation applications, so that it is therefore worth studying further in greater detail. The calculated selectivity and its pressure dependence were in good agreement with experimental results whereas the calculated flux did not agree with experiments, indicating that certain assumptions made in the model were erroneous.

- (1) The partition coefficients were assumed to be independent of the component concentrations; this was shown not to be so by sorption experiments.
- (2) Sorption experiments revealed large differences in concentrations in the membrane when one side of the membrane was in contact with the liquid and the other with the vapour at low partial pressure. This gives rise to a convective transport (Stefan flux) which had earlier been ignored.

After correction of the model with regard to these two points discussed above, good agreement with experimental results was obtained.

The model has been further developed by studies of variations in the feed temperature and composition.

In 1985 Rautenbach and Albrecht<sup>(83)</sup> investigated transport equations for pervaporation based on the sorption-diffusion model, which is widely accepted as a description of the transport mechanism in other membrane processes such as reverse osmosis. The advantages of these phenomenological transport equations are

- (1) a sufficient degree of accuracy;
- (2) a minimum number of free variables (material properties) is needed;
- (3) the material properties can be determined from relatively simple, steady-state experiments.

The validity of the equations has been verified by experiments with the pervaporation of a benzene/cyclohexane system through polyethylene membranes.

Brun *et al.*<sup>(76)</sup> derived a model in which changes in selectivity and fluxes are related to major external conditions, namely, the upstream mole fraction in the feed and the downstream total pressure of the pervaporate. The validity of this model has been tested by applying it to a set of experimental data for the pervaporation of hydrocarbon binary mixtures through rubber membranes.

The introduction of diffusivity of permeants exponentially related to their concentrations in a solution-diffusion model permits the extension of the LONG-model<sup>(76)</sup> to the case of binary mixtures. The model provides a suitable description of the pervaporation of binary mixtures, provided swelling of the membrane is moderate and if strong physico-chemical interactions between permeants and the membrane are absent.

Brun *et al.*<sup>(156)</sup> followed up this study with the modelling of the pervaporation of binary mixtures through moderately swelling, non-reacting membranes.

This was analyzed as a solution-diffusion process, on the assumption that the diffusion coefficient of each permeant is an exponential function of both concentrations. A model was derived in which changes in selectivity and fluxes are related to major external conditions.

This model led to the computation of the pervaporation selectivity and fluxes as functions of the variables of the model. Numerical examples are given for different shapes of curves for selectivity and fluxes. Internal concentration profiles in the membrane may also be computed.

The introduction of diffusivity of permeants exponentially related to their internal concentrations in the solution-diffusion process allows an extension of the Long-model to the pervaporation of binary mixtures as has been mentioned earlier.

Because of its adaptability the "exponential six-coefficients model" can be adjusted to most of the known shapes of pervaporation isotherm, if ideal and moderate swelling of the membrane are assumed. Experimental data are required to enable the coefficients to be computed.

Internal concentration profiles in the membrane under steady-state conditions may also be computed with this model. The model should be applicable to the description of the pervaporation of binary mixtures, and to predict the pervaporation behaviour of the system under other experimental conditions, provided that swelling is moderate and that too strong physiochemical interactions between permeants and the membrane are absent.

Mulder and Smolders<sup>(97)</sup> developed a modified sorption-diffusion model, which described transport and concentration profiles in homogeneous membranes.

In the model the coupled transport is divided into a thermodynamic and a kinetic part. The thermodynamic part takes account of the fact that the change in concentration of one component in the presence of another is a function of the interaction between them, and between the two components and the membrane. The kinetic part of the transport takes account of the combined ability of the two components to solvate the membrane, which varies with the composition of the mixture and which can greatly influence diffusivity. The polymer-liquid and liquid-liquid interactions have been studied in detail in swelling experiments in order to determine the variables of Flory-Huggins thermodynamics. Calculations with concentration-independent diffusion coefficients give a completely erroneous picture of the relations in the membrane, and an exponential concentration dependence has thus been chosen for the diffusion coefficients, where the solvating ability of the mixture has also been included.

As a part of a dissertation, Soukop<sup>(157)</sup> in collaboration with GFT, has developed an empirical model for the dimensioning of a pervaporation plant to separate ethanol from water. In an initial investigation, several mathematical relations were found.

- (1) The selectivity is an exponential function of the feed composition at constant temperature.

- (2) The permeate flux is an exponential function of temperature at constant feed composition, i.e. the flux increases with increasing temperature, as in other membrane processes.
- (3) The permeate flux decreases linearly with  $x$  for  $x > 75$  ( $x$  = % by volume ethanol in the feed) at constant temperature.

Using this model, Soukop<sup>(157)</sup> has performed detailed calculations on a combined distillation-pervaporation plant.

Transport of liquids by pervaporation takes place by a solution-diffusion mechanism. Brun<sup>(76,156)</sup> studied the "diffusion part" of this transport model extensively. In order to investigate the "solution part" of the transport model, Mulder<sup>(100)</sup> compared preferential sorption with preferential permeability.

Theoretical values of preferential sorption have been derived from Flory-Huggins thermodynamics, extended with concentration-dependent interaction variables. These calculated sorption values show reasonable agreement with experimental values. The large difference between the molar volumes of water and ethanol determine, to a great extent, the preferential sorption of water in these systems and this effect increases with decreasing swelling. Comparison of the results of preferential sorption experiments with those of pervaporation experiments indicates that, apart from the effect of differences in diffusivity for the permeating components, preferential sorption contributes to a major extent to selectivity transport.

By use of Flory-Huggins thermodynamics, supplemented with concentration dependent interaction variables reasonable good agreement was established between theoretical and experimental values for the preferential sorption of low molecular mass components in polymeric membranes.

In terms of the solution-diffusion model the conclusion is justified that the component that is adsorbed preferentially will also permeate preferentially. This statement is in agreement with the observations of Aptel<sup>(158)</sup>. Furthermore, it can be concluded that, in general, the assumption of ideal sorption cannot be used.

As mentioned earlier, mass transport in non-porous polymer membranes is usually described within the framework of solution-diffusion models. The overall permeation rate and the selectivity of a membrane can thus be described by basic equations.

The solution-diffusion models assume that mechanical equilibrium prevails, and thus excludes convective or viscous mass transport in the membrane. Microscopic inhomogenities or excessive swelling can give rise to convective transport in seemingly dense membranes and in these cases the pore-flow models are preferably applied.

Laatikainen *et al.*<sup>(26)</sup> described a separation model based on sorption and diffusion equations. The discussion is restricted to the separation of binary mixtures.

A summary of all the models is given in Table 2.4.

TABLE 2.4: MATHEMATICAL MODELS REGARDING BINARY MIXTURES

Authors	Mathematical Models	Ref.
Huang & Lin	Dependence of permeation rate on solubility and diffusivity.	48
Fels & Huang	Theoretical model; permeabilities.	61
Rhim & Huang	Separation factors and permeabilities; Coupling effect; Flory-Huggins thermodynamics; modified <sup>(43)</sup> .	152
Aptel et al.	Dependence of flux and selectivity on the composition of the feed.	40; 153
Aptel et al.	Model derived from film theory, concentration polarization of dilute solutions.	154
Neel et al.	Continued work of <sup>(154)</sup> ; energy consumption calculation; flux and selectivity changes.	82; 155
Hoover & Hwang	Interactions in terms of activity coefficients; effective permeability coefficient including effects of solvation, concentration, pressure and membrane swelling; computer simulations.	87
Rautenbach & Albrecht	Mass transport; concentration dependence and coupled diffusion coefficients; selectivity and pressure dependence; flux, including corrected partition coefficients and convective transport.	43
Rautenbach & Albrecht	Transport equations based on the sorption-diffusion model.	83
Brun et al.	Selectivity and flux related to major external conditions; diffusivity; extension of LONG-model.	76
Brun et al.	Follow-up of <sup>(100)</sup> ; swelling as a solution-diffusion process; internal concentration profiles; adaptable model.	156
Mulder & Smolders	Modified sorption-diffusion model; transport and concentration profiles; thermodynamics and kinetics; swelling; Flory-Huggins thermodynamics.	97
Soukop	Empirical model for dimensioning of a pervaporation plant, selectivity and flux.	157
Mulder	Preferential sorption vs preferential permeability; extension of Flory-Huggins thermodynamics with concentration - dependent interaction variables.	100
Laatikainen	Separation model based on sorption and diffusion.	26

From these discussions of models it is possible to extract those parameters that are important in designing and optimizing membrane chemical structure.

Variables of importance are:

1. Pressure
2. Temperature
3. Composition
4. Solubility
5. Diffusivity
6. Thermodynamics
7. Degree of adsorption
8. Coupling effects
9. Polymer morphology
  - \* Degree of crystallinity
  - \* Degree of crosslinking
10. Chemical structure of membrane
11. Swelling of membrane

#### 2.2.4 INDUSTRIAL APPLICATION<sup>(54)</sup>

During recent years pervaporation processes and membranes have attracted increasing interest from both membrane researchers and potential users of membranes in the chemical industry. The effectiveness of a large number of different types of membranes has been investigated for various separation processes. Membranes originally designed and used for reverse osmosis or electro-dialysis as well as various other polymer films and membranes especially developed for pervaporation have been tested. Only a few membranes were found which do exhibit selectivities sufficiently high to effect separations, although nearly all of them are unsuitable for practical use.

Pervaporation processes for the dehydration of organic mixtures are being introduced widely in the chemical industry. Several plants for the dehydration of ethanol and isopropanol are in operation; their capacities range up to 6 ton of ethanol per day. Systems with larger capacities and/or for other separation processes are under construction or are in the project phase. Based on the interest the chemical industry is showing in pervaporation four main areas for this technology, which overlap unavoidably, can be specified. These areas are mentioned below and some examples are given:

- (1) Dehydration of azeotrope-forming binary mixtures.

Table 2.2 shows typical aqueous mixtures which can be dehydrated by pervaporation.

- (2) Dehydration of multi-component process streams.

Table 2.5 gives some examples of multi-component mixtures which can be separated by pervaporation.

**TABLE 2.5: MULTI-COMPONENT MIXTURES CONTAINING WATER WHICH CAN BE TREATED BY PERVAPORATION**

Ethylacetate-ethanol	Butanol-1 - butylether
Diethylether-ethanol	Chloroform-methanol
Acetate-ethanol	Chloroform-ethanol
Acetone-isopropylether	Ethanol-ethylbutylether
Allylalcohol-allylether	Propylacetate-propanol
Allylalcohol-cyclohexane	Isopropylether-isopropanol
Benzene-ethanol	Methanol-ethanol-isopropanol
Butanol-butylacetate	Ethylacetate-ethanol-acetic acid

(3) Dehydration of recycled solvent streams.

Tests have been done on various mixtures, many of them comprising ethanol with isopropanol as the main solvent, and the first plant for such a separation process has been under investigation since 1985.

(4) Removal of low water concentrations from organic liquids.

Tests have been done on hydrocarbons, such as jet-engine fuels and several halogenated hydrocarbons containing water with concentrations 200 and 500 ppm. Final water concentrations less than 20 ppm have been achieved which compares well with those obtained by dehydration using adsorption processes.

Two pilot plants constructed in 1984 in Brazil and in the Philippines, by GFT (Gesellschaft für Trenntechnik) of Mannheim West Germany, are used to distill a mixture obtained from continuous fermentation of sugar-cane, bagasse, and sweet sorghum and containing 6% ethanol to produce a mash containing 80 to 85% ethanol. Thereafter, the mixture is further concentrated to 96% alcohol by pervaporation. The plant in Brazil produces 1 300 ℓ alcohol per day and consumes 1,4 kg steam per ℓ ethanol (1,4 bar, 109°C,  $h = 2\,690$  kJ per kg). The 20 m<sup>2</sup> membrane area is divided up and used in two stages, the first having a higher flux than the second. The permeate side is kept under vacuum and condensation is effected by the use of cooling water at 20°C. The plant in the Philippines is designed to produce 6 000 ℓ pure ethanol per day.

GFT's composite membrane has an active layer of 0,1 μm polyvinyl-alcohol, and the selectivity is measured in small test cells in which the permeate is condensed by means of ice. The transport phenomena are being studied in collaboration with an unnamed university. The pervaporation is being studied of various mixtures, such as ethyl acetate-water and isopropanol-water, with which higher separation and flux have been achieved than with the ethanol-water system.

During the last four years several large pervaporation plants (all for the dehydration of solvents<sup>(159,160)</sup> have been erected and are in operation. The largest plant is a 150 000 ℓ per day ethanol-dehydration plant (93% b.w. to 99,8% b.w.)<sup>(161)</sup>. Other plants are dehydrating toluene, perchloro-ethylene or acetone. The first semi-industrial plants for removal of solvents from aqueous streams are in operation as well<sup>(162)</sup>.

In France and Italy pervaporation is applied to the production of low alcohol wines<sup>(163)</sup>.



At present, development of new membranes and the understanding of the basic principles on mass transport across non-porous membranes is increasing rapidly. Therefore, in the near future membranes will be available to the chemical industry not only for the removal of water from organic liquids, but also for separating a wide variety of liquids.

## 2.2.5 ECONOMICS OF PERVAPORATION

For many applications pervaporation offers cost savings over alternative solvent extraction systems. Actual costs are sensitive to the solvent being removed, the availability of cooling agent, the temperature of the feed and other factors. A particularly important factor is the amount of solvent required to be removed. Most pervaporation systems operate at 90 to 95% solvent removal. Greater amounts of solvent can be removed but this decreases the permeate concentration and increases the cost of the system<sup>(164)</sup>.

Cogat<sup>(167)</sup> compared the economics of pervaporation and distillation for separating water from ethanol and concluded that pervaporation is the more economic process if no pre-existing distillation equipment is available.

The main advantages of the membrane technique are as follows:

- (1) The cost investment is rather less in the case of pervaporation.
- (2) The use of pervaporation saves approximately 65% of the energy required by triple-stage azeotropic distillation.
- (3) Pervaporation can be readily monitored and the purity grade of the ethanol produced easily adjusted, at will.
- (4) During pervaporation, no problem arises from the eventual presence of traces of organics in the recycled feed mixture.

Nevertheless, in certain cases, triple-stage azeotropic distillation can also be used with advantage.

Soukop<sup>(157)</sup> gives the investment and operation costs for a plant with a daily production of 6 000.ℓ (4 740 kg) pure ethanol. The cost of a combined pervaporation-distillation plant is quoted as 2 to 3 times lower than that of a traditional distillation plant, while the running costs are reduced by a factor of 1,5 to 2,5. Pervaporation purification dispenses with the need for high-pressure steam and entrainers which are used in extractive distillation.

The extractive distillation process is based on a shifting of the vapour-liquid equilibrium by adding a solvent with a high boiling point, which is highly selective for one component. Achievement of high product purity (> 98,5%), leads to rapidly increasing energy consumption, and high investment costs.

In 1985<sup>(77,88,170)</sup> there was only one known (semi) commercial pervaporation process; this was the production of pure alcohol by a hybrid process consisting of distillation and pervaporation stages. Therefore, the only way to locate promising areas of application for pervaporation seems to be a detailed analysis of special cases. This has been done for the fractionation of the system

benzene/cyclohexane, which is commonly separated by extractive distillation because its equilibrium curve is very shallow and, in addition, shows an azeotropic point. Two cases have been analyzed:

Case 1: The substitution of the extractive distillation by a pervaporation cascade.

Case 2: A hybrid process consisting of extractive distillation and pervaporation.

The results of this analysis are given in Table 2.6 which shows comparative costs, given in DM, determined in 1985. (Values are not rounded, but quoted from literature.)

Assuming (in Case 1) membrane costs of only 100 DM per m<sup>2</sup> and an average membrane life of 20 months, investment and cooperating costs become a minimum when the temperature drop in the modules is 3°C. According to this analysis a three-stage pervaporation cascade can never be competitive with an extractive distillation plant.

According to Table 2.6 investment costs, as well as operating costs, are higher for pervaporation than for extractive distillation. One reason is the high costs of condensing - a direct consequence of the relatively low pressure (150 mbar) at the permeate side. (The entrance temperature of the cooling water has been assumed to be 20°C).

The heat consumption and, accordingly, the evaporator investment costs are lower for pervaporation than for extractive distillation. This is a consequence of the relatively low reflux ratio of the membrane cascade. The differences in specific costs are so noticeable that, even allowing for future developments, the situation cannot be changed.

Very likely pervaporation will not replace conventional thermal separation processes in cases similar to the one discussed here.

**TABLE 2.6: COST ANALYSIS OF EXTRACTIVE DISTILLATION AND PERVAPORATION. CORRELATIONS FOR THE CALCULATION OF INVESTMENT<sup>(149)</sup>**

	Specific costs (DM/t <sub>product</sub> )	
	Extractive distillation	Pervaporation
Sieve tray-column	6,11	-
Module (without membranes)	-	4,85
Evaporator/heat exchanger	4,43	2,67
Condensor	1,41	6,33
Pumps	0,45	0,72
Membranes (100 DM/m <sup>2</sup> )	-	43,65
Steam (30 DM/t)	18,81	14,44
Cooling water (0,1 DM/m <sup>3</sup> )	1,38	12,69
<b>Total costs</b>	<b>32,59</b>	<b>85,35</b>

Assumptions: membrane service lifetime 20 months, linear amortization within 5 years and 10% interest, operating time 3 500 hr/a.

Pervaporation:  $\vartheta_a = 75^\circ\text{C}$ ;  $\Delta\vartheta = 3^\circ\text{C}$ ;  $P_2 = 150 \text{ mbar}$ ; membrane thickness;  $\delta_M = 8 \times 10^{-6} \text{ m}$ ; reflux ratio,  $m_1 = 0,75$

Pervaporation seems, however, to be economical where high purities are required - and when used in combination with conventional processes. This statement is based on the result of the analysis of Case 2.

Calculations indicate that a hybrid process, a combination of extractive distillation and one-stage pervaporation, will be superior to the conventional extractive distillation. Use of the hybrid process can achieve cost savings of about 20% compared with the costs of the conventional process. It should be emphasized that the required permeate flux in this case is very low ( $0,027 \text{ kg/m}^2\text{h}$ ). The major factor for cost reduction is the much lower energy consumption of the hybrid process of 1,18 t/h of heating stream against 1,7 t/h for the conventional process.

A further reduction of the specific separation costs is feasible if the effective membrane thickness can be reduced, for example, by employing "optimized" asymmetric membranes. It should be noted that the optimal feed concentration of the pervaporation unit is determined not only by the design of the extractive distillation unit but by the effective membrane thickness (or specific membrane costs) as well. With increasing permeate fluxes, or lower specific membrane costs, the optimal feed concentration is shifted to higher hydrocarbon concentrations. This indicates that the optimization of the hybrid process cannot be achieved by optimization of the two stages independently.

The commercial application of pervaporation will most probably be limited to cases where conventional processes either fail or prove difficult to operate. The economics of multi-stage pervaporation processes seem to be very unpromising.

Hybrid processes, i.e., the combination of a one-stage pervaporation with conventional processes in cases where high-purity products are required, appear to be most promising.

## 2.2.6 ALTERNATIVE PROCESSES

Fractionation of liquid mixtures by selective transport through polymer membranes may be achieved by using various techniques of which pervaporation is one.

### 2.2.6.1 Reverse Osmosis

In 1985 Rautenbach and Albrecht<sup>(77)</sup> compared pervaporation and reverse osmosis. Despite the fact that both processes are based on the same transport mechanism, sorption-diffusion-desorption, the separation potential of pervaporation is much higher than that of reverse osmosis, because the transmembrane pressure difference in pervaporation is small. This causes the convective transport through imperfections to be negligibly small compared to diffusive transport. For the reverse osmosis experiments, thick membranes had to be installed in order to avoid convective flow. The result of this comparison, calculated for a benzene-cyclohexane system and polyethylene membranes, indicate that the selectivities and fluxes of pervaporation can be achieved - at least in theory - by reverse osmosis also. The necessary operating pressures are high and, accordingly, the membrane quality must be extremely high with respect to compaction and to imperfections. Although the separation potential of pervaporation and reverse osmosis can be the same in theory, the potential of reverse osmosis is, in reality, markedly lower.

The same conclusions can be drawn from a paper by Sheldon *et al.*<sup>(165)</sup> who discussed reverse osmosis and pervaporation in detail for different operating conditions.

According to Laatikainen and Lindstrom<sup>(26)</sup> reverse osmosis and pervaporation can be treated as closely related processes as far as the separation and transport mechanism is concerned.

#### 2.2.6.2 Distillation

Ishida and Nakagawa<sup>(166)</sup> compared pervaporation and distillation on the basis of an exergy (Gibb's free energy) analysis. The characteristic features of a pervaporation system from the viewpoint of exergy are shown clearly when it is compared with a distillation system.

The following features were emphasized:

- (1) The heat input for pervaporation is generally less than that for distillation.
- (2) The temperature of the heat input for pervaporation may be lower than that for distillation.
- (3) The temperature of the heat output from pervaporation may be lower than that from distillation.

Hence, when cooling water can be used as coolant, we may say from the exergy viewpoint, that the heat input is utilized more effectively in the pervaporation system than in the distillation system.

Consequently, when the exergy losses from pervaporation and distillation systems are almost equal, pervaporation is superior to distillation. For the time being it would be better to combine pervaporation with distillation, to reduce the heat input and to increase the driving force for pervaporation.

Cogat<sup>(167)</sup> compared the economics of the two processes as noted earlier (see Section 2.2.5).

#### 2.2.6.3 Membrane Distillation

Membrane distillation has recently attracted wide interest as a process for the separation of aqueous mixtures. The potential advantage is the low temperatures involved; on the other hand, if it is compared with pressure-driven membrane processes, membrane distillation has the advantage that it is not subject to strong limitations when large osmotic pressures are involved.

