MODELING AND EXPERIMENTS OF AQUEOUS ALCOHOL SEPARATION VIA PERVAPORATION

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CHAPTER I

INTRODUCTION

Recently, the applications of membrane science and technology have been intensively studied in the field of chemical engineering. In the petrochemical industry, the use of membranes is appropriate for many types of separation, purification, or concentration operations and can reduce energy costs. The main advantages of membrane separation processes are simplicity, continuous operation, flexibility of combining with other separation techniques, and the possibility of operation at low or moderate temperatures. Membrane processes are generally not constrained by vapor-liquid equilibria behavior and do not require the use of additional chemicals for effecting the separation. Furthermore, the energy requirement of a membrane separation process is comparatively lower than that of the conventional technologies and membrane process scale-up is relatively easier to perform.

In spite of all the advantages given above, membrane separation is not an ideal technology, and like other separation techniques it has some disadvantages and problems. Some of these disadvantages are low flow-rates, fouling and noncompatibility of membranes with some chemicals.

The various types of the membrane separation processes are gas permeation, pervaporation, dialysis, electrodialysis, reverse osmosis (or hyperfiltration), ultrafiltration and microfiltration. These processes serve the various needs of mankind like the desalination of brackish water and seawater, oil/water separation, concentration of fruit juices, waste water treatment, recovery of helium from natural gas, dehydration of alcohols, and artificial kidneys.

Pervaporation is a separation process in which the components of a liquid mixture selectively permeate through a membrane under the influence of a chemical potential gradient. On one side of the membrane is a liquid feed and on the other side is a gaseous permeate. The portion of the liquid that permeates through the membrane undergoes a phase change from liquid to vapor and sometimes energy is added to the system to provide the heat of vaporization. Hence, the word pervaporation is a combination of "per" (from permeation) and "vaporation" (from evaporation). The permeation rate varies from one component to another and is related to the molecular shape, size and chemical nature of the permeate. The nature of the membrane, e.g., its hydophillicity or hydrophobicity or affinity for a certain component also affects the separation. Finally, the interaction of one permeant with another and with the membrane has a very strong influence on its permeation rate. In general, the selectivity of the membrane is desired to be in favor of the component that is present in smaller amounts. This desire is due to the reason that a small amount will have to be vaporized and there will be savings in the heat of vaporization. The chemical potential gradient can be created by several means such as creating a vacuum on the permeate side or the use of a sweep gas. The permeate product is usually collected by condensation over a very cold surface.

Pervaporation possesses all the inherent advantages of a membrane-based process. In addition, the nonporous nature of the membrane makes pervaporation less susceptible to fouling, and in-situ cleaning of the commercial pervaporation plants is a normal routine. In contrast to reverse osmosis, the osmotic pressure driving force does not retard the separation process because the permeate is kept under low pressure.

Kober (1917) was the first to coin the term pervaporation and Binning et al. (1961) were the first to experiment with and model the process. Initially, pervaporation was used to separate anhydrous organic mixtures, but later research included applications such as dehydration of alcohols, separation of octane-boosters from their precursors and separation of trace organics from water and wastewater streams.

The art of making membranes developed over the years and so did the design and configuration of the pervaporation process. This technological advancement leads to the first commercial pervaporation plant by GFT (West Germany) in the mid-1970s for the dehydration of ethanol. The commercial plant required only a small vacuum pump because a significant amount of vacuum is developed by the condensing permeate resulting in low capital costs.

Pervaporation finds many applications in the fields of dehydration of organic liquids, water treatment and organic-organic separations. The most successful application has been the dehydration of organic liquids. In particular, the dehydration of ethanol has been very successful and significant research continues for the dehydration of isopropanol, butanol, acetone, tetrahydrofuran, ethyl acetate, ethylene glycol and methylene chloride.

The unique capabilities and the great versatility of pervaporation have made it very competitive with conventional separation technologies. Currently, pervaporation is more advantageous when integrated with existing separation units. There is still considerable need for membrane and process development. The most significant long-term potential application for pervaporation may be for organic-organic separations. There may be considerable research, in the future, on the preparation and use of blend membranes in a quest to achieve exotic properties. Since the strength and fouling characteristics of membranes are extremely important, the future of pervaporation will most likely involve considerable research in inorganic ceramic membranes.

The purpose of this study was to design a pervaporation laboratory where research could be performed on the separation of the mixtures of industrial importance and to develop a mathematical model for predicting the pervaporation behavior.. The design of the apparatus includes special cold traps wherein product removal without dismantling the equipment is possible. In this study, the apparatus was used for the dehydration of ethanol/water and isopropanol/water mixtures. Ethanol can be used as a fuel, either pure or as a blend with gasoline and isopropanol finds use in the pharmaceutical industry. Both ethanol and isopropanol make azeotropes with water that are very hard to separate.

Since pervaporation experiments are very expensive and often time-consuming, there is a need for a mathematical model which can provide a quick estimate of the performance of the process for studies of technical and economical feasibility. For a particular application, the pervaporation model can enable a comparison of the advantages and disadvantages of pervaporation relative to the conventional methods of separation. An optimization of the pervaporation process is also possible through the use of a reliable model. There has been a significant effort in the past to model the pervaporation process, but none of models developed so far have a completely predictive capability. Therefore, a comprehensive pervaporation model has been developed in this study which does not need any experimental data for diffusivity or sorption in the membrane. The model developed in this study is based on free volume theory of diffusion for a ternary mixture and takes into account the coupling of diffusion coefficients.

CHAPTER II

LITERATURE REVIEW

Pioneering Work in Pervaporation Experiments:

Binning et al. (1961) carried out the first major industrial work in pervaporation. The pervaporation membranes which they used did not contain discrete pores, so they were considered as nonporous. They compared pervaporation with gas separation using membranes. They believed that unlike the dry film in gas permeation, pervaporation involves the sorption of the permeating liquid in the polymer film. Hence, they visualized the permeable film under operating conditions as a swollen "solution" of polymer and the permeating organic compounds. Due to the interactions between the permeants and the membrane, it was not possible to calculate the permeate composition from a knowledge of the mixture composition and permeation rates of pure components. Binning et al. (1961) perceived the pervaporation process as consisting of three steps:

1) solution of liquid in the film surface in contact with the liquid feed mixture,
2) migration through the body of the film, and
3) vaporization of the permeating material at the downstream interface where permeate product is immediately swept away.

The mathematical model describing the mechanism of pervaporation given in the above three steps is usually called the solution-diffusion model. This model assumes that the penetrants in the bulk phase of the feed are in equilibrium with the surface of the membrane. Similarly, on the permeate side of the membrane, the penetrants are assumed to be in equilibrium with the bulk phase. In the ideal pervaporation system, the permeate side of the membrane is in contact with complete vacuum so that the equilibrium concentration on the permeate side of the membrane and the bulk phase is zero.

Huang and Lin (1968) conducted several experiments on pervaporation using a low density polyethylene (LDPE) membrane with mixtures of organic compounds. These compounds were n-pentane, n-nonane as well as some aromatic and cyclic compounds. They found that the temperature dependence of the permeation rate can be expressed by an Arrhenius-type relationship for both pure components and binary mixtures. However, the quality of separation was sometimes adversely affected by the increase in temperature, which Huang and Lin (1968) explained by arguing that the increase in kinetic energy or motions of the polymer chains at higher temperatures enhances the passage of the non-solvent. The effects of chemical nature, molecular size, and molecular shape of the diffusing species on the permeation were studied and qualitative guidelines were suggested. The solubility difference depends primarily on the difference in the chemical nature of the permeating species. On the other hand, diffusivity difference is attributed largely to the size and shape of these molecules and to the degree of aggregation among the diffusing species within the polymer.

For molecules with similar shape and chemical nature, Huang and Lin (1968) showed that the permeation rate decreases with increasing molecular length. The permeation rate also decreased with increasing diffusional cross-section of molecule. Table I shows some effects of molecular shape and size on permeation rate. It was noted that n-hexane permeated slowly as compared to benzene although its diffusional cross section is slightly smaller than that of

TABLE I

Effect of Molecular Shape and Size on the Permeation Rate Through LDPE

Permeant	Molecular length $\overline{L}$ (A^0)	Diffusional cross-section, $\overline{V}/\overline{L}$ (A^{02})	Permeation rate at 25 ^0C (g/hr m^2)
Benzene	5.96	24.8	301
n-Hexane	9.10	23.9	203
Cyclohexane	5.74	31.3	152
2,2-Dimethylbutane	6.58	33.8	35

Reference: Huang and Lin (1968)

benzene, which may be because of the smaller molecular length of benzene.

Huang and Lin (1968) also showed that polar compounds tend to permeate polar membranes faster than non-polar compounds and vice versa. Therefore, it was observed that a less polar compound, chloroform, permeated through polyethylene faster than dichloromethane, in spite of the fact that chloroform has a larger molar volume than dichloromethane.

Solvents with solubility parameters, δ, close to that of the polymer sorb to a greater extent than solvents whose δ values are far from that of the polymer (Huang and Lin, 1968). On this basis, chloroform ($\delta = 9.3$) permeates polyethylene ($\delta = 7.9$) faster than dichloromethane ($\delta = 9.7$). In liquid permeation, shape and size effects predominate for molecules with smaller differences in chemical nature. However, molecules with larger differences in chemical nature are affected more by parameters such as solubility, which are related to the chemical nature of the molecule.

Huang and Lin (1968) considered the permeation as ideal when each component in the mixture permeates without any interference from the other. The ratio of the actual to the ideal permeation rate was defined as permeation ratio and denoted by the symbol θ. For $\theta > 1$, the system was said to exhibit a permeation enhancement effect, while for $\theta < 1$, a permeation depression effect was indicated.

The membrane can be considered as a simple molecular sieve or screen, wherein the amorphous region constitutes the holes while the interconnected crystalline regions constitute the mesh (Huang and Lin, 1968). Most of the pervaporation experiments show that higher separations were obtained at lower concentrations of the preferentially permeating component. This can be explained on the basis that the solvent, in general, has a higher solubility and hence more plasticizing effect on the membrane than the non-solvent. An increase in plasticizing effect tends to “loosen up” the amorphous region and increase the permeability of both the solvent and the non-solvent.

Tock et al. (1974) performed pervaporation experiments on water, dioxane, and their mixtures using nylon-6 membranes and later, attempted to predict the selectivities of the mixtures from permeabilities of pure components. They assumed that the pure component permeation rates (q_i^0) and the mixture permeation rates (q_i) are related by:

$$q_A = x_A q_A^0 \tag{2.1}$$

$$q_B = x_B q_B^0 = (1 - x_A)\, q_B^0 \tag{2.2}$$

where x_A and x_B are the mole fractions of the permeant and nonpermeant, respectively. The predictions based on the above equations were found to be inaccurate for non-ideal mixtures like water and dioxane.

Tock et al. (1974) also studied the effects of surface treatment of the membrane on the permeation of one component relative to the other. The results of their experiments in Table II and III shows that both the permeability and sorption are improved by surface treatment of the membrane. They concluded that surface treatment destroys the crystallinity of the barrier surface and thereby increases its sorptive capacity. The etching of the surface of polar nylon-6 membrane increased the sorption of the more polar liquid, water, relative to the less polar paradioxane.

The selectivity factor or separation factor is defined as:

$$\alpha_{A/B} = \frac{y_A / y_B}{x_A / x_B} \tag{2.3}$$

where x_A, x_B, y_A and y_B denote the weight fraction of component A and B in the

Table II

Permeation Parameters. Pure Component Systems, Temperature; 35 °C, Nylon 6 Barrier-Capran, Type 77-C, Allied Chemical Corp.

	Permeate			
	Water		Paradioxane	
Parameter	Untreated film	Treated film	Untreated film	Treated film
J, mass flux	3.305×10^{-7}	5.901×10^{-7}	1.144×10^{-8}	1.181×10^{-8}
P, permeability	1.799×10^{-9}	3.227×10^{-9}	7.686×10^{-11}	6.297×10^{-11}
C*, equilibrium concentration	0.0096	0.119	0.074	0.113
Film thickness, cm	5.11×10^{-3}	5.11×10^{-3}	5.11×10^{-3}	5.11×10^{-3}
C_1, concentration	0.0913	0.086	0.0092	0.0144

Reference: Data taken from Tock et al. (1974).

Table III

Permeation Parameters. Mixtures. Feed: Water and Paradioxane Mixture(50:50), Temperature; 35 ^{0}C, Nylon 6 Barrier

	Total permeate mixture	
Parameter	Untreated film	Treated film
J, mass flux	5.023×10^{-7}	11.210×10^{-7}
P, total permeability	2.679×10^{-9}	6.042×10^{-9}
C*, equilibrium concentration	0.116	0.163
Film thickness, cm	5.11×10^{-3}	5.11×10^{-3}
C_1, concentration	0.094	0.077

Reference: Data taken from Tock et al. (1974).

feed solution and in the pervaporate, respectively, where A is the preferentially pervaporated species. The selectivity factor, α, is analogous to the relative volatility of distillation and is related to the ease of separation of the components. Aptel et al. (1976) observed that α depends on the composition of the feed. They compiled a summary of the previous pervaporation experiments which is presented in Table IV. A view of Table IV shows that, in general, the selectivities are higher for alcohol/water separations than for other separations. Aptel et al. (1976) also introduced the idea of "thermopervaporation" in which the temperature gradient contributes to the driving force for the mass transfer. In thermopervaporation, a "cold wall" is used to condense the permeate and collect it as a liquid, eliminating the need for a separate cold trap. This scheme is presented in Figure 1. Using poly(tetrafluoroethylene), PTFE, films grafted with N-vinylpyrrolidone, NVP, as membranes for a number of binary mixtures, they discovered that an increase in the feed temperature leads to an increase of both selectivity and flux. An advantage of pervaporation is the higher selectivity while a disadvantage is the slow rate of the process which involves transport through a membrane. Aptel et al. (1976) prepared membranes in which functional groups are able to provide specific interactions with one of the components of the mixture. The very small thickness (about 12 μm) of their membranes resulted in high fluxes of the order of 1 kg/h m^2 for mixtures of water with dioxane. High selectivities were observed for the water-alcohol azeotropes.

Aptel et al. (1976) observed that the compounds with higher molecular weight were more easily dehydrated by pervaporation than the lower molecular weight members of the series, especially if the steric hindrance of the carbon bearing the OH group prevents the self-association of the compound. Water is the preferential permeant because of the high affinity of water for the CO groups

Table IV

Some Azeotropic and Close-Boiling Mixtures Separated by Pervaporation

Feed mixture			Pervaporation				
Compounds		Composition (wt. % of A)	Temp. (°C)	Selectivity $\alpha_{A/B}$	Flux (kg/h m²)	Membrane and its Thickness (μm)	References
A	B						
water	EtOH	45	80	8.5	1.95	Cellulose acetate (N.A.)	Binning et al. (1961)
water	iPrOH	12	60	15.6	0.7	Cellophane (N.A.)	Carter et al.(1964)
		12	80	20.0	3.7	Modified cellulose acetate (140)	Manedova et al.(1969)
Benzene	MeOH	60.5	42	11.9	0.3	Polyethylene (N.A.)	Carter et al.(1964)
		60.5	60	7.2	2.1	Polyethylene (N.A.)	Binning et al.(1961)
MeOH	benzene	39.5	60	5.1	3.1	Cellulose acetate (N.A)	Binning et al.(1961)
toluene	heptane	60.0	30	1.4	0.27	Polyethylene (51)	Fels (1972)

Table continued

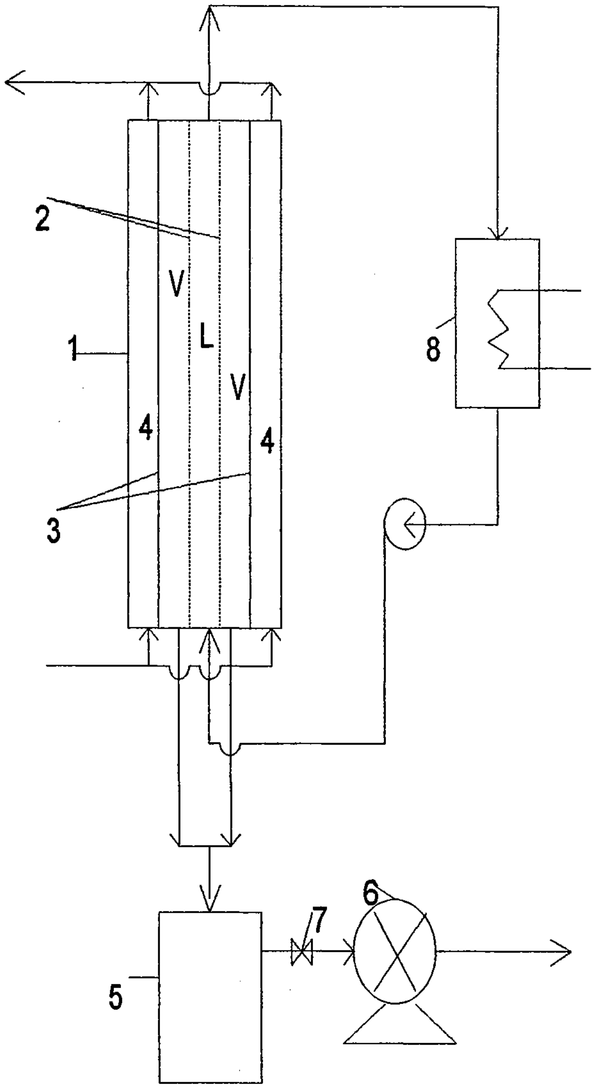
N.A. - not available
Ref: Aptel et al.(1976)

Table IV (continued)

Some Azeotropic and Close-Boiling Mixtures Separated by Pervaporation

Feed mixture			Pervaporation				
Compounds		Composition (wt. % of A)	Temp. (°C)	Selectivity $\alpha_{A/B}$	Flux (kg/h m2)	Membrane and its Thickness (μm)	References
A	B						
benzene	n-hexane	50	30	1.6	1.0	Polyethylene-styrene graft copolymer (24)	Huang et al.(1968)
benzene	cyclo -hexane	50	25	1.6	0.5	Polyethylene (25.4)	Huang et al.(1968)
		50	60	2.6	1.0	Polypropylene (40)	Kucharski et al.(1967)
		50	56	5.5	0.1	Modified vinylidene fluoride (100)	McCandless et al.(1973)
		50	60	11.0	0.32	Polymeric alloys of polyphosphonate and acetyl cellulose (20)	Cabasso et al.(1974)
1,3 butadiene	*trans*-2-butene	0.8	N.A.	4.9	0.02	Aromatic imide (25)	Perry et al.(1974)
1,3-butadiene	Iso -butene	0.38	22	3.1	0.3	1,3-Butadiene-acrylonitrile copolymer (20)	Vasse et al.(1974)

N.A. - not available
Ref: Aptel et al.(1976)



Legend:

1. Thermopervaporation cell
2. Membranes
3. Cold wall
4. Cooling chamber
5. Pervaporate container
6. Vacuum pump
7. Stop-cock
8. Hot feed container

L - Feed compartment

V - Pervaporate compartment

Figure 1. "Thermopervaporation" Apparatus of Aptel et al.(1976)

of the NVP. This affinity, in addition to the tendency of self-association of water molecules, causes a multimolecular layer of sorbed water at the membrane-solution interface. This layer, in turn, increases the concentration gradient of water through the membrane.

In the case of mixtures whose components have different affinities for the membrane, it was observed that as the concentration of the preferentially pervaporated species (A) decreases, the flux decreases, and the selectivity increases. The change in flux is expected while the change in selectivity can be explained in terms of the modifications undergone in the membrane. The decrease in A decreases the plasticizing action so that B sees a "different" membrane and is sorbed in lesser quantities. Aptel et al. (1976) also reported the pervaporation results for some binary negative azeotropes through PTFE-PVP membranes. For these mixtures, the selectivities were relatively smaller than those of positive azeotropic mixtures and hence the separation by pervaporation was found to be difficult.

Hoover and Hwang (1982) demonstrated that by using a continuous membrane column, a mixture of two or more liquids can be separated to a higher degree without cascading several stages of individual pervaporation units. They used hollow fiber (capillary) membranes. The counter-current flow arrangement of the continuous membrane column allows the feed liquid to flow inside the capillary while the permeate is drawn from the outside. Unlike the conventional pervaporator, a continuous membrane column does not pose a limitation on the degree of enrichment. The permeabilities of ethanol-water and isopropanol-water mixtures through silicon rubber [poly(dimethylsiloxane)] were reported as a function of concentration. Silicone rubber has been found to be very durable for gas permeation separations.

The experimental setup used by Hoover and Hwang (1982) is different from a typical pervaporation apparatus in that the membrane cell is arranged in a shell and tube assembly as shown in Figure 2. A liquid mixture of known concentration is circulated through the tubeside at a large enough rate that the concentration remains unchanged due to pervaporation losses to the shell.

The scheme of a continuous pervaporation column of Hoover and Hwang (1982) is presented in Figure 3. The pervaporation system has been arranged in a form which is somewhat similar to the arrangement of a distillation column. The stripping and enriching sections of a continuous membrane column are constructed in a shell and tube configuration. The feed flows in the tubes while the permeate is collected in the shell. Both cells are coiled into spirals to reduce the space requirements for the apparatus. A closed circuit sweep air stream is used to remove the permeate vapor from the shell side and bringing it to the condenser.

In alcohol-water systems, alcohol permeates preferentially through silicone rubber. Hoover et al.(1982) defined an ideal separation factor as:

$$\alpha^* = \frac{Q_A P_A^0}{Q_B P_B^0} \tag{2.4}$$

where Q_i (mol m/s m^2 kPa) is the permeability coefficient and P_i^0 the vapor pressure of component i. Hoover et al. (1982) viewed α^* as a product of separation factor for gas permeation (permeability ratio) and for distillation (vapor pressure ratio). Contrary to the convention used by other investigators, Hoover and Hwang (1982) used the subscript A for alcohol and B for water.

The permeability experiments of Hoover and Hwang (1982) have indicated relatively low permeabilities for ethanol in ethanol-water pervaporation through silicone rubber. However, ethanol vapor pressure is about double that of water in the 25-40 °C temperature range. This is the reason why alcohol is the

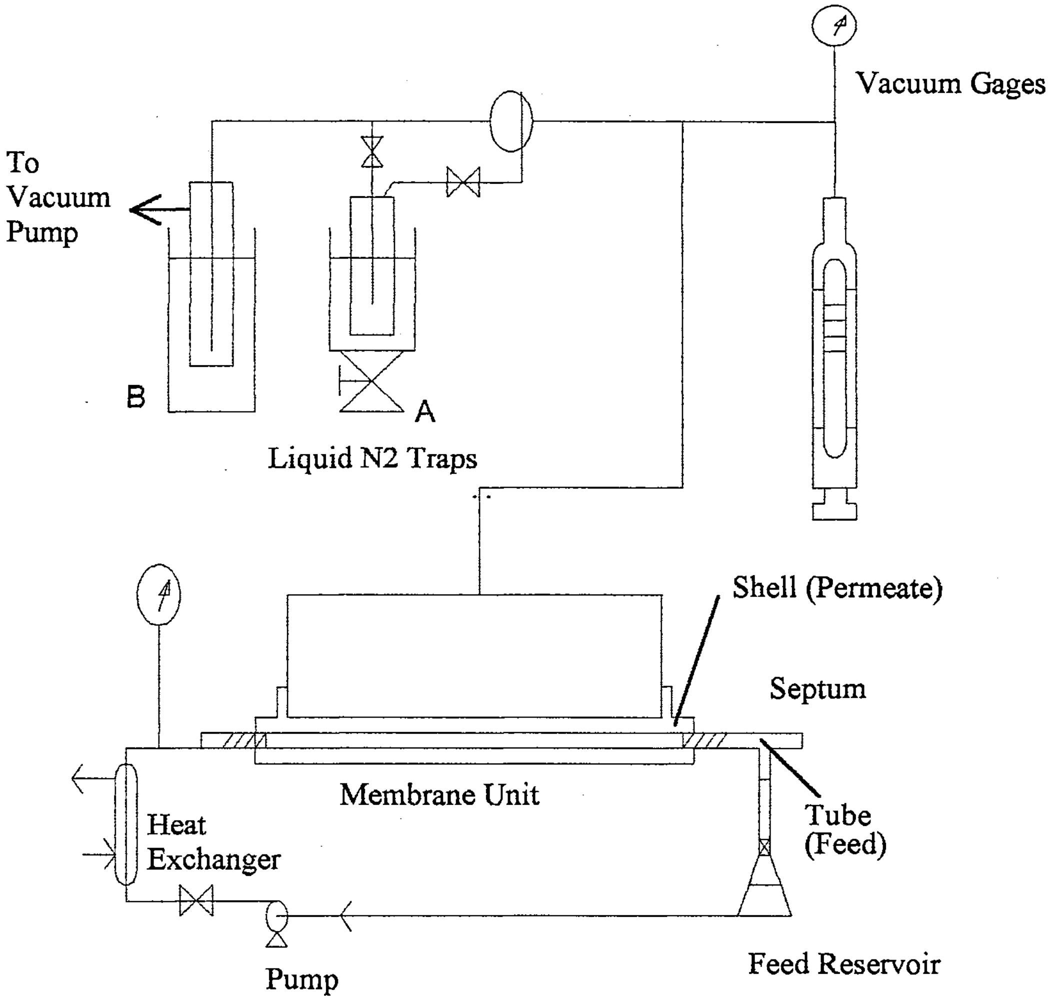


Figure 2. Permeability Determination Apparatus of Hoover and Hwang (1982)

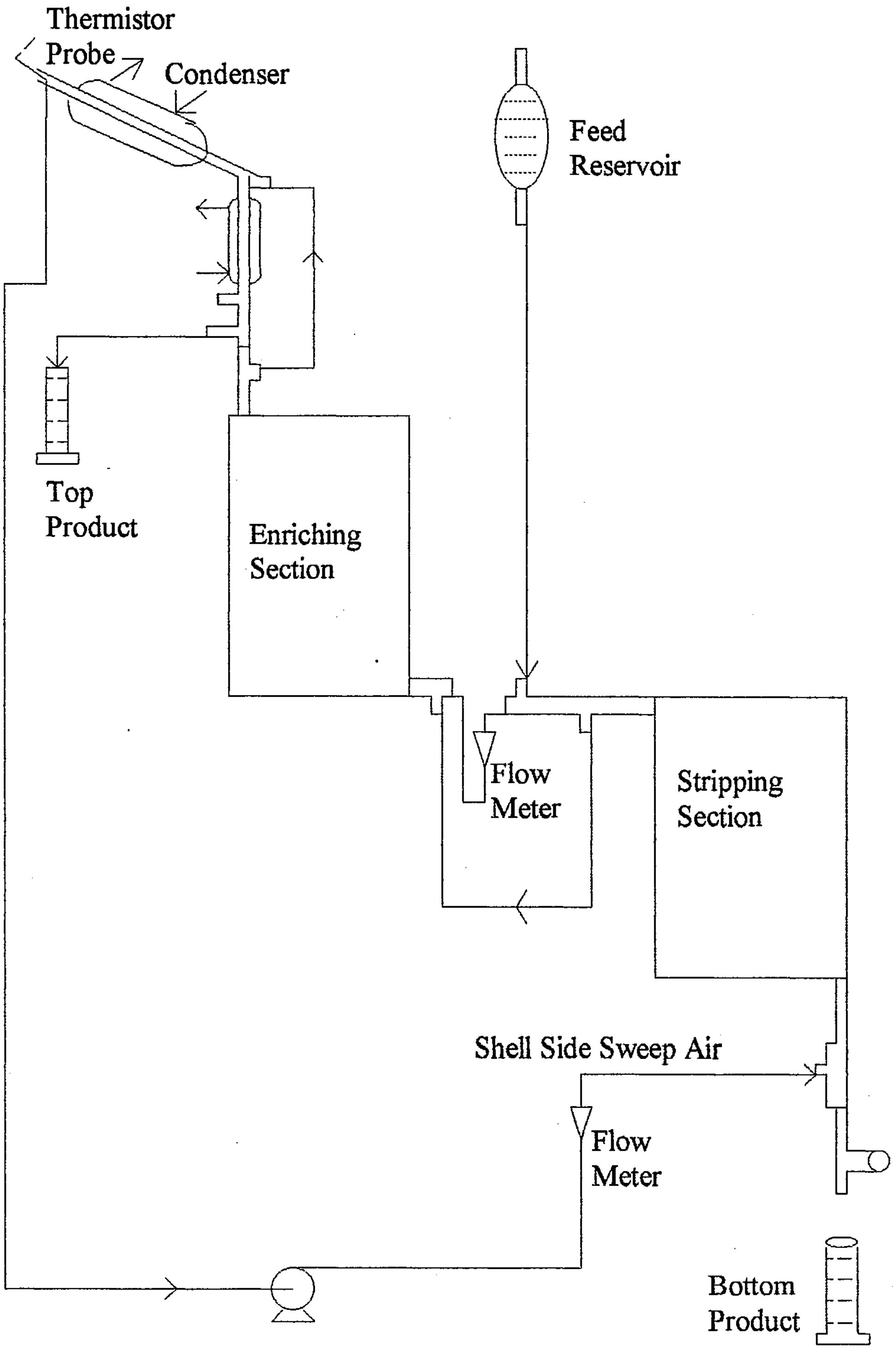


Figure 3. Continuous Membrane Column of Hoover and Hwang (1982) for Pervaporation

component that permeates preferentially in silicone rubber. At low alcohol levels, α is quite large, but decreases as the alcohol is increased. At $\alpha = 1$, the permeating vapor has the same composition as that in the liquid phase. This situation is identical to that of an azeotrope in distillation. In distillation an azeotrope is shifted by a change in pressure. However, in pervaporation a change in temperature has been found to be effective.