Different types of membrane distillation are considered by Sarti and Gostoli<sup>(168)</sup> who analyzed the effects of the relevant process variables and discussed the applicability of the processes to the separation of water-ethanol mixtures.

Ohya *et al.*<sup>(169)</sup>, on the other hand, investigated the transport of mixed vapours in membrane distillation. Although highly efficient processes are available as laboratory curiosities at this stage, the applicability of this technique on an industrial scale is nowhere near acceptance.

#### 2.2.6.4 Vapour Permeation

Vapour permeation, like pervaporation, is of interest in the separation of water-organic or organic-organic mixtures which are difficult to separate by distillation. The advantage of vapour permeation

compared with pervaporation is that the necessity to supply the evaporation enthalpy by the latent heat of the feed is eliminated.

If top product of a fractionation column is to be further purified by vapour permeation or pervaporation, the inlet feed to the membrane stage is already in the vapour phase. Consequently, the installation of a number of heat exchangers for feed reheating, which is typical for pervaporation, can be avoided. A small disadvantage of vapour permeation is the necessity to minimize the pressure losses at the module feed-side and not only at the permeate-side.

Rautenbach *et al.*<sup>(170)</sup> did a comparative study of pervaporation, gas permeation, and reverse osmosis. In Table 2.7 the characteristics of the membrane processes are summarized.

**TABLE 2.7: CHARACTERISTICS OF MEMBRANE PROCESSES<sup>(170)</sup>**

	Reverse osmosis	Pervaporation	Gas permeation
State of Liquid/liquid aggregation	Liquid/vapour	Gas/gas	
Membrane structure	Nonporous Symmetric Asymmetric		Micro-porous
Transport mechanism	Sorption and diffusion		Pore flow (Knudsen)

Rautenbach *et al.*<sup>(147,171)</sup> also reported results of vapour permeation experiments with various water-alcohol mixtures. In these experiments composite membranes, developed for pervaporation, were used.

According to the experiments

- (1) the separation potential of vapour permeation and pervaporation are, in principle, identical;
- (2) the flux of vapour permeation is very sensitive to a decrease of the feed-side pressure ratio.

Most likely, the results presented in their paper are valid in general and are not limited to the water-alcohol mixtures tested in the experiments.

Suematsu *et al.*<sup>(172)</sup> investigated the separation of ethanol-water mixtures by permeation of vapour through cellulose membranes. Vapour permeation was compared with pervaporation under isothermal conditions. The selectivity of vapour permeation was higher than that of pervaporation for the whole

range of feed compositions, while the permeation rate of vapour was lower. It was observed that the membrane used in pervaporation was more swollen than that used in vapour permeation.

Furthermore, where feed vapour was superheated in vapour permeation, the selectivity increased markedly and the permeation rate decreased. The influence of temperature on the permeation rate was investigated as well.

#### 2.2.6.5 Perstraction

Perstraction has been found to be effective for separating azeotropes and other liquid mixtures into their components. In perstraction, the permeate is removed by a stream of non-permeable purge liquid, which is subsequently separated from the permeate by distillation and recycled.

It is sometimes necessary to employ "hybrid" processes, which combine membrane separation with some conventional separation technique, such as fractional distillation or adsorption. The hybrid processes have been found to be economically attractive in terms of capital and energy costs by conventional separation techniques such as extractive distillation<sup>(173)</sup>.

It is interesting to compare the separation of benzene/cyclohexane mixtures which can be achieved by selective permeation through alloy (composites of different polymers) membranes in perstraction and pervaporation processes. Specific permeation rates are compared by Acharaya and Stern<sup>(57)</sup>. Neglecting the small temperature difference in the two types of measurements, pervaporation yields higher permeation rates.

The selectivity of the membranes is reported as a function of feed composition at different temperatures for perstraction and at a single temperature for pervaporation. The selectivity values for perstraction and pervaporation agree within experimental error.

The relative advantages of perstraction and pervaporation, when these processes are compared with distillation or some other conventional separation technique, can be unambiguously assessed only by means of a detailed economic analysis. In comparing perstraction and pervaporation, it appears that the latter process has the advantage of lower membrane area requirements because of the larger driving force required for permeation. The energy requirements of the two membrane processes differ however in several aspects.

#### 2.2.6.6 Adsorption and Air Stripping

During the last few years, volatile organic compounds have come to be present in some ground supplies of water. Adsorption and air stripping are two of the techniques used to remove these compounds. Membrane separation processes, particularly pervaporation, have been viewed with considerable interest as means for reducing solvent contamination in water.

Aptel *et al.*<sup>(175)</sup> compared pervaporation with adsorption and air stripping in respect of their efficiency and operating costs.

## 2.3 THEORETICAL BACKGROUND OF THE SYNTHESIS STUDY

The theoretical bases of the free-radical polymerization reactions, hydrolysis reactions and crosslinking reactions are well described in the literature<sup>(176-181)</sup>.

### 2.3.1 POLYMERIZATION REACTIONS: A BRIEF BACKGROUND

#### 2.3.1.1 General

Details of initiators required, polymerization techniques, kinetics and so on are of extreme importance, but these are readily available in a number of publications<sup>(176,177)</sup>.

Several polymers were synthesized. Crosslinkable polymers with various degrees of hydrophobicity were needed in this study. Various degrees of crosslinking were achieved by using different amounts of hydroxyethyl acrylate (HEA) in the polymer. Various degrees of hydrophobicity were achieved by using different amounts of acetate in the polymer. No literature references to such a compound were found on either pervaporation or synthetic work. Where, however, background could be traced, references to this are included in Table 2.3 to provide an established working basis to the study.

### 2.3.2 COPOLYMERS

#### 2.3.2.1 Poly (vinyl acetate-co-2-acrylic acid)

The only reference on this copolymer found in the literature was a thesis by Van Reenen on dynamic membranes<sup>(182)</sup>.

### 2.3.3 TERPOLYMERS

#### 2.3.3.1 Poly (vinyl acetate-co-hydroxyethyl acrylate-co-acrylic acid)

No literature reference to this terpolymer was found.

### 2.4.1 HYDROLYSIS REACTIONS: A BRIEF BACKFROUND

#### 2.4.1.1 General

Details of the chemicals required and mechanisms of reactions are again of extreme importance, but these are readily available in a number of publications<sup>(178,183,184)</sup>. In this study, base-catalyzed hydrolysis was done.

### 2.4.2 COPOLYMER HYDROLYSIS

#### 2.4.2.1 Poly (vinyl acetate-co-acrylic acid)

The only reference on this hydrolyzed copolymer found in the literature was a thesis by Van Reenen on dynamic membranes<sup>(182)</sup>.

### 2.4.3 TERPOLYMER HYDROLYSIS

#### 2.4.3.1 Poly (vinyl acetate-co-hydroxyethyl acrylate-co-acrylic acid)

No literature reference was found.

## 2.5.1 CROSSLINKING REACTIONS: A BRIEF BACKGROUND

### 2.5.1.1 General

Details of chemicals required and mechanisms of reactions are readily available in a number of publications<sup>(179,180,181,185,186,187)</sup>. The chemistry of crosslinking reactions is well known in the literature. HEMA and HEA were found to be well-known compounds to effect crosslinking in general, so that the degree of crosslinking was varied by the adjusting the ratio of HEA present in the terpolymer.

As some of the polymers that were crosslinked were novel, no reference could be found to the crosslinking of the specific polymers in the literature.

Background could be traced concerning the use of HEMA in crosslinking and this established the working basis to the study undertaken<sup>(190)</sup>.

## 2.5.2 POLYVINYL ALCOHOL CROSSLINKING

References on polyvinyl alcohol crosslinking are readily available. Different crosslinking reagents are used. The most preferred crosslinking reagent is copper sulfate<sup>(187,188)</sup>. It has also been proposed that potassium persulfate is effective as a crosslinking reagent<sup>(187)</sup>. Sulphuric acid has also been used as a crosslinking reagent<sup>(186)</sup>.

## 2.5.3 COPOLYMER CROSSLINKING

### 2.5.3.1 Poly (vinyl acetate-co-acrylic acid)

The only reference on this copolymer found in the literature was a thesis by Van Reenen on dynamic membranes<sup>(182)</sup>.

## 2.5.4 TERPOLYMER CROSSLINKING

### 2.5.4.1 Poly (vinyl acetate-co-hydroxyethyl acrylate-co-acrylic acid)

No literature reference was found.

## 2.6.1 MEMBRANE EVALUATION

### 2.6.1.1 Characterization of a Pervaporation Membrane<sup>(53)</sup>

It is clear that flux and selectivity are the two characteristics which determine the performance of a membrane  $M$  used to separate, by pervaporation, a given binary A-B liquid mixture. Since the permeation of both liquids is influenced by the extent of swelling of the permselective film and therefore dependent on the composition of the facing A-B feed, the complete evaluation of the membrane performance required the knowledge of these dependences. Usually, these investigations are carried out in a discontinuous way, by experimenting with a series of A-B mixtures differing in their compositions and with simple laboratory cells which have been described in the literature<sup>(35)</sup>.

According to Huang and Lin<sup>(48)</sup> the membrane selectivity of a binary system consisting of two liquids A and B can be expressed in terms of a separation factor  $\alpha$ , defined as the concentration ratio B/A in the permeate divided by the ratio B/A in the feed.



The permeation rate of a mixture through a membrane is the sum of the permeation rates of the components in the mixture. Non-ideal behaviour results when one component of the permeating mixture plasticizes the membrane more than the other. The measure of the non-ideal behaviour of liquid permeation can be expressed by a permeation ratio which is defined as the ratio of the actual permeation rate to its ideal permeation rate. If the permeation ratio of a system is greater than unity, the system can be said to exhibit a permeation enhancement effect, while a value lower than unity indicated a permeation depression effect.

### (A) Pervaporation Rate (Flux)

To describe the characteristic data of a pervaporation test, two factors were selected:

- (a) the pervaporation rate (flux), represented by  $\psi$  or  $J$  and expressed in kilograms per hour per square meter,  
 $\psi$  (kg/h.m<sup>2</sup>)

and

- (b) the selectivity factor,  $\alpha$  (see Section 2.2.1).

Pervaporation rates<sup>(53)</sup> are generally expressed in the abovementioned unit since the permeate undergoes a phase change during the pervaporation process. Total flux,  $\psi$  or  $J$ , may be divided into two separate fluxes, namely  $\psi_A$  or  $J_A$  and  $\psi_B$  or  $J_B$ .

In all the figures and tables, the values of  $\psi(J)$  are taken at the initial stage of pervaporation in order to ensure comparable values.

### (B) Selectivity

The simplest parameter characterizing the transport selectivity is the  $\beta$  ratio defined as:

$$\beta = \frac{c'}{c}$$

$c$  and  $c'$  being, respectively, the mass concentration of the more permeative component in the feed ( $c$ ) and in the permeate ( $c'$ ).

This  $\beta$  parameter is very convenient for formulating the chemical engineering equations which govern a continuous separation by pervaporation. However, it has the disadvantage of being devoid of any significance from the physico-chemical point of view. In fact, a perfectly semi-permeable membrane ( $c' = 1$ ) is characterized by  $\beta = 1/c$  which depends on  $c$ .

Selectivity data are therefore more generally reported using the  $\alpha$  parameter.

$$\alpha = \frac{c'}{1 - c'} / \frac{c}{1 - c} = \frac{c'}{c} \frac{1 - c}{1 - c'}$$

This latter ratio is more significant since it assumes an infinite value for a perfectly selective membrane ( $c' = 1$ ). Moreover, it is equivalent to the ratio commonly used in gas permeation and it can be shown that it would be directly related to the partition and diffusion coefficients of both penetrants if these characteristics were not concentration-dependent.

$$\beta = \frac{k_A D_A}{k_B D_B}$$

$k_A$  and  $k_B$  are the partition coefficients of A and B between the swollen upstream membrane layer  $(C_A)_1$ ,  $(C_B)_1$  and the facing liquid feed mixture  $(C_A, C_B)$ .

$$(C_A)_1 = k_A C_A$$

$$(C_B)_1 = k_B C_B$$

$D_A$  and  $D_B$  are the diffusion coefficients of A and B within the membrane.  $(C_A)_1$  and  $(C_B)_1$ : A and B mass concentrations in the upstream layer of the membrane.

A = faster penetrant.

The numerical values of  $\alpha$  and  $\beta$  can be readily interconverted by using the following relationships:

$$\alpha = \frac{1 - c}{1 - \beta c} \quad \beta = \frac{\alpha}{1 + (\alpha - 1)c}$$

These equations show that  $\alpha$  is systematically higher than  $\beta$ .

In order to express the characteristic behaviour of a membrane towards a given liquid mixture, the following conventions<sup>(35)</sup> were selected for this thesis.

Suppose a pervaporation test was carried out with a binary system consisting of two liquids A and B (pervaporant). The total feed volume was  $V$ , the partial volumes were  $V_A$  and  $V_B$  and the volume fractions were  $X_A$  and  $X_B$ :

$$X_A = \frac{V_A}{V} \quad X_B = \frac{V_B}{V}$$

The diffusing species (permeate) were condensed in a trap. Every hour, this trap was removed from the apparatus and another one then connected. The volume  $v$  and the composition (volume fractions  $y_A$  and  $y_B$ ) were measured:

$$v = v_A + v_B \quad y_A = \frac{v_A}{v} \quad y_B = \frac{v_B}{v}$$

These values permit the calculation of the volume fraction  $X$  of the pervaporant and the volume fraction  $Y_A$  and  $Y_B$  of the two compounds which have been pervaporated since time zero:

$$X = \frac{\Sigma v}{v} \quad Y_A = \frac{\Sigma v_A}{v_A} \quad Y_B = \frac{\Sigma v_B}{v_B}$$

Between  $X$ ,  $Y_A$  and  $Y_B$  the following relation may be easily verified:

$$X = x_A Y_A + x_B Y_B$$

or

$$2X = Y_A + Y_B$$

When the initial mixture is composed of equal volumes of A and B. Graphs of  $Y_A$  and  $Y_B$  versus  $X$  can be plotted. The more the graphs diverge, the better the fractionation is.

The membrane selectivity of a binary system composed of two liquids can be expressed in terms of a selectivity factor,  $\alpha$ , defined as the concentration ratio  $y_A/y_B$  by volume in the permeate divided by the ratio  $x_A/x_B$  in the pervaporant (feed):

$$\alpha = \frac{y_A/y_B}{x_A/x_B}$$

A is the species which is preferentially pervaporated. During the pervaporation, the volume fractions  $x_A$  and  $x_B$  vary, so that  $\alpha$  is not constant. Considering  $\alpha_0$  as the selectivity factor at the initial stage of the transfer, it can be easily shown that  $\alpha_0$  is the ratio between the tangent slopes of the two graphs  $Y_A$  vs  $X$  and  $Y_B$  vs  $X$  at the origin.

In all the figures and tables the values of  $\alpha$  can be taken at the initial stage of pervaporation, in order to ensure comparable values.

### 2.6.1.2 Additional Comments on Membrane Evaluation

The literature contains little information on the morphology of membranes, e.g. the swelling of the membrane in reaction to the feed stream, and the measurement of the hydrophobicity of the material.

In general, analysis usually comprises a study of the selectivity, in terms of the following variables:

- feed
- materials used
- temperature
- membrane geometry.

There has been little research on membrane performance. This area deserves more attention in the future.

## CHAPTER 3

### EXPERIMENTAL OBJECTIVES, MATERIALS AND EQUIPMENT

#### 3.1 GENERAL

Two factors largely influence membrane functionality (usability). These are membrane performance, comprising flux and selectivity, and membrane durability.

As discussed in Chapter 2, the present state-of-the-art pervaporation membranes do not include terpolymer membranes.

It was the object of this study to synthesize suitable terpolymers to characterize them, to make membranes and to evaluate the performance of these membranes.

#### 3.2 MATERIALS

Polyvinyl alcohol (PVA) was used for making membranes for the preliminary experiments. PVA was used together with different crosslinking reagents. PVA with different molecular mass was used as well. The making of these membranes is described in Section 4.5.2.

Gantrez AN 119, a fabricated membrane, made according to a patented literature reference<sup>(187)</sup>, was tested to compare with the synthesized membranes. The making of this membrane is summarized in Table 4.5.

Commercial membranes, GFT-standard and GFT-wasserreich, were tested to set a standard to which the synthesized membranes can be compared.

#### 3.3 SYNTHESIS OBJECTIVES

##### 3.3.1 TERPOLYMERS

Terpolymers of the family poly(vinyl acetate-co-hydroxyethyl acrylate-co-acrylic acid) were synthesized.

##### 3.3.2 HYDROLYSIS

Different percentages of the acetate groups on the terpolymer (see Section 3.2.3.1) were hydrolyzed.

#### 3.4 CHARACTERIZATION OBJECTIVES

The polymers were characterized by Nuclear Magnetic Resonance Spectroscopy (NMR). The methods are discussed in Chapter 4.

## 3.5 EVALUATION OBJECTIVES

The polymers were evaluated as pervaporation membrane components. This evaluation was made in terms of:

- (a) membrane performance;
- (b) membrane durability;
- (c) membrane formation.

## 3.6 EQUIPMENT

### 3.6.1 SYNTHESIS EQUIPMENT

#### 3.6.1.1 Distillation Equipment

Standard distillation equipment was connected to a vacuum line in order to facilitate the purification of liquid monomers at relatively low temperatures. The equipment consisted of a double-necked 50 mL round-bottomed flask, a 6-inch Vigreux-column, adaptor, thermometer, jacketed distillation head and a monomer trap.

#### 3.6.1.2 Polymerization Equipment

The polymerization equipment consisted of a double-necked 50 mL round-bottomed flask, a 6-inch long Vigreux column and a glass stopper.

#### 3.6.1.3 Vacuum Pump

A SPEEDIVAC model was used to provide the vacuum for degassing the reaction mixtures.

### 3.6.2 CHARACTERIZATION EQUIPMENT

#### 3.6.2.1 Nuclear Magnetic Resonance Spectrograph

A VARIAN model FT 80 Nuclear Magnetic Resonance Spectrograph, as well as a VARIAN model VXR 300 were used for characterization purposes.

### 3.6.3 EVALUATION EQUIPMENT

#### 3.6.3.1 Membrane Coating Equipment

The membrane coating equipment consisted of a polyurethane roller, two clamps and a glass plate. A Perspex frame with clamps was also used.

#### 3.6.3.2 Gas Chromatograph

A VARIAN model 3700 Gas Chromatograph (GC) coupled to either a VARIAN CDS 111 model 9176 recorder or a HP 3380 A HEWLETT PACKARD integrator was used for evaluation purposes. Details of the column used in the gas chromatograph are given in Table 3.1.

**TABLE 3.1: GAS CHROMATOGRAPH COLUMN SPECIFICATIONS**


---

Column material	Stainless steel
Length	1 828,8 mm
Outside diameter	6,4 mm
Inside diameter	5,3 mm
Support	Chromosorb WHP
Mesh range	80/100
Liquid phase	Carbowax 20 M
Weight %	10
Date	5/2/80
Comments	Temperature: 60 to 225 <sup>o</sup> C

---

The parameters (see Table 3.2) of the gas chromatograph-integrator were kept constant throughout the experiments.

**TABLE 3.2: GAS CHROMATOGRAPH - INTEGRATOR PARAMETERS****GC:**

Temperature control	
Injector	100 <sup>o</sup> C
Ionization detector	100 <sup>o</sup> C
Column temperature	70 <sup>o</sup> C
Program	not used
Column limit	200 <sup>o</sup> C
Attenuator	256
Output	+

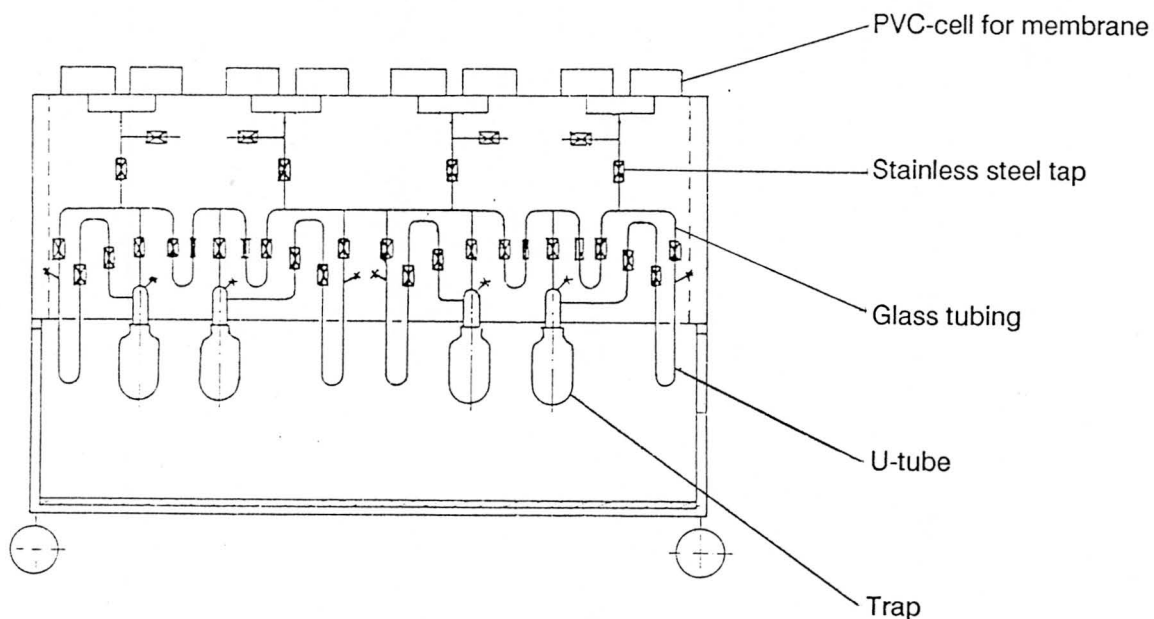
**Integrator:**

Report	Area %
Start delay	not used
Stop timer	5 minutes
Area reject	not used
Chart speed	0,5 cm/min
Chart	Auto
Slope sensitivity	0,3 mV/min
Attenuation	32

---

**3.6.3.3 Pervaporation Test Apparatus**

A pervaporation test apparatus (Figure 3.1) was designed and constructed.