Hoover and Hwang (1982) argued that the membrane which shows $\alpha^* >1$ throughout the concentration range of interest is the most desirable. In this respect, they found the silicone membrane to be desirable for concentrating ethanol from ethanol/water mixtures. However, for the system isopropanol-water-silicone, the feed concentration showed $\alpha^* >1$ until 80 % isopropanol, above which $\alpha^* <1$ was observed. On the other hand, isopropanol-water shows a normal distillation azeotrope at 68.5 mole % isopropanol. Hence the separation by membranes has the advantage of giving a purer product. Also, since high temperatures are not required, heat sensitive materials can potentially be separated.

A potential application of pervaporation can be the immersion of silicone rubber tubes in the fermenting mixture (Hoover and Hwang, 1982). The ethanol level reached in a fermenter is about 8 mol percent. The ethanol will selectively permeate into the tubes under the influence of a vacuum or sweep gas. The membrane will also act as a filter, preventing particulate matter from entering the later processing equipment. Alternatively, azeotrope produced by distillation can be broken by pervaporation.

Mulder et al. (1983) showed that separations of ethanol from biomass are possible using membranes which are preferentially permeable for ethanol in combination with others which are preferentially water permeable. This process has the advantage that fuels are produced from renewable resources.

Pervaporation is such a membrane process which can be used to separate ethanol-water of any composition. On the other hand, a disadvantage of pervaporation is the relatively high energy consumption as compared to pressure-driven membrane processes such as reverse osmosis and ultrafiltration where no phase transition occurs. The slow permeation rate can be compensated by membrane configurations with a large area to volume ratio such as hollow fiber systems.

Mulder et al. (1983) also discussed the preparation of several types of membranes (homogeneous, asymmetric, and composite) and described a membrane-controlled process flow diagram for the fermentation of sugars to ethanol which is presented in Figure 4. The ethanol-selective membranes were used in the first stage while water-selective ones were used in the second stage. The ethanol productivity was limited by ethanol inhibition and also by a low cell mass concentration. Hence the removal of ethanol in the first stage of the process shifted the equilibrium in the direction of increased ethanol production.

Cabasso et al. (1985) reported that water is the preferred permeate when its mixture with alcohol is pervaporated through Nafion hollow fiber membranes. This is because the hydration shells of the counter-ions control the mass transport characteristics of the membrane over a wide range of feed composition. In the cases studied, the permselectivity of the membrane is dictated solely by the ion-pairs, rather than by the chemical nature of the membrane's polymer chains. Nafion membranes [copolymer of poly(sulfonylfluoride vinylether) and poly(tetrafluoroethylene)] consist of a heterogeneous network. The perfluorinated ethylene backbone (mostly crystalline) does not attract water and absorbs an insignificant quantity of organic liquid. The side chains have a strong affinity for water and have the following composition:

$$-O-CF_2(CF-CF_2)_n-O-CF_2-CF_2-SO_3M \qquad (M = H^+, Li^+, \ldots..)$$

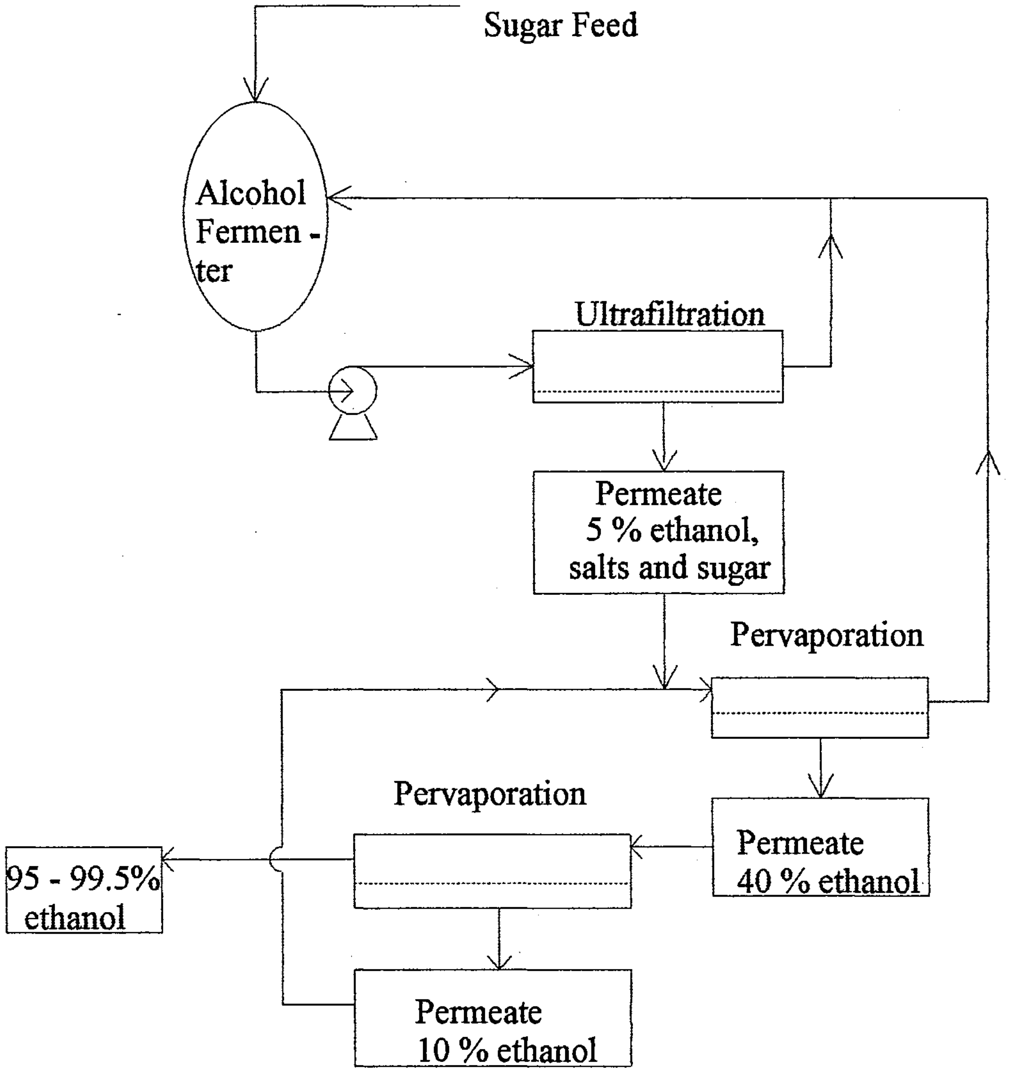


Figure 4. Schematic Presentation of Membrane-Controlled Continuous Fermentation Process of Mulder et al.(1983)

The hydrophilicity of a membrane can be increased by imparting ion-exchange capacity to the polymer matrix. The ion-exchange capacity alters the absorption characteristic of the membrane, and the ion-pairs show higher affinity towards water.

Mass transport characteristics can be altered at will merely by loading the membrane with the proper counterions. For the alkali cation series (elements of Group IA of the periodic table), flux decreases in the sequence: H > Li > Na > K > Cs; the sequence is reversed for the separation factor. The experimental apparatus used by Cabasso et al. (1985) is presented in Figure 5, and the results of their experiments are summarised in Tables V and VI. The alcohol/water feed was circulated through the hollow fiber membrane at a rate of 145 ml/min, the vacuum used was 10-100 Pa. The binary mixtures used for the experimentation were isopropanol-water and ethanol-water. The results show that the changes observed by the change of counterions are extremely high, which can be explained by selective and coupled absorptions into the ionic and perfluorinated domains. In order to explain the higher values of diffusivities and selectivities, characterizations of the state of existance (self-association) of the permeates in the membrane are needed.

Chen et al. (1989) developed a Total Recovery Improvement for Methyl tert-butyl Ether (MTBE), or TRIM, process. MTBE is an important blending agent to improve the octane rating of gasoline. MTBE that has been produced in a reactor must be separated from its mixture with methanol and other C_4 compounds. In the TRIM process, a pervaporation unit placed between the reactor and the debutanizer selectively permeates methanol. The recovered methanol is recycled to the reactor. Hence the separation of methanol from its azeotropic mixtures with C_4 compounds is avoided.

Shah et al. (1989) considered a hybrid membrane process (pervaporation

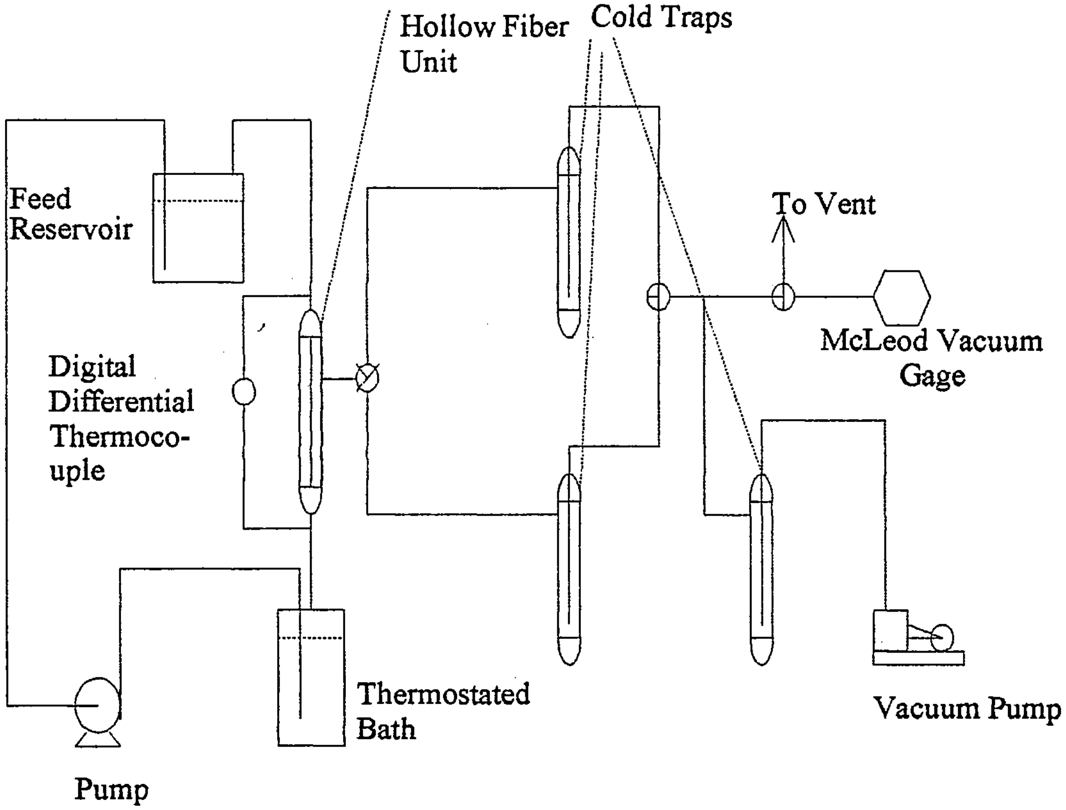


Figure 5. Schematic Presentation of Pervaporation Apparatus of Cabasso et al. (1985)

Table V

The Effect of Different Counter-Ions on Separation Factors and Flux of Nafion 811 Hollow Fiber (feed composition water/isopropanol 12/88 % w/w)

Counter ion	Permeate composition		Separation factor, α	Flux	
	Water	i-PrOH	(w/i-PrOH)	(g/m² h)	(ml/m² h)
Li^+	57.4	42.6	10.2	742	816.4
Na^+	76.6	23.4	25.1	364	383.9
K^+	86.2	13.8	46.7	124	128.0
Cs^+	87.5	12.5	54.9	107	110.3
Ca^{+2}	56.0	44.0	9.3	351	586.9
Al^{+3}	50.0	50.0	7.3	232	260.4

Reference: Cabasso et al. (1985)

Table VI

The Effect of Different Counter-Ions on Separation Factors and Flux of Ethyl Alcohol/Water Mixture in Nafion Hollow Fibers

Counter-ion	Feed composition		Permeate composition		Separation factor, α (w/EtOH)	Flux (g/m²h)
	Water	EtOH	Water	EtOH		
K^+	21.7	78.3	74.3	25.7	10.4	179.5
Cs^+	21.5	78.5	69.5	30.4	8.4	264.3

* Feed temperature: 29 °C

Reference: Cabasso et al. (1985)

coupled with distillation) for breaking the azeotrope between dimethyl carbonate (DMC) and methanol (MeOH). The azeotrope is formed at a pressure of one atmosphere for a mixture containing 69 % MeOH. DMC has been considered as an additive in gasoline-based fuels. A composite membrane of PVA supported on PAN shows high selectivity for methanol. The hybrid process shows better economics than high pressure distillation.

Changlou et al. (1989) used several kinds of membranes such as cellulose triacetate (CTA), polysulfone (PSf), polyvinyl acetate/poly sulfone (PVAc/PSf), polyacrylamide-polyacrylonitrile/cellulose acetate (PAA-PAN/CA) for separating various mixtures of ethanol and water. They found all these polar membranes to be feasible for this separation. They also explained the reason for better selectivity and permeation of water at high ethanol concentrations. When the concentration of water is large, hydrogen bonding is significant, and the association of water molecules results in the formation of clusters which hinders the permeation of molecules through membrane. However, in water, clustered and non-clustered water molecules are in equilibrium. When the concentration of ethanol is high, the ethanol molecules fit into the interstices between the water clusters, associate with and even destroy the clusters. The equilibrium is shifted towards fewer clusters and more monomeric water. Therefore, the solubility of water in the membrane increases as alcohol concentration increases.

Although vacuum induced pervaporation is the most common, other possibilities also exists as mentioned by Baker (1990). For example, a carrier gas can be used for removing the permeate. Furthermore, the carrier gas may be condensable itself. These different possibilities require different design of the pervaporation system. Baker (1990) lists these design features and discusses the advantages and disadvantages of each. He envisions five important areas of pervaporation research which are:

(1) Dehydration of solvents,

(2) Water purification,

(3) Pollution control,

(4) Solvent recovery, and

(5) Organic-organic separations.

Baker also discussed the various possibilities of integrating pervaporation with other separation techniques such as distillation. The cost of a pervaporation plant for producing 1,000 l/day of 99.5 % ethanol is also estimated and compared with a distillation and absorption unit performing the same service. A comparison of costs is presented in Table VII. On the basis of these costs, Baker (1990) concludes that pervaporation is less capital and energy intensive than distillation or adsorption processes. However, pervaporation costs increases linearly with production capacity, while distillation costs increases at a rate proportional to 0.6-0.7 times the power consumption. Thus distillation becomes more economical than pervaporation for large plants and according to Baker (1990), the cross-over point is 5000 l/hr for the separation of 99.5 % EtOH from an aqueous mixture.

Ahsan et al. (1991) synthesized mechanically tough, cross-linked, ionic polyurethane membranes and conducted pervaporation experiments at room temperature with ethanol-water mixtures. The ionic membrane was found to be selective to water over the entire range of liquid mixture compositions.

Yamaguchi et al. (1991) discusses a novel membrane prepared by Plasma-Graft Filling Polymerization. The idea is to suppress membrane swelling and enhance solubility difference. A polymer fills the pores of a porous substrate film. The substrate is inert to organic liquids and restrains the swelling of the polymer contained in the substrate pores. Ideally, the graft chains are formed only on the surface of the pores and not on the surface of the film. The authors

Table VII

Separation Options for Small Scale EtOH/Water
(Basis: 1,000 l/day, 99.5 wt % EtOH)

	Pervaporation	Distillation	Adsorption
System cost	$ 75,000	$ 140,000	$ 90,000
Pumps	3 kW	2 kW	2 kW
Steam	45 kg/h @ 1.8 bar	70 kg/h @ 7.3 bar	90 kg/h @ 7.3 bar
Entrainer	--	3 l/day	--

Reference: Baker (1990)

achieved this by controlling the grafting conditions and the extent of grafting. They claim that unlike radiation-induced grafting, the solubility of the substrate matrix remains unaltered in case of Plasma-induced grafting. When poly(methyl acrylate) (PMA) was grafted in high-density polyethylene (HDPE), benzene permeated selectively from a benzene-cyclohexane mixture.

Mathematical Modeling of Pervaporation:

Lee (1975) categorized pervaporation as a nonmediated transport process and developed a model based on the solution-diffusion theory by combining the diffusive transport equations with thermodynamic correlations. According to the solution-diffusion theory, the flux, J_i, of the component i at any point X in the membrane can be given by:

$$J_i(X) = \frac{-D_i(X)C_i(X)}{RT}\nabla\mu_i(X) \tag{2.5}$$

where Ji is the mass flux relative to the mass average velocity, D_i is the self diffusion coefficient, C_i the concentration and μ_i the chemical potential of the component i at location X in the membrane; R is the gas constant and T the absolute temperature.

Lee (1975) defined the chemical potential as:

$$\mu_i(X) = \mu_{io} + RT\ln a_i(X) + \int_{P_{ref}}^{P(X)} V_i dP - \int_{T_{ref}}^{T(X)} S_i dT \tag{2.6}$$

where μ_{io} is the chemical potential at a reference state and a_i is the activity, V_i the partial molar volume and S_i the entropy of the component i; P denotes the pressure. For a stationary membrane, Lee (1975) used the following form of the Fick's first law equation:

$$n_1 = \frac{\rho_1 D}{1 - w_1} \nabla w_1 \tag{2.7}$$

where n_1 is the mass flux relative to the stationary co-ordinates, ρ_1 the density and w_1 the weight fraction of the penetrant.

Solving Fick's law for the boundary conditions specific to pervaporation, Lee (1975) obtained an equation analogous to equation (17.2-10) of Bird et al. (1968) which is presented as follows:

$$1 - w_1(X) = [1 - w_1(l_1)] \left[\frac{[1 - w_1(l_2)]}{[1 - w_1(l_1)]} \right]^{(X - l_1)/(l_2 - l_1)} \tag{2.8}$$

where l_1 refers to the length at the upstream and l_2 to the downstream end of the membrane.

The above equation can be used for the calculation of the concentration profile of the permeants through the membrane. However, it does not have any bearing on the physical and chemical nature of the permeating species.

The final form of Lee's (1975) model can be represented by:

$$J_i = \frac{P_i}{l} C_{i1}{}^{S} \left(1 - \frac{P_{i2}{}^{S}}{P_{i1}{}^{S}} \right) \tag{2.9}$$

where

$$P_i = D_i K_i, \tag{2.10}$$

D_i is the diffusivity and K_i is the solubility constant for the component i in the membrane. $C_{i1}{}^S$ is the concentration and $P_{i1}{}^S$ the partial pressure of component i in the upstream solution. $P_{i2}{}^S$ is the partial pressure of component i in the downstream solution, l is the length of the membrane and P_i is the permeability constant of component i in the membrane.

The model developed by Lee (1975) was one of the earliest pervaporation models and is valid under the following conditions:

(1) Membrane pressure is constant and equal to that in upstream phase solution.

(2) The diffusion constant, activity coefficient, and partial molar volume for all penetrants are independent of concentration.

(3) The concentration of each penetrant in the membrane is very small.

(4) The partial molar volume of the penetrant in the membrane is the same as that in the upstream phase solution.

Assumptions (1) and (4) are normally true in most cases but (2) and (3) are not. Lee (1975) used a diffusion coefficient independent of concentration and also ignored the coupling of fluxes which does not hold true for most of the species. As a result, the treatment becomes far too simple for highly non-ideal mixtures like ethanol-water. The assumption of a very small concentration of penetrant in the membrane is also invalid in the case of highly swollen membranes.

For a continous membrane column, Hoover and Hwang (1982) calculate the permeation rate of component A, F_A (mol/s), through the membrane by the relation:

$$F_A = \frac{Q_A A(P_A^0 x_A - f_A P_2 y_A/\gamma_A)}{t} \qquad (2.11)$$

where Q_A = effective permeation coefficient (mol m/s m² kPa)
A = membrane area (m^2)
$P_A{}^0$ = vapor pressure of the permeant at the upstream conditions (kPa)
P_2 = pressure at the downstream side (kPa)
x_A = liquid side mole fraction of component A
y_A = vapor side mole fraction of component A
“f_A = fugacity coefficient of component A”
γ_A = activity coefficient of component A
t = membrane thickness (m).

Although the units of Q_A can be mol/s m kPa after simplification, they are conventionally written as mentioned above to stress the point that Q_A is the product of permeate flux and membrane thickness divided by the pressure drop across the membrane. The mathematical model developed by Hoover and Hwang (1982) is applicable only to countercurrent flow in a capillary permeator. Furthermore, it requires an appropriate activity coefficient model for the calculation of γ_A and such models are rare for a system of one polymer and two solvents. For a cylindrical geometry, the permeability of component A (alcohol) and component B (water) can be calculated from the following equations:

$$Q_A = \frac{y_A m \ln(r_o/r_i)}{2\pi L M_A(P_A^0 x_A - P_2 y_A/\gamma_A)} \tag{2.12}$$

$$Q_B = \frac{(1 - yA) m \ln(r_0/r_i)}{2\pi L M_B(P_B^0(1 - x_A) - P_2(1 - y_A)/\gamma_B)} \tag{2.13}$$

where m = mass permeation rate (kg/s)
r_0 = outside radius of capillary (m)

r_i = inside radius of capillary (m)

L = total capillary length (m)

M_A = molecular weight of component A.

Mulder and Smolders (1984) also developed a solution-diffusion model to describe the pervaporation process. They studied the separation of ethanol and water using a cellulose acetate polymer membrane, and concluded that interactions of the permeating components with one another and with the polymer affect the thermodynamics of the process. Polymer-liquid interaction parameters were determined by swelling experiments, and the liquid-liquid interaction parameters were calculated from excess free energy of mixing data taken from the literature. They concluded that the transport of ethanol-water mixture cannot be explained by using concentration independent diffusion coefficients. The assumptions involved in their model were:

- One dimensional steady state diffusion,
- Neglegible convection,
- Diffusion through the membrane is the rate limiting step,
- The surfaces of the membranes are in equilibrium with the bulk phases on either side of the membrane, and
- The chemical potential of the penetrants in the membrane can be described by Flory-Huggins theory.

From these assumptions, the flux of the components of a ternary mixture is given by the following equations:

$$J_1 = -\Phi_1 D_1(\Phi_1, \Phi_2) \times$$

$$\frac{d}{dx}\left[\ln \Phi_1 + (1-\Phi_1) - \Phi_2 \frac{V_1}{V_2} - \Phi_3 \frac{V_1}{V_3} + (\chi_{12}\Phi_2 + \chi_{13}\Phi_3)(\Phi_2 + \Phi_3) - \chi_{23}\frac{V_1}{V_2}\Phi_2\Phi_3\right] \tag{2.14}$$

$$J_2 = -\Phi_2 \, D_2(\Phi_1, \Phi_2) \times$$
$$\frac{d}{dx}\left[\ln\phi_2 + (1-\phi_2) - \phi_1\frac{V_2}{V_1} - \phi_3\frac{V_2}{V_3} + (\chi_{12}\phi_1\frac{V_2}{V_1} + \chi_{23}\phi_3)(\phi_1+\phi_3) - \chi_{13}\frac{V_2}{V_1}\phi_1\phi_3\right] \tag{2.15}$$

where J_i is the permeation rate of component i through the membrane; Φ_i is the volume fraction and D_i the diffusivity of component i in the membrane; x is the coordinate in the direction of the penetrant diffusion; V_i is the molar volume of component i; and χ_{km} is the Flory-Huggins interaction parameter between components k and m.

Mulder et al. (1985) experimentally measured the ethanol-water concentration profiles in cellulose acetate by using a stack of 3 - 6 layers of the membrane in a special pervaporation cell and finding the concentration of permeants in each layer. The pervaporation cell was submersed in the feed liquid for pervaporation. When steady state was reached, the membranes were removed from the apparatus, the surface was wiped with tissue paper, the layers were peeled off and weighed individually in weighing tubes. The difference between the weight of the dry membrane layer and its weight after reaching steady state was considered the total weight of the permeate. The composition of the permeate was determined by extracting the permeate by a distillation technique and measuring the composition by gas chromatography. The thickness of each layer was at least 100 μm, and the vacuum used for the process was 0.1 mm Hg.

The systems investigated by Mulder et al. (1985) were water-cellulose acetate, ethanol-cellulose acetate and water-ethanol-cellulose acetate. The equilibrium sorption of each pure liquid was measured by sorption experiments. The concentration just inside the membrane was measured by pervaporation experiments using the layers technique discussed above. The concentration profiles were determined when steady-state conditions were reached and the product samples were taken every hour. Their findings are presented in Tables VIII, IX and X. The results indicate that the sorption of ethanol and water from an ethanol/water mixture is different from the sorption of pure ethanol and pure water. The permeation of the mixtures proceed in a coupled way and cross-diffusion coefficients need to be considered. Based on this need they modified their model. The modified equations in their model are as follows:

$$\begin{aligned}-J_1 = {} & \frac{D_{11}\Phi_1}{\Delta x}\left[\left(\frac{\partial \ln a_1}{\partial \Phi_1}\right)\Delta\phi_1 + \left(\frac{\partial \ln a_1}{\partial \Phi_2}\right)\Delta\phi_2\right] \\ & + \frac{D_{12}\Phi_2}{\Delta x}\left[\left(\frac{\partial \ln a_2}{\partial \Phi_1}\right)\Delta\phi_1 + \left(\frac{\partial \ln a_2}{\partial \Phi_2}\right)\Delta\phi_2\right] \qquad (2.16)\end{aligned}$$

$$\begin{aligned}-J_2 = {} & \frac{D_{21}\Phi_1}{\Delta x}\left[\left(\frac{\partial \ln a_1}{\partial \Phi_1}\right)\Delta\phi_1 + \left(\frac{\partial \ln a_1}{\partial \Phi_2}\right)\Delta\phi_2\right] \\ & + \frac{D_{22}\Phi_2}{\Delta x}\left[\left(\frac{\partial \ln a_2}{\partial \Phi_1}\right)\Delta\phi_1 + \left(\frac{\partial \ln a_2}{\partial \Phi_2}\right)\Delta\phi_2\right] \qquad (2.17)\end{aligned}$$

where D_{12}, D_{21} are cross-diffusion coefficients while D_{11} is the same as D_1 and D_{22} is the same as D_2.

As a result of their experimentation, Mulder et al. (1985) also noted the following differences in the systems water-cellulose acetate and ethanol-cellulose acetate:

(1) Water shows much larger permeation rate through cellulose acetate.

(2) The concentration of ethanol in cellulose acetate falls much more rapidly in the downstream half of the membrane.

(3) For ethanol-cellulose acetate, the difference between the equilibrium sorption value and the concentration just inside the

Table VIII

Permeation Characteristics for the Binary System Water-Cellulose Acetate

Temperature	17 °C
C_{eq}, Equilibrium sorption	0.125 g/g
C_0^m	0.125 g/g
J, Permeation rate	1.1×10^{-3} cm/h
l, Membrane thickness	500 μm
Number of layers	3 - 5
Diffusion coefficient at infinite dilution, D_0	5.5×10^{-9} cm^2/s

Reference: Mulder and Smolders (1985)

Table IX

Permeation Characteristics for the Binary System Ethanol-Cellulose Acetate

Temperature	20 °C
C_{eq}, Equilibrium sorption	0.177 g/g
C_0^m	0.109 g/g
J, Permeation rate	7.8×10^{-4} cm/h
l, Membrane thickness	500 μm
Number of layers	3
Diffusion coefficient at infinite dilution, D_0	1.1×10^{-10} cm^2/s

Reference: Mulder and Smolders (1985)

Table X

Permeation Characteristics for the Ternary System Water-Ethanol-Cellulose Acetate

Temperature	17 °C
Composition of water in the feed	35 % by weight
C_{eq}, Equilibrium sorption	0.253 g/g
C_0^m (overall)	0.169 g/g
J, Permeation rate	1.6×10^{-3} cm/h
l, Membrane thickness	500 μm
Number of layers	4 - 6
C_0^m (water)	0.100 g/g
C_{eq} (water)	0.147 g/g
C_0^m (ethanol)	0.069 g/g
C_{eq} (ethanol)	0.106 g/g
α, Separation factor	9.8

Reference: Mulder and Smolders (1985)

membrane is much more pronounced than that for water-cellulose acetate.

(4) The D_0 value for ethanol is 50 times smaller than that for water.

The above treatment of pervaporation flux in terms of cross-diffusion coefficients becomes too complex and the experimental determination of these coefficients is too cumbersome. Since four diffusion coefficients need to be evaluated, the model will require a large amount of diffusivity data. Furthermore, it is very unlikely that the experimental apparatus used by Mulder and Smolders (1985) for finding the concentration profile in the membrane will be free from errors, because of the possibility that the permeants will vaporize from each layer of membrane while measuring its weight.

Dutta and Sikdar (1991) used a perfluorosulfonic acid (PFSA) film casted on a porous Teflon support and Nafion membranes for pervaporation studies on various azeotropic mixtures. The membranes were more permeable to the component which had a higher polarity. The fluxes increased with increasing alcohol content of the feed and with increasing temperature. Dutta and Sikdar developed a model based on solution-diffusion mechanism which accounts for membrane swelling and the effects of plasticization on the diffusion coefficients. In their equations, they included plasticization parameters as well as the diffusion parameters. However, these parameters were estimated by least-squares fit of the experimental data. Their model is based solely on diffusive transport equations.

The following assumptions are involved in Dutta and Sikdar's model:

(1) An interfacial equilibrium exists between the membrane and the feed liquid.

(2) Diffusional resistances outside the membrane are negligible.

(3) The concentrations of the solute at the downstream face of the membrane are negligible.

(4) The temperature drop across the membrane is negligible.

(5) Diffusion through the membrane is governed by Fick's law.

(6) Mass transport takes place at steady-state.

The fluxes of components is given by:

$$J_1 = -D_1 \frac{d\Phi_1}{dx'} \tag{2.18}$$

$$J_2 = -D_2 \frac{d\Phi_2}{dx'} \tag{2.19}$$

where x' refers to the position in the swollen membrane.

If l_d is the thickness of the dry membrane and l_s that of the swollen one,

$$dx' = (l_s/l_d)dx = (1+\beta(\Phi_1,\Phi_2)).\ dx \tag{2.20}$$

where β is a function relating the dry and swollen membrane thickness.

Since the diffusivities are also dependent on concentration, the flux equations can be written as:

$$J_1 = -\frac{D_{10} f(\Phi_1,\Phi_2)}{1+\beta(\Phi_1,\Phi_2)} \frac{d\Phi_1}{dx} \tag{2.21}$$

$$J_2 = -\frac{D_{20} f(\Phi_1,\Phi_2)}{1+\beta(\Phi_1,\Phi_2)} \frac{d\Phi_2}{dx} \tag{2.22}$$

where D_{10} and D_{20} are the limiting values of D_1 and D_2 at very low concentrations.

Dutta et al. assumed the following functional forms of f_1, f_2 and β:

$$f_1(\Phi_1,\Phi_2) = 1 + \alpha_1 \Phi_1 \tag{2.23}$$

$$f_2(\Phi_1,\Phi_2) = 1 + \alpha_2 \Phi_1 \tag{2.24}$$

$$1+\beta(\phi_1,\phi_2) = 1+\beta_1\phi_1 \tag{2.25}$$

where α_1 and α_2 relates the diffusion coefficients at non-zero concentrations to the diffusion coefficients at infinite dilution of the permeants. The boundary conditions for the system are:

$$\text{B.C. 1: } @\, x = 0,\ \Phi_1 = \Phi_{10} \tag{2.26}$$

$$\text{B.C. 2: } @\, x = 0,\ \Phi_1 = \Phi_2 = 0 \tag{2.27}$$

The solution of the differential equations based on the boundary conditions leads to the final form of Dutta model:

$$J_1 = \frac{D_{10}}{\beta_1}\left[\left(1-\frac{\alpha_1}{\beta_1}\right)\ln(1+\beta_1\Phi_{10})+\alpha_1\Phi_{10}\right] \tag{2.28}$$

$$J_2 = \frac{J_1\Phi_{20}}{(1-\frac{\alpha_1}{\alpha_2})\ln(1+\alpha_2\Phi_{10})+\alpha_1\Phi_{10}}\cdot\frac{\alpha_2 D_{20}}{D_{10}} \tag{2.29}$$

where D_{10} and D_{20} are the limiting values of D_1 and D_2 at very low concentrations.

Dutta and Sikdar (1991) claimed that their estimated diffusivities compare well with the diffusivities reported by Mulder and Smolders (1984). Figure 6 shows the experimental set-up used by Dutta et al. (1991) and the pervaporation data gathered by them is presented in Table XI. The proposed model satisfactorily predicted the pervaporation data for a typical alcohol-hydrocarbon system. However, a major disadvantage is the need for a significant amount of experimental data for estimating the parameters by a least square fit.

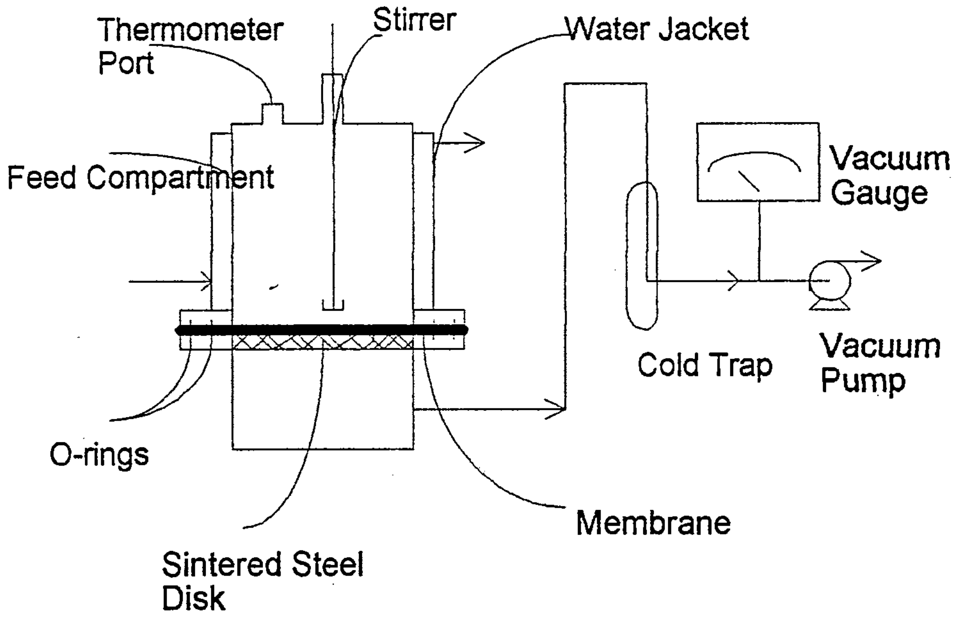


Figure 6. Experimental Set-up of Dutta et al. (1991)

Table XI

Flux and Selectivity for Pervaporation of Some Organic Mixtures

System	Feed wt, % Comp. 1	Flux kg/h.m^2	Selectivity Comp. 1
Methanol (1)- Carbon Tetrachloride (2)	15.4	6.06	14.6
Ethylacetate (1)- Carbon Tetrachloride (2)	44	0.653	1.29
Acetonitrile (1)- Carbon Tetrachloride (2)	15.5	0.885	2.35
Ethylacetate (1)- Cyclohexane (2)	54	0.483	1.73
Methanol (1)- Benzene (2)	32.5	10.280	9.56

* Temperature = 45 °C; membrane, composite, H-form

Reference: Dutta et al. (1991)

Applications In Biochemical Engineering:

Pervaporation has potential applications in biochemical engineering. Several materials such as sugars, starch, whey and cellulosic materials are first converted to fermentable sugars by use of certain enzymes. These fermentable sugars are subsequently converted to ethanol in fermentors with the help of micro-organisms. Prolonged exposure to high alcohol concentrations result in sporulation of the micro-organisms which ceases the microbial activity. Mulder and Smolders (1986) argue that a fermentor can be coupled to a membrane module for the recovery of the product ethanol. Fermentation broth is pumped continuously through a membrane filtration unit which is permeable to the inhibitory end-products but not to the micro-organisms. The complete flow-diagram for the conversion of substrate (glucose, lactose) to 99% ethanol is presented in Figure 7. It involves a combination of hyperfiltration, microfiltration as well as pervaporation membranes. Hyperfiltration is used to concentrate the substrate while pervaporation is used to remove the alcohol product and the aldehydes and ketones byproducts. The second pervaporation unit is comprised of a water-selective membrane which dehydrates the permeate from the first pervaporation unit.

Mulder and Smolders (1986) compares the performance of microfiltration, membrane distillation and pervaporation in a membrane bioreactor. Their findings are presented in Table XII. They conclude that pervaporation is the most promising membrane process in a membrane bioreactor. No product/substrate separation is obtained with microfiltration/ultrafiltration because all the low molecular weight components pass freely through the membrane. On the other hand, pervaporation membrane allows only the product to pass through and rejects the substrate, nutrients and micro-organisms.

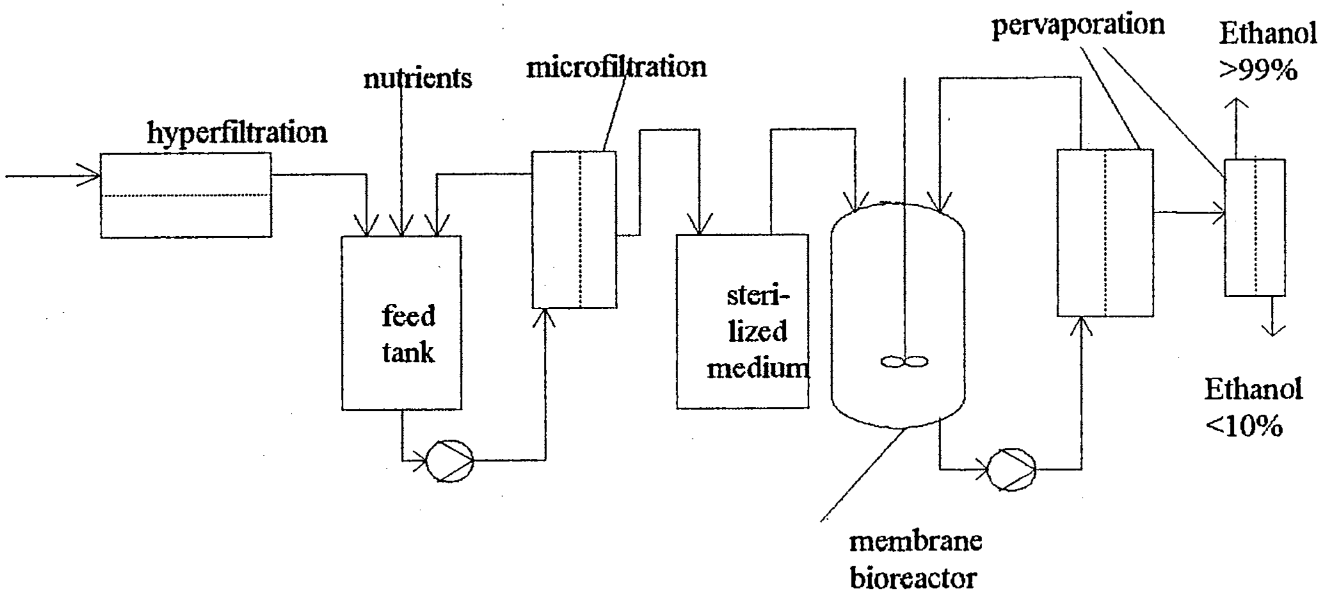


Figure 7. Schematic Process Diagram of Continuous Alcohol Fermentation Controlled by Membrane Process

Table XII. Evaluation of the Membrane Processes in a Membrane Bioreactor.

Characteristic	Microfiltration/ ultrafiltration	Membrane distillation	Perva- poration
Continuous fermentation	yes	yes	yes
Solid/liquid separation	yes	yes	yes
Product/substrate, nutrient separation	no	yes	yes
Product purification	no	little	moderate
Membrane fouling	high	low	low
Membrane area	small	medium	high
Pervaporation rate	high	medium	low
Dead volume	small	medium	large

Concentration polarization and membrane fouling are also found to be lower in pervaporation.

Groot et al. (1984) produced butanol and isopropanol by the action of immobilized Clostridia on glucose. They applied sweep-gas pervaporation to remove the product butanol; isopropanol also permeated to some extent. The result was a 65-70 % increase in the glucose conversion as well as in the alcohol production. The fermentation broth was circulated through a pervaporation module at a rate of 60 ml/min. The selectivity was found to be 30. However, the type of membrane used was not mentioned.

Groot et al. (1987) discovered that a mixture of glucose and xylose can be converted to butanol using immobilized Clostridia. Some ways of improving the process are:

(1) pretreatment of the feed,
(2) the selection of the optimal strains,
(3) better understanding of the fermentation kinetics on a mixed hexose and pentose substrate, and
(4) energy efficient product recovery system.

The use of an immobilized strain made possible a fixed bed rather than a fluid bed fermenter. Xylose is consumed only when glucose is completely consumed and the biocatalyst is not fully inhibited by butanol. The in-situ product recovery lowered the butanol concentration and thus reduced the product inhibition. This enables the complete conversion of glucose, and also increases the consumption of xylose. The pervaporation rate was 2.6 ml/hr, and the selectivity for butanol/water separation was 11.

The substrate range for the butanol fermentation process is larger and includes a range of hexose and pentose sugars (Friedl et al., 1991). However, butanol starts inhibiting fermentation even at low concentrations resulting in a total solvent concentration that never exceeds 20 g/L if the product is not removed. Friedl et al. (1991) used cells of immobilized Clostridia to convert a lactose solution to an acetone-butanol-ethanol (ABE) mixture. By employing an integrated fermentation and product recovery system, they achieved a solvent productivity of 3.5 g/L h. The previous attempts of increasing the productivity by increase in the cell density in continuous reactors were not very successful because of culture degeneration problems. On the other hand, the system remained stable in the integrated process. The hollow fiber polypropylene membrane allowed the solvents to pass through, but retained the lactose. The membrane flux was 7.1 g/m^2h with a selectivity of 5 and the system proved to be very reliable. The specifications of the membrane were: fiber length, 470 mm; inner fiber diameter, 1.8 mm; membrane thickness, 0.4 mm; pore diameter, 0.2 μ m; membrane area (based on the inner fiber diameter), 0.10 m^2; and calculated total module volume, ~ 0.24 L.

The circulation rate through the pervaporation unit was 25 L/h, i.e., high enough to prevent membrane fouling. The temperature difference between the inlet and the outlet was 3 to 4 °C. Nitrogen was used as the sweep gas in a flow path countercurrent to the liquid. The coolant used for condensing the product was 30 % (w/v) ethylene glycol in water.

Friedl et al. (1991) compared the different product removal techniques that were integrated with continuous ABE fermentation. This comparison is presented in Table XIII and it shows that pervaporation is competitive with other product removal techniques. If butanol were recovered by distillation, the energy demand would be higher than the energy content in the fermentation product itself. However, pervaporation is expected to be less energy intensive.

Table XIII.

Continous ABE Fermentation with Various Types of Integrated Product Removal Systems

Product removal system	Substrate	Productivity (g/l h)	Sugar utilization (%)	Solvent yield (gs/gl)	Selectivity of the used system	Reference
Gas stripping	glucose	4.2	75	0.34	--	Park et al. (1989)
Gas stripping	glucose	1.0	70	0.30	4	Groot et al. (1989)
Gas stripping	whey	5.12	75	0.40	29	Qureshi et al. (1991)
Extraction	glucose	1.96	95	0.30	--	Eckert & Schuegerl (1987)
Perstraction	glucose	0.92	75	0.27	--	Shukla et al. (1989)
Pervaporation	glucose	1.70	54	--	30	Groot et al. (1984)
Pervaporation	glucose xylose mixture	0.4 - 1.0	>98	0.33	11	Groot et al. (1987)
Pervaporation	whey permeate	3.5	97.9	0.39	3 - 5	Friedl et al. (1991)

Reference: Friedl et al. (1991).

CHAPTER III

DESCRIPTION OF EXPERIMENTS

This chapter contains the details of the construction and operation of the experimental pervaporation apparatus used in this study. The construction of the pervaporation equipment will be discussed along with the design and modification of each piece of equipment involved. The specifications of the equipment used for product analysis is also presented in this chapter. The last part of this chapter covers the method by which nonporous cellulose acetate membranes used in this study were prepared.

The apparatus for pervaporation experiments was designed to ensure continuous and safe operation. A support structure, made of steel rods, was first installed on a plywood table on which the pervaporation equipment was constructed. All lines were made up of 1/4" stainless steel tubing except the coil in the constant temperature bath which was made of copper for better heat transfer and the connections to the vacuum pump and the vacuum indicator which were made of vacuum tubing. All connections in the apparatus were made using Swagelok fittings. The only equipment susceptible to breakage were the glass cold traps which required careful installation for convenient product recovery. Therefore, clamps were used to support the cold traps and the associated tubes above the surface of the table.

A schematic of the equipment is given in Figure 8. The feed is prepared in a tank where the composition is adjusted to the required value. Samples are injected into a gas chromatograph and the compositions are calculated from the

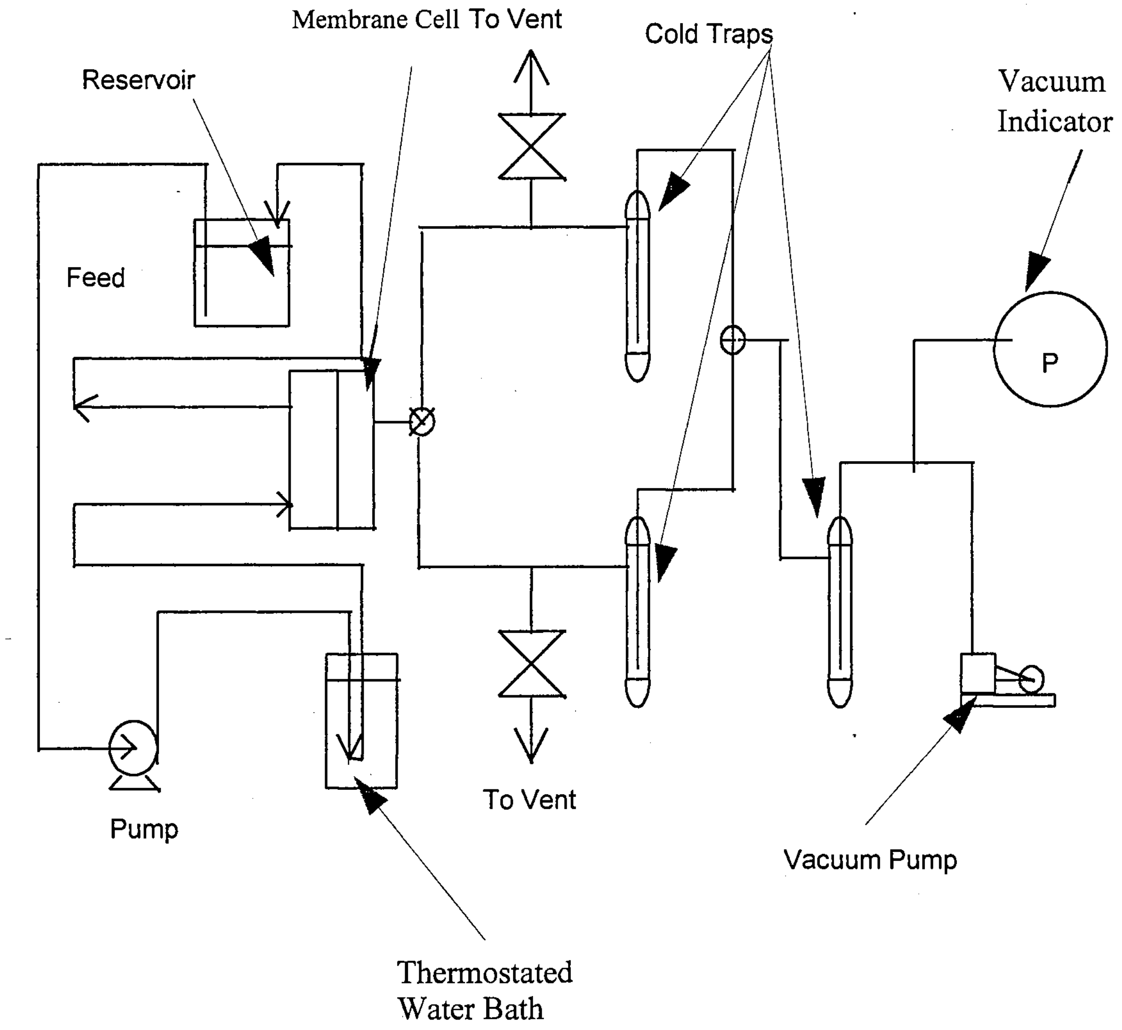


Figure 8. Schematic of the Pervaporation Apparatus Used in this Study

resulting peaks. The feed tank can accomodate 20 liters of feed liquid. The feed is circulated in the copper coils through temperature bath using a centrifugal pump. After attaining an appropriate temperature in the bath, the feed flows through the pervaporation cell. The flow rate of the feed through the cell is about 35 l/hr. The permeate is drawn towards the cold traps under the influence of vacuum while the retentate is sent back to the feed tank. Since the feed tank is a very large reservoir of liquid, the loss of permeate does not change the feed composition significantly. The pressure of the feed entering the pervaporation cell is measured using a pressure gage. Two thermocouples measure the temperature at the inlet and outlet of the pervaporation cell. The thermocouples' readings are displayed on a digital panel. A temperature drop across the pervaporation cell indicates that pervaporation is taking place. The amount of vacuum is indicated by an electronic vacuum indicator. In this study, the vacuum was maintained aroud 0.1 μm Hg.

The heart of the process is the pervaporation cell where the actual pervaporation process takes place. In the pervaporation cell, the components of the liquid feed permeate through the membrane towards the permeate side which is kept under vacuum. The body of the cell is made up of stainless steel and is circular in shape. The membrane is held in place using two Teflon O-rings and a stainless steel support gauze. By tightening the three nuts near the circumference of the cell, the system can be made air-tight. The effective area offered by the cell for pervaporation is 45.36 cm^2. A stainless steel prefilter screen can also be installed inside the cell if so desired, but was not used in this work.

There are two connecting points on the top of the cell (feed side), one of which was used in this study for connecting the feed line and the other for the removal of the retentate. These fluid connections are made leak-proof by using Teflon tape on the male pipe thread (MPT) portion of the Swagelok connectors.

The feed is circulated in this fashion with a high velocity so that the concentration polarization and fouling near the membrane surface can be minimized. On the bottom side of the cell (permeate side), there is one connecting point which is used for removing the permeate. The permeate side is also made leak-proof by the same method as used for the feed side. The pervaporation cell is supported above the plywood table with a three-legged stand.

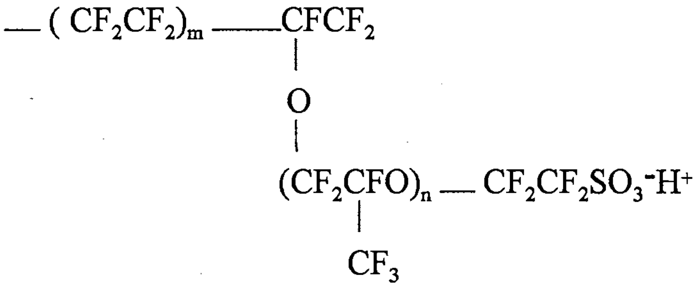
The permeate is collected in cold traps cooled with liquid nitrogen. In order to keep the process continuous, two cold traps are arranged in parallel by fitting two-way valves in the apparatus as shown in Figure 8. Each route to the cold traps is equipped with a vacuum relieving ~~value~~ valve which can be opened to vent this portion of the system for sample collection. To collect a sample, the two-way valves are switched to cause the permeate to flow to the other cold trap in the system. While one cold trap is in operation, the other can be vented for product removal and made ready for subsequent operation. The removal of the product requires that the dewar flasks containing liquid nitrogen be removed and the outside of the cold trap gently heated by some means like a hot air blower. This is necessary because the product collects in the cold traps as a solid mass and has to be melted for removal and analysis. Nevertheless, overheating of the cold trap must be avoided to minimize the possibility of a fire hazard due to any flammable solvent. The outlets from these two sample cold traps are connected to a third liquid nitrogen cold trap to prevent permeate from reaching the vacuum pump and also to prevent vacuum pump oil from entering the sample cold traps when the equipment is switched off. The liquid nitrogen is placed in dewar flasks which surround the cold traps. These dewar flasks are, in turn, mounted on the support structure using caged clamps.

Each end of every cold trap was initially connected to a small piece of steel tube by using Kovar seals. This piece of tube was, in turn, connected to the other tubes by Swagelok unions or union elbows. However, the Kovar seal was very brittle and nonflexible, and therefore, resulted in breakage while tightening the Swagelok fittings. Therefore, the Kovar seals were replaced by flexible Ultra-torr fittings which were found to be very useful and manageable. Another change in the initial design of the cold traps was made to provide increased convenience in the product removal. Initially, the cold trap was dismantled each time the product was to be removed. This tedious procedure was eliminated by creating a sample port in the bottom of the cold trap and attaching a stopcock at this point. The stopcock was kept close during pervaporation and was opened only for product removal. However, it was considered very important to keep the stopcock tightly closed during pervaporation, otherwise liquid nitrogen could be sucked inside the cold trap.

The vacuum pump was hooked to vacuum tubing which was in turn connected to a stainless steel tube. The probe of the vacuum gage was also connected to a stainless steel tube in a similar fashion. Finally, these two tubes were connected to the rest of the system by using a union tee connection. A small amount of vacuum grease was applied over each metal-to-rubber connection before tightening with a clamp. When the leaks were properly eliminated, the vacuum pump could achieve a vacuum as low as 7 torr. However, the vacuum pump oil was replaced frequently in order to maintain the vacuum to such low values.

Membrane Materials and Other Chemicals:

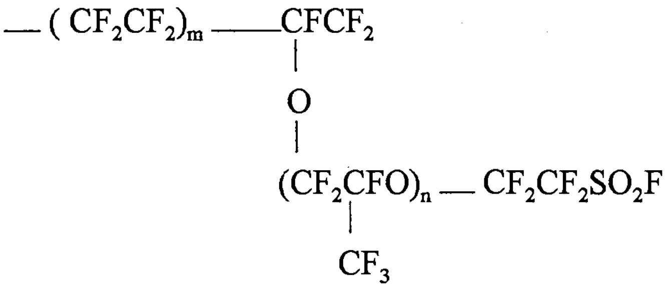
In this study, the pervaporation experiments were performed using Nafion and cellulose acetate membranes. The Nafion membrane (K^+ form) was supplied by du Pont. According to du Pont, this is the most popular Nafion membrane presently in existence. The thickness of these membranes was 5 mil (127 μm). Nafion, in acid form, is a copolymer of tetrafluoroethylene and a vinyl sulphonic (or carboxylic) acid. The sulphonic acid form of Nafion can be represented by the following structure:



$$-(CF_2CF_2)_m-\underset{\underset{(CF_2\underset{CF_3}{\underset{|}{C}}FO)_n-CF_2CF_2SO_3^{-}H^{+}}{\underset{|}{\overset{|}{O}}}}{C}FCF_2$$

where m = 5 - 12 and n is usually equal to 1.

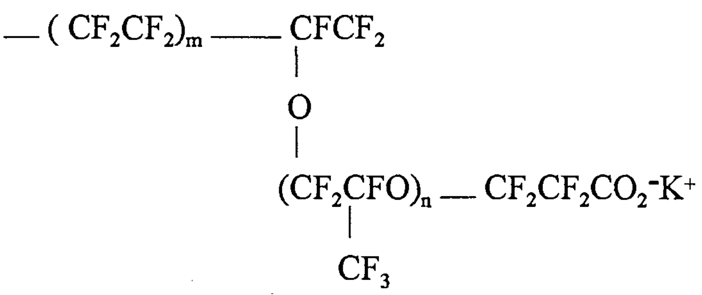
The Nafion precursor is known as XR Resin which can be hydrolyzed to give Nafion perfluorosulfonate polymer (H^+ form) or treated with an appropriate base to give Li^+, Na^+, K^+ or Cs^+ salts. The structure of the XR Resin is presented as follows:



$$-(CF_2CF_2)_m-\underset{\underset{(CF_2\underset{CF_3}{\underset{|}{C}}FO)_n-CF_2CF_2SO_2F}{\underset{|}{\overset{|}{O}}}}{C}FCF_2$$

where m = 5 - 12 and n is usually equal to 1.

Similarly, the Nafion in the K^+ and carboxylic acid form (which was used in this study) can be represented by:



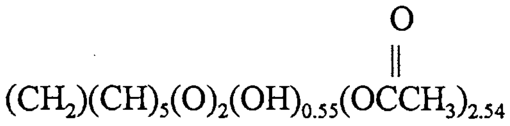
$$\begin{array}{ll} -(\mathrm{CF_2CF_2})_m - & \mathrm{CFCF_2} \\ & \;| \\ & \mathrm{O} \\ & \;| \\ & (\mathrm{CF_2\underset{\underset{\displaystyle CF_3}{|}}{C}FO})_n - \mathrm{CF_2CF_2CO_2^-K^+} \end{array}$$

where m = 5 - 12 and n is usually equal to 1. However, the exact value of m or n was not specified by the manufacturer.

Ethanol (200 proof) was used for all of the experiments except the pervaporation of 73 % aqueous ethanol through Nafion (K^+ form) where denatured ethanol was used. The 200 proof ethanol was purchased from Aaper Alcohol and Chemical Company while the denatured ethanol was purchased from Fluka Chemika. Five percent methanol and traces of some other compounds were included in the denatured ethanol. All the aqueous mixtures were prepared by using distilled water obtained from the Unit Operations Laboratory of the School of Chemical Engineering. The isopropanol used in the experiments was purchased from Fisher Scientific and was 99.9 % pure. The acetone used for preparing cellulose acetate membrane was also purchased from Fisher Scientific and was 99.7 % pure. The solvents were used as supplied from both manufacturers. The cellulose acetate powder purchased from Aldrich Chemical Company had an acetyl content of 39.8 %, the approximate number average molecular weight was reported to be 30,000 and the specific gravity was reported to be 1.3.