**FIGURE 3.1: SCHEMATIC REPRESENTATION OF THE PERVAPORATION TEST APPARATUS**

A schematic representation of this equipment is given in Figure 3.1. (The apparatus is connected to a vacuum pump.) The feed mixture was circulated at a set rate past four flat-sheet membranes (the formation of these membranes is discussed in Section 4.5.2). Permeate passed through the membranes, to the vacuum-side of the system, and was condensed in the liquid-nitrogen traps. By returning the permeate to the feeding tank, the feed concentration could be kept constant.

## CHAPTER 4

### EXPERIMENTAL METHODS

#### 4.1 MONOMERS

The monomers used were:

- (a) Acrylic acid, AR grade from FLUKA.
- (b) Vinyl acetate, AR grade from FLUKA.
- (c) Hydroxyethyl acrylate, AR grade from FLUKA.

#### 4.2 POLYMERIZATION REACTIONS

##### 4.2.1 PRE-REACTION SEQUENCE

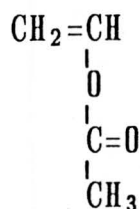
Equipment used for polymerization reactions was assembled as described in Section 3.6.1.2. An oil bath was used for heating.

Standard practice, before initiation of a reaction (by adding benzoylperoxide), was to remove all traces of oxygen from the reaction mixture. This was done by flushing with N<sub>2</sub> (Air Products; High Purity Grade).

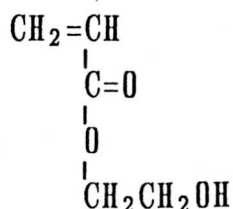
##### 4.2.2 TERPOLYMERIZATION

###### 4.2.2.1 Vinyl acetate and hydroxyethyl acrylate and acrylic acid

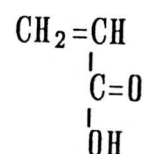
###### (a) Monomer structures



Vinyl acetate



Hydroxyethyl acrylate



Acrylic acid

The monomers vinyl acetate (JF 3), hydroxyethyl acrylate (JF 4) and acrylic acid (006) were proved to have a high purity and correct composition by NMR spectroscopy. The carbon-13 spectra of these monomers can be seen in Figures 5.15, 5.16 and 5.17.



**(b) Method of Polymerization**

All reagents were freshly distilled before use. In a typical polymerization reaction, a mixture of (0,61 g;  $8,46 \times 10^{-3}$  moles) acrylic acid, (3,00 g;  $2,94 \times 10^{-3}$  moles) hydroxyethyl acrylate and (18,04 g;  $2,10 \times 10^{-2}$  moles) vinyl acetate in (100,05 g; 1,14 moles) 1,4-dioxane was flushed with  $N_2$  and (1,21 g;  $5,01 \times 10^{-3}$  moles) benzoylper oxide was added. The reaction mixture was stirred under constant reflux, at 343 K for 30 minutes. The reaction was terminated with the addition of (2,04g;  $1,82 \times 10^{-2}$  moles) hydroquinone. The terpolymer produced was recovered from the reaction mixture by precipitation in (231,26 g; 3,12 moles) diethyl ether. The material was filtered and dried under vacuum at 298 K. The reaction mixtures ratios used in the preparation of the various terpolymers are shown in Table 4.1. The yields obtained are given in Table 4.2. The four terpolymers were characterized by NMR-spectroscopy. The carbon-13 spectra can be seen in Figures 5.18, 5.19, 5.20 and 5.21. (Numerical values are rounded to two significant digits.)

**TABLE 4.1: AMOUNTS OF CHEMICALS USED FOR THE POLYMERIZATION REACTIONS**

Chemicals	Terpolymers			
	010	011	012	013
Acrylic acid	0,61 g; $8,5 \times 10^{-3}$ moles	0,40 g; $5,6 \times 10^{-3}$ moles	0,2 g; $2,9 \times 10^{-3}$ moles	0,0 g; 0 moles
Hydroxyethyl acrylate	3,0 g; $2,9 \times 10^{-3}$ moles	3,0 g; $2,9 \times 10^{-3}$ moles	3,0 g; $2,9 \times 10^{-3}$ moles	3,1 g; $3,0 \times 10^{-3}$ moles
Vinyl acetate	18,0 g; $2,1 \times 10^{-1}$ moles	18,0 g; $2,1 \times 10^{-1}$ moles	18,0 g; $2,1 \times 10^{-1}$ moles	18 g; $2,1 \times 10^{-1}$ moles
1,4-Dioxane	100,0 g; 1,1 moles	100,0 g; 1,14 moles	100,0 g; 1,1 moles	100,0 g; 1,1 moles
Diethyl ether	$2,3 \times 10^2$ g; 3,1 moles	$2,3 \times 10^2$ g; 3,12 moles	$2,3 \times 10^2$ g; 3,1 moles	$2,3 \times 10^2$ g; 3,1 moles
Benzoyl peroxide	1,2 g; $5,0 \times 10^{-3}$ moles	1,8 g; $3,4 \times 10^{-3}$ moles	0,8 g; $3,4 \times 10^{-3}$ moles	0,8 g; $3,4 \times 10^{-3}$ moles
Hydroquinone	2,0 g; $1,8 \times 10^{-2}$ moles	2,2 g; $2,0 \times 10^{-2}$ moles	2,1 g; $2,1 \times 10^{-2}$ moles	2,2 g; $1,5 \times 10^{-2}$ moles
Reaction time	30 min	60 min	60 min	75 min

TABLE 4.2: YIELD OF POLYMERIZATION REACTIONS

Terpolymers	g	%
010	4,51	21
011	4,97	23
012	4,32	20
013	3,91	19

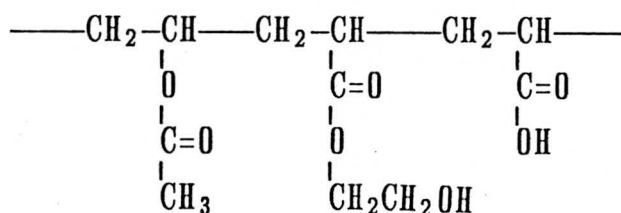
### 4.3 TERPOLYMER HYDROLYSIS

#### 4.3.1 PRE-REACTION SEQUENCE

All the reactions were carried out in 250 ml Schott bottles. After all the ingredients had been added, the reaction mixture was stirred at 298 K for 72 hours.

##### 4.3.1.1 Poly (vinyl acetate-co-hydroxyethyl acrylate-co-acrylic acid)

###### (a) Terpolymer structure (prior to hydrolysis)



###### (b) Method

Typically, a solution of (0,50 g) watersoluble terpolymer in (29 ml) 0,1 M (standardized) sodium hydroxide was diluted with (71 ml) distilled water. The amounts employed in the series of experiments are detailed in Table 4.3.

The stirred hydrolysis reaction was performed at room temperature for 72 hours. The material was filtered and dried under vacuum at 298 K to obtain sodium salts. The yields obtained are given in Table 4.4. Selected hydrolyzed terpolymers were characterized by NMR-spectroscopy. The carbon-13 spectra can be seen in Figures 5.22, 5.23, 5.24, 5.25, 5.26, 5.26 and 5.27. The integration of these spectra can be seen in Figures 5.28, 5.29, 5.30, 5.31, 5.32 and 5.33.



100% Hydrolysis:

Neutralize acid and hydrolyze acetate:

$$\begin{aligned} \text{Moles of sodium hydroxide} &= \text{moles of acid} + \text{moles of acetate} \\ &= 1 \times 10^{-3} + 2 \times 10^{-3} \\ &= 3 \times 10^{-3} \end{aligned}$$

$$\text{Grams of sodium hydroxide} = 0,12$$

Volume of sodium hydroxide

$$(0,1M) \text{ solution} = \frac{0,12}{4 \times 10^{-3}} = \frac{0,12}{4} \times 10^3$$

\*Hydrolysis of acrylate not taken into account in calculation.

TABLE 4.4: YIELD OF HYDROLYSIS REACTIONS

Hydrolyzed polymers	Calculated amount of hydrolysis (%)	Yield (g)
010 : 100	100	0,50
011 : 100	100	1,14
012 : 100	100	0,36
013 : 100	100	0,17
010 : 70	70	0,47
011 : 70	70	0,48
012 : 70	70	0,47
013 : 70	70	0,16
010 : 50	50	0,49
011 : 50	50	0,41
012 : 50	50	0,50
013 : 50	50	0,49
010 : 30	30	0,26
011 : 30	30	0,50
012 : 30	30	0,50
013 : 30	30	0,35
010 : 0	0	0,36
010 : 0	0	0,44
012 : 0	0	0,47
013 : 0	0	0,05

## 4.4 POLYMER CHARACTERIZATION

### 4.4.1 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Thirty percent solutions of the terpolymers were made in deuterized dimethyl siloxane (DMSO -  $d_6$ ). Ten percent solutions of the hydrolyzed terpolymers were made in deuterized water ( $D_2O$ ).

The standard method was used to record the NMR spectra.

## 4.5 MEMBRANE FORMATION AND EVALUATION

### 4.5.1 INTRODUCTION

Many techniques can be used to form thin-film composite membranes<sup>(188-190)</sup>. For this research project a roll-on and a pour-on technique were tested.

The membrane formation techniques were practiced with a 2% polyvinyl alcohol (Mn = 72 000; % hydrolysis: 86 - 89) solution containing 0,1% concentrated sulphuric acid. The variables of the crosslinking reaction can be found in Table 4.5. The membranes were cut out with a oval template (approximately 42,5 cm<sup>2</sup>). For testing, two membranes cut from the same sheet were mounted in polyvinyl chloride cells which were placed in series in the test apparatus and were sealed with O-rings. The effective membrane area is approximately 31,1 cm<sup>2</sup> inside the O-ring.

Based on these test results, decisions were made regarding the following variables:

- (a) Number of polymer layers for membranes.
- (b) Time needed for a standard pervaporation experiment.
- (c) Time between readings for a pervaporation experiment.
- (d) Composition of feed mixture:
  - Components.
  - Relative ratio of components.

The results of these preliminary experiments are given in Section 5.2.

### 4.5.2 MEMBRANE FORMATION

Two techniques for membrane formation were tested. These techniques are the following:

- (1) The roll-on technique.
- (2) The pour-on technique.

The roll-on technique comprises the following. After a small volume of a polymer solution had been poured onto the substrate, it was spread evenly by a rubber roller. Each layer was heated to 120°C for 30 minutes. It was impossible to obtain reproducible results. The variation in the results was caused by the variation in the layer thickness which could not be kept constant because the polymer solution was spread by hand. It was decided to test an alternative method of forming the membrane.

The pour-on technique comprises the following. In a typical case the polymer solution is poured onto the smooth side of the substrate, (5 min) and drained (5 min). Each polymer layer was heated to 120°C for 10 minutes. This method was successful. Details of the actual conditions used are given in Table 4.5.

#### 4.5.2.1 Crosslinking Reactions

The crosslinking reactions were part of the membrane formation technique as described in Section 4.5.2. Crosslinking reagents were added to the polymer solution before it was poured onto the

substrate or the membrane was soaked in a solution of the crosslinking reagent. Heat initiated the crosslinking reaction. Details of the crosslinking reactions done during this research project are summarized in Table 4.5.

**TABLE 4.5: VARIABLES OF THE CROSSLINKING REACTIONS**

Polymer (Mol. Mass)	Solvent (% Polymer)	Crosslinking Reagent (%)	Temp. (°C)	Time (min)	Ref.
<b>I: Reagents in Polymer Solutions:</b>					
Polyvinyl alcohol (72 000)	Water (2)	H <sub>2</sub> SO <sub>4</sub> (0,1)	120	10	186
Polyvinyl alcohol (72 000)	Water (2)	H <sub>2</sub> SO <sub>4</sub> (0,1)	120	30	186
Polyvinyl alcohol (72 000)	Water (2)	H <sub>2</sub> SO <sub>4</sub> (0,1)	120	25	186
Gantrez AN 119	Water (2)	H <sub>2</sub> SO <sub>4</sub> (2,5)	120	20	-
Polyvinyl alcohol (72 000)	Water (2)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (0,5)	80	20	187
Polyvinyl alcohol (15 000)	Water (2)	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (0,5)	80	20	187
Hydrolyzed terpolymers	Water (2)	Not needed - inherent in structure	5	120	186
<b>II: Reagent solution with dehydrated polymer:</b>					
Polyvinyl alcohol-co- acrylic acid	Water (2)	CuSO <sub>4</sub> (0,5)	-	1 400	180, 185

#### 4.5.3 MEMBRANE PRETREATMENT<sup>(191,192)</sup>

In the course of some experiments, pretreatment of membranes was considered. It was decided to use an ethanol-hexane mixture for this pretreatment. The membrane was soaked in a 30% ethanol solution for 8 hours. After the pretreated membrane was then tested with a 5% ethanol feed.

#### 4.5.4 MEMBRANE EVALUATION

The membranes were evaluated in terms of a percentage of ethanol in the permeate in comparison with the percentage of ethanol in the feed-mixture. These values were obtained by injecting 0,5  $\mu\text{l}$  of both the feed and permeate mixtures into a gas chromatograph (see Section 3.5.3.2).

Both a 50% and a 30% ethanol feed-mixture were used for each of the membranes. The flux of the membrane was estimated, based on the amount of permeate in the trap. Each run lasted for 8 hours.

To establish the performance of the synthesized membranes, they were tested against the commercial membranes, e.g. GFT-standard, GFT-wasserreich and a fabricated Gantrez AN 119 membrane, made according to a patented literature reference<sup>(187)</sup>. Polyvinyl alcohol membranes with differing molecular mass (72 000 vs 15 000) were tested as well. All these results can be found in Appendix A.

# CHAPTER 5

## RESULTS AND DISCUSSION

### 5.1 INTRODUCTION

This chapter describes the new polymers and presents the results of their properties as pervaporation membranes. This work was undertaken without the knowledge of reactivity ratios and chemical proportions were therefore empirically chosen. The polymers were regarded as original because of this, and similar polymers have not previously been used in pervaporation.

In the following sections an endeavour will be made to describe the properties of pervaporation membranes formed with these polymers in terms of selectivity (separation factors) and/or flux. Preliminary experiments with polyvinyl alcohol membranes were used as a reference. The data obtained will be used to determine trends and to evolve ideas.

### 5.2 PRELIMINARY EXPERIMENTS

Pervaporation facilities were built and commissioned, experiments were carried out to determine the variables important in standardizing an experimental procedure.

#### 5.2.1 POLYMER LAYERS

Experiments concerning the number of polymer layers used to make a membrane were carried out with a 2% polyvinyl alcohol ( $M_n = 72\ 000$ ; % hydrolysis: 86 - 89) solution containing 0,1% concentrated sulphuric acid. Polysulphone was used as a substrate. The pour-on technique, as discussed in Section 4.5.2, was used to make the layers. Pervaporation was carried out for 3 hours at room temperature with 30% ethanol in the feed mixture. The vacuum approached 101,3 kPa. The results of these experiments can be found in Table 5.1, (average of 2 results, rounded to two significant digits).

**TABLE 5.1: THE SELECTIVITY OF MEMBRANES CONSISTING OF DIFFERENT AMOUNTS OF POLYMER LAYERS**

Number of layers	Selectivity ( $\alpha$ )	Flux ( $\text{kg/m}^2 \cdot \text{h}$ )
2	4	740
3	60	480
4	140	370
5	400	300

A membrane consisting of one layer of polymer was too thin and it was sucked through the substrate by the vacuum pump.

If the results of these experiments were displayed graphically (see Figure 5.1), the selectivity increases with the increasing number of polymer layers. These results are for specific experimental conditions.

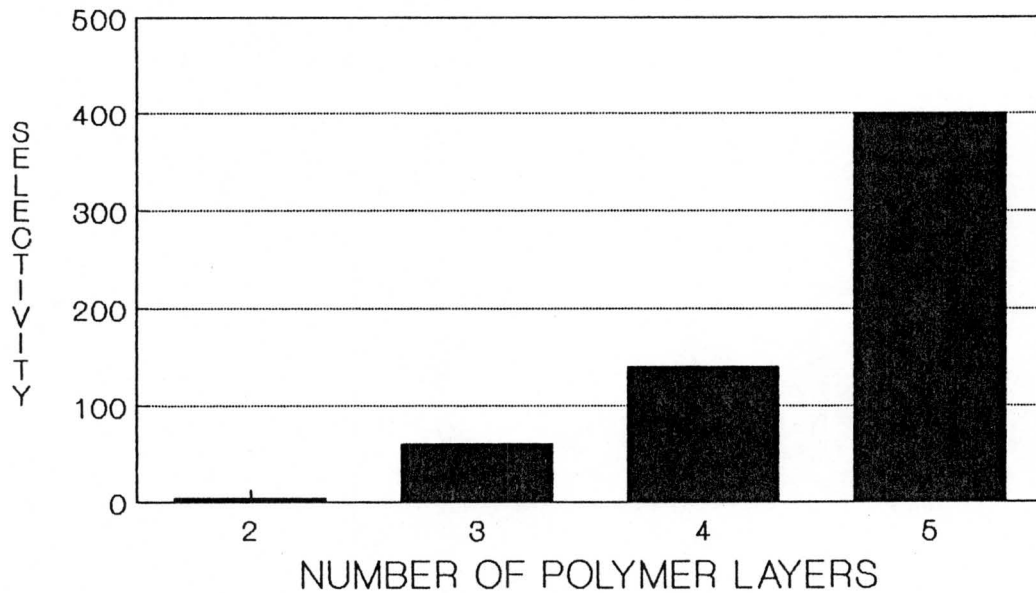


FIGURE 5.1: GRAPH OF NUMBER OF POLYMER LAYERS VS SELECTIVITY

Aptel *et al.*<sup>(153)</sup> state that selectivity is not affected by membrane thickness. Spitzen *et al.*<sup>(144)</sup> agrees with them in one case but found in another that flux decreases and selectivity increases with increased membrane thickness. Most research<sup>(137,138)</sup> agrees with the latter phenomenon, which agrees with the results found in this experiment.

### 5.2.2 CUMULATIVE TIME

The change in selectivity and flux was measured over a 12 hour period under the conditions used in Section 5.2.1. To make the membrane, two layers of polymer were used.



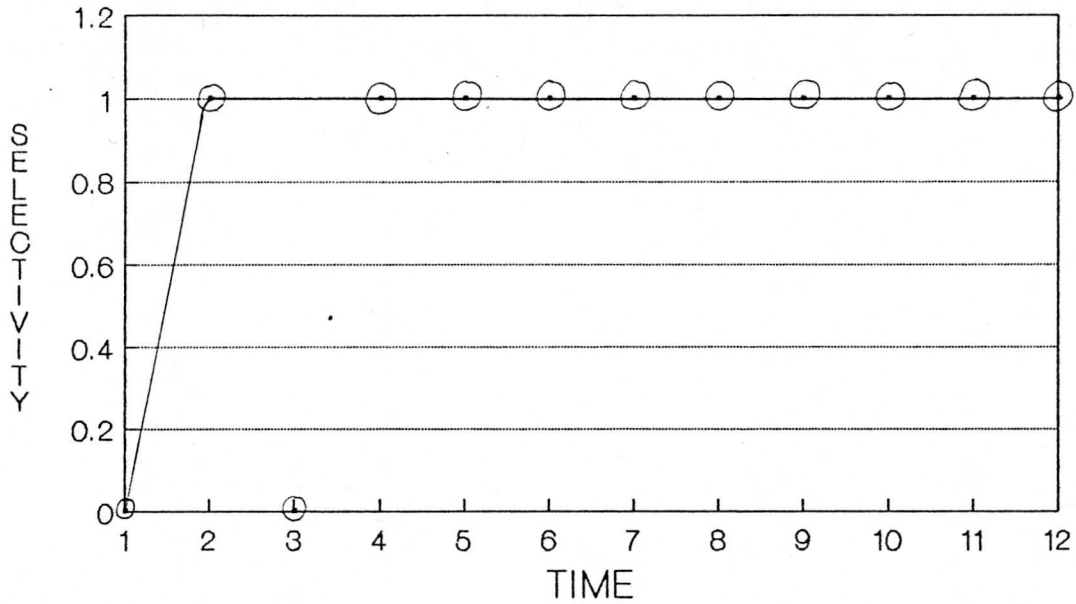


FIGURE 5.2: GRAPH OF SELECTIVITY VS TIME

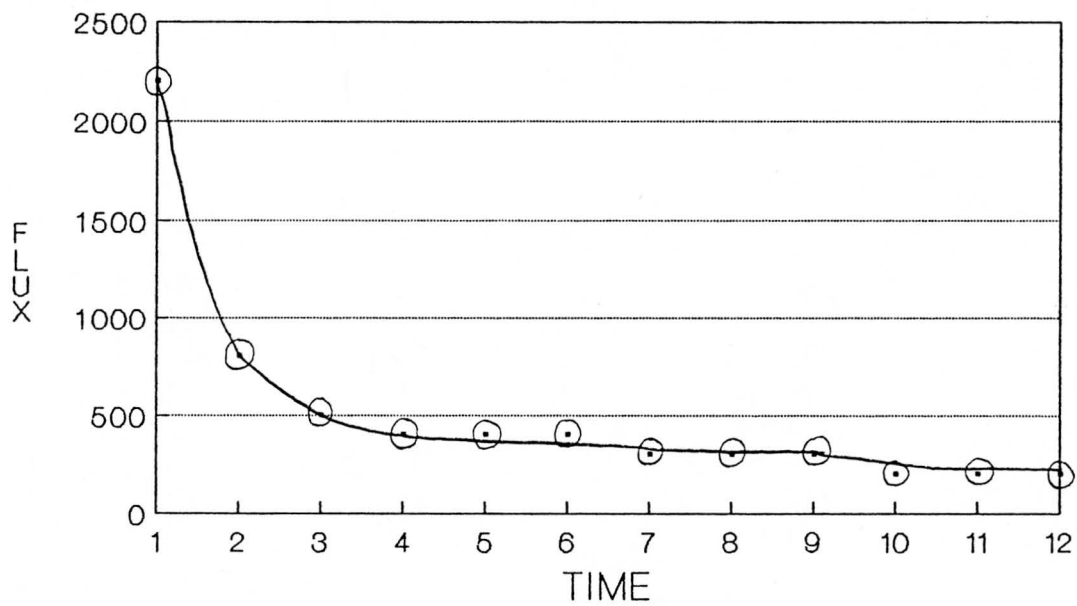


FIGURE 5.3: GRAPH OF FLUX VS TIME

Figures 5.2 and 5.3, it can be seen that the change in selectivity and flux values minimize in 3 to 4 hours. It was decided that 8 hours was suitable to ensure a constant value (average of 2 results).

In the literature a range of cumulative time values is reported<sup>(24,137,138)</sup>. Rautenbach *et al.*<sup>(98)</sup> also use 8 hours as the cumulative time for their experiments.

### 5.2.3 SAMPLE TIME

The size of the trap in which the sample for GC analysis is collected, determines the maximum time, while the volume needed for the GC analysis determines the minimum time needed between sampling. Bearing this in mind and comparing it with values from the literature<sup>(137)</sup>, it was decided to take samples one hour apart.

### 5.2.4 FEED COMPOSITION

#### 5.2.4.1 Components

Organic/organic separations were previously little investigated. Therefore, sparse information was available in this area of research. The objective of this study was to add to knowledge in this field. Ethanol was chosen because it is an inexpensive alcohol which is readily available. Hexane was chosen to be similar to hexene. (SASOL has a hexene-dilute alcohol mixture.) Thus, the two components of the feed mixture are ethanol and hexane.

#### 5.2.4.2 Ratio of Components

A range of experiments was done with different component ratios in the feed mixture. The experimental conditions are described in Section 5.2.1. To make the membrane, two layers of polymer were used. Pervaporation was carried out for 8 hours at room temperature (average of 2 results). The results of these experiments show (see Figure 5.4 and 5.5) that selectivity, as well as flux, increases with increasing amounts of ethanol in the feed mixture.

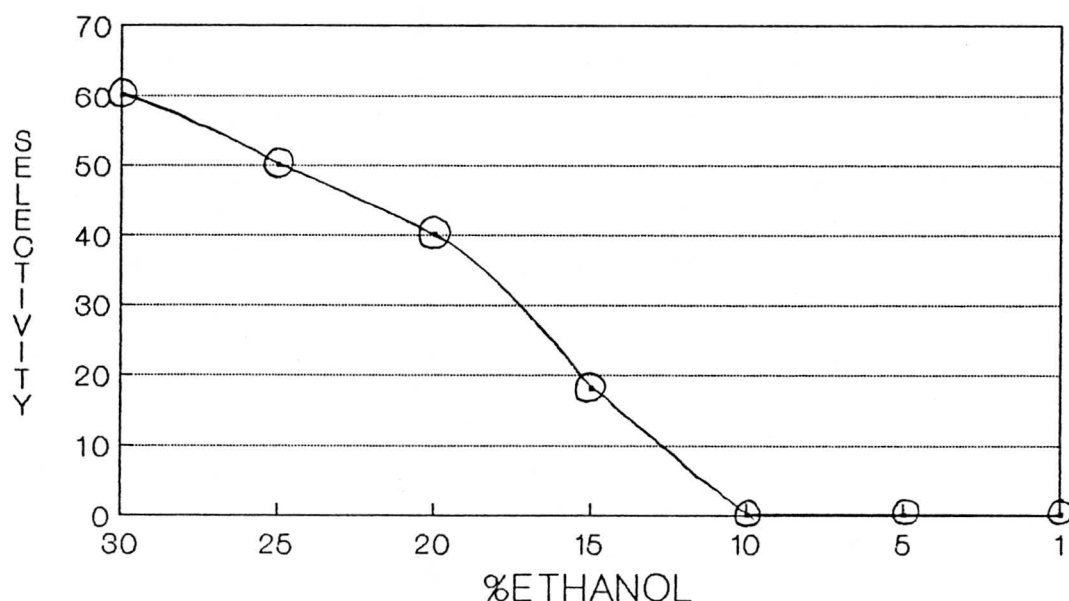
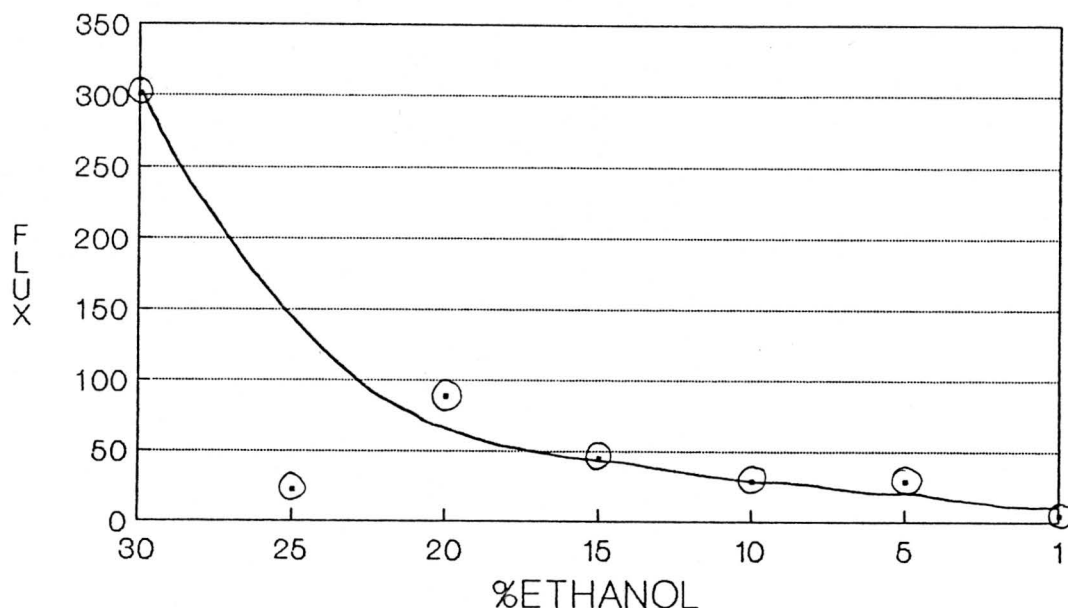


FIGURE 5.4: GRAPH OF SELECTIVITY VS % ETHANOL IN THE FEED MIXTURE



**FIGURE 5.5: GRAPH OF FLUX VS % ETHANOL IN THE FEED MIXTURE**

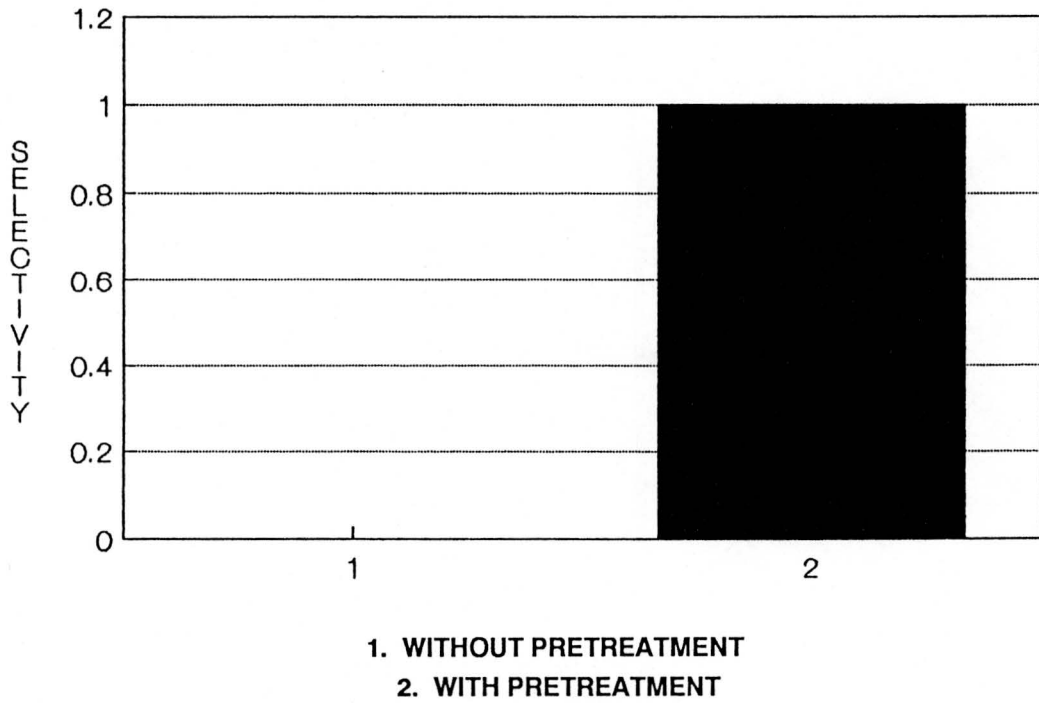
In order to achieve representative results, it was decided to use a 30% ethanol mixture, representing the high selectivity and flux values, as well as a 5% ethanol mixture, representing the low selectivity and flux values. All further tests of membranes were therefore done with a 30% and a 5% ethanol mixture.

The dependence of selectivity and flux on the feed mixture is due to different amounts of swelling of the membrane. The swelling of the membrane on the other hand is dependent on the amount of crosslinking and the chemical composition of the polymer structure<sup>(187-191)</sup>.

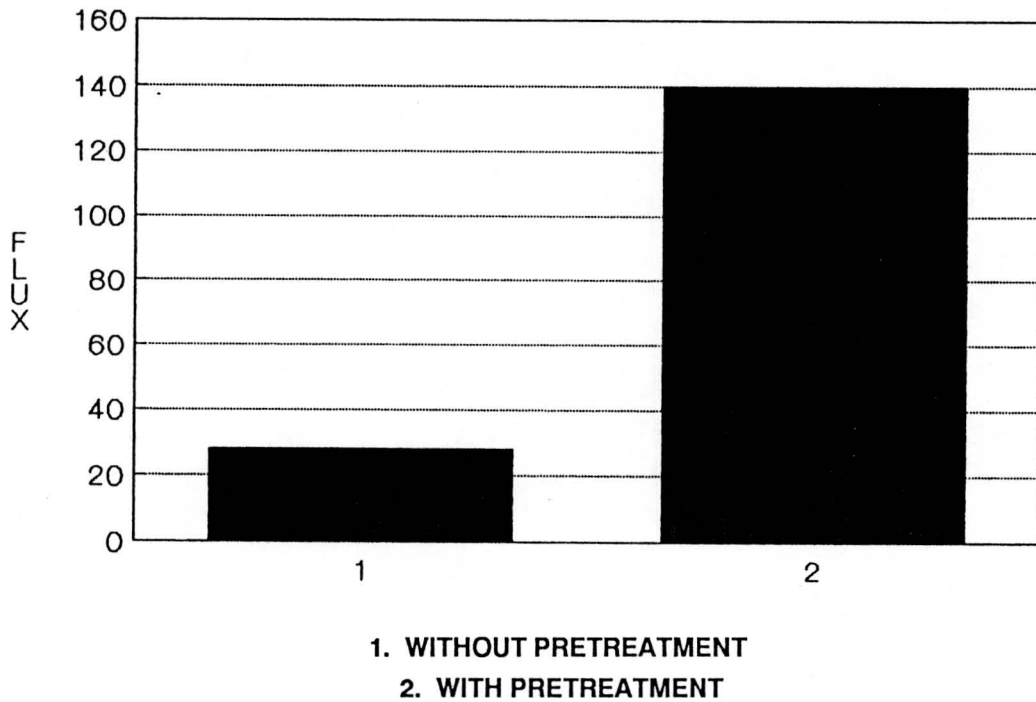
The dependence of selectivity and flux on the feed mixture was thoroughly researched in the past. Experiments with ranges of different feed mixtures were done<sup>(33,57,69,80,87,92,93,137,138,140,141,172)</sup>. The more complete ranges of feed mixtures show that selectivity and fluxes go through a minimum/maximum value<sup>(29,43,78,127,136)</sup> while some of the ranges used only show trends in one direction. The experiments done for this study can be compared with the latter<sup>(29)</sup>.

### 5.2.5 PRETREATMENT OF MEMBRANES

Experiments concerning the pretreatment of membranes were carried out with the same polymer and substrate that were used for the membrane under the same conditions as in Section 5.2.1. The pretreatment of the membranes is discussed in Section 4.5.3. To make the membrane, 2 layers of polymer were used. Pervaporation was carried out for 8 hours at room temperature with a feed of 5% ethanol in hexane (average of 2 results).



**FIGURE 5.6: GRAPHIC REPRESENTATION OF SELECTIVITY OF A MEMBRANE WITH/WITHOUT PRETREATMENT**



**FIGURE 5.7: GRAPHIC REPRESENTATION OF FLUX OF A MEMBRANE WITH/WITHOUT PRETREATMENT**

In Figures 5.6 and 5.7, the selectivity and flux of an untreated membrane are compared to that of a pretreated membrane. Figure 5.6 shows that the selectivity of the membrane increases. Flux increases as well (see Figure 5.7). The exact values of these increases are in Table 5.2, where it can be seen that the selectivity changes from preference for hexane ( $\alpha = 0$ ) to no preference ( $\alpha = 1$ ) for one particular compound.

**TABLE 5.2: TABLE OF FLUX AND SELECTIVITY VALUES OF AN UNTREATED MEMBRANE VS A PRETREATED MEMBRANE**

	Untreated Membrane	Pretreated Membrane
Flux	28	140
Selectivity	0	1

Neel *et al.*<sup>(53)</sup> explain the changes due to the swelling of the membrane after immersion in the pretreatment mixture. In the swollen phase the content of one component of the feed mixture is higher, while the other component passes through the membrane more rapidly. Brun *et al.*<sup>(101)</sup> and Nibrega *et al.*<sup>(136)</sup> also looked at pretreatment of membranes, but no definite findings were achieved due to scatter in the results.

The swelling of a membrane is controlled by the amount of crosslinking. A decrease in the amount of crosslinking, implies an increase in the amount of swelling. Preswelling of a membrane, where it results in a change of selectivity, implies a chemical change in the membrane. The chemical change would most probably be due to crosslink breakage by mechanical swelling forces rather than major change in the chemistry of the membrane.

Different amounts of crosslinking are obtained by different amounts of hydrolysis (see Section 4.3) before treating with the crosslinking agent. In the following section, therefore, membranes with different amounts of hydrolysis are tested and evaluated after a standard heat treatment for crosslinking.

### 5.3 MEMBRANE TESTING

Once the preliminary experiments were carried out for determining the variables important in standardizing an experimental procedure (see Section 5.2), the following membranes were tested:

- GFT-standard
- GFT-wasserreich
- PVA ( $M_r = 72\ 000$ )
- GANTREZ AN 119
- PVA ( $M_r = 15\ 000$ )
- Poly(vinyl acetate-co-acrylic acid)

- Synthesized terpolymers:           010 : 100  
   010 : 50  
   010 : 0  
  
   011 : 50  
   012 : 50  
   013 : 50

For discussion of the results, smoothed values have been used to show trends in data. The errors (10%) can be explained by the accuracy of the GC-integrator combination, accuracy of volumetric data and measurement of data.

### 5.3.1 COMMERCIAL MEMBRANES

Selectivity and flux are compared for two commercial membranes (GFT-standard and GFT-wasserreich) and a fabricated copy of a patented membrane Gantrez AN 119 ( 2 layers of polymer), as seen in Figures 5.8 and 5.9. The experimental conditions were described in Section 5.2. These membranes were not pretreated. Pervaporation was carried out for 8 hours at room temperature (average of 2 runs).

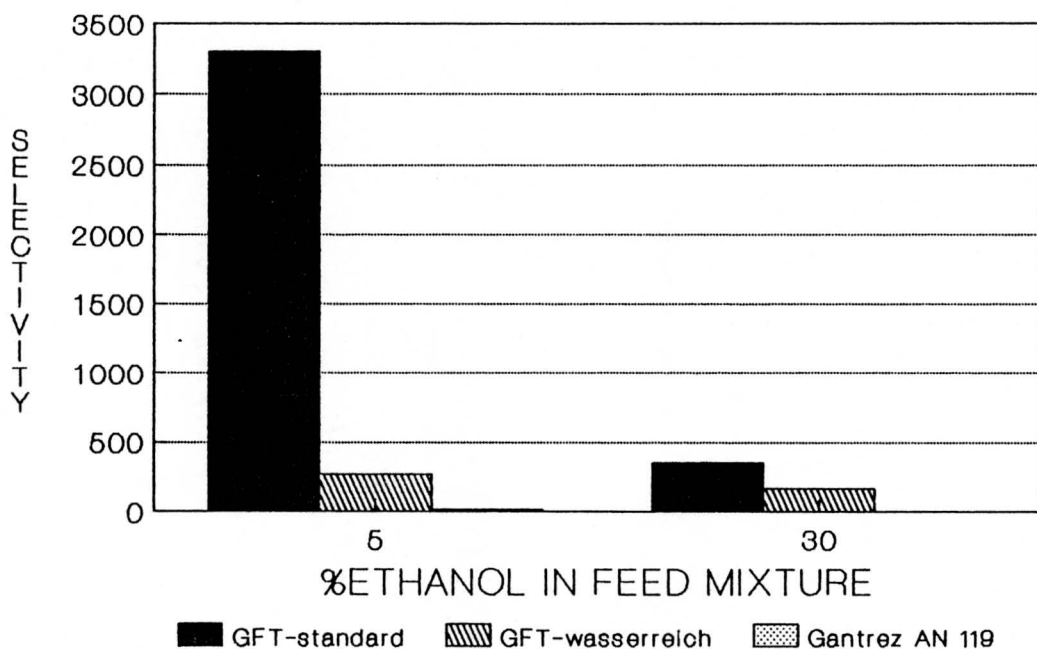
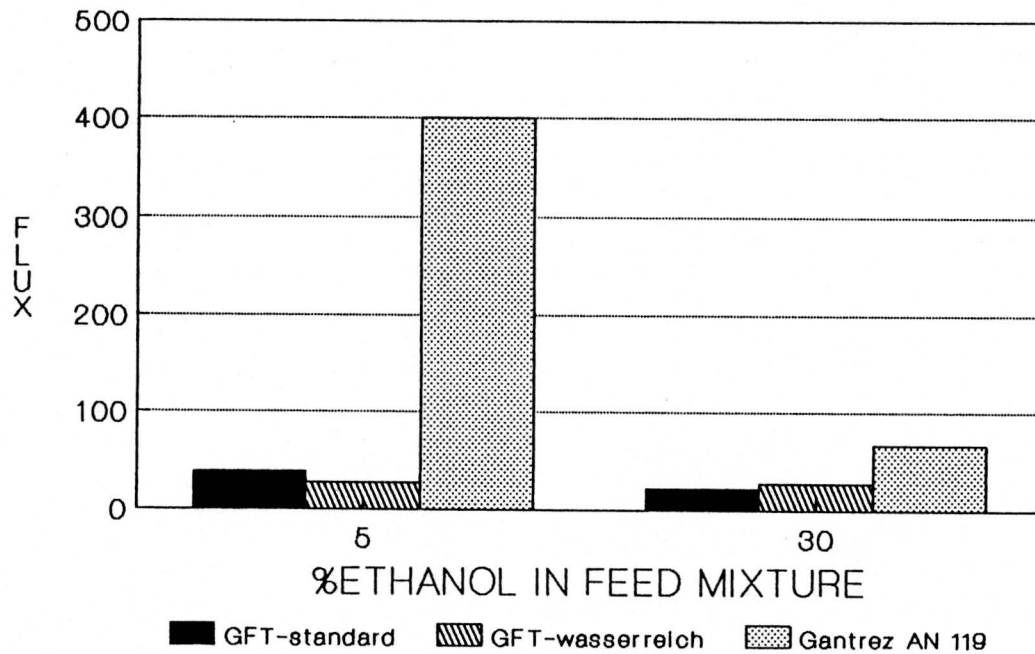


FIGURE 5.8: GRAPHIC REPRESENTATION OF THE SELECTIVITY OF COMMERCIAL MEMBRANES WITH TWO FEED MIXTURES



**FIGURE 5.9: GRAPHIC REPRESENTATION OF THE FLUX OF COMMERCIAL MEMBRANES WITH TWO FEED MIXTURES**

It is obvious that the selectivity of the GFT-standard membrane is far superior to the other membranes, while the flux of the Gantrez AN 119 membrane seems the best. The average selectivity and flux values can be found in Table 5.3 (average of last 4 results).