Preparation of Cellulose Acetate Membrane:

The structure of cellulose acetate is complex. The polymer molecule of cellulose acetate involves repetition of cyclic rings. The repeat unit consists of two such rings. Ohya et al. (1993) indicated that the structure of the repeat unit of cellulose acetate is:



$$(CH_2)(CH)_5(O)_2(OH)_{0.55}(OC\overset{\overset{O}{\|}}{C}H_3)_{2.54}$$

The basic method of preparing cellulose acetate membrane was taken from Loeb and Sourirajan (1963) who used Magnesium perchlorate ($MgClO_4$) as a membrane setting agent. However, because of the strong oxidizing potential and toxicity of $MgClO_4$, it was not used in this work for membrane preparation and the procedure deviated to some extent. The cellulose acetate membranes were prepared by making a mixture of 22.5 % powdered cellulose acetate, 67.5 % acetone and 10 % water by weight, in a flask. When the powder was completely dissolved and a homogeneous solution was formed, the contents were transferred to a glass dish with a smooth surface. The dissolved mixture was transparent and very thick. As soon as a small ripple appeared on the surface, the glass dish was covered and placed in an ice box filled with crushed ice. At this stage, extreme care was taken to maintain the level of the dish. The glass dish was kept in the ice for about 30 minutes. The dish was then taken to a level surface and a paper towel was placed between the top cover and the bottom part of the glass dish. The glass dish was then placed in the fume hood for at least 12 hours. The condition of the membrane was monitored for the indications of solidification.

As soon as the membrane solidified and enough solvent has vaporized, a mixture of about 2.5 % acetone and distilled water was added so that the membrane was submerged. Adding the acetone/distilled water mixture before significant solidification of the membrane was important, otherwise the membrane could wrinkle and become very brittle. The paper towel was removed and the glass dish was covered and placed on a hot plate. The temperature of the hot plate was kept at 60 ^{O}C and the glass dish was placed over it for about 24 hours. More distilled water was added into the glass dish if needed. The membrane thus prepared was transparent. The porosity of the membrane was examined using a scanning electron microscope (SEM) which confirmed that the membrane was nonporous. Once relatively thick membranes (700-1000 μm) were successfully prepared, thinner membranes (100-300 μm) were also prepared, but they lacked mechanical strength and failed in the pervaporation cell under the influence of vacuum. Hence, all the pervaporation experiments with cellulose acetate membrane were performed by using thicker membranes.

Techniques Used for Product Analysis:

The permeate product was analyzed by refractometry and gas chromatography. The dependence of refractive index on ethanol composition for the aqueous mixtures prepared by denatured ethanol is presented in Figure 9, which shows that the curve is reproducible to the extent shown by the error bars. The details of the equations used in the error analysis is presented in Appendix A. However, this curve is not very convenient for product analysis because a maxima exists at some point between 75 % and 85 % ethanol by weight. Also, in the range from 60 % to 100 % ethanol, the refractive index changes very slowly with composition and the use of the curve becomes very difficult. Therefore, the results from the refractometer were considered only as rough estimates for composition and the product was also analyzed by gas chromatography.

A Carle Analytical Gas Chromatograph (GC) model 111H was used for measuring the compositions of the feed and the permeate product. The GC was equipped with a column of 80/120 Carbopack B/3% SP-1500 and was attached to a HP 3390A integrator. The detector used in the column was a thermal conductivity detector which was kept at a temperature of 110 °C. Helium was

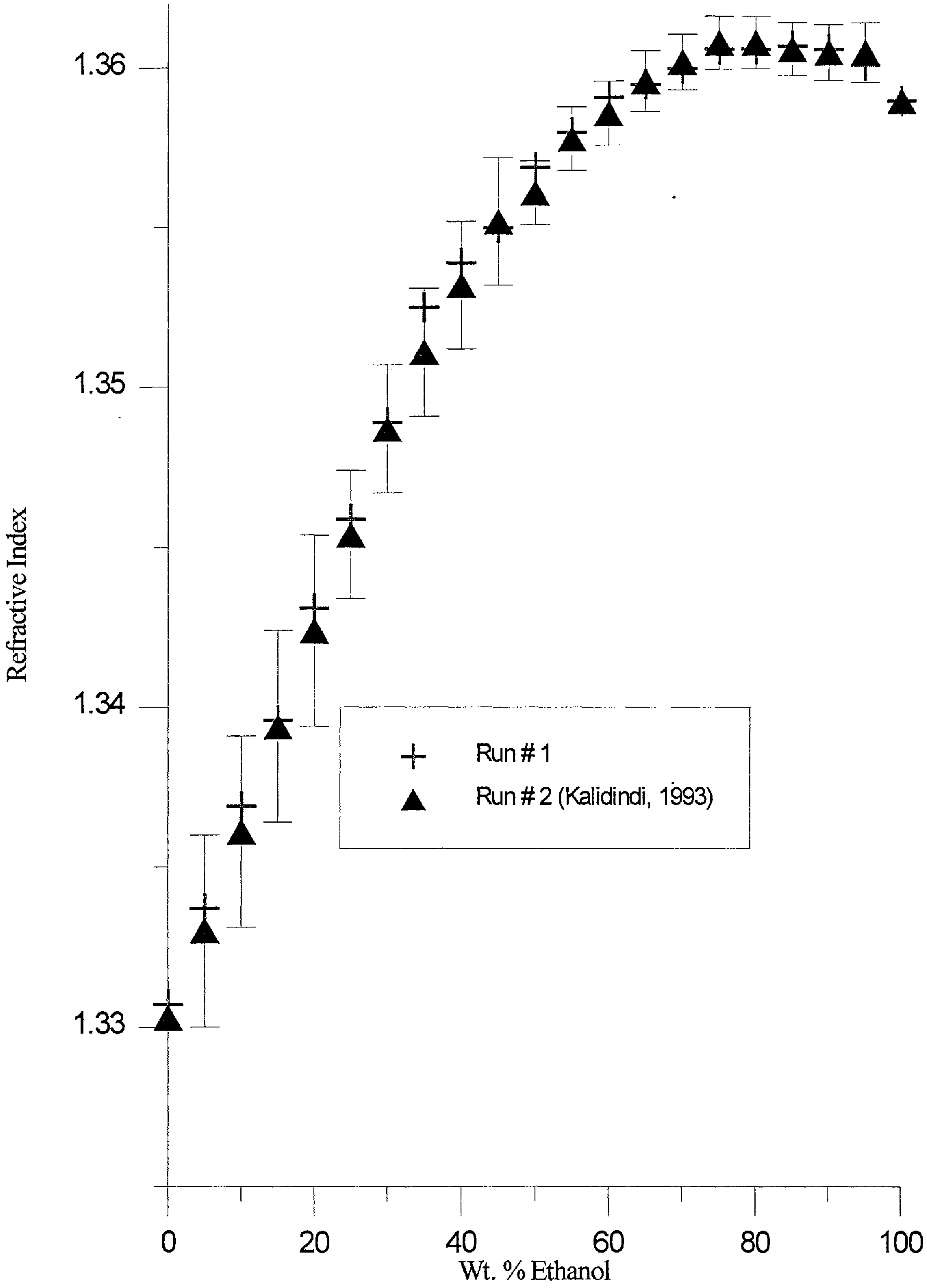


Figure 9. The Refractive Index Curve for Ethanol/Water Mixtures
Prepared from Denatured Ethanol.

used as a carrier gas for the GC and the attenuation of the integrator was set at 5. The pressure of the Helium was constant at 13 psi. The output from the GC were peaks for the various compounds present in the injected sample and a record of the area percent covered by each peak. The sample size normally used was 0.1 μl into which 0.4 μl of air was added as an internal standard. Since the residence time of air was ~~the~~ shorter than that of the solvents in the sample, the output from the GC often contained a first peak of air. However, due to the smaller mass of air in the sample compared to the solvents in the sample, the area percentage of the air-peak was very small and sometimes the air-peak did not appear at all. The second peak was water and the third peak was ethanol. Sometimes the compounds used to denature the ethanol also appeared as a separate peak. In such cases, the area percents were normalized for the compounds of interest. The weight percentage of the alcohol in an alcohol/water mixture was calculated by the following relationship:

$$\text{Wt. \% of alcohol} = \frac{A_a w_{fa}}{A_a w_{fa} + A_w w_{fw}} \qquad (3.1)$$

where A_a is the normalized area percentage of alcohol, A_w is the normalized area percentage of water, w_{fa} is the weight factor of alcohol and w_{fw} is the weight factor of water.

Figure 10 shows the graph of wt.% ethanol obtained by gas chromatography versus the wt. % of (denatured) ethanol in known mixtures (standards). The error bars on Figure 10 show that the precision is better than the refractive index graph The diagram shows that the results from GC are not only reproducible, but also convenient to use because there is no maxima and the graph is linear. Therefore, it was decided that the GC curves results will be used rather than the refractive index curves to determine the compositions of the

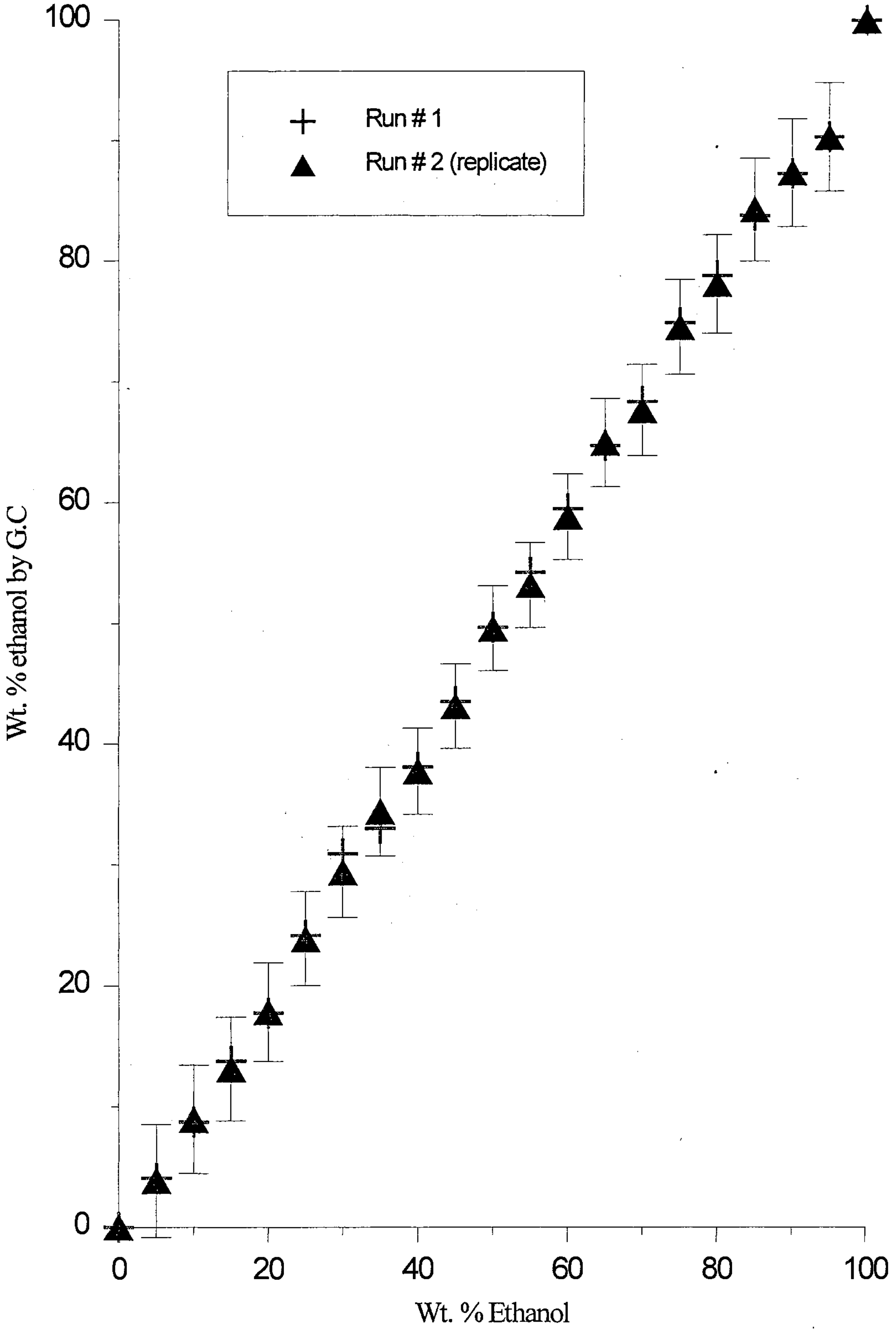


Figure 10. The Gas Chromatographic Results for Ethanol/Water Mixtures Prepared from Denatured Ethanol.

pervaporation streams.

The refractive index versus weight percent ethanol curve for the mixtures prepared from 200 proof ethanol is presented in Figure 11. Since the refractive index graph is not used for product analysis, Figure 11 is presented here only for completeness. Figure 12 shows the dependence of ethanol composition measured by GC on the ethanol composition in standard samples of aqueous ethanol mixtures prepared from 200 proof ethanol. The graph is fairly linear, reproducible and was convenient to use. In addition, there was no peak due to impurity and so the product analysis was simpler.

The refractive index versus weight percent isopropanol curve for the isopropanol/water mixtures is presented in Figure 13. Once again, the refractive index graph is presented here only for completeness and is not used for product analysis. Figure 14 shows the graph of weight % isopropanol obtained by GC versus the weight % isopropanol in standard samples of isopropanol/water mixtures. As previously observed for the graphs based on GC results, this graph is also linear, reproducible and can be conveniently used. As observed in the case of ethanol, the peak of the alcohol (isopropanol) appears last. However, the retention time of isopropanol was found to be much greater than that of ethanol.

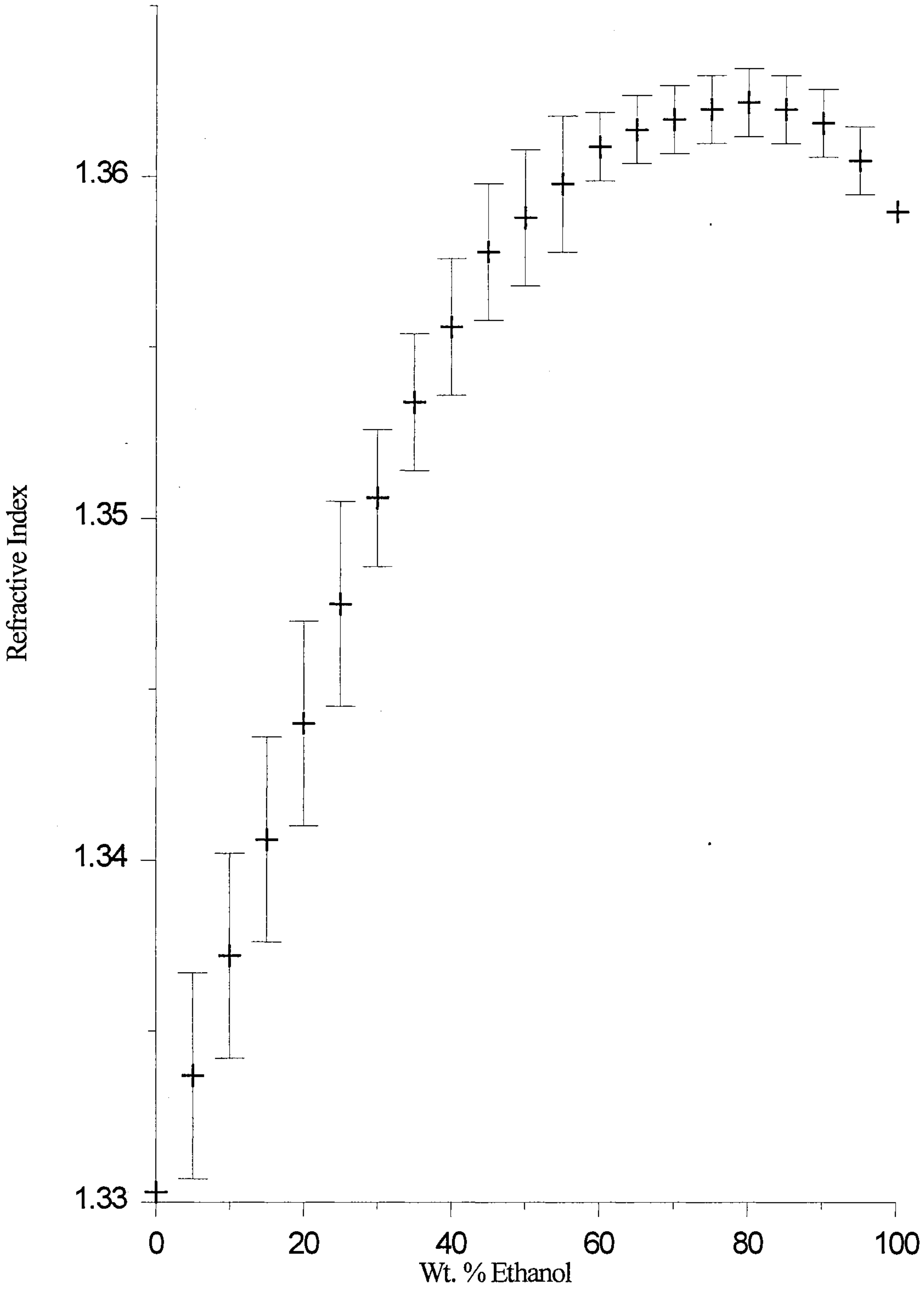


Figure 11. The Refractive Index Curve for Ethanol/Water Mixtures Prepared from 200 Proof Ethanol.

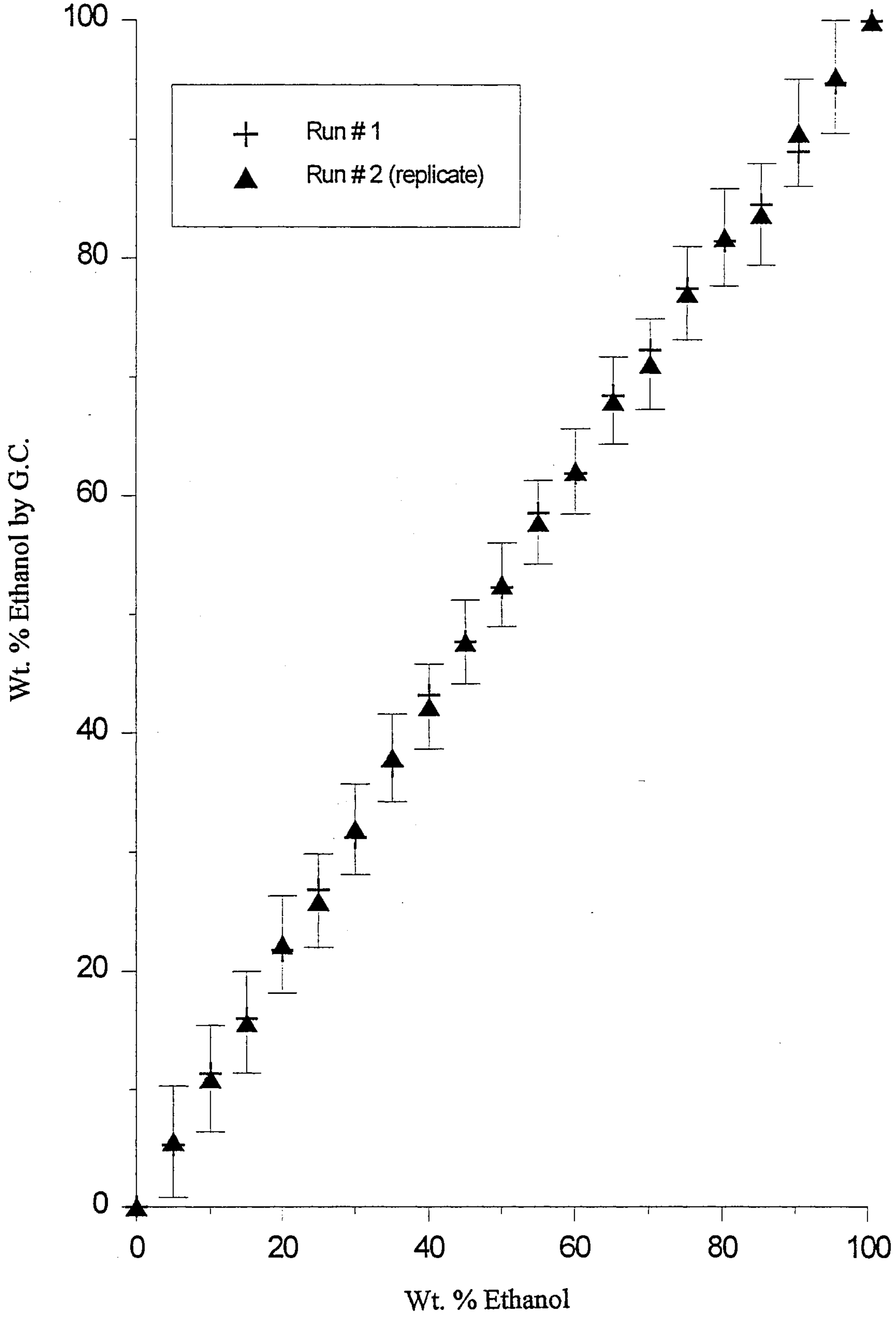


Figure 12. The Gas Chromatographic Results for Ethanol/Water Mixtures Prepared from 200 Proof Ethanol.

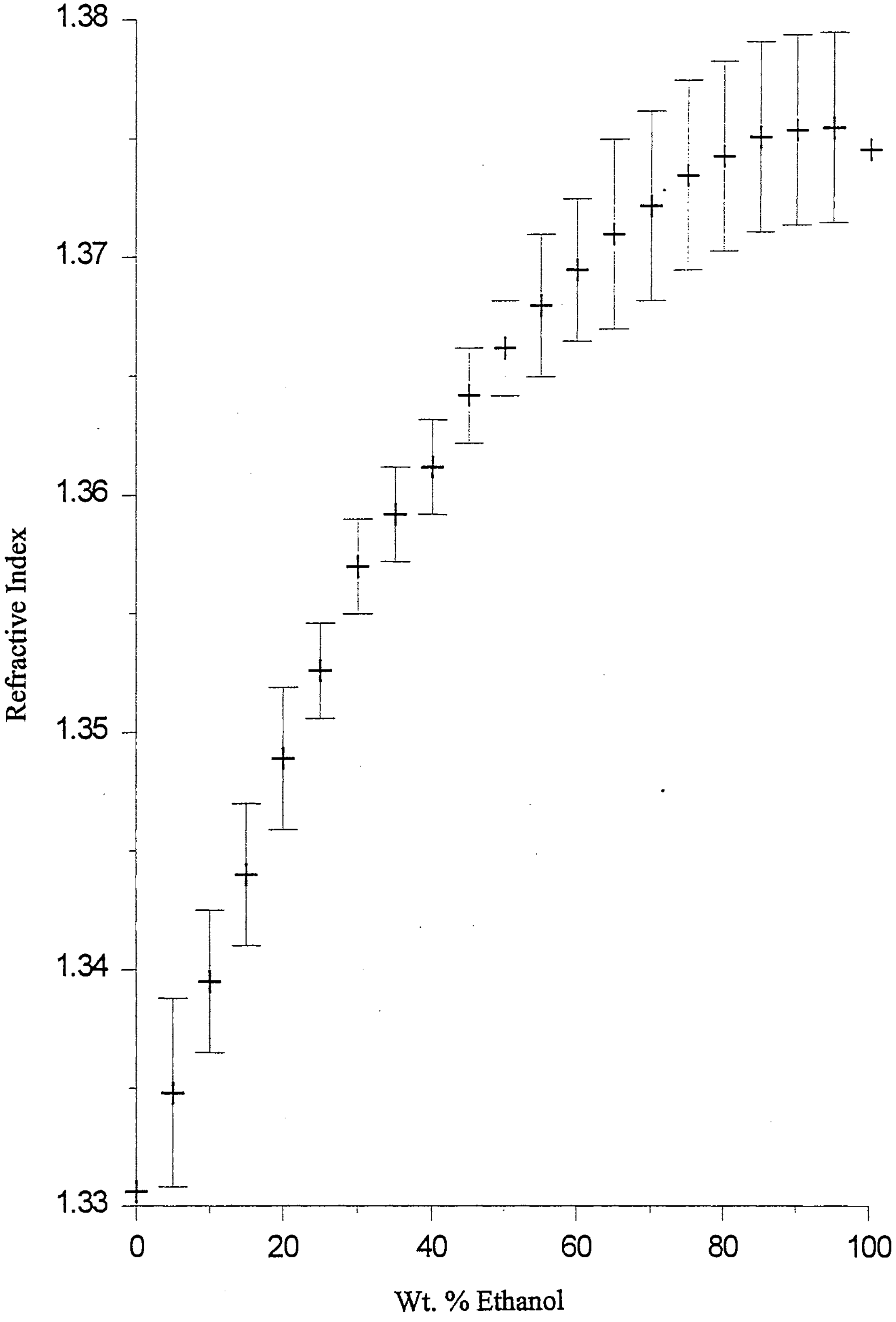


Figure 13. The Refractive Index Curve for Isopropanol/Water Mixtures.

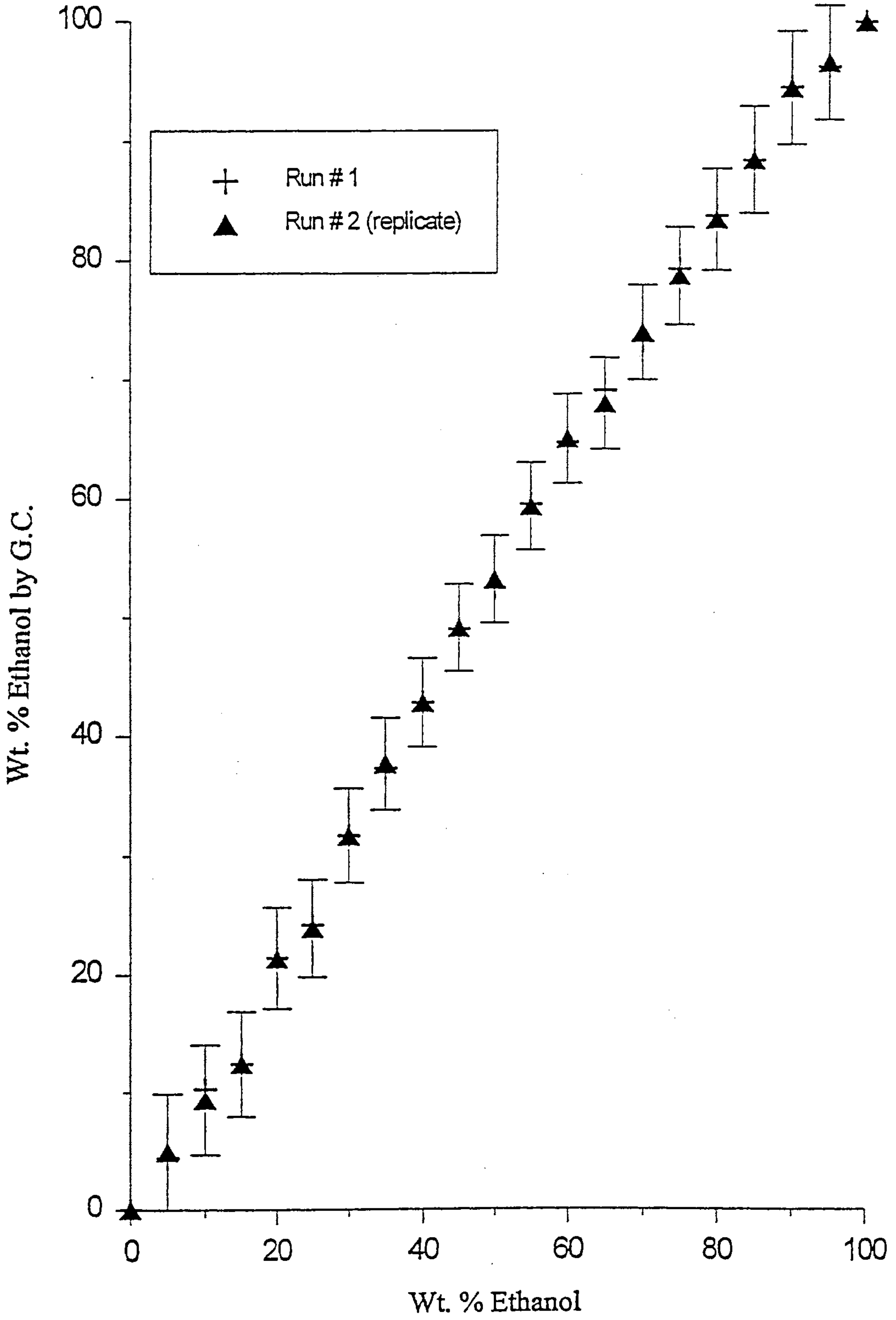


Figure 14. The Gas Chromatographic Results for Isopropanol/Water Mixtures.

CHAPTER IV

DEVELOPMENT OF PERVAPORATION MODELS

This chapter contains a step-by-step development of the models developed in this study. The appropriate assumptions made are included at each stage and the methods of calculating the various parameters of the model are also presented.. The last portion of this chapter describes the use of the model.