**TABLE 5.3: TABLE OF SELECTIVITY AND FLUX VALUES FOR THE COMMERCIAL MEMBRANES**

Membrane	% Ethanol in Feed Mixture	Selectivity ( $\alpha$ )	Flux (kg/m <sup>2</sup> .h)
GFT-standard	5	3 300	39
	30	350	22
GFT-wasserreich	5	270	28
	30	170	28
Gantrez AN 119	5	15	400
	30	0	67

The best membrane for pervaporation of this mixture is the GFT-standard membrane because high selectivity together with a moderate flux is preferable to a low selectivity with a high flux.

In the literature, there are references to GFT membranes<sup>(12,13)</sup>, their advantages and disadvantages<sup>(162)</sup> and their use in the chemical industry<sup>(54)</sup>. Membranes made for this study will be compared to these commercial membranes.

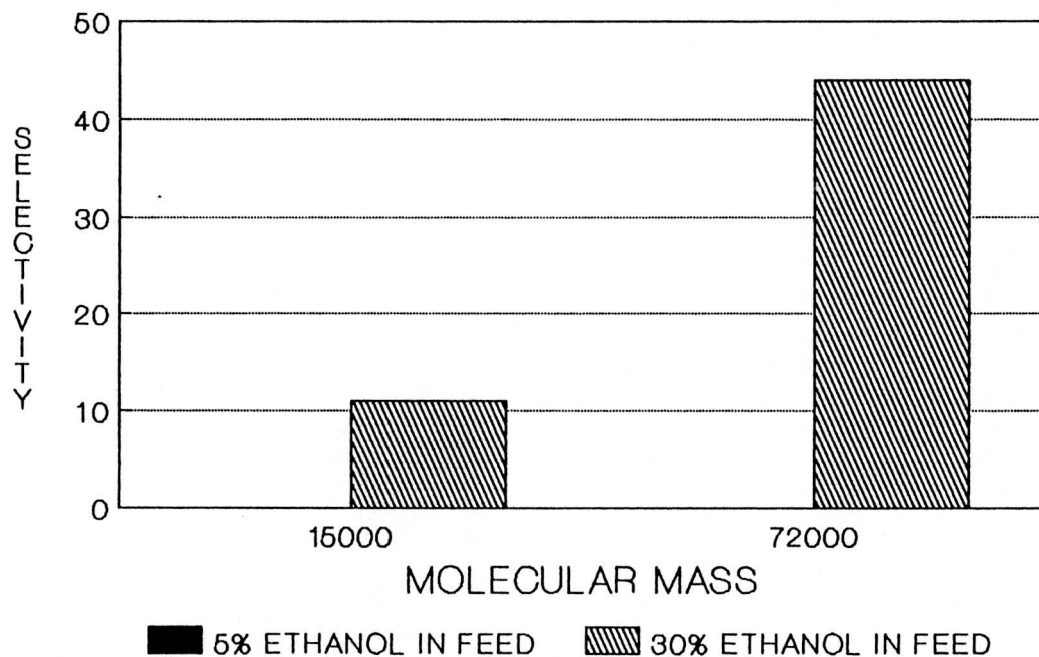
### 5.3.2 INFLUENCE OF MOLECULAR MASS

Experiments to determine the influence of molecular mass on the selectivity and flux of a membrane were carried out with a polyvinylalcohol ( $M_n = 15\ 000$ ;  $M_n = 72\ 000$ ) solution containing 0,5% potassium persulphate on a polysulphone substrate. The experimental conditions were described in Section 5.2. The selectivity and flux values can be seen in Table 5.4.

**TABLE 5.4: TABLE OF FLUX AND SELECTIVITY VALUES FOR PVA-MEMBRANES OF DIFFERENT MOLECULAR MASS**

Molecular Mass	% Ethanol in Feed Mixture	Selectivity ( $\alpha$ )	Flux ( $\text{kg/m}^2\cdot\text{h}$ )
15 000	5	0	430
	30	11	440
72 000	5	0	120
	30	44	120

A graphic representation of the experimental results makes it very obvious that selectivity increases with increasing molecular mass (see Figure 5.10). This agrees with the results of Nobrega *et al.*<sup>(136)</sup>.



**FIGURE 5.10: GRAPHIC REPRESENTATION OF THE INFLUENCE OF MOLECULAR MASS ON THE SELECTIVITY OF A MEMBRANE**

The influence of the 5% ethanol on the selectivity is insignificant in this PVA membrane. This indicated the need for well selected membrane chemistry to suit specific separation requirements.



### 5.3.3 INFLUENCE OF SYNTHETIC CHANGE IN MEMBRANE CHEMISTRY

#### 5.3.3.1 Hydrolysis before crosslinking by heat

Experiments to determine the influence of amount of hydrolysis on the selectivity and flux of a membrane, were carried out with some of the terpolymers (010:100, 010:50, 010:0) as described in Section 4.2 and 4.3. The experimental conditions were described in Section 5.2. To make the membrane, six layers of polymer were used. This was done because the two to five layer-membranes gave no results due to too thin layers which are sucked through the substrate by the vacuum pump. The selectivity and flux values can be seen in Table 5.5 (average of last 4 results, rounded to 2 significant digits).

**TABLE 5.5: TABLE OF SELECTIVITY AND FLUX VALUES FOR MEMBRANES WITH DIFFERENT AMOUNTS OF HYDROLYSIS**

Terpolymers	Amount of Hydrolysis (%)	% Ethanol in Feed	Selectivity ( $\alpha$ )	Flux ( $\text{kg/m}^2\cdot\text{h}$ )
010:0	0	5	290	50
		30	73	140
010:50	49	5	250	2 200
		30	5	4 600
010:100	58	5	27	1 400
		30	21	3 100

A graphic representation of the experimental results makes the decrease of selectivity for the 5% ethanol in the feed with increasing amounts of hydrolysis obvious (see Figure 5.11).

The flux, on the other hand, goes through a maximum value at approximately 50% hydrolysis (see Figure 5.12).

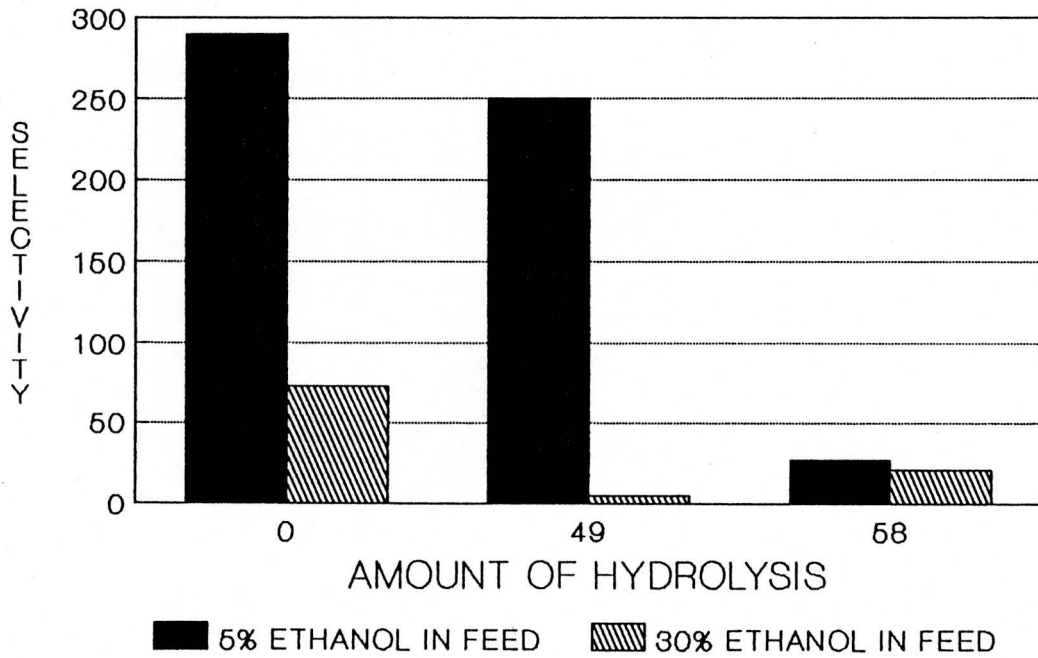


FIGURE 5.11: GRAPHIC REPRESENTATION OF THE INFLUENCE OF THE AMOUNT OF HYDROLYSIS ON THE SELECTIVITY OF A MEMBRANE

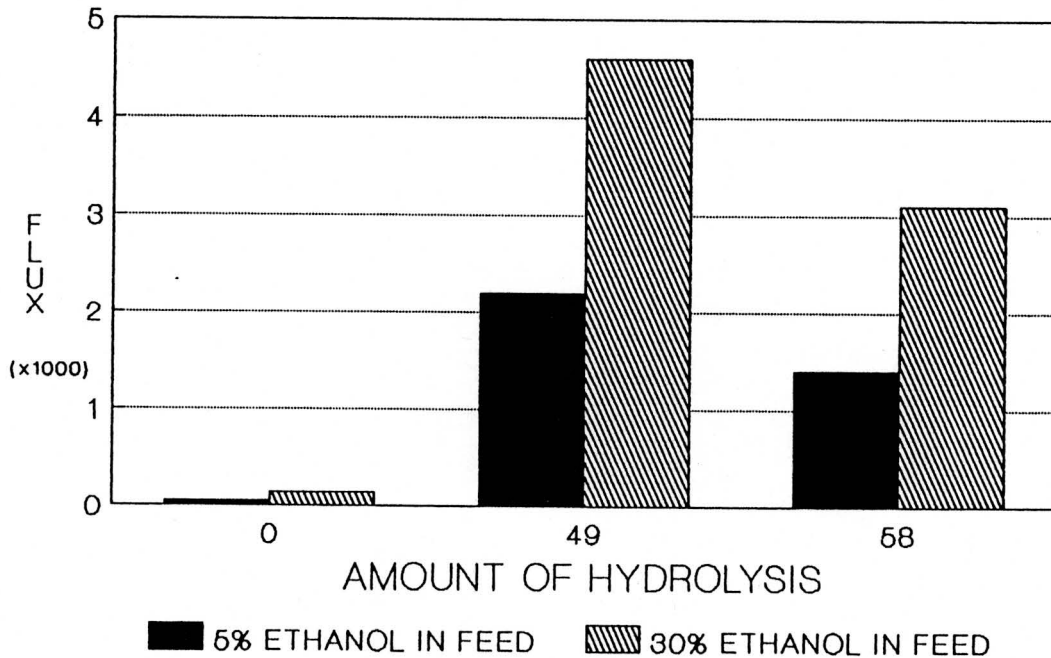


FIGURE 5.12: GRAPHIC REPRESENTATION OF THE INFLUENCE OF HYDROLYSIS ON THE FLUX OF A MEMBRANE

The results disagree with those of Nobrega *et al.*<sup>(136)</sup> who found that the selectivity of a membrane increases with an increase in the amount of hydrolysis. The flux values agree with literature values<sup>(136)</sup>. Their experiments were done between 80 and 100% of hydrolysis. Xu *et al.*<sup>(127)</sup> agree with the abovementioned results. There is more literature available on this subject<sup>(31,33,106)</sup>. These influences arise from the differing chemical compositions compared to the present work.

### 5.3.3.2 Hydrophilicity

Experiments to determine the influence of hydrophilicity on the selectivity and flux of a membrane, were carried out with some of the quaterpolymers as described in Sections 4.2 and 4.3. However, there is one deviation from the abovementioned experimental conditions (see Section 5.3.3) in that 6 layers were used in membrane formation. The selectivity and flux values for different hydrophilicities can be seen in Table 5.6.

**TABLE 5.6: TABLE OF SELECTIVITY AND FLUX VALUES FOR MEMBRANES WITH DIFFERENT AMOUNTS OF HYDROPHILICITY**

Hydrophilicity (% Acrylic Acid)	% Ethanol in Feed Mixture	Selectivity	Flux
0	5	2 200	88
	30	49	290
5	5	240	89
	30	15	170
10	5	110	120
	30	11	350
15	5	250	2 200
	30	5	4 600

A graphic representation of the experimental results makes the decrease of selectivity and increase of flux with increasing hydrophilicity obvious (see Figures 5.13 and 5.14).

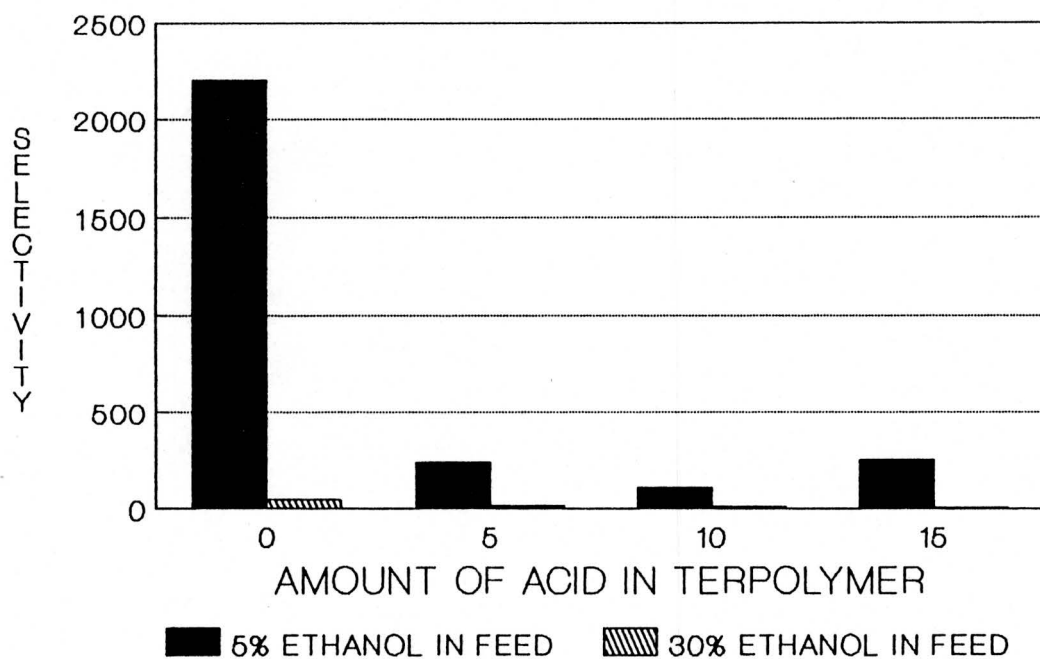


FIGURE 5.13: GRAPHIC REPRESENTATION OF THE INFLUENCE OF AMOUNT OF HYDROPHILICITY ON THE SELECTIVITY OF A MEMBRANE

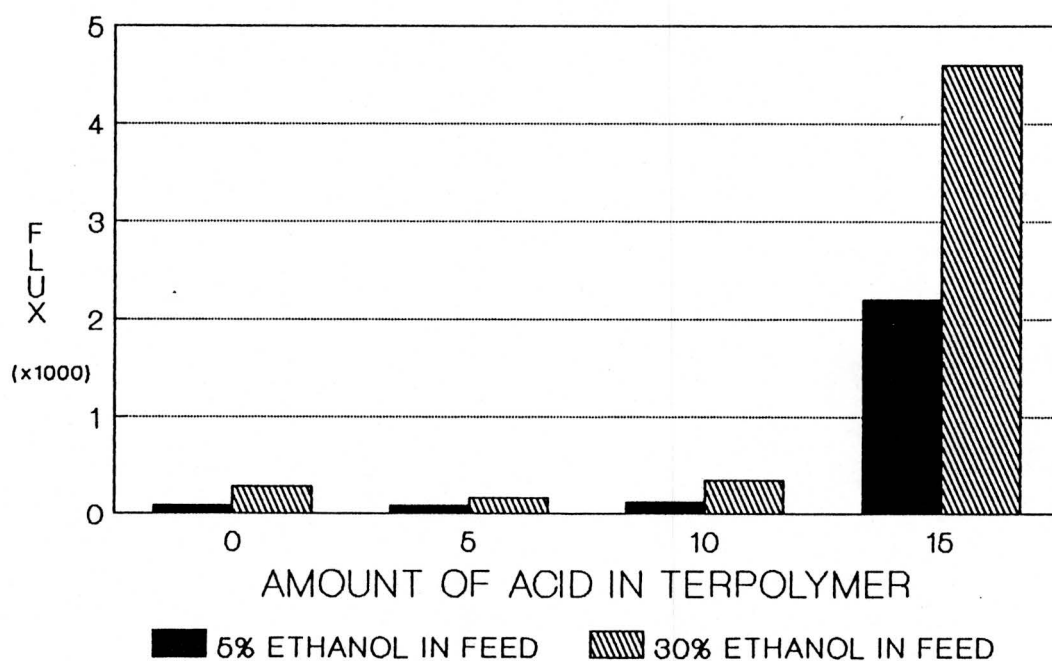


FIGURE 5.14: GRAPHIC REPRESENTATION OF THE INFLUENCE OF AMOUNT OF HYDROPHILICITY ON THE FLUX OF A MEMBRANE

The importance of the hydrophilic-hydrophobic balance, when choosing polymers for specific membranes, is also described in more general terms in the literature<sup>(75,135,142)</sup>. More specifically, Xu *et al.*<sup>(127)</sup>, also use polyacrylic acid to alter the hydrophilicity of the membrane.

### 5.3.3.3 NMR Analysis

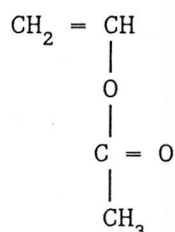
#### (a) Monomers

The monomers were characterized and checked for impurities. These spectra can be found in Figures 5.15, 5.16 and 5.17.

#### NMR Spectrum 5.15 (VXR 300):

- (a) Type:  $^{13}\text{C}$
- (b) Sample preparation: Vinyl acetate (VA) monomer (approximately 0,30 ml) was dissolved in DMSO (approximately 1 ml) in a NMR-tube. A homogeneous mixture was found.
- (c) Solvent: DMSO -  $\text{d}_6$
- (d) Temperature:  $26^\circ\text{C}$
- (e) Spintempo: 26 rps
- (f) Tube diameter: 5 mm
- (g) External/Internal standard: TMD
- (h) Spectral recording time:  $1\ 360 \times 0,800$  s
- (i) Interpretation: The four characteristic peaks of the four carbon atoms in vinyl acetate can be distinguished. The chemical shift (rounded to the nearest integer) of the different carbon atoms relative to TMS  $\delta$  (ppm) = 0, is as follows:
  - (i)  $\text{CH}_3$   $\delta$  (ppm) = 20
  - (ii)  $\text{CH}_2$   $\delta$  (ppm) = 97
  - (iii)  $\text{CH}$   $\delta$  (ppm) = 141
  - (iv)  $\text{C}=\text{O}$   $\delta$  (ppm) = 168

The peaks at  $\delta$  (ppm) = 39 can be allocated to the solvent, DMSO.
- (j) The chemical structure of vinyl acetate is as follows:



#### NMR Spectrum 5.16 (VXR 300):

- (a) Type:  $^{13}\text{C}$
- (b) Sample preparation: Hydroxyethyl acrylate (HEA) monomer (approximately 0,30 ml) was dissolved in DMSO (approximately 1 ml) in a NMR-tube. A homogeneous mixture was found.
- (c) Solvent: DMSO -  $\text{d}_6$
- (d) Temperature:  $26^\circ\text{C}$
- (e) Spintempo: 26 rps
- (f) Tube diameter: 5 mm
- (g) External/Internal standard: TMS
- (h) Spectral recording time:  $320 \times 0,800$  s

- (i) Interpretation: The three characteristic peaks of the four carbon atoms in hydroxyethyl acrylate can be distinguished. The chemical shift (rounded to the nearest integer) of the different carbon atoms relative to TMS  $\delta$  (ppm) = 0, is as follows:

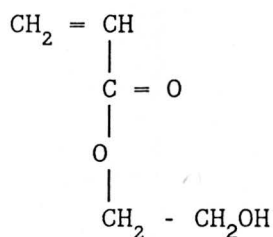
(i) CH  $\delta$  (ppm) = 129

(ii) CH<sub>2</sub>  $\delta$  (ppm) = 131

(iii) C=O  $\delta$  (ppm) = 168

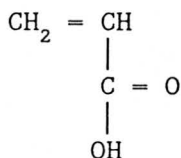
The peaks at  $\delta$  (ppm) = 39 can be allocated to the solvent, DMSO.