None of the models mentioned in Chapter II are predictive models. They all require experimental data for determining the value of one or more parameters. Specifically, the treatment of the concentration dependence of the diffusion coefficient is not properly accounted for in any of the models developed so far. Therefore, a major goal of this study is to develop a predictive model for pervaporation. The first step in the development of this model is the continuity equation for the permeants in the membrane. For steady state one dimensional transport, the continuity equation becomes:

$$\frac{\partial}{\partial z}\left(-\rho D_i \frac{\partial w_i}{\partial z}\right)=0 \qquad (4.1)$$

where D_i is the diffusion coefficient of the ith component and w_i is its weight fraction, ρ is the total species density and z is the spatial coordinate perpendicular to the membrane.

An assumption inherent in equation (4.1) is that the flux of permeants can be described by the Fick's law of diffusion. The term inside the parenthesis represents the mass flux of permeants relative to the mass-average velocity. Since the mass transport is assumed to occur only in the z direction, the partial derivatives with respect to z can be replaced by the total derivatives. It is worth noting that if z is written in terms of the relative dimensionless distance through the membrane, $x_R = z/L$, the above equation remains the same except that z is replaced by x_R. The differentiation of the term inside the parenthesis of equation (4.1) and simplification leads to the following equation:

$$\left(D_i\frac{\partial\rho}{\partial w_i}+\rho\frac{\partial D_i}{\partial w_i}\right)\left(dw_i/dx_R\right)^2+\rho D_i\frac{d^2 w_i}{dx_R{}^2}=0 \tag{4.2}$$

The second step in the development of pervaporation model is the inclusion of the concept of free volume for the calculation of the diffusion coefficients. According to the free volume theory, a liquid is considered to consist of a volume occupied by the liquid molecules, V_o, and some empty space between the molecules called free volume, V_f (Zielinski and Duda, 1988). If the molecule is assumed spherical, V_o is associated with the van der Waals radius of the liquid molecules plus the volume associated with vibrational motions. The rest of the volume is free volume which can be divided into two parts. The first type of free volume is the interstitial free volume which is assumed to be uniformly distributed among the molecules. The interstitial free volume requires a large energy for redistribution and therefore it is not affected by random thermal fluctuations. The other part of free volume which requires negligible energy for its redistribution is known as hole free volume. Therefore, the hole free volume is continuously being redistributed due to random thermal fluctuations. It is this hole free volume ~~which~~ that determines the transport properties of a polymer and permeant. According to the free volume theory, the permeant transport will occur if a hole of sufficient size occurs adjacent to a molecule and the molecule possesses enough energy to jump into the hole. In other words, the rate of permeant transport is determined by the amount of hole free volume available and the size of the migrating molecule. Also, in the glassy state (i.e., below the glass transition temperature, T_g), the polymer segments do not have adequate mobility which is required to reach their equilibrium configurations. The result is the trapping of some extra hole free volume in the glassy state. It should also be noted that the membranes used in this study are glassy polymers.

Since free volume concepts have successfully described the transport properties of polymeric systems (Ganesh et al., 1992), it has been assumed that they will also describe the diffusive transport in the pervaporation process. Since most of the work done on pervaporation involves the separation of a binary mixtures in which the membrane material is considered the third component, the swollen membrane is a ternary mixture. Therefore, such a diffusion coefficient model is sought for modeling pervaporation which should be based on a ternary mixture. The diffusion coefficient model of Vrentas et al. (1984) meets this requirement and is also based on free volume concepts. This model has been recasted according to the nomenclature used in this study as:

$$D_1 = D_{01}\exp\left(\frac{-(w_1 V_1^* + w_2 V_2^* \xi_{13}/\xi_{23} + w_3 V_3^* \xi_{13})}{V_{FH}/\gamma}\right) \quad (4.3)$$

$$D_2 = D_{02}\exp\left(\frac{-(w_1 V_1^* \xi_{23}/\xi_{13} + w_2 V_2^* + w_3 V_3^* \xi_{23})}{V_{FH}/\gamma}\right) \quad (4.4)$$

$$\frac{V_{FH}}{\gamma} = \frac{K_{11}}{\gamma}(K_{21} - T_{g1} + T)w_1 + \frac{K_{12}}{\gamma}(K_{22} - T_{g2} + T)w_2$$
$$+ \frac{K_{13}}{\gamma}(K_{23} - T_{g3} + T)w_3 \quad (4.5)$$

where V_i^* (cm³/g) is the specific critical hole free volume, w_i is the mass fraction and T_{gi} (K) is the glass transition temperature of component i. D_{10} and D_{20} are the limiting values of D_1 (cm²/s) and D_2 (cm²/s) at very low concentrations. The parameter γ is an overlap factor which is introduced because the same free volume is available to more than one molecule. K_{11} (cm³/g K) and K_{21} (K) are free-volume parameters for solvent 1 (which is the faster permeant), K_{12} (cm³/g K) and K_{22} (K) are free-volume parameters for solvent 2 (which is the slower permeant) and K_{13} (cm³/g K) and K_{23} (K) are those of polymer. Finally, ξ_{13} is the ratio of the critical molar volumes for the solvent 1 and polymer jumping units and ξ_{23} is the ratio of the critical molar volumes for the solvent 2 and polymer jumping units. The convention which is followed assigns the subscript 1 to the faster permeating solvent, 2 to the slower permeating solvent and 3 to the polymer. The parameter V_{FH} is the average hole free volume per gram of mixture. The parameters in this model are not simply adjustable parameters that allow for good experimental fits to data, but have physical significance and are rooted in the free-volume theory.

The pervaporation model has been developed by combining the diffusivity model of Vrentas et al. (1984) with the continuity equation of the permeants. The final form of the model is a set of two coupled second-order ordinary differential equations (ODEs) which are:

$$\begin{aligned}&\left[\frac{(\rho_1-\rho_3)}{\rho}+\frac{(s-t+q_1)w_2+t}{\{(c-p)w_1+(e-p)w_2+p\}^2}\right]\left(\frac{dw_1}{dx_R}\right)^2\\&\quad+\left[\frac{(\rho_2-\rho_3)}{\rho}-\frac{(s-t+q_1)w_1-q_1}{\{(c-p)w_1+(e-p)w_2+p\}^2}\right]\left(\frac{dw_1}{dx_R}\right)\left(\frac{dw_2}{dx_R}\right)+\frac{d^2w_1}{dx_R^2}=0\end{aligned} \tag{4.6}$$

$$\left[\frac{(\rho_2-\rho_3)}{\rho}+\frac{(u-v+q_2)w_1+v}{\{(c-p)w_1+(e-p)w_2+p\}^2}\right]\left(\frac{dw_2}{dx_R}\right)^2$$
$$+\left[\frac{(\rho_1-\rho_3)}{\rho}-\frac{(u-v+q_2)w_2-q_2}{\{(c-p)w_1+(e-p)w_2+p\}^2}\right]\left(\frac{dw_1}{dx_R}\right)\left(\frac{dw_2}{dx_R}\right)+\frac{d^2w_2}{dx_R^2}=0 \qquad (4.7)$$

Equation (4.6) involves the change in slope of component 1 while Equation (4.7) involves the change in slope of component 2. The above equations are coupled because both w_1 and w_2 as well as their slopes (dw_1/dx_R and dw_2/dx_R, respectively) appear in each equation. The symbol ρ_i in the above equations denote the species density of the permeant i, where i=1 for the faster permeant (water in this study), i=2 for the slower permeant (alcohol in this study) and i=3 for the polymer. The symbol ρ denotes the total density of the ternary mixture, which can be calculated by the following relationship:

$$\rho = w_1\rho_1 + w_2\rho_2 + w_3\rho_3 \qquad (4.8)$$

All the other symbols involved in the above equations are various combinations of the free-volume parameters which are described in the free-volume theory of Vrentas et al. (1984) earlier in this chapter. The relationships between these symbols and the free-volume parameters are:

$$s = b_1c - a_1e \qquad (4.9)$$

$$t = p_1c - pa_1 \qquad (4.10)$$

$$q_1 = p_1 e - b_1 p \quad (4.11)$$

$$u = b_2 e - c a_2 \quad (4.12)$$

$$v = p_2 e - p a_2 \quad (4.13)$$

$$q_2 = p_2 c - b_2 p \quad (4.14)$$

$$c = \frac{K_{11}}{\gamma}(K_{21} - T_{g1} + T) \quad (4.15)$$

$$e = \frac{K_{11}}{\gamma}(K_{12} - T_{g2} + T) \quad (4.16)$$

$$p = \frac{K_{13}}{\gamma}(K_{23} - T_{g3} + T) \quad (4.17)$$

$$b_1 = V_2^* \xi_{13}/\xi_{23} \quad (4.18)$$

$$b2 = V_1^* \xi_{23}/\xi_{13} \quad (4.19)$$

$$p_1 = V_3^* \xi_{13} \quad (4.20)$$

$$p_2 = V_2^* \xi_{23} \quad (4.21)$$

$$a_1 = V_1^* \quad (4.22)$$

$$a_2 = V_2^* \quad (4.23)$$

The simultaneous solution of equations (4.6) and (4.7) provides the concentration profile of the two permeants through the polymer membrane. The boundary conditions for solving the equations is the concentrations of the two permeants on the feed side and the permeate side of the membrane. More specifically, permeants on the feed side are in equilibrium with the feed solution while the permeate side concentrations are assumed to be equal to zero because of the presence of the vacuum. The membrane is divided into many parts (usually 100) between $x_R=0$ to $x_R=1$ for calculating the concentration profile. However, the solution of the second-order ODE(s) for the concentration profile additionally requires the knowledge of the derivative of concentration with distance (slope) at the start of the profile (Riggs, 1988). This means that for the case of two coupled ODEs, a total of two slopes must be known at the start of the profile, i.e. one slope for each permeant. Since this slope is not known, a shooting method can be used for solving the coupled ODEs. This can be accomplished relatively easily on a commercial software package, such as Mathcad, where the luxury of repeatedly changing the slopes and watching the results of the change is possible.

Methods of Calculating Free Volume Parameters:

In order to use the model, the free volume parameters of the two solvents as well as the polymer must be calculated. The parameter $\hat{V}_i^*$ can be assumed to be the same as the molar volume at 0 K which, in turn, can be estimated by the group contribution methods developed by Sugden (1927) and Biltz (1934). In case of the polymer, a better estimate can be obtained by using a relatively more recent group contribution method presented by Van Krevelen (1976). For the estimation of the polymer free volume parameters, the polymer glass transition temperature, T_g, the molecular weight of repeat unit, and the Williams-Landel-

Ferry (WLF) constants must be known or estimated. For the estimation of the free volume parameters of the solvents, viscosity and specific volume versus temperature data must be available or generated by a correlation.

In this study, the V_i^* for the polymer (i.e. V_3^*) has been estimated by the method of Van Krevelen (1976). In this method, the molar volume in the glassy state (V_g) is first estimated by a group contribution method. Then, the van der Waals volume (V_w) is traced out by using a graphical relationship between V_g and V_w (Fig. 4.2 of van Krevelen, 1976). Finally, V_3^* is calculated by the following relationship:

$$V_3^* = \frac{1.3V_g}{M_{RU}} \tag{4.24}$$

where M_{RU} is the molecular weight of the repeat unit of the polymer.

The other free volume parameters of the polymer can be calculated by making use of the WLF constants of the polymer. Zielinski and Duda (1992) have provided the relationship for calculating these parameters which has been recasted according to the nomenclature used in this study as follows:

$$\frac{\gamma V_3^*}{K_{13}} = 2.303C_{13}C_{23} \tag{4.25}$$

$$K_{23} = C_{23} \tag{4.26}$$

where C_{13} and C_{23} are the WLF constants.

The WLF equation describes the temperature dependence of the viscosity of glass forming liquids. This equation can be recasted according to the nomenclature used in this study as:

$$\log\left(\frac{\eta}{\eta_g}\right) = \frac{-C_{13}(T-T_g)}{C_{23}+(T-T_g)} \qquad (4.27)$$

For a wide variety of glass forming liquids of differing molecular weight and chemical structure, the WLF equation fits well when C_{13}=17.4 and C_{23}=51.6. These standard values of the WLF constants have been used in this study since the WLF constants for cellulose acetate are not available in literature.

The calculation of the free volume parameters of the solvents requires the knowledge of the chemical structure of the solvents as well as their viscosity and specific volume versus temperature data. The parameter V_i^* can be estimated by the group contribution methods developed by Sugden (1927) and Biltz (1934). If the viscosity and specific volume versus temperature data are available, the other free volume parameters of the solvents can be obtained by performing a four-parameter regression using the equation presented by Zielinski and Duda (1992). This equation has been recasted according to the nomenclature used in this study as:

$$\ln\left(\frac{0.124\mathrm{x}10^{-16}V_c^{2/3}RT}{\eta M_i V_i}\right) = \ln D_0 - \frac{E(w_i \rightarrow 1)}{RT} - \frac{\frac{\gamma V_i^*}{K_{1i}}}{K_{2i}-T_{gi}+T} \qquad (4.28)$$

where i=1 or 2 based on the faster or the slower permeant. V_c (cm^3/mol) is the solvent's critical molar volume and M_i is its molecular weight. 0.124x10^{-16} is a constant having units of mol$^{2/3}$. η (g/cm s) and V_i (cm^3/g) are the viscosity and the specific volume of the pure solvent, respectively.

Zielinski and Duda (1992) have shown that converging to a set of parameters that uniquely represents the viscosity and specific volume data is often impossible. They suggest neglecting energy effects, $E(w_i) = 0$ which reduces the number of regression parameters to three and tremendously improves the likelihood of convergence. This assumption has been used in this study and three parameters have been regressed for each permeant.

The parameter ξ_{13} should be calculated for the faster permeant/polymer pair while ξ_{23} should be calculated for the slower permeant/polymer pair. These parameters are calculated by using the equation suggested by Zielinski and Duda (1992) which can be recasted according to the nomenclature used in this study as:

$$\xi_{i3} = \frac{M_i V_i^*}{M_{3j} V_3^*} = \frac{M_i V_i^*}{V_{3j}} \tag{4.29}$$

where i=1 or 2 based on the faster or the slower permeant respectively. M_i is the molecular weight of the solvent jumping unit and M_{3j} is the molecular weight of the polymer jumping unit.

Since the polymer molecules exhibit segmental motion rather than moving as single unit, the determination of the size of a polymer jumping unit is tricky. However, Zielinski and Duda (1992) have presented a linear relationship between V_{3j} and T_{g3} which can be recasted as:

$$V_{3j}(\text{ cm}^3/\text{mol}) = 0.6224\, T_{g3}(\text{K}) - 86.95 \tag{4.30}$$

Rigorous and Modified Model:

In most of the cases, the solvent molecules are expected to move as single units, but the transport of very small molecules, especially water, is unusual and different in nature than large solvent molecules such as ethanol. According to Vrentas and Duda (1976), the movement of water molecules requires more than three times the average hole free volume than what is associated with three polymeric jumping units. The key assumption implicitly introduced by Fujita is that the molecular weight of the solvent is equal to the molecular weight of a jumping unit of the polymeric chain:

$$M_1 = M_j \qquad (4.31)$$

For organic solvents, the two molecular weights are expected to be close since the polymer is often formed from a monomer which itself is an organic solvent. On the other hand, for small molecules of low molecular weight like water, M_1 will be significantly less than M_j, and the predictions based on this notion will no longer be acceptable. Therefore, the Fujita free volume theory describes diffusion of ethyl acetate ($M_1 = 88$) in poly(methyl acrylate) (PMA), but not diffusion of water ($M_1 = 18$) in the same polymer. Vrentas and Duda (1976) also mentioned that for two polymer-solvent systems with equivalent values of fractional hole free volumes, f_1 and f_2, the increase in diffusivity with concentration is more pronounced for the system which has the higher molecular weight solvent if the solvents have comparable values of specific critical hole free volume. Aptel et al. (1976) pointed out that water molecules form three dimensional networks of strong hydrogen bonds, and in liquid water a large fraction of the molecules is self-associated in clusters. In the light of these arguments, the free volume parameters of water were also calculated for a presumed dimer of water (i.e., a cluster of two self-associated water molecules). This was done by considering the jumping unit molecular weight as twice the molecular weight of water in the free volume calculations. Using this assumption, the pervaporation model was modified and the concentration profile as well as pervaporation parameters calculated.

At this stage, two different models emerge out the description of the pervaporation process. The model which assumes and is based on the movement of single water molecules has been named the rigorous model because it does not contain any assumptions other than those inherent in the free volume theory, the Vrentas diffusion coefficient model and the Fick's law of diffusion. The other model assumes the self-association of water molecules as clusters and is based on a presumed dimer structure of water (i.e., a cluster of two self-associated water molecules). The free volume parameters are calculated separately for each model and some of them are found to be significantly different. In particular, the parameters ξ_{13} and D_{01} have come out to be significantly different for the two models.

The Use of the Models:

The calculations start at the feedside of the membrane, where an equilibrium is established between the feed liquid and the liquid absorbed in the membrane. The equilibrium sorption is calculated by the Mulder and Smolders (1984) model and is used as input for the models developed in this study. According to the Mulder and Smolders (1984) model, the chemical potential of each permeant in the liquid feed is equal to its chemical potential in the feed side of the membrane. This equality results in the following equations:

$$\begin{aligned} \ln \upsilon_1 + (1 - \frac{V_1}{V_2})\, \upsilon_2 + \chi_{12}\upsilon_2^{\,2} &= \ln\phi_1 + (1 - \phi_1) - \phi_2\frac{V_1}{V_2} - \phi_3\frac{V_1}{V_3} \\ &\quad + (\chi_{12}\phi_2 + \chi_{13}\phi_3)(\phi_2 + \phi_3) - \chi_{12}\frac{V_1}{V_2}\phi_2\phi_3 \qquad (5.32) \\ \ln \upsilon_2 + (1 - \frac{V_2}{V_1})\, \upsilon_1 + \chi_{12}\frac{V_2}{V_1}\upsilon_1^{\,2} &= \ln\phi_2 + (1 - \phi_2) - \phi_1\frac{V_2}{V_1} - \phi_3\frac{V_2}{V_3} \\ &\quad + (\chi_{12}\phi_1\frac{V_2}{V_1} + \chi_{23}\phi_3)(\phi_1 + \phi_3) - \chi_{13}\frac{V_2}{V_1}\phi_1\phi_3 \qquad (5.33) \end{aligned}$$

where V_i is molar volume and υ_i is the volume fraction of species I in the binary liquid feed. The symbol, χ_{ij} is the binary interaction parameter and ϕ is the volume fraction in the ternary system.

The other parameters which are used, besides the free volume parameters, as input to the pervaporation model are the temperature of the membrane, the thickness of the membrane, and the densities of the solvents at the temperature of operation. The molecular weights of the solvents are needed for the calculation of the parameter, ξ_{i3}. The equilibrium sorption of the permeants at the feed side of the membrane (i.e. the first boundary condition) as calculated by the Mulder and Smolders model is also used as input for the calculation of selectivity of the membrane. The shooting method has been used, employing the Runge-Kutta method for solution at every point in the membrane, for calculation of the concentration profile of the permeants. The other boundary condition (i.e. the zero concentrations at the end of the membrane or permeate side) is matched by trial and error on the initial slopes.

Once the concentration profile is obtained, the mass flux relative to the mass-average velocity can be calculated for each permeant by using the following equation:

$$j_i = \frac{\rho D_i}{L} \frac{\partial w_i}{\partial x_R} \tag{4.34}$$

where x_R is the relative distance through the membrane which can be obtained by dividing the local distance, z by the total thickness of the membrane, L. Since the slope varies at all points throughout the membrane, the flux should be calculated at each point using Equation (4.31) and it should come out as constant.

The selectivity of the membrane for the faster permeant A over the slower permeant B can be defined as:

$$\alpha_{A/B} = \frac{Y_A/Y_B}{X_A/X_B} \tag{4.35}$$

where Y denotes the concentration in the permeate and X denotes the concentration in the feed. Since the ratio of the permeate concentrations of A to B are the same as ratio of the fluxes of permeant A to B, the selectivity can be calculated from the fluxes.

An indication of a correct output from the model is that for each permeant, the flux should come out as a constant value at all the points throughout the membrane. This has been observed for both of the models developed in this study, when applied to predict the pervaporation behavior.

A limitation of the models developed in this study has been observed at the point where the concentration of both the solvents approached zero. It should be remembered that the concentration of both the solvents becomes virtually zero (actually, very low values) at the downstream end of the membrane. In this point at the end of the membrane, the predictions of diffusivities and hence the fluxes are poor. Therefore, the results have been computed by including all but the last point in the membrane.

CHAPTER V

RESULTS

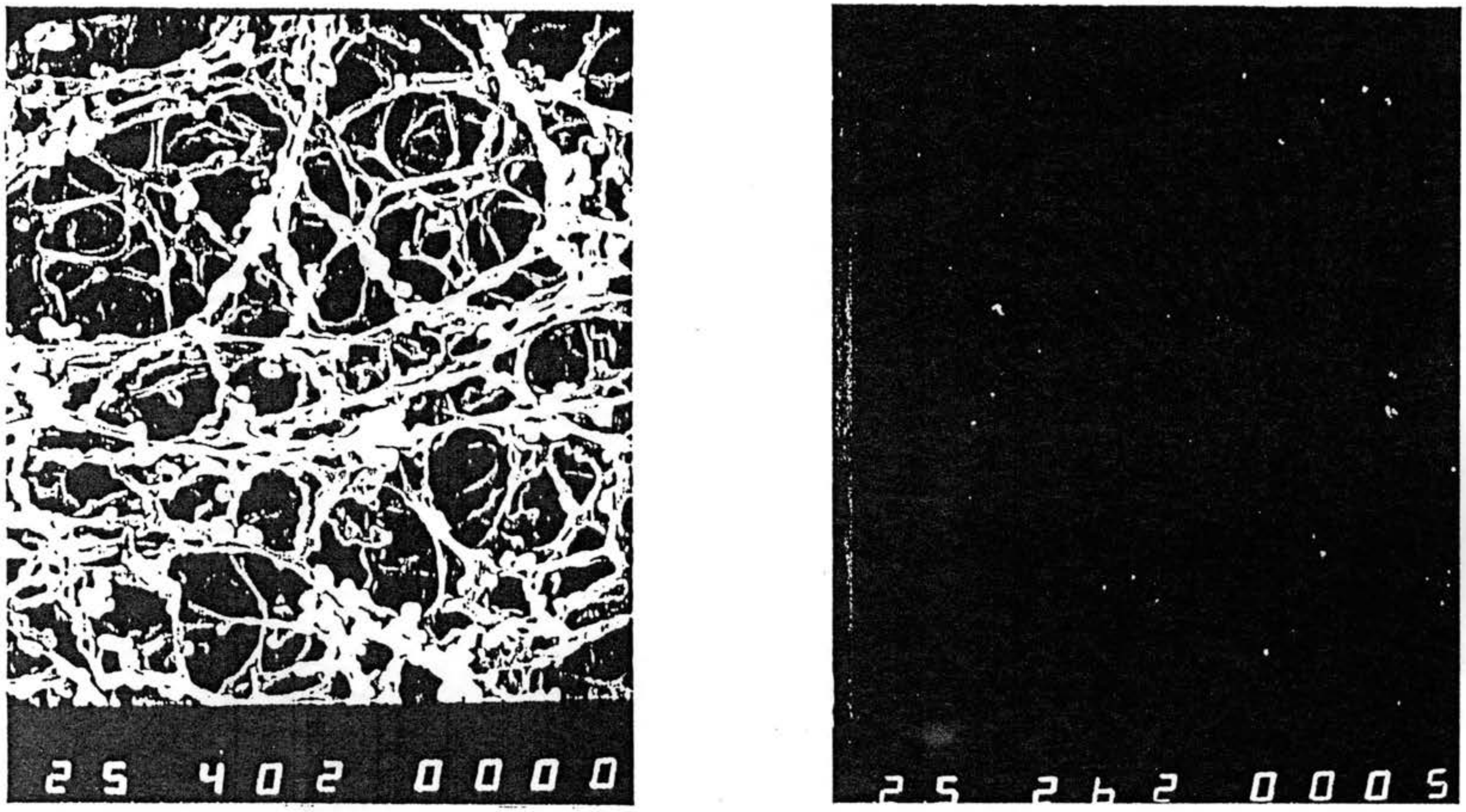
This chapter contains the experimental results obtained in this work and comparės the results with the predictive pervaporation model discussed in Chapter IV as well as the experimental results of Mulder and Smolders (1984). A scanning electron microscope (SEM) photograph of the cellulose acetate membrane prepared and used in the experiments is also presented in order to characterize the porosity of the membrane. Results from the gas chromatograph analysis of the ethanol/water mixture are discussed. The discussion of the pervaporation model includes the results from the rigorous as well as the modified model.

Results from Pervaporation Experiments

Pervaporation experiments were performed using Nafion™ (K^+ form) and cellulose acetate membranes. The experimental setup used for performing pervaporation experiments is discussed in detail in Chapter III. For each experiment a fresh membrane was used after soaking in the feed solution prior to the experiment for at least 10 hours so that the membrane could swell to its maximum extent. Nafion™ (K^+ form) membranes were supplied by Du Pont while the cellulose acetate membranes were casted in the laboratory as discussed in Chapter III. The Nafion™ (K^+ form) membranes used in the experiments had a thickness of 5 mil (127 μm). The thickness of the cellulose acetate membranes was much higher and varied widely in the range of 786 to 972 μm. While measuring the glass transition temperature (T_g) of Nafion™ (K^+ form) membranes, Yeo and Eisenberg (1977) observed two peaks. By dynamic mechanical studies, the α-transition was observed at 225 °C while the β-transition was observed at 160 °C. Since the T_g of cellulose acetate was not found in the literature, the glass transition temperature of cellulose acetate propionate was assumed to be close to that of cellulose acetate and was used for calculations. Brandrup (1966) reports the T_g of cellulose acetate propionate as 312 K.

Pervaporation experiments should be conducted using nonporous membranes and the porosity of the membranes prepared in this study has been estimated from SEM photographs. Figure 15 shows an SEM photograph of a typical cellulose acetate membrane used in the experiments. The pore size of the commercially available cellulose acetate membrane, Figure 15(a) is 0.2 μm. The magnification in Figure 15(a) is 4000x while that in Figure 15(b) is 2600x. The membrane prepared in the lab was sensitive to the beam of electrons under the SEM and so the magnification could not be increased above 2600x. However, it can be seen that even though the magnification in Figure 15(b) is more than half the magnification in Figure 15(a), the pore size in Figure 15(b) is much smaller than that in Figure 15(a). Therefore, membranes prepared in this work are considered nonporous and suitable for pervaporation experiments.

The feed was prepared in the feed tank by matching the mixture composition to the required values with the help of results obtained from a gas chromatograph. The permeate samples collected in the cold traps were transferred into sampling bottles and then weighed. Finally, the compositions of the samples were obtained by gas chromatography as described in Chapter III.



(a)

(b)

Figure 15. The SEM Photograph of: (a) Commercially Available Porous Cellulose Acetate Membrane (4000×); (b) Nonporous Cellulose Acetate Membrane Prepared in the Laboratory (2600×)

A typical example of the GC peaks is presented in Figure 16. These peaks were obtained from a permeate sample collected after 12 hours of pervaporation of 21.5 % aqueous ethanol through Nafion membrane. Helium used as a carrier gas, was introduced into the chromatographic column at 13 psi and the attenuation of the integrator was set at 5. The sample size used was 0.1 μl into which 0.4 μl of air was added as an internal standard. The first peak in Figure 16 is air, the second is water while the last is ethanol. Since, in this work, only water and ethanol concentrations are of interest, the effects of the air peak must be cancelled. This is accomplished by normalizing the area percentages for the compounds of interest. The compositions of these compounds are calculated by using their normalized area percentages and weight factors.

Pervaporation experiments were normally conducted for very long periods of time (i.e., approximately 40 hours). A profile of the permeate collected versus time (permeation profile) for the pervaporation of 73 % aqueous ethanol (EtOH) through Nafion™ (K^+ form) membrane is presented in Figure 17. The error bars on Figure 17 are due to the random errors associated with measuring the weight of the permeate. Since every sample is collected separately and the cumulative permeate collection is plotted with time, the error bars are smaller for the initial data points and grow larger for the later data points. Hence, the uncertainties are the smallest for the initial data points and largest for the later data points. However, in addition to these random errors, systematic errors also exist which are due to the trace amount of permeate which sticks to the wall of the cold trap and cannot be removed. Because of the difficulties in estimating the systematic errors, they are not plotted in Figure 17. However, it can be visualized that contrary to the random errors, the systematic errors will have a bias in the positive y-axis direction. Like random errors, systematic errors are also expected to be the smallest for the initial data points and largest for the later data points.