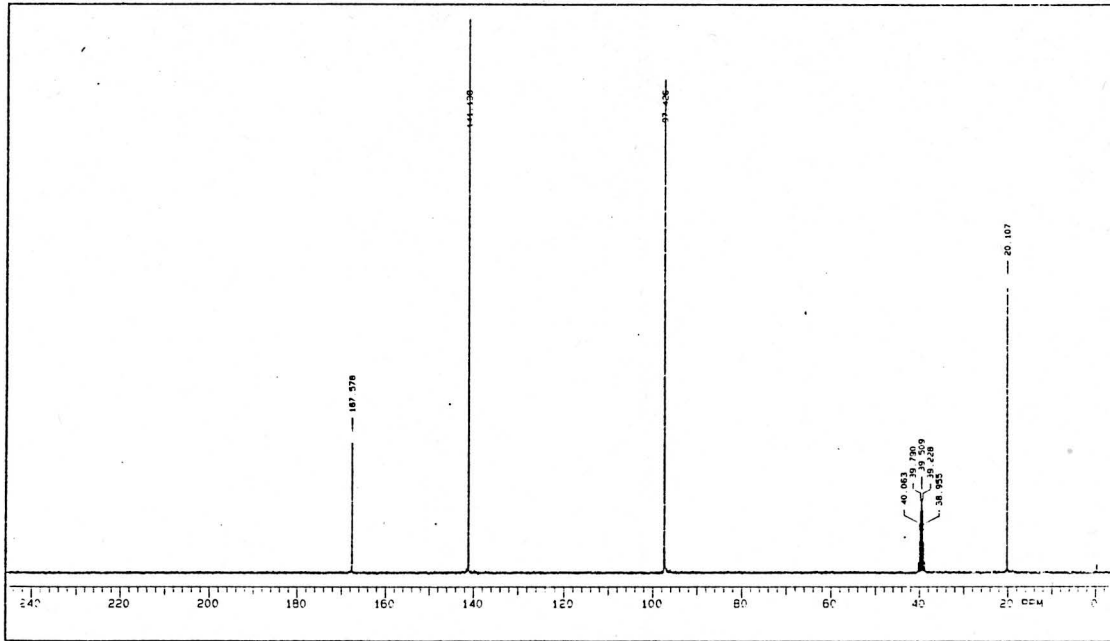
- (j) The chemical structure of hydroxyethyl acrylate is as follows:



#### NMR Spectrum 5.17 (FT 80):

- (a) Type: <sup>13</sup>C
- (b) Sample preparation: Acrylic acid (AA) monomer (approximately 0,30 ml) was dissolved in DMSO (approximately 1 ml) in a NMR-tube. A homogeneous mixture was found.
- (c) Solvent: DMSO - d<sub>6</sub>
- (d) Temperature: 34°C
- (e) Spintempo: 24 rps
- (f) Tube diameter: 5 mm
- (g) External/Internal standard: TMS
- (h) Spectral recording time: 0,409 s
- (i) Interpretation: The four characteristic peaks of the three carbon atoms in acrylic acid can be distinguished. The chemical shift (rounded to the nearest integer) of the different carbon atoms relative to TMS  $\delta$  (ppm) = 0, is as follows:
- (i) CH  $\delta$  (ppm) = 130
- (ii) CH<sub>2</sub>  $\delta$  (ppm) = 130
- (iii) C=O  $\delta$  (ppm) = 167
- The peaks at  $\delta$  (ppm) = 39 can be allocated to the solvent, DMSO.
- (j) The chemical structure of acrylic acid is as follows:





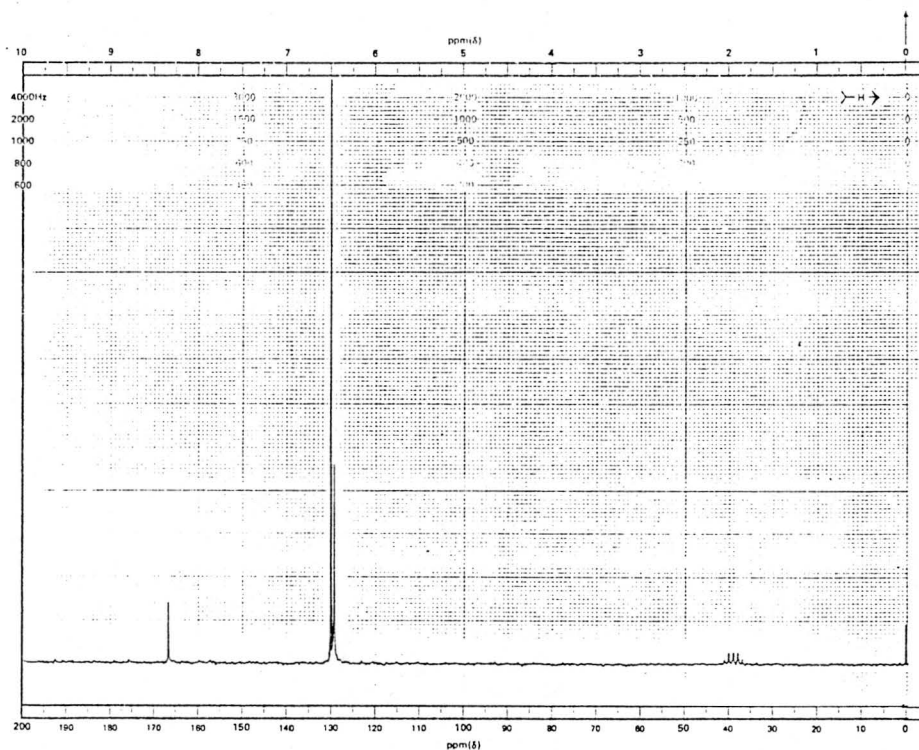


FIGURE 5.17:  $^{13}\text{C}$  NMR SPECTRUM OF ACRYLIC ACID

## (b) Polymers

The polymers were characterized by NMR. The relative monomer ratios in the polymers were determined, as well as the amount of hydrolysis present. These spectra can be found in Figures 5.18 to 5.33.

### NMR Spectrum 5.18 (VXR 300):

- (a) Type:  $^{13}\text{C}$
- (b) Sample preparation: Polymer 010 (approximately 0,30 g) was dissolved in DMSO (approximately 1 ml) in a NMR-tube. A homogeneous mixture was found.
- (c) Solvent: DMSO -  $\text{d}_6$
- (d) Temperature:  $26^\circ\text{C}$
- (e) Spintempo: 26 rps
- (f) Tube diameter: 5 mm
- (g) External/Internal standard: TMS
- (h) Spectral recording time:  $10\,560 \times 0,800$  s
- (i) Interpretation: One each of the characteristic peaks of the three monomers were chosen to identify them in the polymer. Integration was done over these peaks to calculate the relative ratios of monomers in the polymer. The results are as follows:
  - (i) HEA  $\delta$  (ppm) = 170
  - (ii) VA  $\delta$  (ppm) = 174
  - (iii) AA  $\delta$  (ppm) = 176



The peaks at  $\delta$  (ppm) = 39 can be allocated to the solvent, DMSO.

- (j) The relative ratio of the monomers incorporated in the 010 polymer is:

HEA	:	VA	:	AA
1,5		1,8		0,6

#### NMR Spectrum 5.19 (VXR 300):

- (a) Type:  $^{13}\text{C}$
- (b) Sample preparation: Polymer 011 (approximately 0,30 g) was dissolved in DMSO (approximately 1 ml) in a NMR-tube. A homogeneous mixture was found.
- (c) Solvent: DMSO -  $d_6$
- (d) Temperature:  $26^\circ\text{C}$
- (e) Spintempo: 26 rps
- (f) Tube diameter: 5 mm
- (g) External/Internal standard: TMS
- (h) Spectral recording time:  $83\,968 \times 0,800$  s
- (i) The results are as follows:
- (i) HEA  $\delta$  (ppm) = 170
- (ii) EA  $\delta$  (ppm) = 174
- (iii) PA  $\delta$  (ppm) = 176
- (j) The relative ratio of the monomers incorporated in the 011 polymer is:

HEA	:	VA	:	AA
1,8		1,9		0,4

#### NMR Spectrum 5.20 (VXR 300):

- (a) Type:  $^{13}\text{C}$
- (b) Sample preparation: Polymer 012 (approximately 0,30 g) was dissolved in DMSO (approximately 1 ml) in a NMR-tube. A homogeneous mixture was found.
- (c) Solvent: DMSO -  $d_6$
- (d) Temperature:  $26^\circ\text{C}$
- (e) Spintempo: 26 rps
- (f) Tube diameter: 5 mm
- (g) External/Internal standard: TMS
- (h) Spectral recording time:  $63\,689 \times 0,800$  s
- (i) The results are as follows:
- (i) HEA  $\delta$  (ppm) = 170
- (ii) EA  $\delta$  (ppm) = 174
- (iii) PA  $\delta$  (ppm) = 176
- (j) The relative ratio of the monomers incorporated in the 012 polymer is:

HEA	:	VA	:	AA
1,8		1,8		0,2

**NMR Spectrum 5.21 (VXR 300):**

- (a) Type:  $^{13}\text{C}$
- (b) Sample preparation: Polymer 013 (approximately 0,30 g) was dissolved in DMSO (approximately 1 ml) in a NMR-tube. A homogeneous mixture was found.
- (c) Solvent: DMSO -  $d_6$
- (d) Temperature:  $26^\circ\text{C}$
- (e) Spintempo: 26 rps
- (f) Tube diameter: 5 mm
- (g) External/Internal standard: TMS
- (h) Spectral recording time:  $96\ 056 \times 0,800\ \text{s}$
- (i) The results are as follows:
- (i) HEA  $\delta$  (ppm) = 170
- (ii) EA  $\delta$  (ppm) = 174
- (iii) PA absent
- (j) The relative ratio of the monomers incorporated in the 013 polymer is:
- |     |   |     |   |    |
|-----|---|-----|---|----|
| HEA | : | VA  | : | AA |
| 1,7 |   | 2,1 |   | 0  |

Based on the NMR results a comparison between the reagent addition ratios and practical incorporated ratios of the monomers in the polymer (see Table 5.7), can be made.

**TABLE 5.7: TABLE OF RELATIVE RATIOS**

Polymer	Reagent Ratio			Incorporated Ratio						
	HEA	:	VA	:	AA	HEA	:	VA	:	AA
010	3	:	18	:	0,6	1,5	:	1,8	:	0,6
011	3	:	18	:	0,4	1,8	:	1,9	:	0,4
012	3	:	18	:	0,2	1,8	:	1,8	:	0,2
013	3	:	18	:	0	1,7	:	2,1	:	0

**TABLE 5.8: TABLE OF AMOUNT OF ACID IN POLYMER**

Polymer	Reagent Value (%)	Incorporated Value (%)
010	3	15
011	2	10
012	1	5
013	0	0

## NMR Spectra 5.22 to 5.33 (FT 80):

- (a) Type:  $^{13}\text{C}$
- (b) Sample preparation: Approximately 0,07 g of each of the following hydrolyzed polymers were dissolved in approximately 0,8 ml  $\text{D}_2\text{O}$  in NMR tubes. Homogeneous mixtures were found.
- (c) Solvent:  $\text{D}_2\text{O}$
- (d) Temperature:  $34^\circ\text{C}$
- (e) Spintempo: 24 rps
- (f) Tube diameter: 5 mm
- (g) External/Internal standard: Dioxane
- (h) Spectral recording time: 0,409 s
- (i) Interpretation: To follow the amount of hydrolysis, the characteristic peaks of the vinyl acetate and hydroxyethyl acrylate monomer is watched. Integration was done over the three characteristic peaks of the monomers in order to calculate the change in the vinyl acetate and hydroxyethyl acrylate peaks. The results are as follows:
- (i) 010 : 0  $\delta$  (ppm) = 178;  $\delta$  (ppm) = 174
- (ii) 010 : 50  $\delta$  (ppm) = 178;  $\delta$  (ppm) = 174
- (iii) 010 : 100  $\delta$  (ppm) = 179;  $\delta$  (ppm) = 175
- (iv) 011 : 50  $\delta$  (ppm) = 178;  $\delta$  (ppm) = 174
- (v) 012 : 50  $\delta$  (ppm) = 178;  $\delta$  (ppm) = 174
- (vi) 013 : 50  $\delta$  (ppm) = 178;  $\delta$  (ppm) = 174
- The peaks at  $\delta$  (ppm) = 40 can be allocated to the solvent,  $\text{D}_2\text{O}$ .
- (j) The difference in amount of hydrolysis, is calculated as a percentage value. The results are as follows:

		VA	HEA
(i)	010 : 0	0%	0%
(ii)	010 : 50	49%	25%
(iii)	010 : 100	58%	37%
(iv)	011 : 50	36%	0%
(v)	012 : 50	34%	0%
(vi)	013 : 50	17%	0%

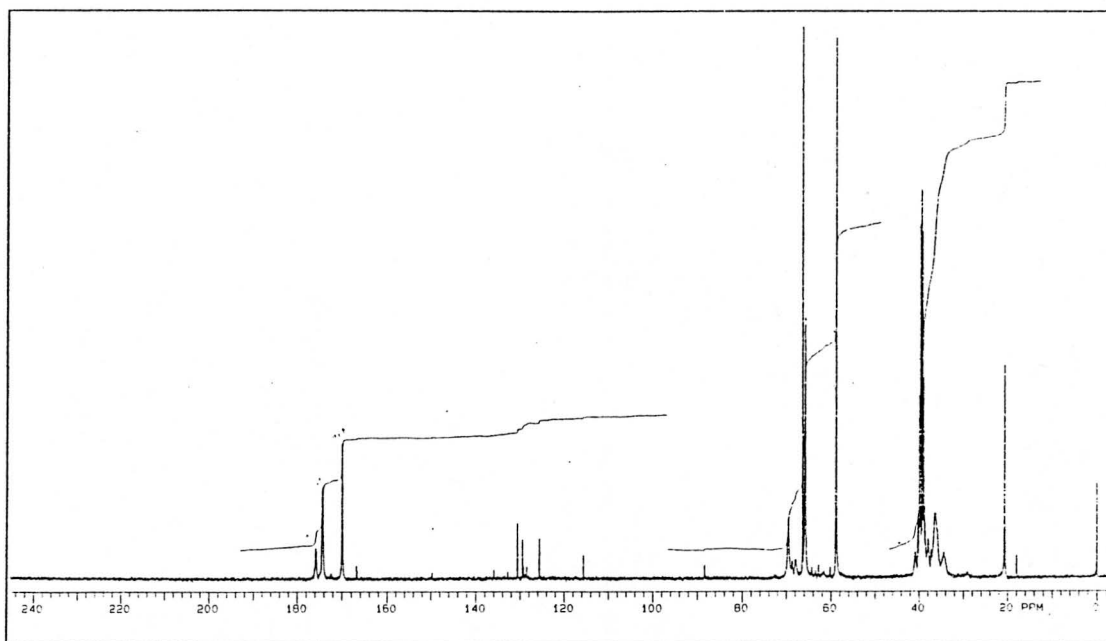
Quantities of the other polymers were sufficient for 2 layer membranes, but since the membranes were leaky, resynthesis was necessary. The quantities of polymer left were insufficient for further membrane formation.

As the VXR 300 was not available, the FT 80 had to be used. There is less accuracy when using the FT 80 to monitor degree of hydrolysis.

Based on the NMR results, a comparison between the theoretical and practical values of the percentage of hydrolysis in the polymer (see Table 5.10) can be made.

TABLE 5.9: TABLE OF PERCENTAGE HYDROLYSIS IN THE POLYMER

Polymer	Calculated Percentage		Experimentally found Percentage	
	Acetate	Acrylate	Acetate	Acrylate
010 : 0	0	0	0	0
010 : 50	50	0	49	0
010 : 100	100	0	58	40
011 : 50	50	0	36	0
012 : 50	50	0	34	0
013 : 50	50	0	17	0

FIGURE 5.18:  $^{13}\text{C}$  NMR SPECTRUM OF POLYMER 010

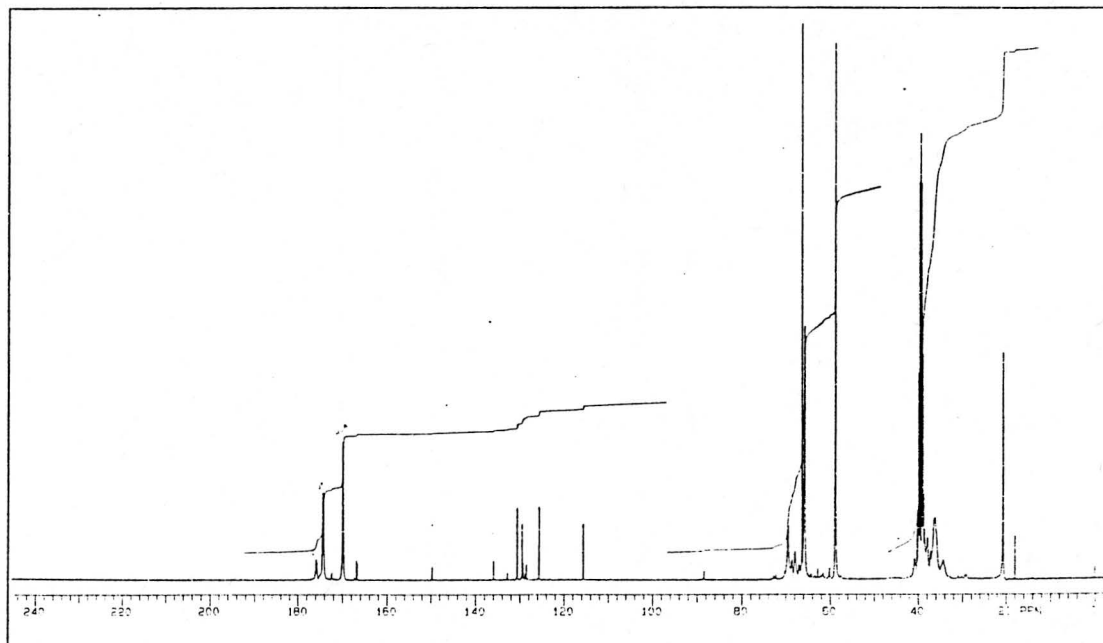


FIGURE 5.19:  $^{13}\text{C}$  NMR SPECTRUM OF POLYMER 011

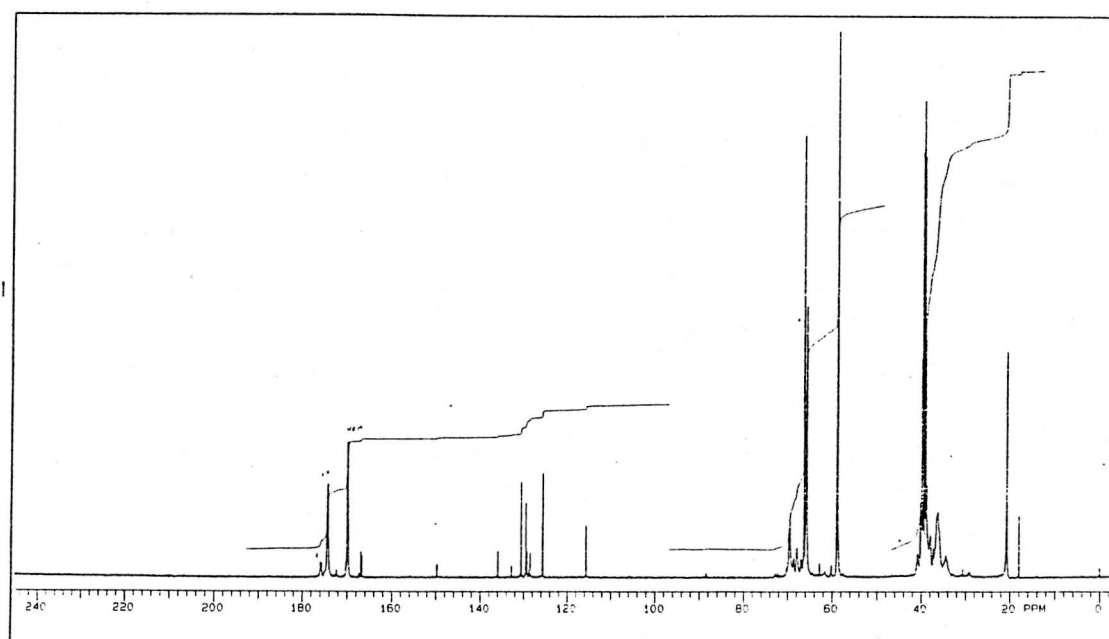


FIGURE 5.20:  $^{13}\text{C}$  NMR SPECTRUM OF POLYMER 012

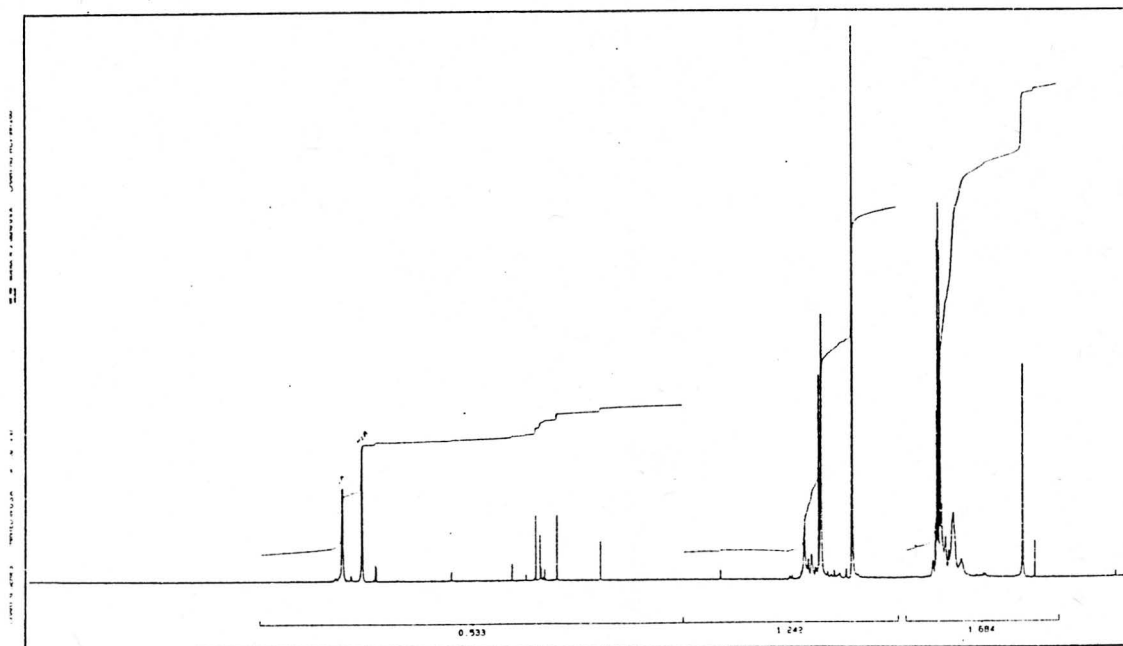


FIGURE 5.21:  $^{13}\text{C}$  NMR SPECTRUM OF POLYMER 013

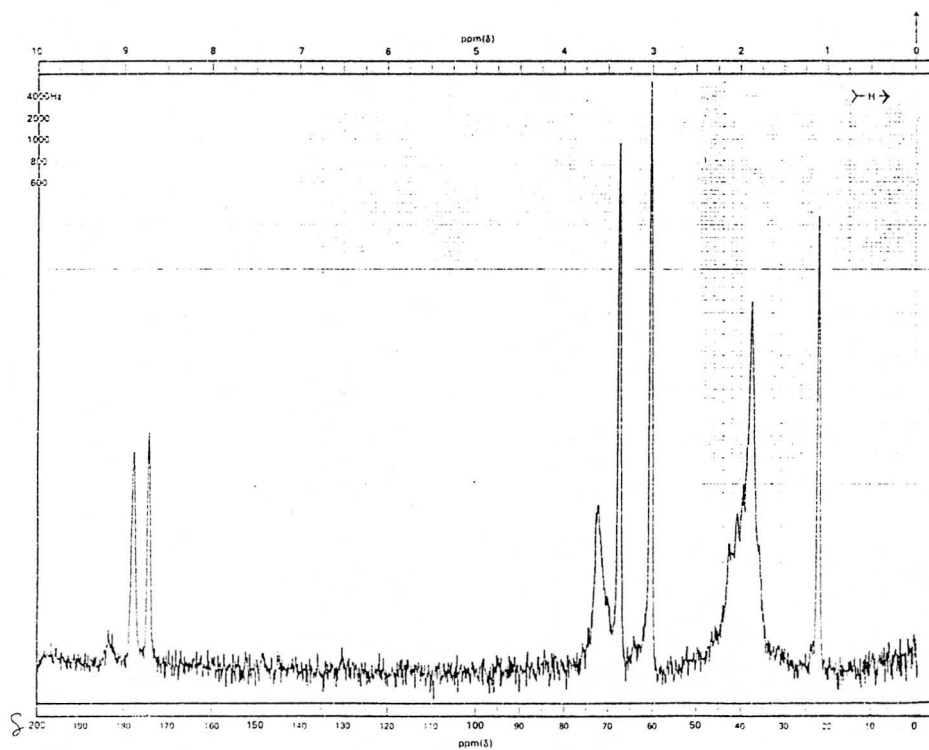


FIGURE 5.22:  $^{13}\text{C}$  NMR SPECTRUM OF POLYMER 010 (0% HYDROLYSIS)

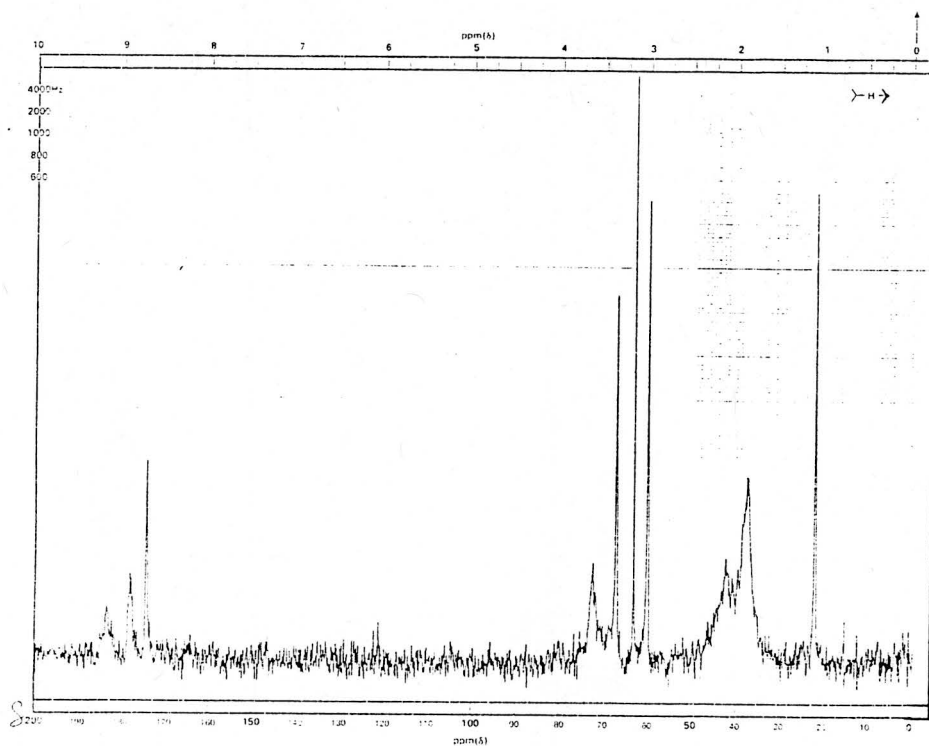


FIGURE 5.23:  $^{13}\text{C}$  NMR SPECTRUM OF POLYMER 010 (50% HYDROLYSIS)

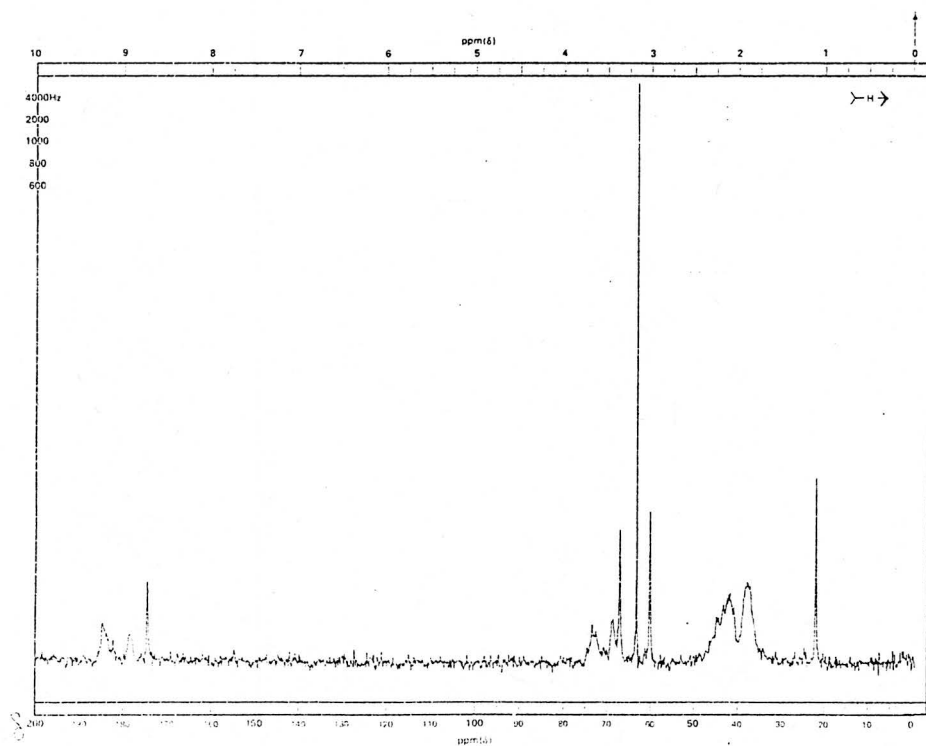


FIGURE 5.24:  $^{13}\text{C}$  NMR SPECTRUM OF POLYMER 010 (100% HYDROLYSIS)

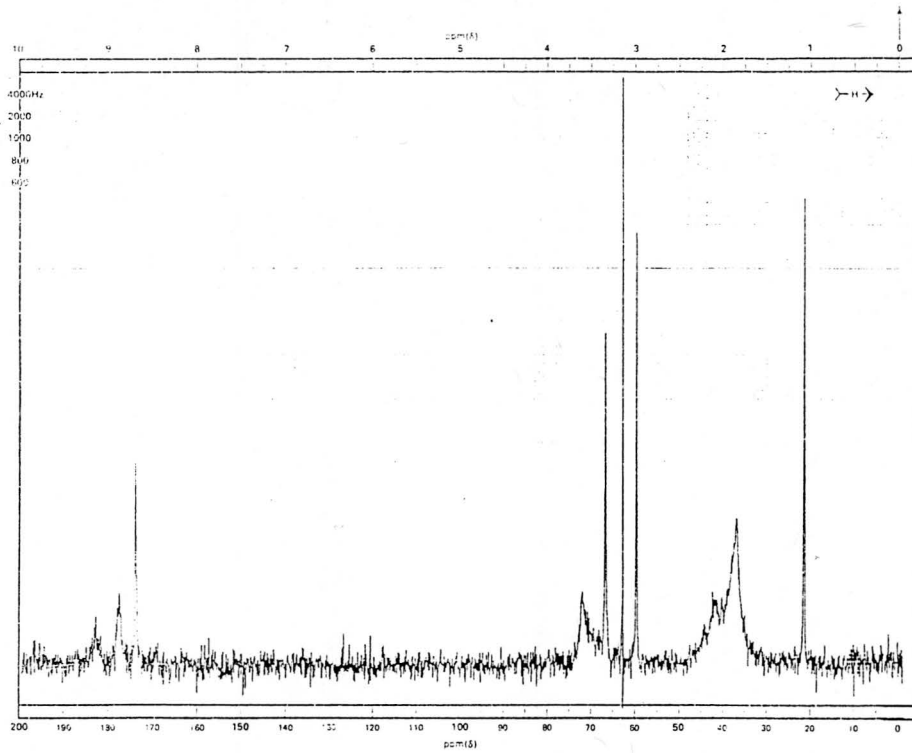


FIGURE 5.25:  $^{13}\text{C}$  NMR SPECTRUM OF POLYMER 011 (50% HYDROLYSIS)

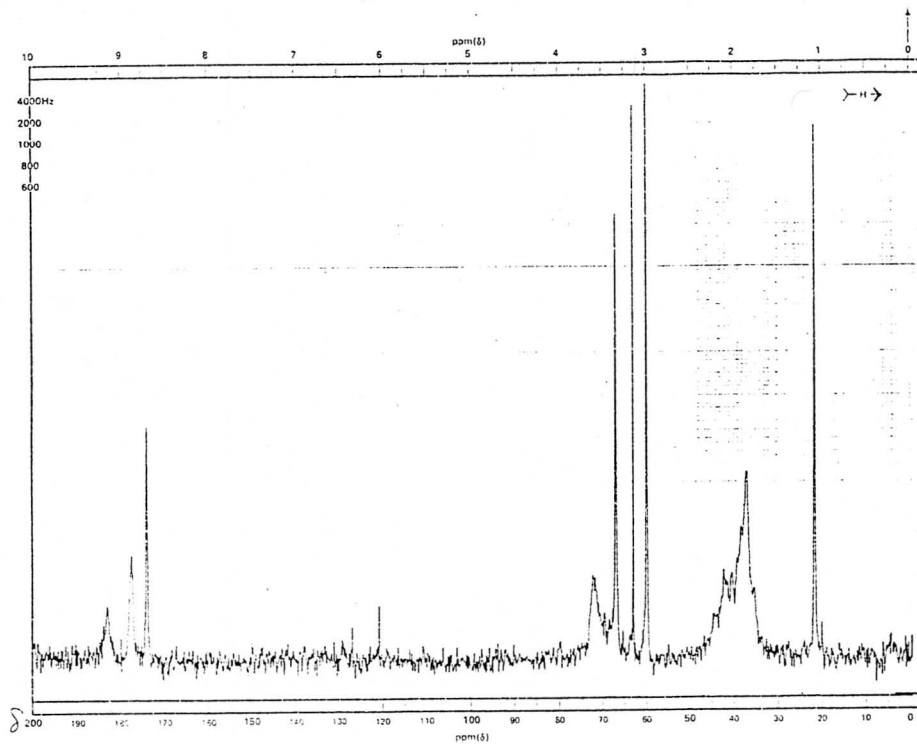


FIGURE 5.26:  $^{13}\text{C}$  NMR SPECTRUM OF POLYMER 012 (50% HYDROLYSIS)



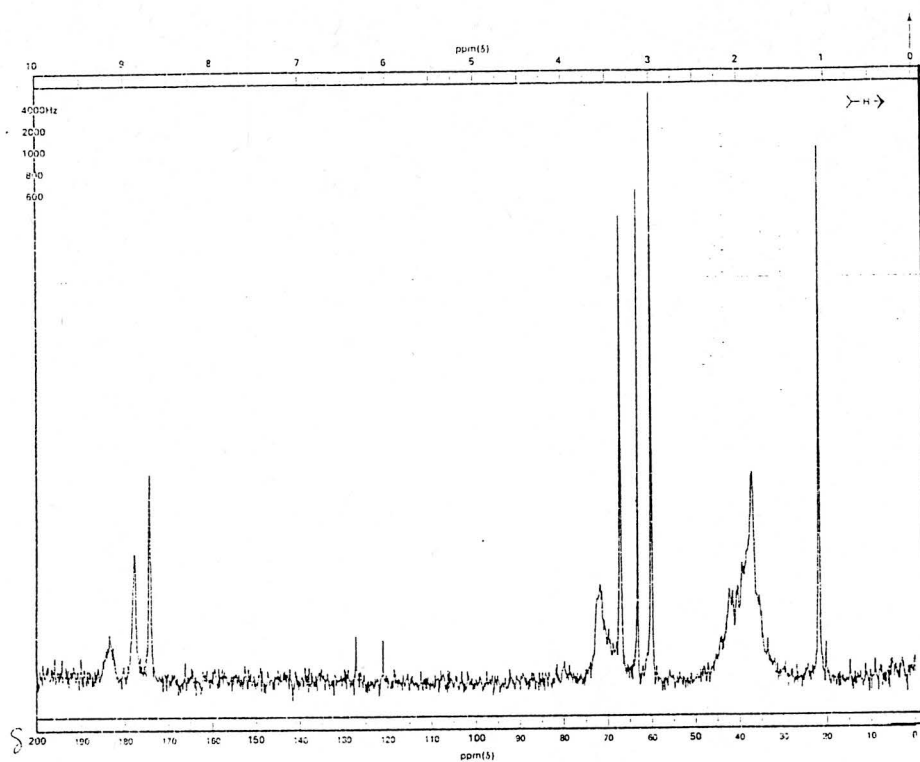


FIGURE 5.27:  $^{13}\text{C}$  NMR SPECTRUM OF POLYMER 013 (50% HYDROLYSIS)

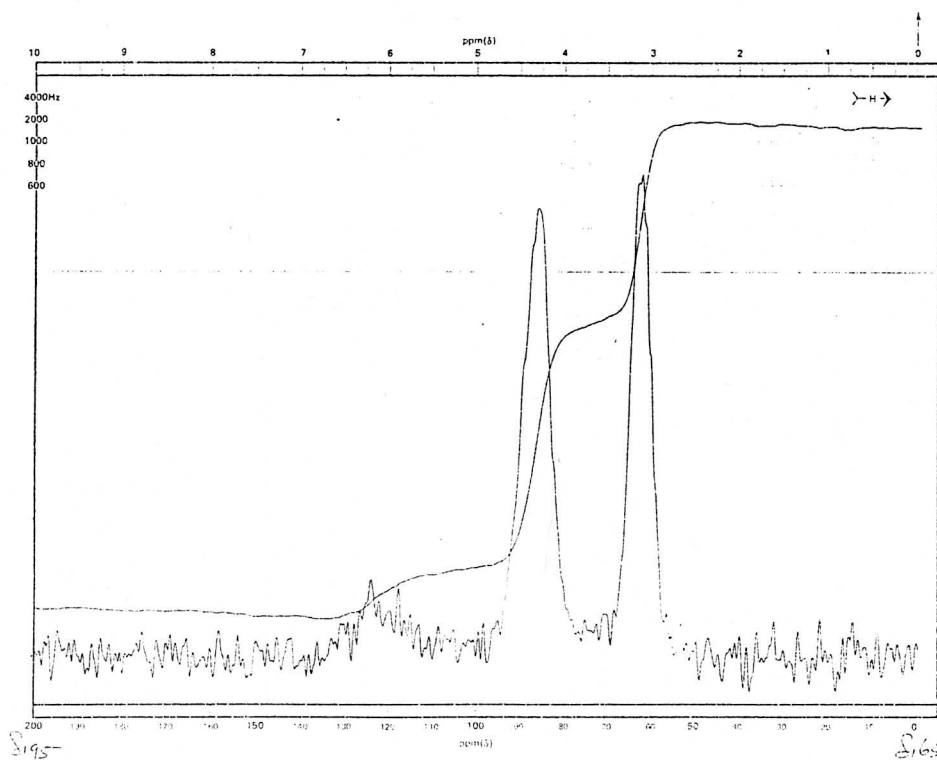


FIGURE 5.28:  $^{13}\text{C}$  INTEGRATED SPECTRUM OF POLYMER 010 (0% HYDROLYSIS)

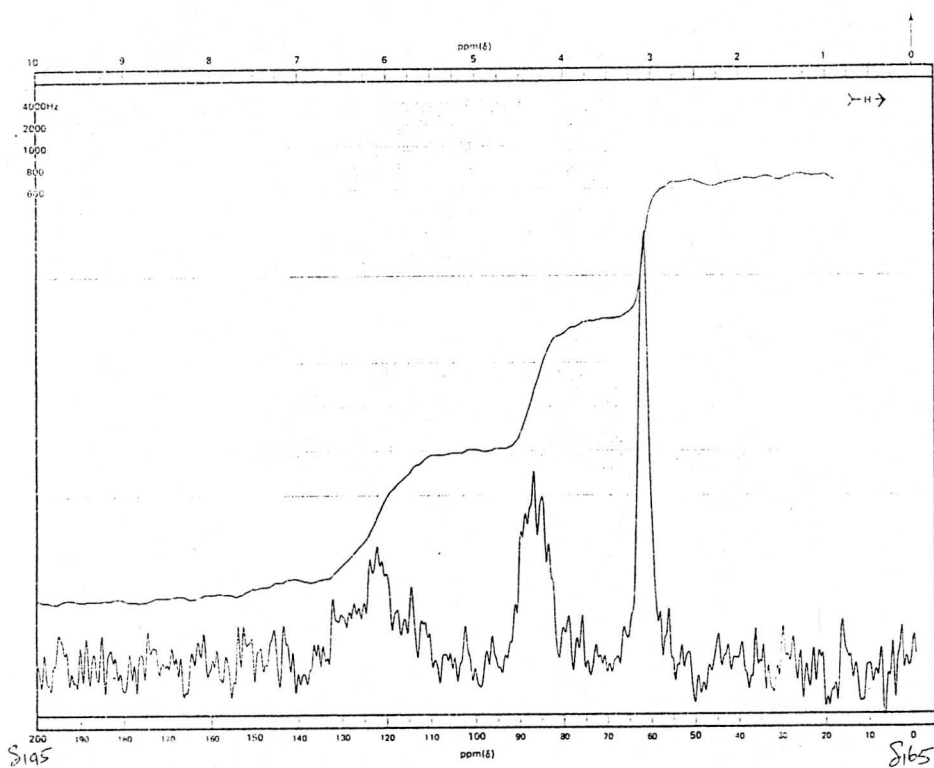


FIGURE 5.29:  $^{13}\text{C}$  INTEGRATED SPECTRUM OF POLYMER 010 (50% HYDROLYSIS)

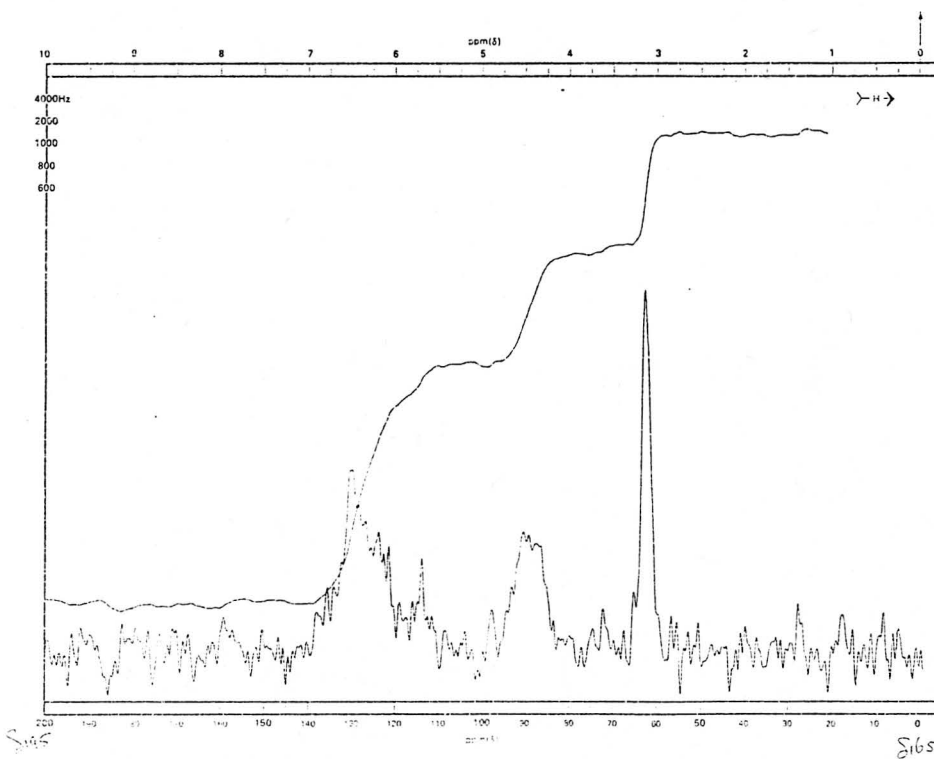


FIGURE 5.30:  $^{13}\text{C}$  INTEGRATED SPECTRUM OF POLYMER 010 (100% HYDROLYSIS)