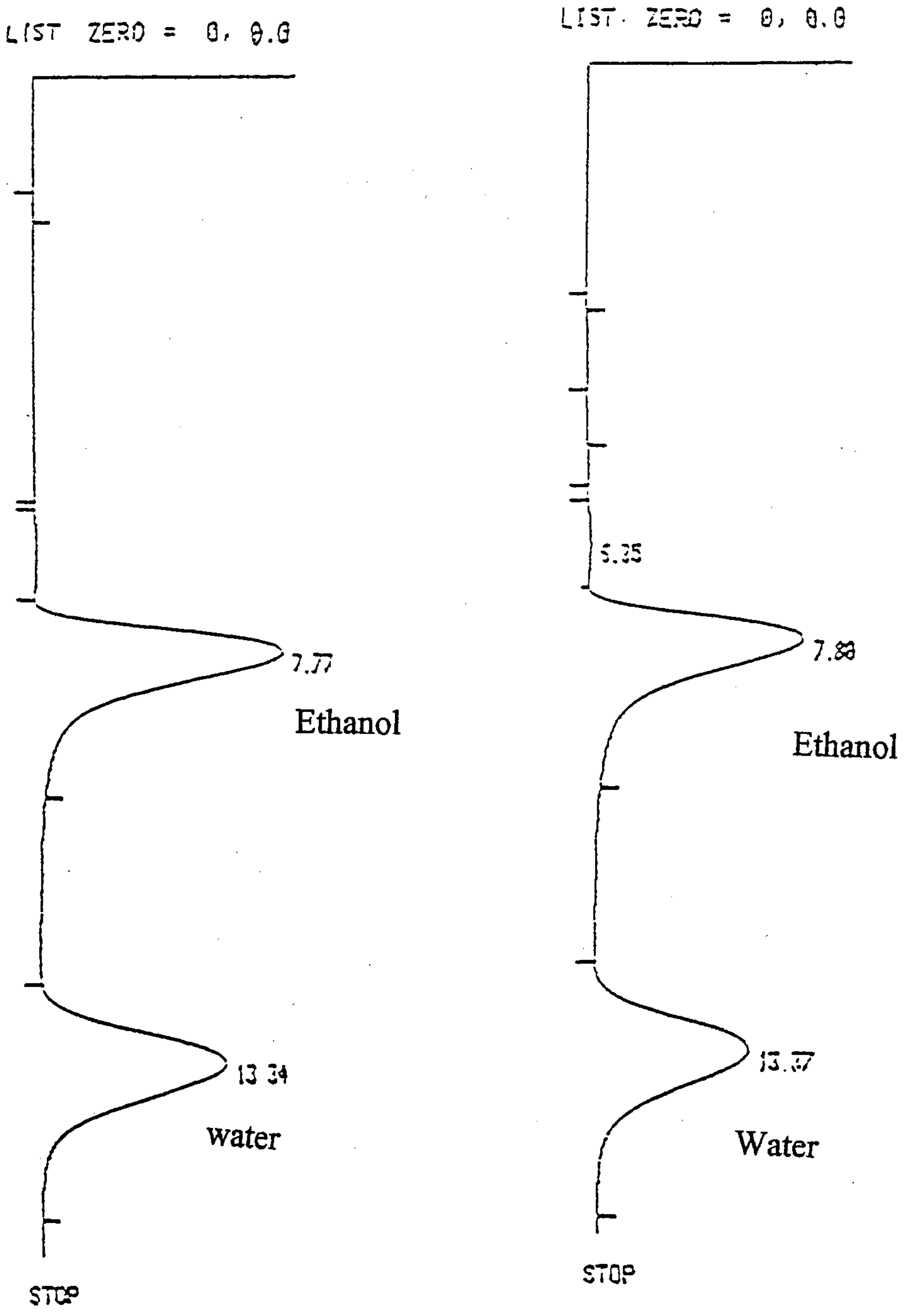


Figure 16. Typical Gas Chromatograms of Water/Ethanol Mixtures

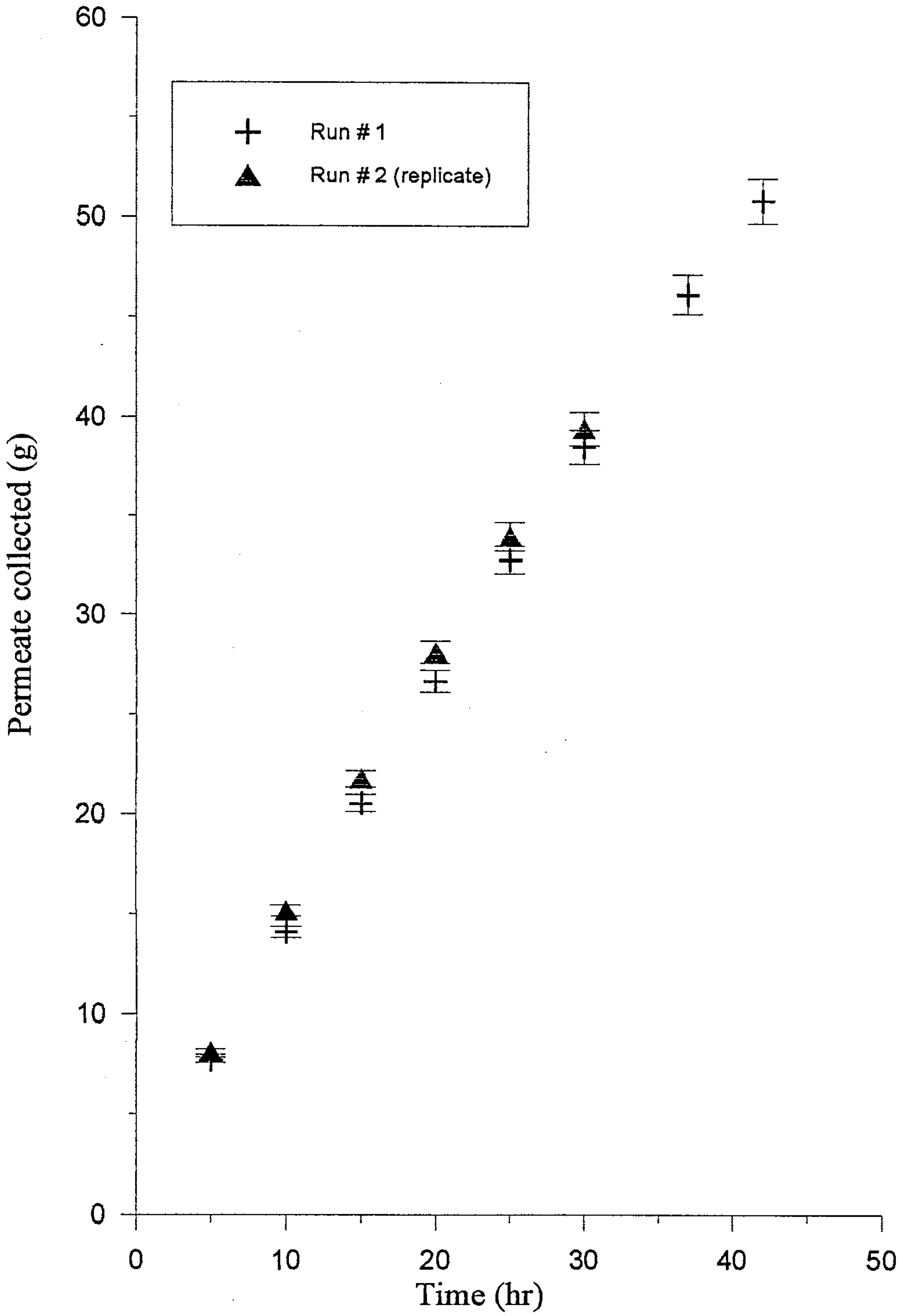


Figure 17. Pervaporation of 73 % Aqueous EtOH Through Nafion (K^+) Membrane

Therefore, it can be concluded that within the bounds of the existing errors, Figure 17 shows a predominantly linear behavior. Figure 18 also shows a linear increase in the permeation profile for the pervaporation of 21.5 % aqueous EtOH. Similar behavior was observed for other experiments with Nafion™ for pervaporating isopropanol/water mixtures. Figure 19 shows a linear permeation profile for a 5.2 % aqueous isopropanol (i-PrOH) while Figure 20 shows a similar behavior for 88 % isopropanol.

As observed with the Nafion™ membrane, the permeation profiles for cellulose acetate membranes also show a linear increase. Figure 21 shows this behavior for the pervaporation of 73 % aqueous EtOH while Figure 22 shows the same trend for 95.6 % aqueous EtOH. The break in the data of Figure 22 may be due to some vacuum fluctuations overnight. The profiles observed for mixtures of water and isopropanol also depict similar behavior as shown in Figure 23 for the pervaporation of 88 % isopropanol and in Figure 24 for the pervaporation of 5.2 % isopropanol.

Although the permeation profiles show a predominantly linear behavior, some of them do not have a zero y-intercept. This nonzero y-intercept in some cases is due to the relaxation of the glassy polymer membrane initiated by its interaction with the solvent. The relaxation phenomenon moves the polymer towards its equilibrium or relaxed position, where the extra-hole free volume associated with the glassy polymers is decreased. As a consequence, the total flux is decreased. Since the relaxation rate is maximum during the earlier stages of pervaporation than the later stages, the flux is maximum during the earlier stages and progressively reaches a constant value at a time when substantial relaxation has occurred.

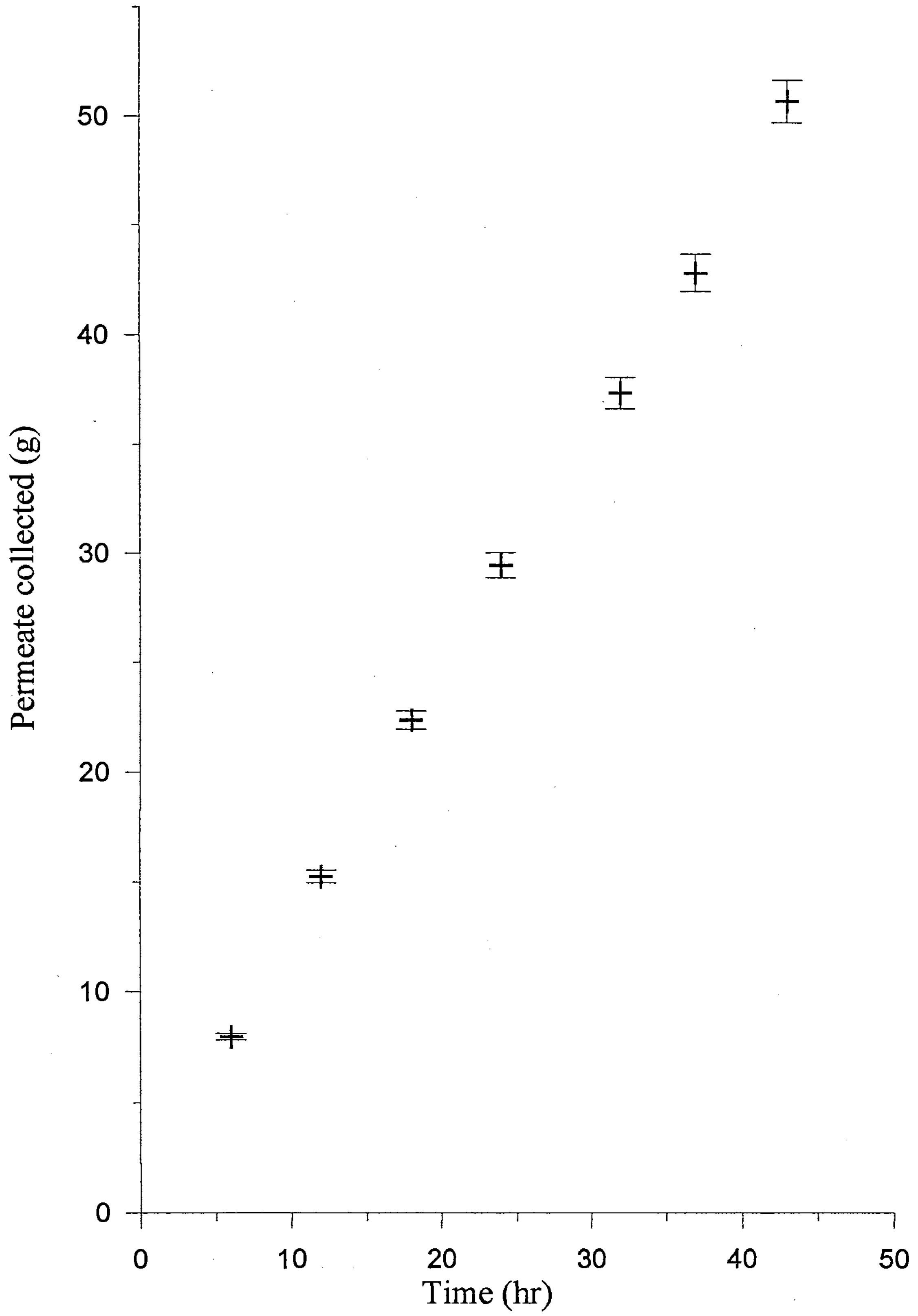


Figure 18. Pervaporation of 21.5 % Aqueous EtOH Through Nafion (K^+) Membrane

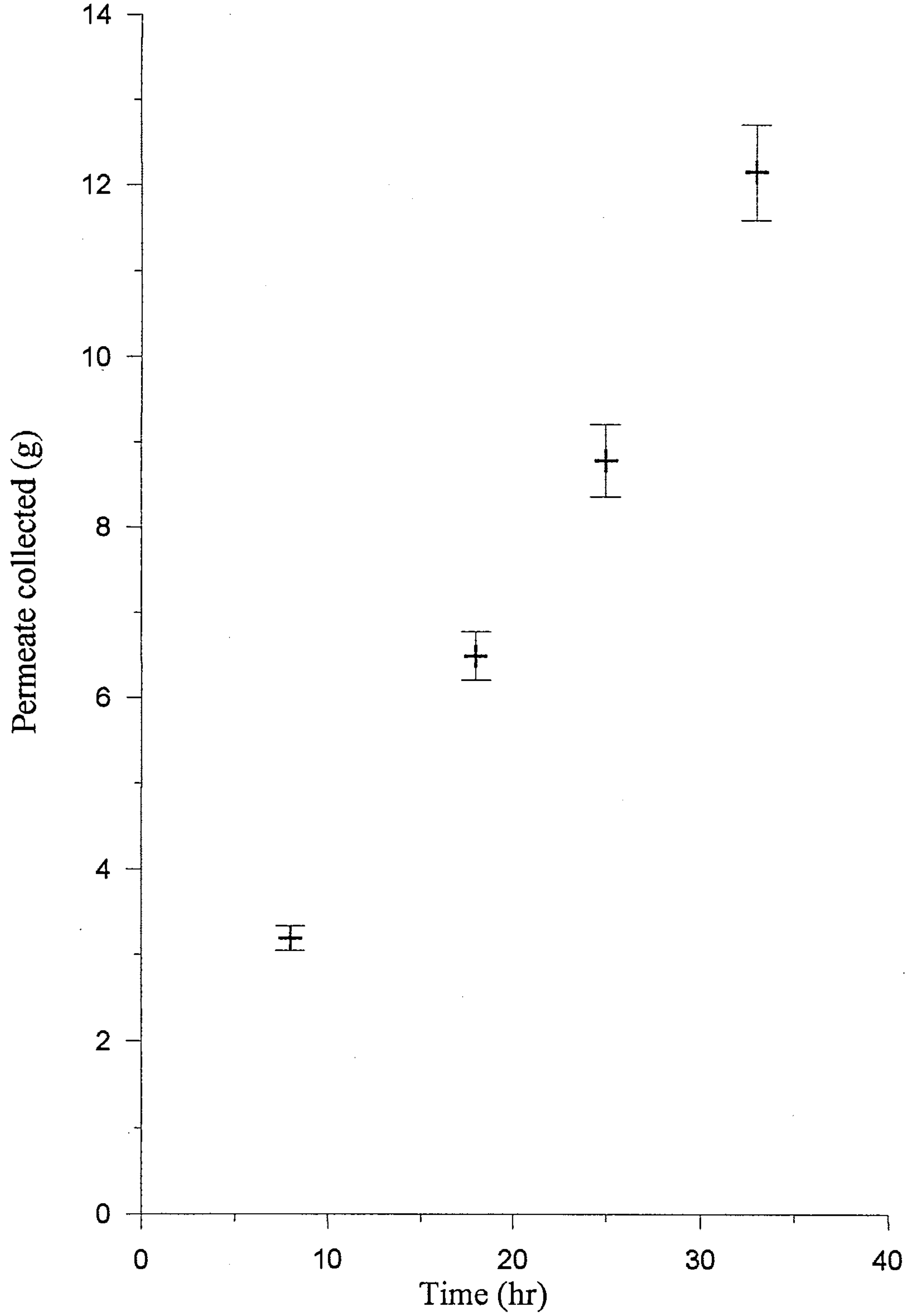


Figure 19. Pervaporation of 5.2 % Aqueous I-PrOH Through Nafion (K^+) Membrane

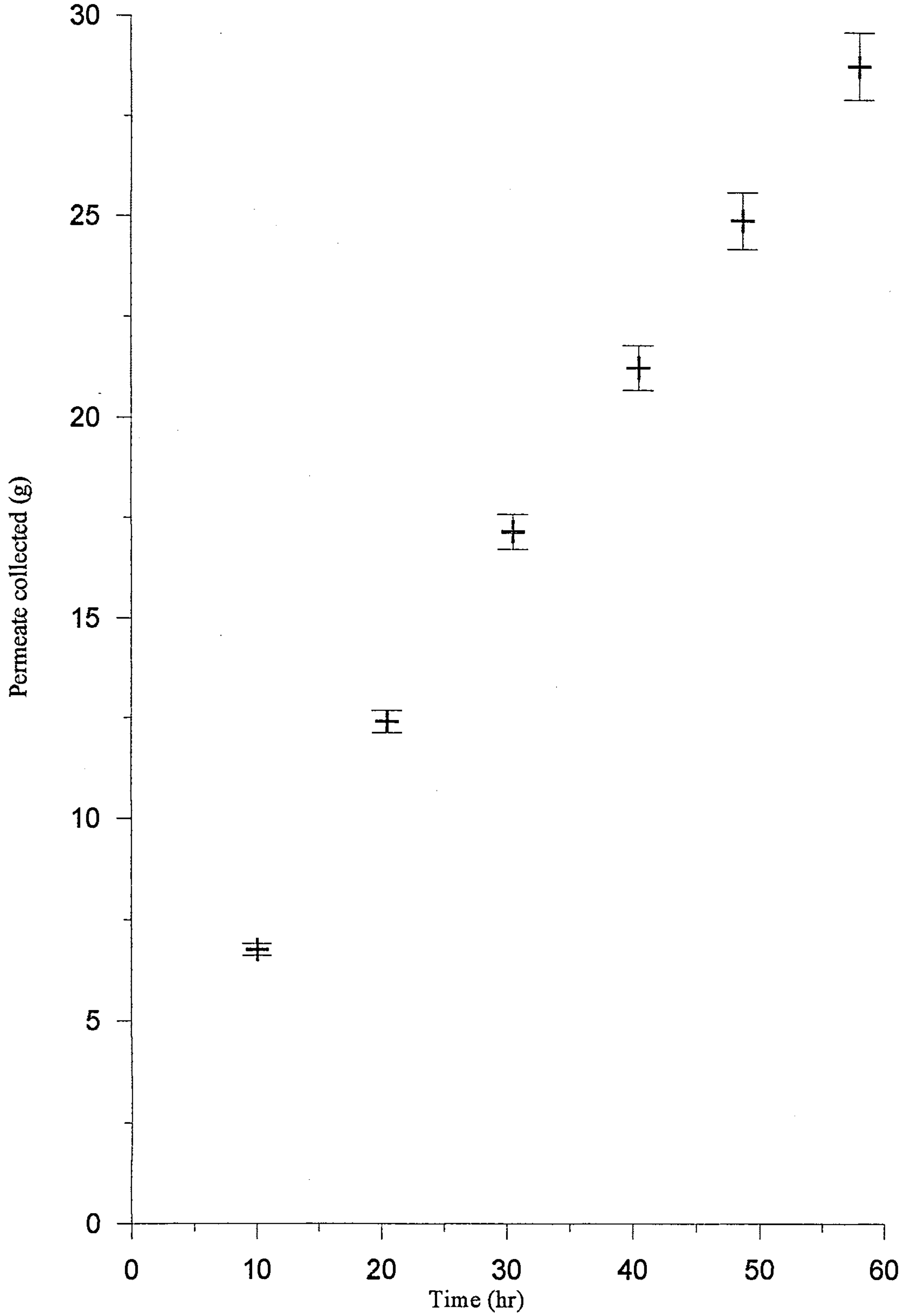


Figure 20. Pervaporation of 87.8 % Aqueous I-PrOH Through Nafion (K+) Membrane

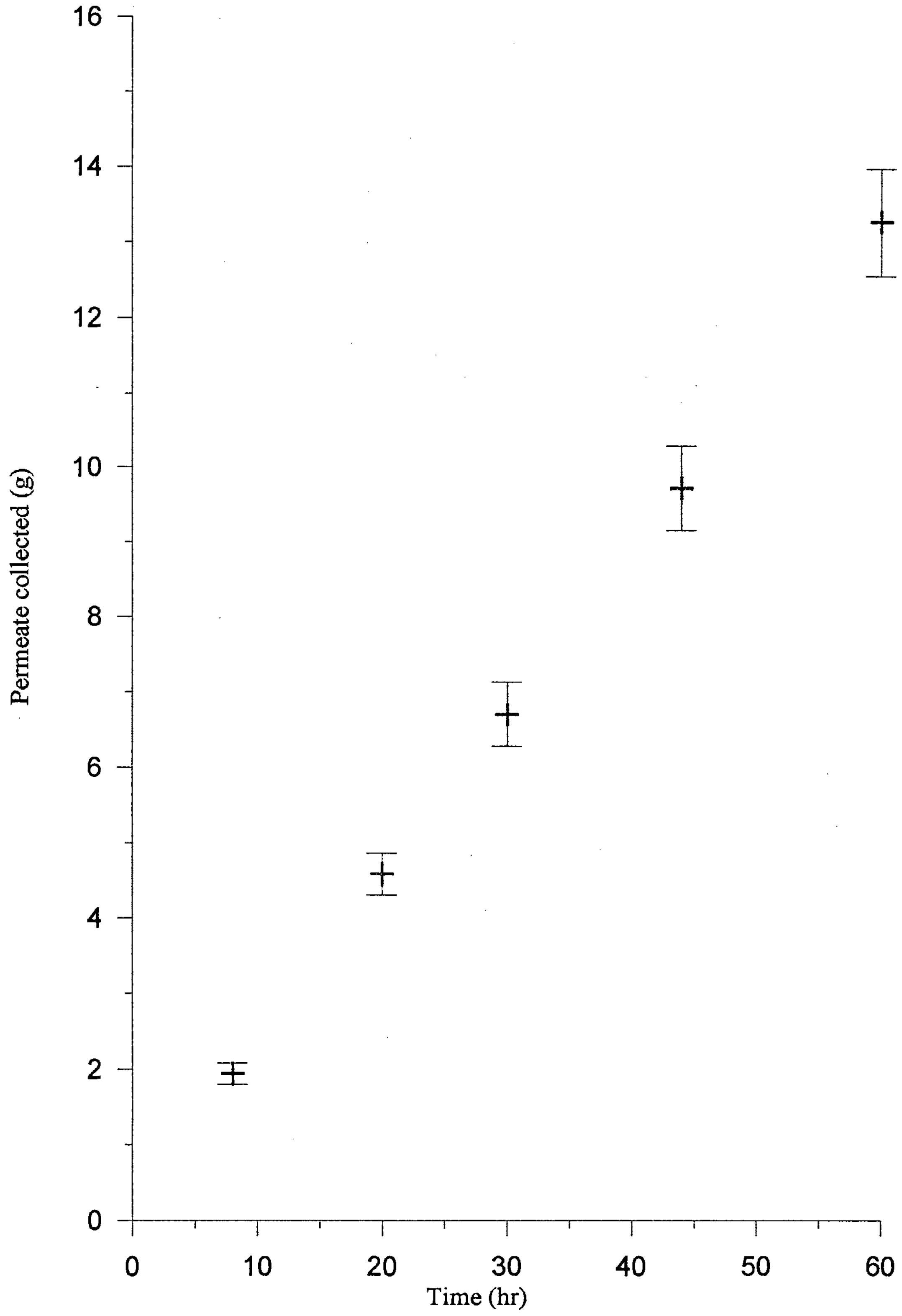


Figure 21. Pervaporation of 73 % Aqueous EtOH Through Cellulose Acetate Membrane

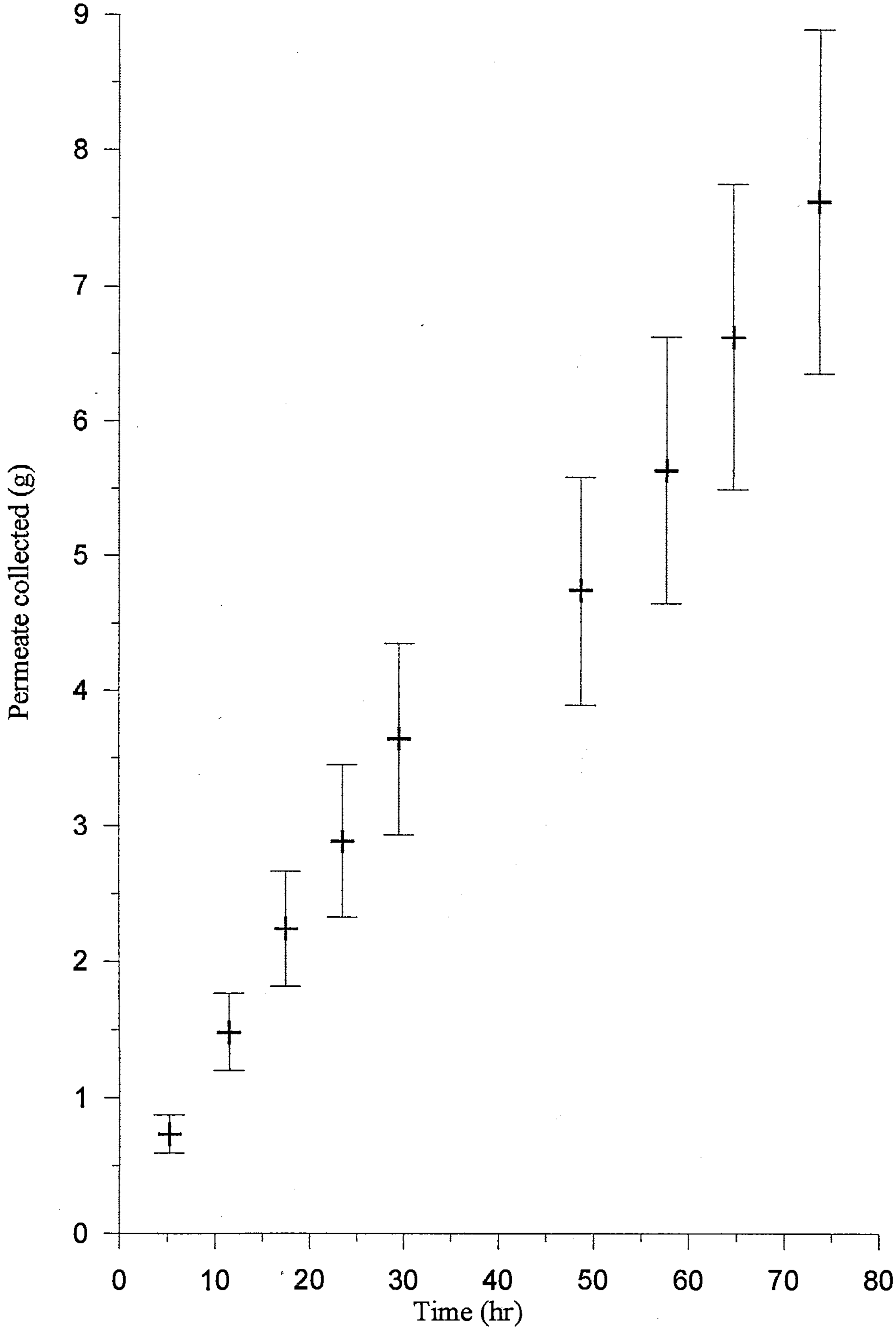


Figure 22. Pervaporation of 95.6 % Aqueous EtOH Through Cellulose Acetate Membrane