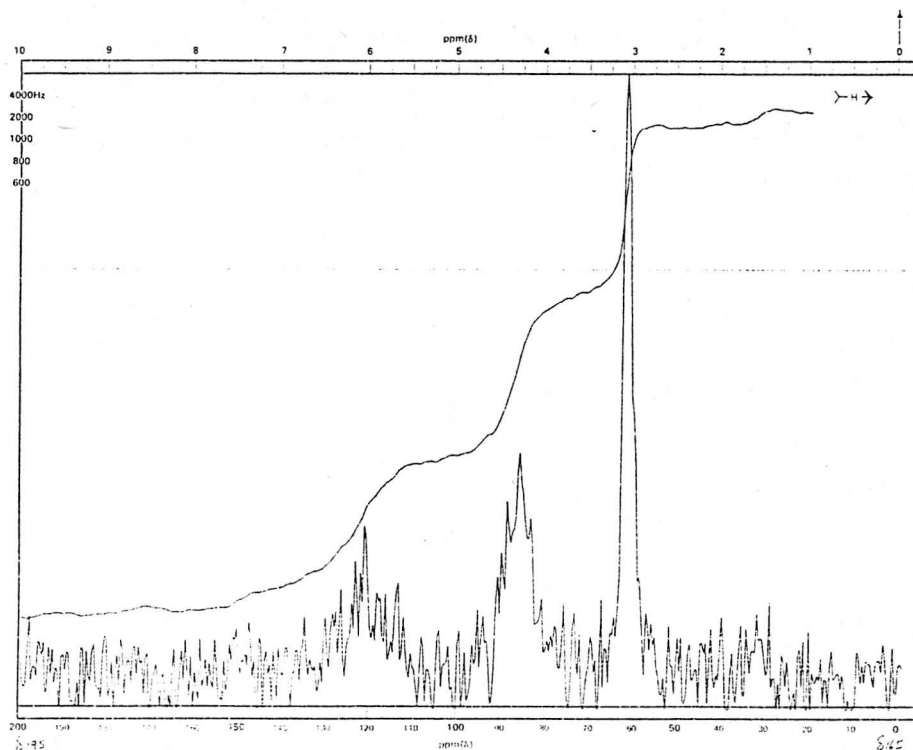


FIGURE 5.31:  $^{13}\text{C}$  INTEGRATED SPECTRUM OF POLYMER 011 (50% HYDROLYSIS)

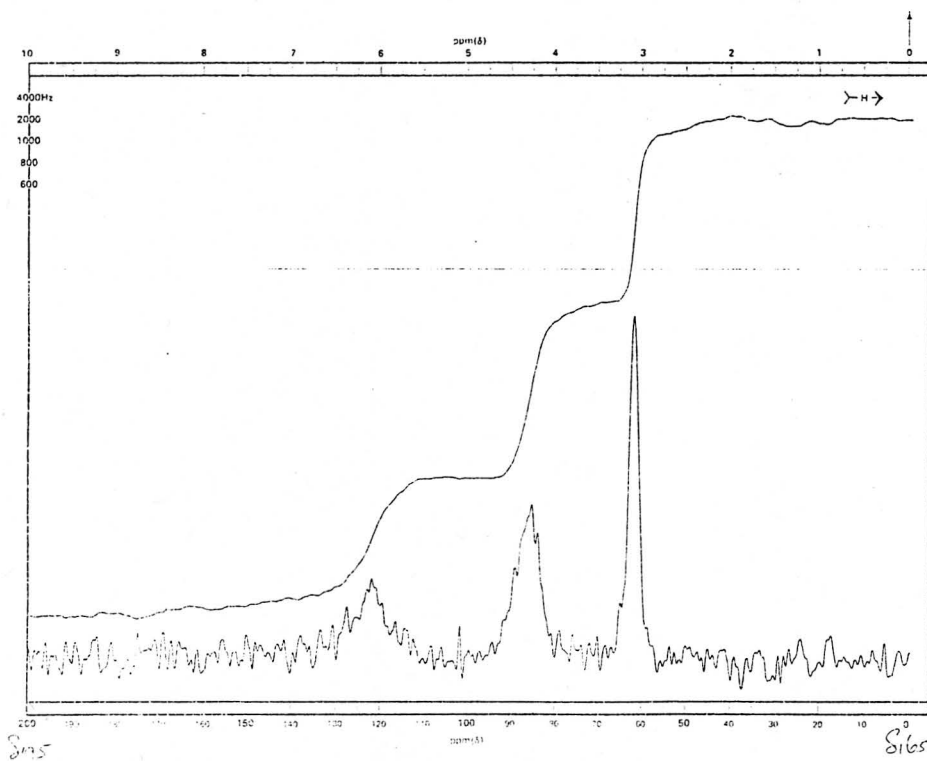


FIGURE 5.32:  $^{13}\text{C}$  INTEGRATED SPECTRUM OF POLYMER 012 (50% HYDROLYSIS)

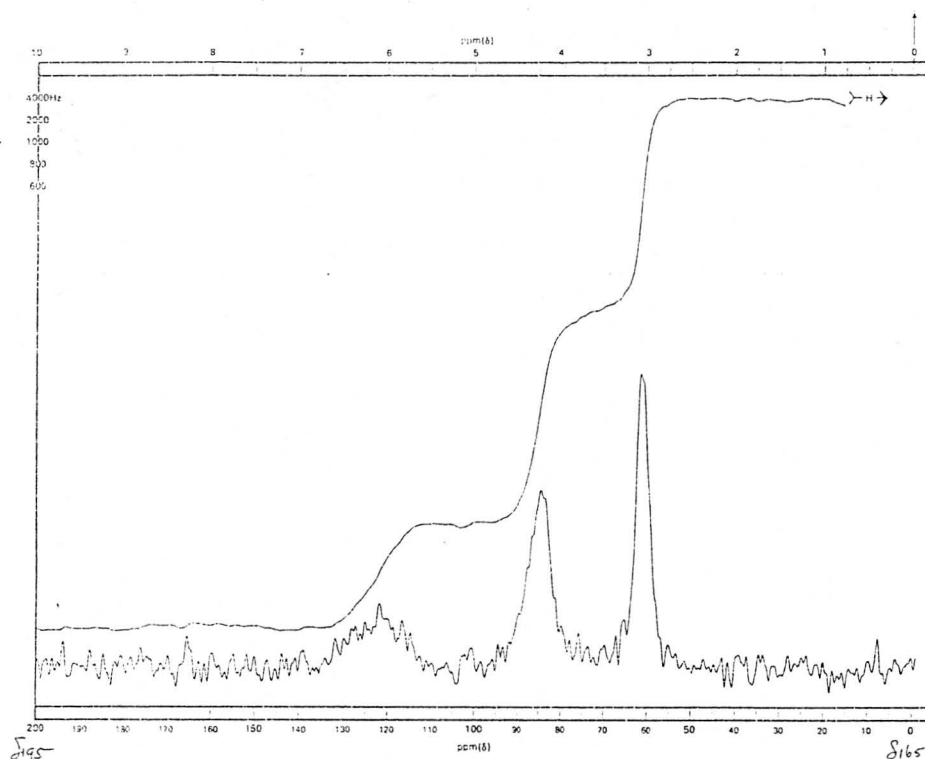


FIGURE 5.33:  $^{13}\text{C}$  INTEGRATED SPECTRUM OF POLYMER 013 (50% HYDROLYSIS)

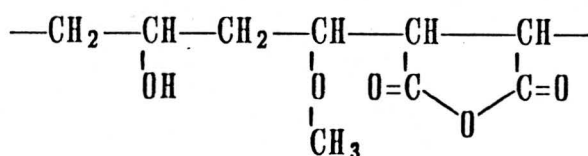
## 5.4 DISCUSSION

The two commercial GFT-membranes are based on crosslinked (86-89% hydrolyzed PVAC) polyvinyl alcohol<sup>(131)</sup>. The selectivity of these membranes was poorer with the wasserreich GFT membrane. This finding is in keeping with the present result that selectivity decreases as the polyvinyl acetate groups are progressively hydrolysed to polyvinyl alcohol groups. There is a great deal of general information concerning GFT membranes available<sup>(12,54,162)</sup>, but knowledge of organic-organic separations is limited.

The selectivity of the GFT-standard membrane is higher for lower amounts of alcohol in the organic media. Thus, future research programmes could move to the stripping of trace amounts of alcohols.

The differences in selectivities and in fluxes for GFT-standard compared to GFT-wasserreich, makes it obvious that chemical modification plays an important role in membrane effectivity. Future research into chemical modification of membranes will be very valuable.

It is obvious from the chemical structure of Gantrez AN 119, that this membrane is more hydrophilic than GFT-wasserreich (see Figure 5.34).



**FIGURE 5.34: CHEMICAL STRUCTURE OF GANTREZ AN 119**

From the results of this study it is obvious that, for higher selectivity, research should go in the direction of less hydrophilic membranes (see Figure 5.13).

This research concentrated on the hydrophilicity-hydrolysis balance in order to find an optimum chemical structured balance in the membrane. Pure polyvinyl alcohol membranes did not show sufficient selectivities (see Figures 5.2, 5.4 and 5.10). The values were even lower for lower alcohol contents of the feed mixture (see Figure 5.10).

On the other hand, the chemically modified membranes from GFT gives higher selectivity values. These values are better for lower alcohol contents of the feed mixture (see Figure 5.8). Therefore, varying chemical nature of a membrane was the selected route for this research.

Vinyl acetate was chosen as one of the monomers to make varying degrees of hydrolysis possible. Hydroxyethyl acrylate and acrylic acid were incorporated in the membrane structure in order to vary the degree of crosslinking. Higher degrees of crosslinking are preferable due to increased membrane stability. Compromises had to be made for the best membrane results.

To study the degree of hydrophilicity required, the polymer with 50% hydrolysis were chosen due to measurable fluxes. The chemical structure used to study the degree of hydrolysis required strong crosslinking, hence, the polymer with the highest acrylic acid ratio, namely 15%, was used.

The hydrophilic effect of acrylic acid is balanced by not hydrolysing the acetate to give good selectivity. In choosing the degree of hydrolysis with which to vary the acid content from 0% to 15%, hydrophilicity changes were caused.

Results are comparable to GFT-membranes for this particular separation. These results prove that there is a need to change chemical structure of a membrane in order to obtain the best benefit out of specific separation situations. There is obviously more benefit to be gained by further fine tuning of the membrane chemistry with regard to degree of hydrolysis, degree of crosslinking and the variation of the polysulphone substructure in order to allow a thinner polymer layer to be used.

The best synthesized membrane gave a selectivity value of 2 200 with a 5% ethanol feed mixture, and only a value of 49 with a 30% ethanol feed mixture. This opens the possibility of even better results with even lower amounts of alcohol in the feed mixture.

Unfortunately, the experimental facilities and GC analysis of the permeates at high selectivities, precluded accurate analysis in such a situation.

# CHAPTER 6

## CONCLUSIONS

### 6.1 GENERAL

Membrane separations should be considered as a complement to existing conventional separation operations, but are not likely to be capable of performing a complete purification and completely displacing conventional separations for any particular purification process. The separation capabilities of membranes should be examined carefully to identify the best concentration range in which to use the membrane in question. A membrane operation may be capable of performing a small portion of a total separation and greatly improving the overall process.

### 6.2 SPECIFIED CONCLUSIONS

#### 6.2.1 PERVAPORATION APPARATUS

Pervaporation facilities were designed and built. A schematic representation of this equipment is given in Figure 3.1.

#### 6.2.2 POLYMER SYNTHESIS

Terpolymers, consisting of vinyl acetate, hydroxyethyl acrylate and acrylic acid, were synthesized (see Section 4.2). Four different monomer ratios were used.

#### 6.2.3 VARIATIONS IN CHEMISTRY

##### 6.2.3.1 Hydrophilicity

Variations in the degree of hydrophilicity were achieved by incorporating different amounts of acrylic acid in the polymer (see Table 4.1). The experimental values of amount of acid in the polymer differs from the reagent feed values. Four terpolymers varying in acrylic acid from 0 to 15% were successfully synthesized.

##### 6.2.3.2 Hydrolysis

Different degrees of hydrolysis were attempted by controlling the reaction with specific amounts of sodium hydroxide (see Table 4.3). The actual hydrolysis values were determined by NMR analysis of the polymer chemical structure.

#### 6.2.4 CHARACTERIZATION OF POLYMERS

The characterization of the polymers was done by NMR spectroscopy. All the spectra and their analysis can be found in Section 5.3.3.3. Integration was done over certain areas for further calculations.

### 6.2.5 MEMBRANE FORMATION

The pour-on technique was applied in membrane formation. The technique is discussed fully in Section 4.5.2.

### 6.2.6 MEMBRANE EVALUATION

The membrane testing procedure was standardized in order to achieve comparable results. Membranes were tested in different groups so that individual attributes could be investigated.

#### 6.2.6.1 Commercial Membranes

The selectivity of the GFT-standard membrane is higher for lower amounts of alcohol in the organic media. The differences in selectivities and in flux for GFT-standard compared to GFT-wasserreich, makes it obvious that chemical modification plays an important role in membrane effectiveness. Future research into chemical modification of membranes will be very valuable.

#### 6.2.6.2 Influence of Molecular Mass

Higher selectivity is achieved using higher molecular mass but a compromise is necessary, because flux decreases with increasing molecular mass. This only underlines the fact that future research regarding chemical modification of membranes will be very valuable.

#### 6.2.6.3 Influence of Synthetic change in Membrane Chemistry

Varying the chemical nature of membranes was the selected route for this research. Results prove that there is a need to change the chemical structure of a membrane in order to obtain the best benefit out of specific separation situations. There is obviously more benefit to be gained by further fine tuning of the membrane chemistry.

The best membrane 013:50 poly(vinyl acetate-co-vinyl alcohol-co-acrylic acid-co-hydroxyethyl acrylate) gave a selectivity average of 2 200 at a 5% ethanol feed mixture in comparison with the GFT-standard membrane that gave a selectivity of 3 300 with the same feed mixture. This membrane gave a flux of 88 kg/m<sup>2</sup>.d in comparison with the GFT-standard membrane of 39 kg/m<sup>2</sup>.d. The values are all calculated averages.

The terpolymer, poly(vinyl acetate-co-hydroxyethyl acrylate-co-acrylic acid) is therefore a useful membrane material.

## 6.3 FUTURE RESEARCH

This can involve chemical modifications around the above terpolymer structure; using substrates of fine microporosity in order to produce thinner active films; using hollow fine fibre supports to maximize surface area; using preheated feed to the pervaporation membrane; studying trace amount removal of hydrophilic substances from organic media.



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## APPENDIX A

## A1 TABLE OF RESULTS

The complete results of the pervaporation membranes are tabled below (see Table A.1). The GC values are multiplied by a correction factor (derived from the mass of ethanol in the feed relative to the GC reading) and rounded to two significant digits and/or to the nearest integer, instead of using a calibration curve.

TABLE A.1: TABLE OF TEST RESULTS OF PERVAPORATION MEMBRANES

Membrane Tested	Time (hrs)	% Ethanol in Feed		% Ethanol in Permeate Found	Flux <sub>2</sub> (kg/m <sup>2</sup> h)	Selectivity $\alpha$	
		Theoretical	Found				
PVA (72 000) + H <sub>2</sub> SO <sub>4</sub>	0	30	30	-	-	-	
	1		29	0	260	0	
	2		32	87	89	14	
	3		32	85	130	12	
	4		29	87	130	16	
	5		27	90	130	24	
	6		27	91	110	27	
	7		28	91	89	26	
	8		27	92	67	31	
	0	5	5	5	-	-	-
	1		5	5	1	420	0
	2		5	5	1	130	0
	3		5	5	1	89	0
	4		5	5	0	44	0
	5		5	5	0	44	0
	6		4	4	1	22	0
7		4	4	0	22	0	
8		4	4	0	22	0	
GFT-standard	0	30	30	-	-	-	
	1		23	98	44	160	
	2		16	99	44	520	
	3		23	99	22	330	
	4		20	99	22	400	
	5		19	99	22	420	
	6		23	99	22	330	
	7		23	99	22	330	
	8		23	99	22	330	

	0	5	5	-	-	-
	1		3	94	110	510
	2		17	99	110	480
	3		8	100	44	1 100
	4		3	100	44	3 200
	5		3	99	44	3 200
	6		5	100	44	1 900
	7		2	99	44	4 900
	8		3	99	22	3 200
GFT-wasserreich	0	30	30	-	-	-
	1		27	81	89	12
	2		26	96	89	68
	3		26	99	89	280
	4		27	99	44	270
	5		26	99	44	280
	6		26	99	22	280
	7		27	99	22	270
	8		27	99	22	270
	0	5	5	-	-	-
	1		9	84	220	53
	2		6	87	180	100
	3		16	91	44	53
	4		5	86	22	120
	5		6	91	22	160
	6		6	92	22	180
	7		7	94	22	210
	8		7	90	44	120
Gantrez AN 119	0	30	30	-	-	-
	1		26	1	1 400	0
	2		25	1	440	0
	3		26	1	350	0
	4		25	1	180	0
	5		26	1	180	0
	6		26	87	44	19
	7		25	88	22	22
	8		25	87	22	20
	0	5	5	-	-	-
	1		5	1	4 400	0
	2		7	2	1 200	0
	3		6	1	840	0
	4		5	0	580	0
	5		8	0	500	0
	6		6	0	400	0
	7		6	0	400	0

	8		5	0	300	0
PVA (15 000) + $K_2S_2O_8$	0	30	30	-	-	-
	1		27	76	750	9
	2		27	77	620	9
	3		27	78	600	10
	4		26	78	490	10
	5		27	79	490	11
	6		26	81	440	12
	7		26	77	440	10
	8		26	79	400	10
	0	5	5	-	-	-
	1		6	5	5 000	1
	2		6	2	980	0
	3		6	3	400	0
	4		6	3	310	0
	5		6	3	270	0
	6		6	3	270	0
	7		6	2	750	0
	8		5	3	440	1
PVA (72 000) + $K_2S_2O_8$	0	30	30	-	-	-
	1		19	88	490	31
	2		19	84	440	22
	3		25	86	310	18
	4		25	94	310	47
	5		26	92	180	33
	6		25	94	177,4	47
	7		25	95	89	57
	8		25	93	44	40
	0	5	5	-	-	-
	1		5	3	4 300	1
	2		5	1	1 200	0
	3		5	3	1 100	1
	4		5	1	580	0
	5		5	2	270	0
	6		5	2	130	0
	7		5	0	44	0
	8		5	3	22	1
Poly(vinyl acetate-co-acrylic acid)	0	30	30	-	-	-
	1		29	69	1 100	5
	2		30	92	4 400	27
	3		27	99	3 900	270
	4		29	98	3 700	120
	5		27	68	2 700	6

		6	28	85	2 400	15
		7	27	87	2 300	18
		8	27	85	2 100	15
		0	5	5	-	-
		1	5	53	2 600	21
		2	5	50	2 100	19
		3	6	40	1 870	10
		4	5	56	1 600	24
		5	6	61	1 500	25
		6	5	64	1 200	34
		7	6	62	1 100	26
		8	6	68	1 000	33
010 : 100		0	30	30	-	-
		1	24	97	3 400	100
		2	23	82	3 900	15
		3	24	78	3 500	11
		4	22	90	3 100	32
		5	23	90	3 500	30
		6	23	83	3 100	16
		7	23	83	3 100	16
		8	23	86	2 700	21
		0	5	5	-	-
		1	4	95	11 000	460
		2	4	65	3 300	45
		3	3	69	2 000	72
		4	4	40	1 700	16
		5	3	44	1 600	25
		6	3	51	1 400	34
		7	3	34	1 300	25
		8	2	33	1 100	24
010 : 50		0	30	30	-	-
		1	27	65	3 500	5
		2	27	65	5 300	5
		3	26	59	4 100	4
		4	25	59	5 000	4
		5	25	61	4 600	5
		6	25	61	4 900	5
		7	25	70	4 500	7
		8	26	53	4 400	3
		0	5	5	-	-
		1	4	3	14 000	1
		2	4	99	4 700	2 400
		3	3	92	4 000	370

		4	4	94	2 800	380
		5	4	94	2 800	380
		6	3	71	2 000	79
		7	3	92	2 100	370
		8	3	84	1 800	170
010 : 0		0	30	30	-	-
		1		28	98	440
		2		28	99	310
		3		28	97	290
		4		27	97	220
		5		28	97	180
		6		28	97	180
		7		28	96	89
		8		27	96	89
		0	5	5	-	-
		1		5	95	220
		2		5	96	130
		3		6	97	89
		4		6	96	89
		5		6	96	89
		6		6	95	44
		7		6	94	44
		8		6	94	22
011 : 50		0	30	30	-	-
		1		31	80	440
		2		30	84	440
		3		30	87	340
		4		30	85	440
		5		31	83	340
		6		30	84	340
		7		30	83	360
		8		30	83	360
		0	5	5	-	-
		1		5	91	530
		2		6	83	180
		3		5	85	130
		4		5	85	180
		5		5	82	130
		6		5	85	130
		7		5	86	110
		8		5	87	100
012 : 50		0	30	30	-	-
		1		25	92	220

		2	26	88	220	21
		3	26	84	220	15
		4	29	83	220	12
		5	26	84	220	15
		6	26	85	180	16
		7	26	84	130	15
		8	26	81	130	12
		0	5	5	-	-
		1		5	97	610
		2		6	90	140
		3		5	92	220
		4		5	94	300
		5		5	93	250
		6		5	92	220
		7		5	93	250
		8		6	94	250
013 : 50		0	30	30	-	-
		1		27	89	22
		2		26	82	13
		3		26	91	29
		4		27	94	42
		5		26	95	54
		6		26	94	45
		7		27	95	51
		8		26	94	45
		0	5	5	-	-
		1		6	100	1 600
		2		4	100	2 400
		3		4	100	2 400
		4		4	99	2 400
		5		4	98	1 200
		6		4	98	1 200
		7		3	99	3 200
		8		3	100	3 200

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