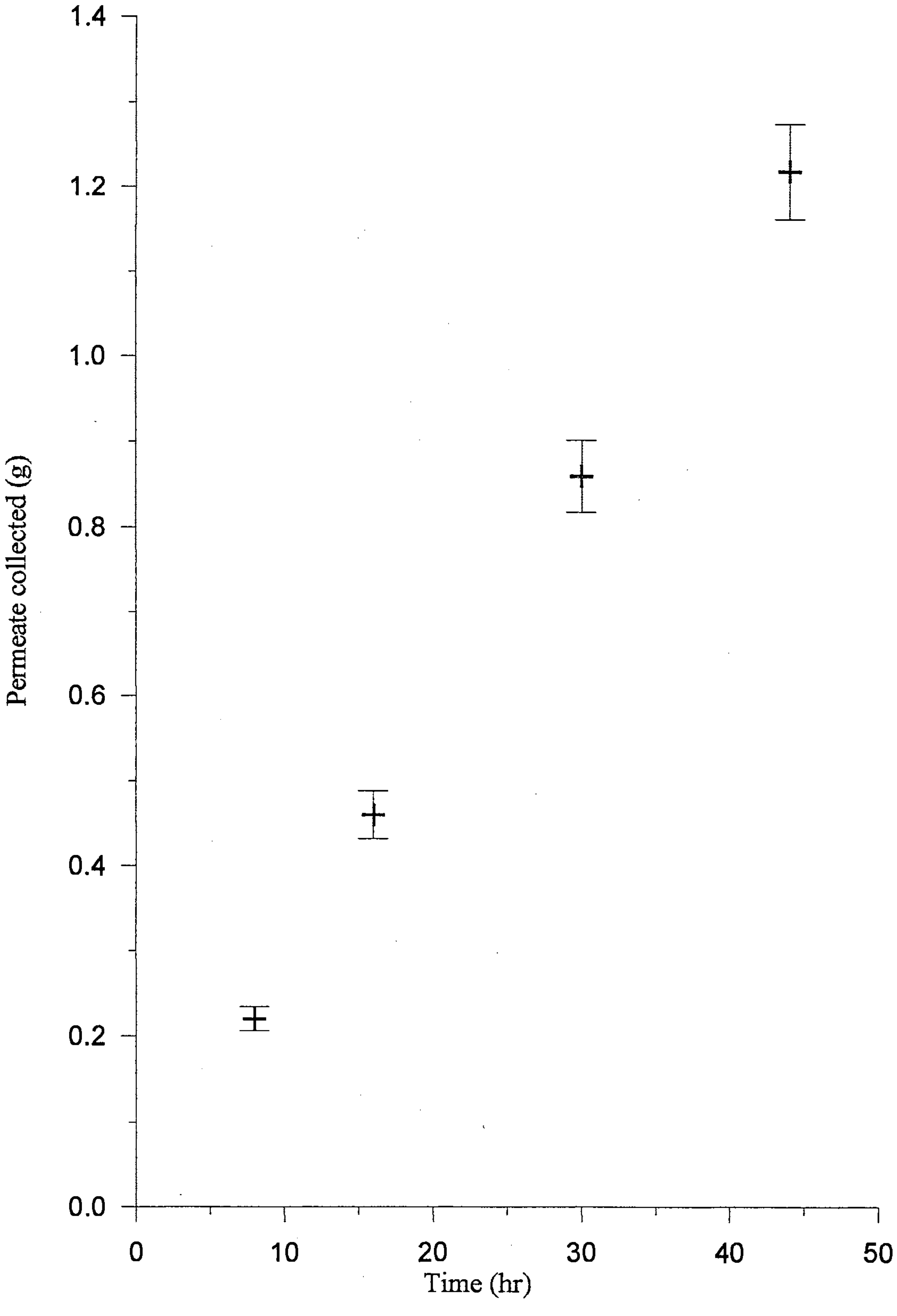


Figure 23. Pervaporation of 87.8 % Aqueous I-PrOH Through Cellulose Acetate Membrane

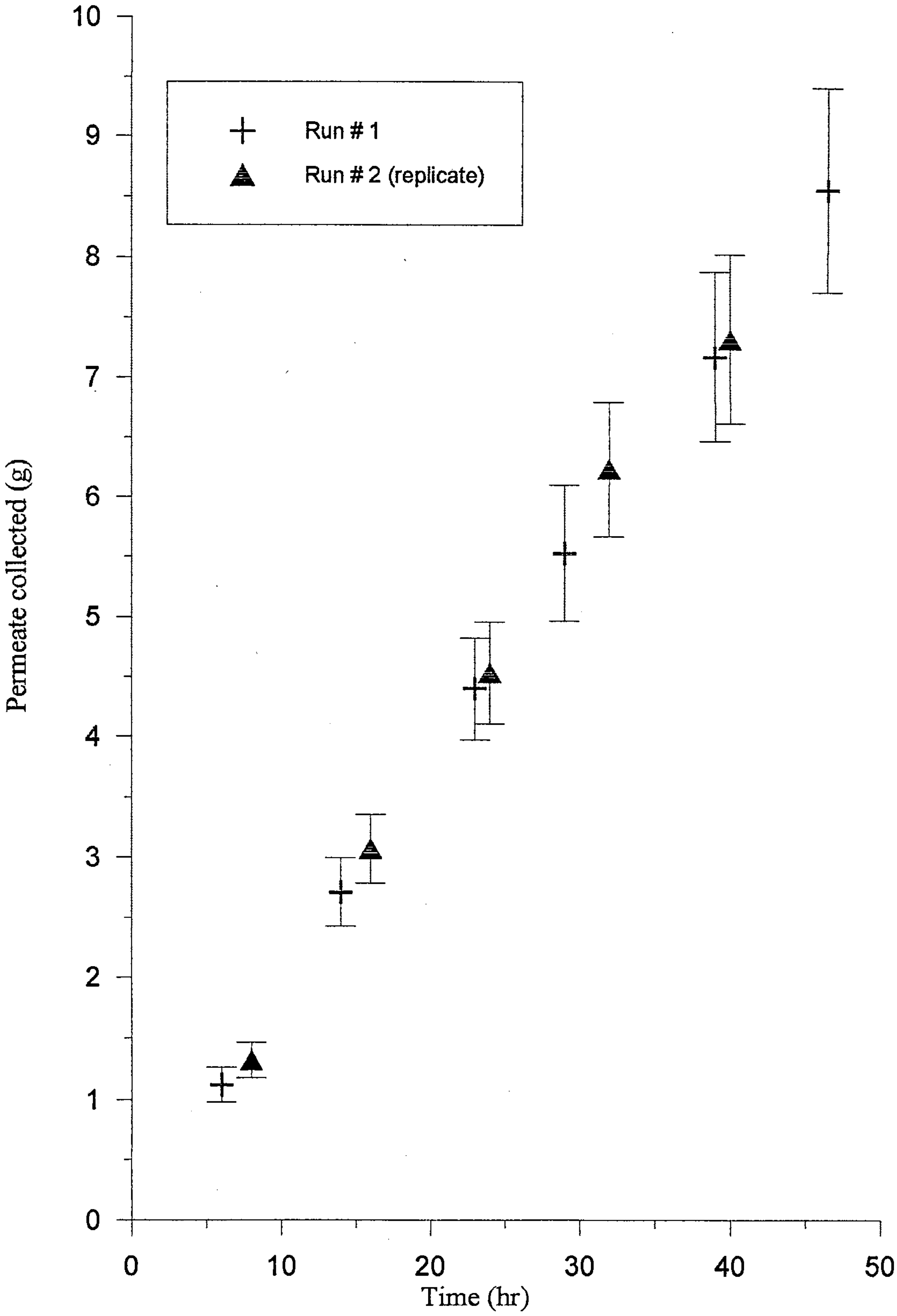


Figure 24. Pervaporation of 5.2 % Aqueous I-PrOH Through Cellulose Acetate Membrane

Pervaporation Parameters from Experiments:

The results based on the pervaporation experiments on EtOH and water mixtures are presented in Table XIV. The pervaporation of 78.5 % aqueous EtOH through Nafion™ (K^+ form) has been conducted to compare with a similar experiment performed by Cabasso et al. (1985). The pervaporation of the other compositions (21.5 % and 73 %) through Nafion™ (K^+ form) has been conducted as new cases to understand the performance of this membrane for pervaporation. Similarly, the pervaporation of 73 % aqueous EtOH through cellulose acetate has been conducted to compare with an experiment performed by Mulder and Smolders (1984) while the other experiment using this membrane, i.e., pervaporating 95.6 % EtOH was conducted as a new case. Since, 95.6 % EtOH (200 proof) in water forms an azeotropic mixture, this experiment has been an excellent demonstration of the advantage of pervaporation. The new case of the pervaporation of 73 % aqueous EtOH through Nafion™ (K^+ form) allows a comparison with the cellulose acetate membrane in pervaporating this mixture.

In general, the values of permeation flux for all components through Nafion™ (K^+ form) are an order of magnitude higher than those for cellulose acetate membranes as observed in Table XIV. The most probable reason for the higher flux is the difference in the thickness of the membranes. For a particular membrane, the flux decreases as the thickness of the membrane increases. A parameter that takes into account the variation of flux with the thickness is the effective permeation coefficient, Q_{eff}, defined by Hoover and Hwang (1982) as:

$$Q_{eff} = \frac{jL}{\Delta P} \tag{5.1}$$

where j (g/cm^2 h) is the total flux of permeants, L (cm) is the thickness of the membrane and ΔP (atm) is the pressure gradient across the membrane. The units

Table XIV. Pervaporation of Aqueous EtOH

Wt. % EtOH in feed	Membrane	Selectivity (water/ EtOH)	Total Flux ($g/cm^2.h$)	Effective Permeation Coefficient Q_{eff} ($g.cm/cm^2.h.atm$)
21.5	Nafion™ (K^+)[1]	0.3±0.06	0.026 ±0.0003	$3.2x10^{-4}$ $\pm 5.1x10^{-5}$
73	Nafion™ (K^+)[1]	0.6±0.17	0.052 ±0.0002	$6.4x10^{-4}$ $\pm 1.1x10^{-4}$
78.5	Nafion™ (K^+)[1]	1.1±0.29	0.011 ±0.0002	$1.3x10^{-4}$ $\pm 2.1x10^{-5}$
73	Cellulose acetate[2]	6.8±1.6	0.0053 ±0.0002	$3.8x10^{-4}$ $\pm 1.6x10^{-5}$
95.6	Cellulose acetate[3]	36±12	0.0023 ±0.0002	$1.7x10^{-4}$ $\pm 1.0x10^{-5}$

1. 127 μm thick
2. 790±20 μm thick
3. 790±20 μm thick

of Q_{eff} in this case will be g cm/cm^2 h atm. The effective permeation coefficient, Q_{eff} is a more useful parameter for comparison between pervaporation experiments because it accounts for the flux variation due to thickness.

The Nafion™ membrane is EtOH-selective for feeds of low EtOH concentration and water-selective for feeds of high EtOH concentrations as observed in Table XIV. A similar behavior is also observed for the cellulose acetate membrane where the selectivity for water is higher for feeds of higher EtOH concentrations. A plausible reason for this difference might be that water exerts a more plasticizing effect on the membranes than EtOH and hence the flux of EtOH is higher for EtOH-lean feed and lower for EtOH-rich feed. The variation of total flux versus weight percent of EtOH in the feed shows that a maximum flux is observed for a feed of 73 % EtOH. Cabasso et al. (1985) has also observed a similar trend, for total flux versus weight fraction isopropanol in feed, during the pervaporation studies of aqueous alcohols. Since the membrane selectivity can also vary with thickness, any conclusions regarding the selectivity of a membrane of certain thickness cannot be applied for the membranes of same material but different thicknesses. The results also show that for the feeds of 73 % or higher EtOH concentrations, cellulose acetate was found to be preferable to Nafion™ (K^+ form) because it has greater selectivity and also a reasonable value of Q_{eff}.

The error analyses of the results show that the uncertainty in selectivity is higher for the separations in which the selectivities are higher. As compared to the uncertainties in selectivity, the variations in the uncertainties in flux and Q_{eff} are relatively smaller. The reason for the larger variations in the uncertainties in selectivity lies in the definition of selectivity which is a complex function of the feed and permeate compositions.

The results based on the pervaporation experiments involving isopropanol (i-PrOH) and water mixtures are presented in Table XV. The pervaporation of 5.2% aqueous i-PrOH through Nafion and 87.8 % aqueous i-PrOH through cellulose acetate has been conducted so that the results could be compared with published results. The rest of the systems have been studied as new cases. The Nafion™ membrane is i-PrOH-selective for low i-PrOH concentrations and becomes water-selective for high i-PrOH concentrations. The cellulose acetate membrane remains highly selective for water for an i-PrOH-rich feed as well as for an i-PrOH-lean feed, but the flux is very low for pervaporating 87.8 % aqueous i-PrOH feed. A plausible reason for this difference might be that water exerts a more plasticizing effect on cellulose acetate membrane than i-PrOH and hence the flux is higher for i-PrOH-lean feed and lower for i-PrOH-rich feed. The results also show that for the dehydration of 87.8 % aqueous i-PrOH, Nafion ™ (K^+ form) was found to be preferable to cellulose acetate because it showed a selectivity greater than one and also a reasonable value of Q_{eff}. As observed for EtOH/water separations, the uncertainty in selectivity for i-PrOH/water separations also strongly depends on the magnitude of selectivity.

Comparison with Other Investigators:

A comparison of the results of EtOH /water separation with the results published by other investigators is presented in Table XVI. Here, water is the selective permeant in all the cases. The values of Q_{eff} are closer to the published results than the values of flux and selectivities. The difference in the values of selectivities may be due to the different thickness and the different temperatures used by the other investigators. However, the results of this study agree with the other investigators in the observed selective solvent. The parameter Q_{eff} was calculated from the results of the other investigators and was not present as such

Table XV. Pervaporation of Aqueous I-PrOH

Wt. % i-PrOH in feed	Membrane	Selectivity (water/ i-PrOH)	Total Flux (g/cm^2.h)	Effective Permeation Coefficient Q_{eff} (g.cm/ cm^2.h.atm)
5.2	Nafion™ (K$^+$)[1]	0.22±0.20	0.008 ±0.0002	9.1x10^{-5} ±1.5x10^{-5}
87.8	Nafion™ (K$^+$)[1]	3.4±1.35	0.0109 ±0.0002	1.2x10^{-4} ±1.9x10^{-5}
5.2	Cellulose acetate[2]	11.2±7.75	0.004 ±0.0002	2.9x10^{-4} ±1.4x10^{-5}
87.8	Cellulose acetate[3]	9.2±3.73	0.0006 ±0.0002	5.2x10^{-5} ±1.4x10^{-5}

1. 127 μm thick
2. 830±20 μm thick
3. 970±20 μm thick

Table XVI. Comparison of Pervaporation Results of Aqueous EtOH with the Results of Other Investigators

Parameter	78.5 % Aqueous EtOH Through Nafion™ (K$^+$) Membrane		73 % Aqueous EtOH Through Cellulose Acetate Membrane	
	Cabasso et al.# (1985)	This study	Mulders and Smolders (1984)	This study
Temperature (°F)	84.2	81.0	68.0	80.0
Membrane Thickness (μm)	90	127	20	790±20
Selectivity (water / EtOH)	8.4	1.1±0.29	2.1	6.8±1.6
Flux (g/cm^2 h)	0.026	0.011 ±0.0002	0.0920	0.0023 ±0.0002
Effective Permeation Coefficient Q_{eff} (g.cm/cm^2.h.atm)	2.3×10^{-4}	1.3×10^{-4} $\pm 2.1 \times 10^{-5}$	1.8×10^{-4}	3.8×10^{-4} $\pm 1.6 \times 10^{-5}$

- Hollow-fiber membrane module (1120 μm outside diameter)

in their publication. The usefulness of Q_{eff} is obvious from Table XVI where the flux is different for membranes of different thicknesses, but Q_{eff} does not vary considerably. It can be observed from Table XVII that the selectivities can be significantly different for two experiments with the same feed composition and the same membrane. Hence the difference between selectivities as observed in this study and those reported by other investigators is not unusual. In the case of Nafion™ membrane, the difference in selectivities may also be due to the difference in the membrane modules. The agreement between the values of Q_{eff} of this study and those of other investigators becomes better when the uncertainty associated with Q_{eff} is accounted for.

A comparison of the results of i-PrOH / water separation with the results published by other investigators is presented in Table XVIII. The results for 87.7 % i-PrOH feed show that the selectivity is lower than what was observed by Carter et al. (1964). The difference may be due to the small difference in the type of membrane employed. However, it may also be due to the different thicknesses of the membranes. Since the thickness of the membrane used by Carter et al. (1964) is not reported, Q_{eff} could not be calculated for their experiments. However, for the comparison of the experiments performed with Nafion™ membranes, Q_{eff} is again found to be a more useful parameter than flux. Also, the agreement between the values of Q_{eff} of this study and that of Cabasso et al. (1985) becomes better when the uncertainty associated with Q_{eff} is accounted for.

The results of this study show that for the pervaporation of 5.2 % aqueous i-PrOH, Nafion™ membrane is selective for i-PrOH, while Cabasso et al. (1985) report that the membrane is selective for water. From an industrial standpoint, the results of this study are more fruitful because high selectivity is desired for the minor component in the feed. As far as the reason for the difference in

Table XVII. Comparison of Pervaporation Results of One Research Group with the Other

Parameter	60.5 % Benzene/39.5 % Methanol Through Through Polyethylene Membrane	
	Carter et al. (1964)	Binning et al. (1960)
Temperature (°F)	107.6	140
Selectivity (benzene / methanol)	11.9	7.2
Flux (g/cm^2 h)	0.03	0.21

Table XVIII. Comparison of Pervaporation Results of Aqueous I-PrOH With the Results of Other Investigators

Parameter	5.2 % Aqueous i-PrOH Through Nafion™ Membrane		87.8 % Aqueous i-PrOH	
	Cabasso et al.[1] (1985)	This study	Carter[2] et al. (1964)	This study[3]
Temperature (°F)	84.2	85.3	140	88.2
Membrane Thickness (μm)	90	127	unknown	970±20
Selectivity (water / i-PrOH)	36.5	0.22±0.20	15.6	9.2±3.73
Flux (g/cm^2 h)	0.0997	0.008 ±0.0002	0.07	0.0006 ±0.0002
Effective Permeation Coefficient Q_{eff} (g.cm/cm^2.h.atm)	87x10^{-5}	9.1x10^{-5} ±1.5x10^{-5}	--	5.2x10^{-5} ±1.4x10^{-5}

1. Hollow-fiber membrane module (1120 μm outside diameter)
2. Cellophane membrane
3. Cellulose acetate membrane

selectivities is concerned, it may be largely due to the difference in the membrane module. The characteristics of the hollow-fiber membrane module is expected to be similar to capillary module but different from that of the flat-sheet module. It has been illustrated by Hoover and Hwang (1982) that the composition of the liquid flowing through a capillary membrane changes significantly with axial position and so is a function of the length of the capillary membrane. Due to the change in the feed composition, the composition of the permeate (and hence the selectivity) is also expected to change with axial position in a capillary membrane. In this manner, the hollow-fiber membrane can be considered as equivalent to several flat-sheet membrane modules in series.

Results From Pervaporation Models

Mulder and Smolders (1984) developed a pervaporation model which laid strong emphasis on the thermodynamics of the process. They used their model for predicting the equilibrium sorption of the permeants on the first layer of the membrane on the feed side. Their model was based on the Flory-Huggins model for the thermodynamics of polymer solutions. In this study, all the equilibrium sorption calculations are based on Mulder and Smolders model (1984). The computer program for calculating the equilibrium sorption of permeants in the membrane based on Mulder and Smolders (1984) model is given in Appendix B.

Using their model, Mulder and Smolders (1984) also tried to predict the concentration profile of the permeants through the membrane. However, this was not a predictive model because it did not predict the individual fluxes of permeants and the diffusion coefficients. The individual fluxes and diffusion coefficients of permeants were obtained from experiments and used as input parameters to generate the concentration profile of the permeants which was the only output from the model. Mulder and Smolders (1984) defined an "apparent diffusion coefficient" which was calculated from their experimental results and considered as constant throughout the membrane. In fact, the diffusion coefficient varies significantly with concentration and the concentration of permeants decreases towards the permeate side of the membrane. As an alternative approach, Mulder and Smolders (1984) related the diffusion coefficients to the concentration by introducing an empirical proportionality constant called plasticization parameter. This treatment was also insufficient because the relationship between diffusion coefficient and concentration can be highly non-linear.

A comprehensive pervaporation model has been developed in this study by incorporating the ternary diffusivity model of Vrentas et al. (1984) into the continuity equation of the permeants. The development of the model has been described in detail in Chapter IV. The free volume parameters used in this model can be calculated solely from the physical properties of the permeants and the membrane material without need of any diffusivity or permeation data. In this manner, the pervaporation model emerges as a completely predictive model. Furthermore, this model can be used for the generation of the concentration profile of the permeants in the membrane as well as for the prediction of pervaporation parameters. The final form of this model is a set of two coupled second-order ordinary differential equations (ODEs) which are highly nonlinear. The boundary conditions are the concentrations of the permeants on the feed and the permeate side. The solution of the second-order ODEs for the concentration profile additionally requires the knowledge of the derivative of concentration with distance (slope) at the start of the membrane (Riggs, 1988). Since this slope is not known, a shooting method is suitable for solving the ODEs. The equations are solved using the software package Mathcad, which employs the fourth-order Runge-Kutta method (rkfixed) for solution at each point in the membrane.

Since water molecules form three dimensional networks of strong hydrogen bonds, the model developed in this study has been modified by considering a presumed dimer of water instead of a single water molecule. In other words, two different models have been developed in this study for predicting pervaporation behavior. The model that assumes water as a single molecule has been named the rigorous model while the other model which assumes water as a dimer has been named the modified model. It must be noted that the free volume parameters have been calculated separately for each model and some of them are found to be significantly different. The regressed free volume parameters for cellulose acetate, EtOH and water (for both the models) are presented in Table XIX. The free volume parameters of EtOH and water have been regressed from their physical properties by using the Nelder-Mead pattern search method. The computer programs utilizing this method are annexed in Appendix C. The free volume parameters for cellulose acetate have been calculated from its physical properties. Since the Williams-Landel-Ferry (WLF) constants of cellulose acetate are not found in the literature, the so called "standard" WLF constants have been used in the calculations.

Concentration Profile of Permeants:

The concentration profile generated by the rigorous model is compared with that generated by Mulder and Smolders (1984) in Figure 25 while a comparison with the profile generated by the modified model is presented in Figure 26. The main difference is that the models developed in this study generates a concentration profile which is concave downwards while the concentration profile of Mulder and Smolders is concave upwards. The curves

Table XIX. Free Volume Parameters Used in the Pervaporation Models

Parameter	EtOH/Cellulose Acetate	Water/Cellulose[1] Acetate	Water/Cellulose[2] Acetate
D_{0i} (cm^2/s)	0.006332	0.012896	0.006448
K_{i1}/γ ($cm^3/g\ K$)	0.00054213	0.00060644	0.00060644
K_{13}/γ ($cm^3/g\ K$)	0.0002362	0.0002362	0.0002362
$K_{2i}-T_{g_i}$ (K)	-3.517	-2.106	-2.104
$K_{23}-T_{g_3}$ (K)	-260.4	-260.4	-260.4
V_i^* (cm^3/g)	0.987	1.072	1.072
V_3^* (cm^3/g)	0.49	0.49	0.49
ξ_{i3}	0.423	0.18	0.36

1. Rigorous pervaporation model
2. Modified pervaporation model

$i = 1$ (water); $i = 2$ (EtOH)

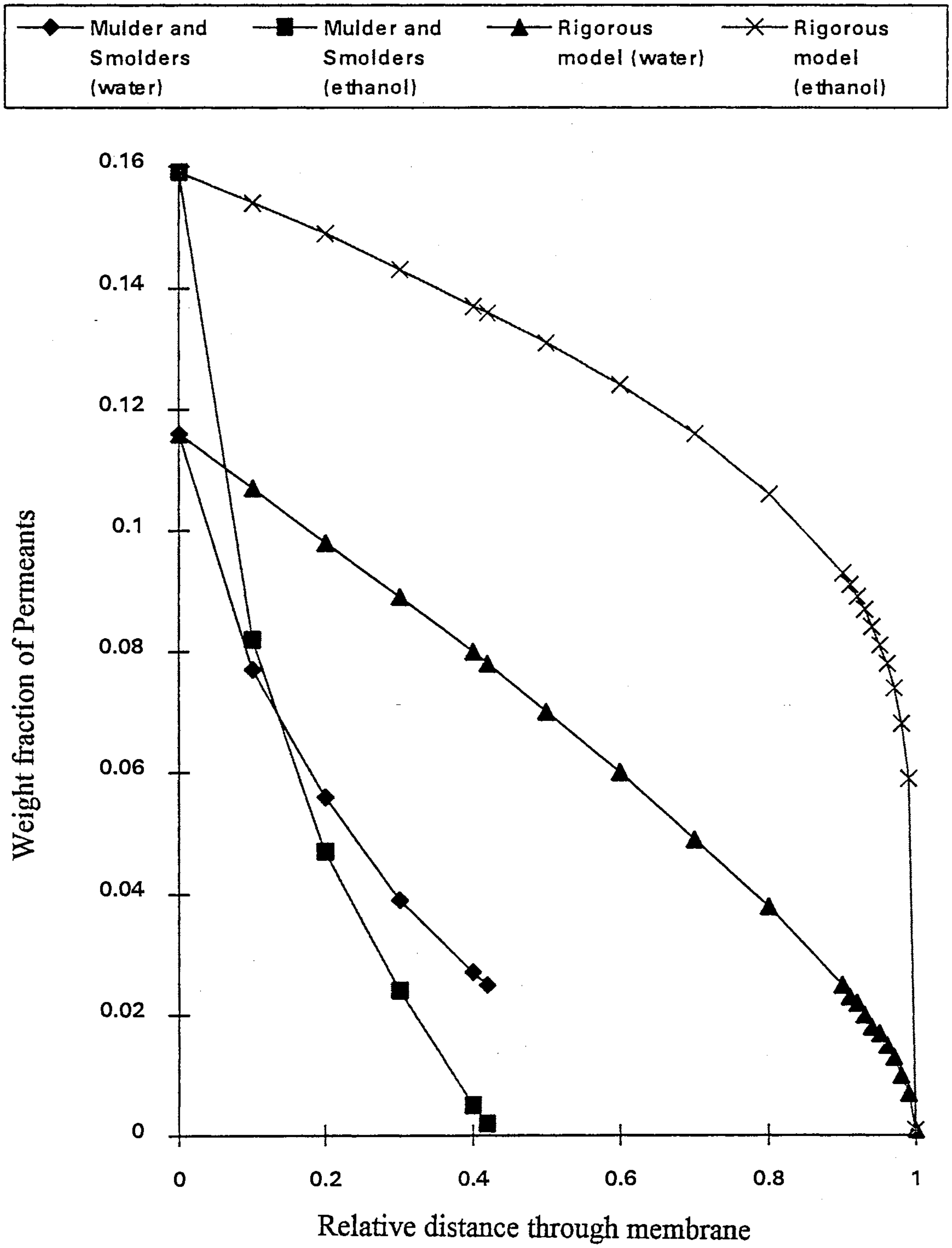


Figure 25. Concentration Profile of Permeants from 73 % Aqueous EtOH Feed Through 20 μm Cellulose Acetate Membrane

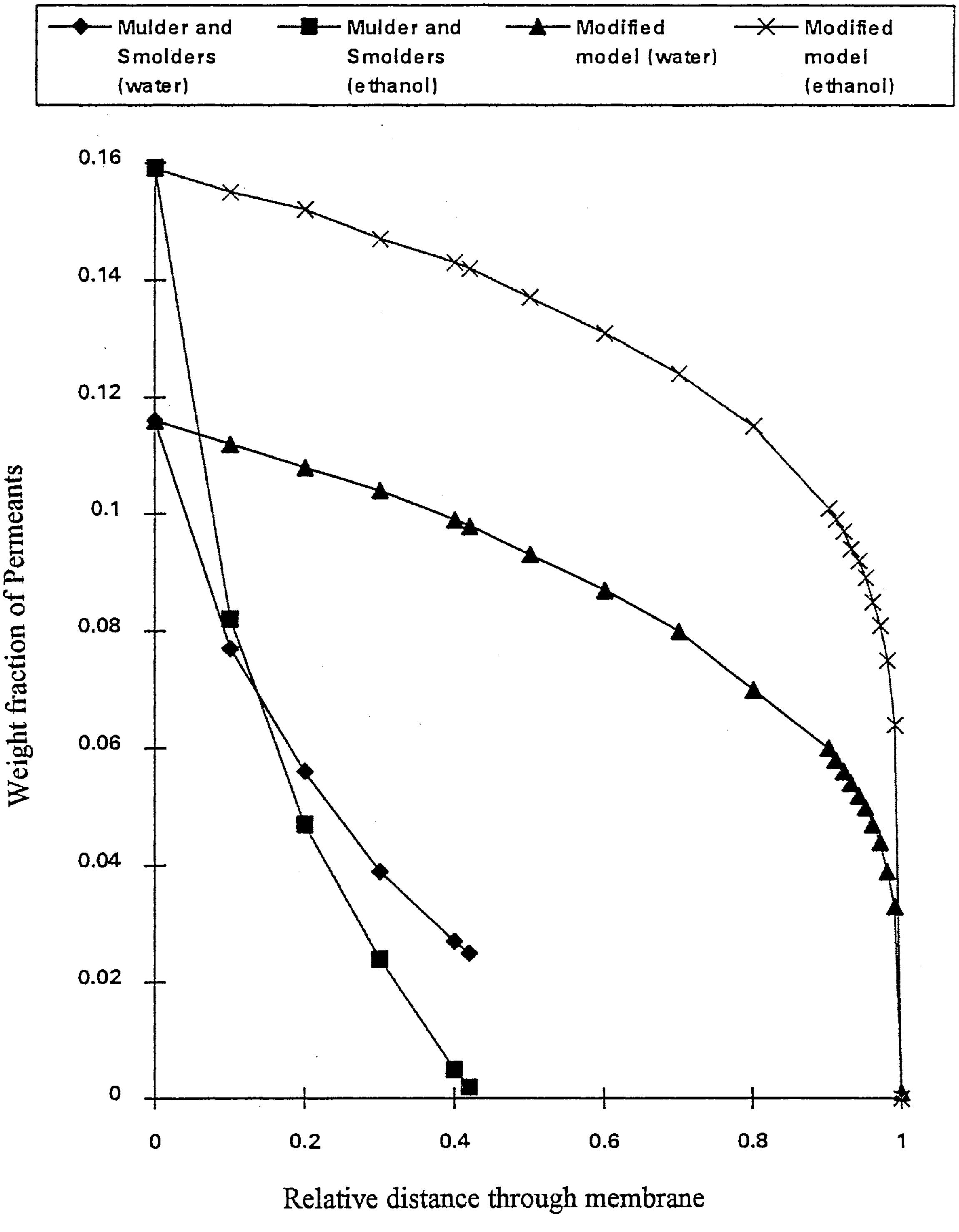


Figure 26. Concentration Profile of Permeants Based on Modified Model for Permeating 73 % Aqueous EtOH Feed Through 20 μm Cellulose Acetate Membrane

generated by Mulder and Smolders (1984) model are reproduced here by digitizing the graph presented in their article in which they have mentioned that the concentration of EtOH falls to negative concentrations somewhere within the membrane, which is obviously not possible. They have generated the concentration profile of water only upto the point where the profile of EtOH falls to zero. A mutual comparison of Figure 25 and Figure 26 shows that the concentration profile of EtOH generated by the modified model is virtually the same as that generated by the rigorous model while the concentration profile of water becomes more concave downwards for the modified model. Figure 26 shows that the curve for EtOH as well as water (this study) changes slope more rapidly in the last 10 % region of the membrane than in the earlier region and falls to zero concentration at the end of the membrane. This behavior indicates that the diffusivity of EtOH and water remains very high in the major part of the membrane and then drops very rapidly as the permeate (vacuum) side is approached. This is in conformity with the idea of two phases in the membrane, the solution phase and the vapor phase, as proposed by Binning et al. (1961) by assuming that the region where the diffusivity is very high represents the solution phase and the region where it drops rapidly represents the vapor phase. A plot of diffusivity versus relative distance through the membrane (Figure 27) also supports the presence of two phases in the membrane.

The diffusivity model of Vrentas et al. (1984) was developed for a ternary system of two solvents in a polymer. For the case of pervaporation the polymer is the membrane and for this study the solvents are water and an alcohol. The diffusivity model of Vrentas et al. (1984) assumes that the diffusion coefficient of a solvent depends not only on its own concentration, but also on the concentration of the polymer and that of the other solvent. Hence, the diffusion coefficient as a function of concentration for one solvent should be plotted for

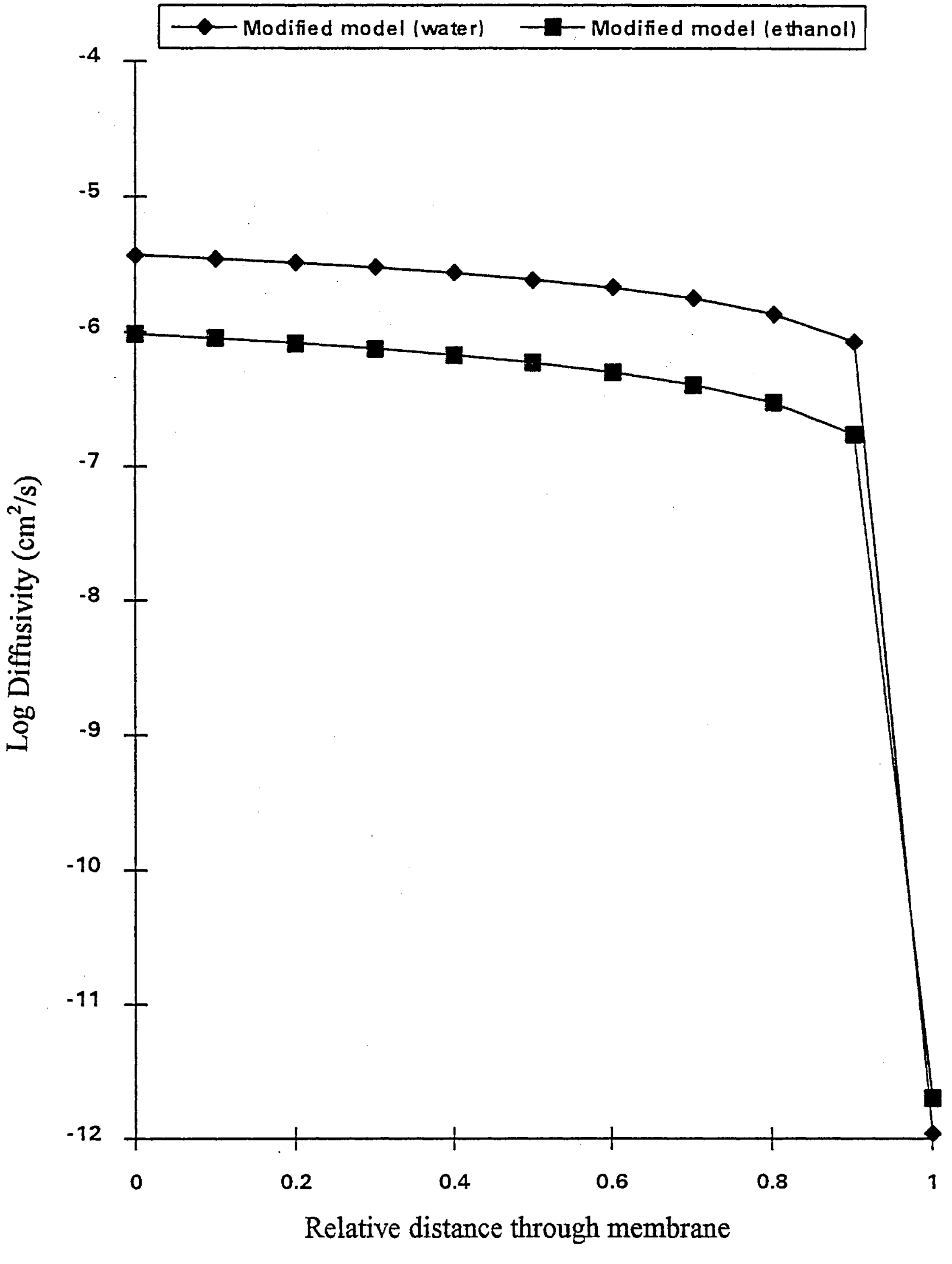


Figure 27. Diffusion Coefficient of Permeants Based on the Pervaporation of 73 % Aqueous EtOH Feed Through 20 μm Cellulose Acetate Membrane

constant values of the other solvent. Such a plot for water is presented in Figure 28 while that of EtOH is presented in Figure 29. These plots should not be taken as the profiles of diffusion coefficients in the membrane because the concentrations of both the solvents as well as the polymer change while traveling through the membrane.

Figure 28 shows that in case of the rigorous model, the diffusion coefficient of water decreases with its concentration keeping the concentration of EtOH as constant at any value between 0.1 and 0.15. This is contrary to what is normally observed for the diffusion coefficients of many other solvents. For the case of 0.05 EtOH concentration, the diffusion coefficient of water shows the usual behavior and increases with its concentration. The modified model shows an increase in the diffusion coefficient of water with its concentration and this is true for all the constant concentrations of EtOH. It is also noticeable for the modified model, that the profiles of the diffusion coefficient of water are almost identical for the various constant concentrations of EtOH.

Figure 29 shows that the diffusion coefficient of EtOH increases with its concentration keeping the concentration of water as constant. This behavior is true in case of the rigorous as well as for the modified model. However, it is noticeable again for the modified model, that the diffusion coefficient profiles of EtOH are almost identical for the various constant concentrations of water.

Predictions from the Models:

A comparison of the predictions from the models developed in this study and the experimental results for the pervaporation of 73 % aqueous EtOH are presented in Table XX. The results show that the rigorous pervaporation model overpredicts the flux of water and hence also the total flux. Since the selectivity can vary from 0 to ∞, depending strongly on the flux of the permeants, the

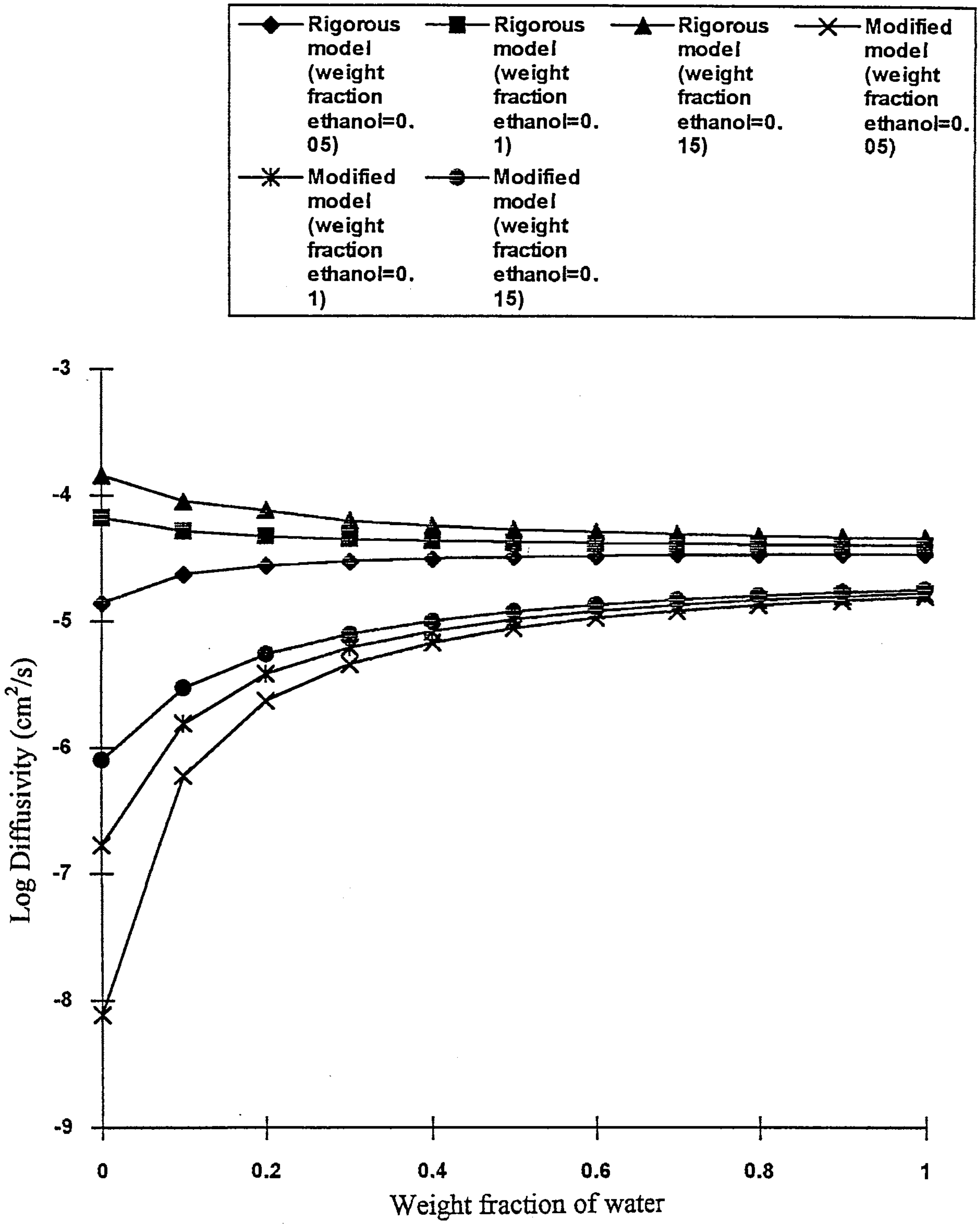


Figure 28. Variation of the Diffusion Coefficient of Water with its Concentration

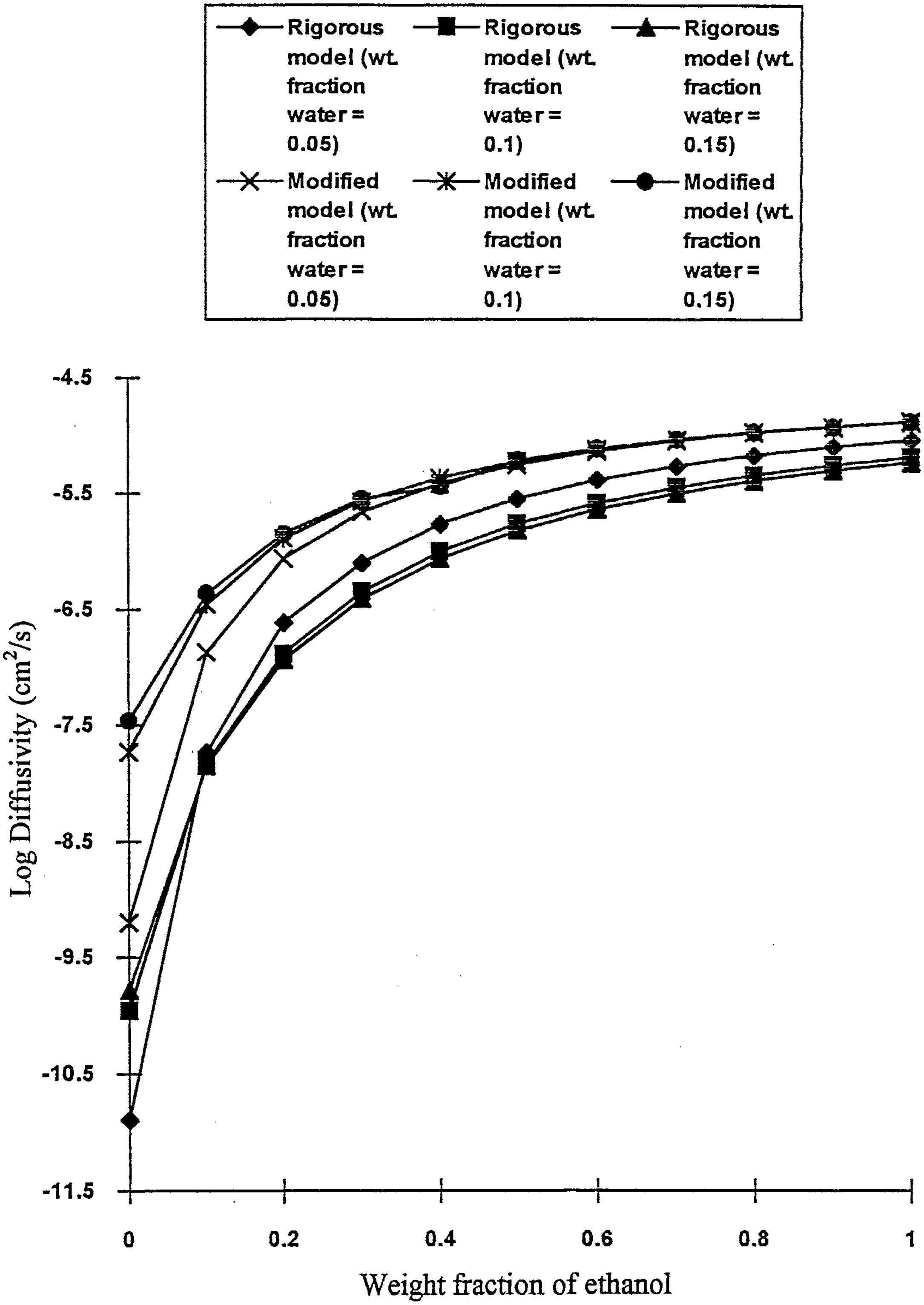


Figure 29. Variation of the Diffusion Coefficient of EtOH with its Concentration

Table XX. Comparison of the Results From the Pervaporation Models with the Experimental Results (This Study) For Pervaporating 73 % Aqueous EtOH Through Cellulose Acetate Membrane

Parameter	This study (experiments)	This study (Rigorous model)	This study (modified model)
Temperature (°F)	80.0	80.0	80.0
Membrane Thickness (μm)	786.0	786.0	786.0
Pressure Gradient (atm)	1.096	1.096	1.096
Total Flux ($g/cm^2.h$)	0.0053 ±0.0002	0.056	0.0138
Flux of Water ($g/cm^2.h$)	0.0038 ±0.0004	0.0557	0.0109
Flux of EtOH ($g/cm^2.h$)	0.0015 ±0.0004	0.0003	0.0029
Selectivity (water / EtOH)	6.8±1.6	5264	10.2
Effective Permeation Coefficient Q_{eff} ($g.cm/cm^2.h.atm$)	$3.8x10^{-4}$ $\pm1.6x10^{-5}$	$4.0x10^{-3}$	$9.9x10^{-4}$

significant overprediction of the flux of water results in the prediction of a considerably large selectivity. The results show that the predictions made by the modified model are more reasonable than those made by the rigorous model. It must also be kept in mind, that the results from the prediction of the model are based solely on the physical properties of the permeants and the membrane. The agreement between the experimental results and the model predictions appears to become better when the uncertainties in the experimental values are accounted for.

A comparison of the predictions from the models developed in this study and the experimental results of Mulder and Smolders (1984) for the pervaporation of 73 % aqueous EtOH is presented in Table XXI. Mulder and Smolders have reported the individual flux of permeants in cm/h and hence fluxes are compared in these units too. The rigorous pervaporation model overpredicts the flux of water and underpredicts the flux of EtOH. As a consequence of this, the selectivity is overpredicted. Mulder and Smolders (1984) have not reported the total flux ($g/cm^2.h$) of the permeants and the species density. Therefore these results (for their experiment) have been estimated using the average species density based on the concentration profiles obtained by the model developed in this study. It has been observed again that the predictions made by the modified model are much more improved and closer to the experimental values than those made by the rigorous model. Furthermore, the agreement between the experimental results and the model predictions appears to become better when the uncertainties in the experimental values are accounted for.

Table XXI. Comparison of the Results From the Pervaporation Models with the Experimental Results of Mulder and Smolders (1984) For Pervaporating 73 % Aqueous EtOH Through Cellulose Acetate Membrane

Parameter	Mulder and Smolders (experi-ments)	This study (Rigorous pervaporation model)	This study (Modified pervaporation model)
Temperature (°F)	68.0	68.0	68.0
Membrane Thickness (μm)	20.0	20.0	20.0
Flux of Water			
(cm/h)	0.033	13.417	0.224
(g/cm^2 h)	0.041	17.404	0.029
Flux of EtOH			
(cm/h)	0.042	0.005	0.060
(g/cm^2 h)	0.052	0.006	0.071
Total Flux ($g/cm^2.h$)	0.092	17.41	0.1
Selectivity (water / EtOH)	2.1	7751	11.2
Effective Permeation Coefficient Q_{eff} ($g.cm/cm^2.h.atm$)	$1.8x10^{-4}$	$3.5x10^{-2}$	$5.6x10^{-4}$

Verification of the Numerical Solution of the Models:

The correctness of the results obtained by the numerical solution of the models using Mathcad has been ascertained by matching the boundary conditions. As mentioned in Chapter IV, the first boundary condition (i.e., the equilibrium concentration at the feed side of the membrane) is used as input to the model. For the numerical solution to be correct, the second boundary condition (i.e., the zero concentrations at the permeate side of the membranes) must be matched by the output from the model. The weight fraction of the permeants in the last 10 % of the membrane has been reproduced from the Mathcad output in Table XXII, which shows that the second boundary condition is indeed matched for the cases run by the rigorous and modified models and at the end of the membrane, the weight fractions of the permeants are so small that they can be considered as zero.

If the flux of each penetrant remains constant throughout the membrane, then this is also an indication of the correct output from the model. The flux of the permeants in various parts of the membrane has been reproduced from the Mathcad output in Table XXIII. The constant flux criterion can be considered a relatively strict one because the parameters, density, diffusivity and concentration profile are all changing through the membrane, yet the flux, which is a function of these parameters, remains constant. However, the profile of flux shows that for the rigorous as well as the modified model, the flux of each permeant does remain constant throughout the membrane in all the cases studied.

In the last approach for checking the validity of the numerical solution, the flux calculated by the pervaporation model is compared with the flux calculated by the Fick's law of diffusion with constant density and diffusivity. Using the boundary conditions of pervaporation, the continuity equation for constant density and diffusivity results in the following equation:

Table XXII. Composition Change of Permeants in the Last Portion of the Membrane

	Rigorous Pervaporation Model				Modified Pervaporation Model			
	Experimental conditions of Mulder and Smolders (1984)		Experimental conditions of this study		Experimental conditions of Mulder and Smolders (1984)		Experimental conditions of this study	
x_R	W_{water}	W_{EtOH}	W_{water}	W_{EtOH}	W_{water}	W_{EtOH}	W_{water}	W_{EtOH}
.90	.0247	.0926	.0233	.0848	.0595	.1008	.0562	.0957
.92	.0217	.0888	.0203	.0807	.0562	.0968	.0528	.0913
.94	.0184	.0841	.017	.0757	.0522	.0918	.0486	.0861
.96	.0147	.0781	.0134	.0693	.0471	.0851	.0434	.0791
.98	.0103	.0684	.009	.0593	.0395	.0745	.0357	.0680
1.0	.0008	.0009	.0004	.0004	.0009	.0000	.0008	.0004

Table XXIII. Flux of Permeants Throughout the Membrane

	Rigorous Pervaporation Model				Modified Pervaporation Model			
	Experimental conditions of Mulder and Smolders (1984)		Experimental conditions of this study		Experimental conditions of Mulder and Smolders (1984)		Experimental conditions of this study	
	Flux (g/cm^2 h)		Flux (g/cm^2 h)		Flux (g/cm^2 h)		Flux (g/cm^2 h)	
x_R	J_{water}	J_{EtOH}	J_{water}	J_{EtOH}	J_{water}	J_{EtOH}	J_{water}	J_{EtOH}
0.00	17.40	0.006	0.056	0.0003	0.294	0.071	0.011	0.003
0.20	17.40	0.006	0.056	0.0003	0.294	0.071	0.011	0.003
0.40	17.40	0.006	0.056	0.0003	0.294	0.071	0.011	0.003
0.60	17.40	0.006	0.056	0.0003	0.294	0.071	0.011	0.003
0.80	17.40	0.006	0.056	0.0003	0.294	0.071	0.011	0.003
0.90	17.40	0.006	0.056	0.0003	0.294	0.071	0.011	0.003
0.99	17.40	0.006	0.056	0.0003	0.294	0.071	0.011	0.003

$$w_i = (1 - x_R)\, w_i^e \tag{5.1}$$

where w_i is the weight fraction of the permeant 'i' at the relative distance x_R through the membrane and w_i^e is the equilibrium concentration at the feed side of the membrane.

The flux of the permeants, using this approach, can be calculated as:

$$j_i = \frac{\rho_i D_i}{L}\, w_i^e \tag{5.2}$$

where L is the thickness of the membrane.

The density and diffusivity used in Equation (5.2) are average values from the Mathcad solution. In Table XXIV, a comparison of the flux obtained by this method with the flux obtained by model calculations show that the values are reasonably close.

Table XXIV. Comparison of the Fluxes of Permeants Calculated by This Model With Those Obtained by Using Fick's Law For Constant Density and Diffusivity

Parameter	Rigorous pervaporation model		Modified pervaporation model	
	Experimental conditions of Mulder and Smolders (1984)	Experimental conditions of this study	Experimental conditions of Mulder and Smolders (1984)	Experimental conditions of this study
Avg. ρ_i (g/cm^3)	1.214	1.216	1.205	1.206
Avg. D_i of water (cm^2/s)	7.639x10^{-5}	9.44x10^{-5}	2.296x10^{-6}	3.146x10^{-6}
Avg. D_i of EtOH (cm^2/s)	3.861x10^{-8}	6.325x10^{-8}	5.665x10^{-7}	8.200x10^{-7}
j_{water} using average values (g/cm^2 h)	19.364	0.610	0.578	0.020
Model Prediction of j_{water} (g/cm^2 h)	17.404	0.556	0.295	0.011
j_{EtOH} using average values (g/cm^2 h)	0.013	0.0006	0.1954	0.0072
Model Prediction of j_{EtOH} (g/cm^2 h)	0.006	0.0003	0.0714	0.0029

CHAPTER VI

CONCLUSIONS

1. The experimental apparatus constructed in this study can be successfully used for pervaporation.
2. The experiments proceeded at near steady state over long periods of time as demonstrated by the permeation profiles.
3. The cellulose acetate membranes prepared in this study and the commercially available Nafion™ (K^+ form) membrane could be successfully used for pervaporation.
4. The SEM photographs of the prepared cellulose acetate membrane show that the membrane was nonporous.
5. The product analysis could be done more conveniently by using gas chromatographic technique than by refractometry.
6. Permeant flux and membrane selectivity are significantly affected by the thickness of the membrane.
7. For a comparison between membranes of different thicknesses, the effective permeation coefficient, Q_{eff} was found to be a more useful pervaporation parameter than flux because it accounts for the flux variation due to thickness.
8. The Nafion™ membrane was found to be ethanol-selective for feeds of low ethanol concentration and water-selective for feeds of high-ethanol concentration. The same behavior of Nafion™ membrane was observed for pervaporation of aqueous isopropanol.

9. The cellulose acetate membrane was found to be water-selective for all the feed concentrations of aqueous ethanol and aqueous isopropanol mixtures.
10. The selectivity of cellulose acetate membrane for water was found to be higher for the feed of higher ethanol concentration than for feed of lower ethanol concentration.
11. The cellulose acetate membrane was found to be almost equally selective towards water for isopropanol-rich and isopropanol-lean feeds but the Q_{eff} was found to be very low for the isopropanol-rich feed.
12. The experimental values of Q_{eff} and selectivity for ethanol/water separations were less than one order of magnitude different from the results of other investigators.
13. For the pervaporation of 87.8 % aqueous isopropanol through cellulose acetate, the value of selectivity was closer to the results of Carter et al. (1964).
14. For the pervaporation of 5.2 % aqueous isopropanol through Nafion membrane, the results from this study are more useful than those of Cabasso et al. (1985) from an industrial point of view.
15. A mutual comparison of the two membranes for ethanol dehydration from 73 % aqueous ethanol feed, appears to favor cellulose acetate membrane because it was found to be water-selective.
16. A mutual comparison of the two membranes for isopropanol dehydration from 87.8 % aqueous isopropanol feed, appears to favor Nafion™ membrane because of its significantly higher Q_{eff} although it shows lower selectivity than that shown by cellulose acetate.
17. The comprehensive pervaporation models developed in this study are completely predictive models.

18. The concentration profile of the permeants, generated by the models developed in this study, confirms the “two-zone” process proposed by Binning et al. (1961) in which two distinct phases (i.e., solution and vapor phase) are assumed to exist in the membrane
19. The predictions made by the Modified model are significantly closer to the experimental values than those made by the Rigorous model.

CHAPTER VII

RECOMMENDATIONS

This chapter is concerned with the directions in which this pervaporation research can be extended. The possibility of any further improvement in the design of the experimental apparatus or any piece of equipment has been covered in this chapter. Recommendations have also been made for applying the pervaporation models to other systems.

This study has covered only the K^+ form of the Nafion membranes™. The other forms of this membrane, i.e., the H^+, Li^+, Na^+ and Cs^+ forms should also be studied for pervaporation of the mixtures covered in this study. In this way, the effects of the different forms of ions in these membranes could be ascertained.

The product analysis has been done much more conveniently with the mixtures prepared by using 200 proof ethanol than those prepared by denatured ethanol. Therefore, for future pervaporation experiments, the mixtures should be prepared from only 200 proof ethanol.

Although some of the cellulose acetate membranes prepared in this study were successfully employed for conducting pervaporation experiments, all the successful membranes were relatively thick and hence the permeation flux through them was low. The thinner membranes prepared in this study were not strong enough to avoid rupture under the influence of vacuum. Therefore attempts should be made in future for preparing thin, but strong cellulose acetate membranes. In particular there is a strong need for finding a suitable plasticizer that could avoid brittleness in the membrane. In this regard a more comprehensive literature search should be made about the methods of membrane preparation and about the plasticizers that have been used in similar materials. Since membrane preparation is, till now, an art rather than science, experiments with any technique might be fruitful.

Considerable research is being done for the preparation of new membranes of better quality and for improving the properties of existing membranes by methods like surface treatment and grafting. Blending of different polymer membranes for improving properties is also being researched by many scientists. Attempts should be made to study the pervaporation behavior of such new polymer-blend membranes of better quality.

Until now, pervaporation has been used mainly for the dehydration of alcohol/water mixtures. The domain of pervaporation research should also be expanded to include organic-organic separations and the removal of trace organics from water and other waste streams for pollution abatement.

The flat-sheet membrane modules do not provide a large area for pervaporation and, therefore, the flux is usually low in such modules. In this study, the gaps between sample collections were at least 3 hours and to check the steady state, the total duration of experiments was several hours. Therefore, the flat-sheet membrane module should be replaced by a membrane module offering larger area for pervaporation. Spiral-wound membrane modules are known to provide a very large area per unit volume and are readily available in market. Detailed information is provided for a commercially available spiral-wound membrane module in Table XXI. The same experiments conducted in this study using flat-sheet membrane should be repeated with the spiral-wound membrane so that a comparison regarding the two systems could be made.

Table XXI Detailed Information for Buying a Spiral-Wound Membrane Module from Ionpure Chemical Company

No.	Part	Size	Part #	Cost ($)
1.	Cellulose acetate membrane (CARO)	3.5"x25"	CDR0025S1	491.05
2.	Bulb (for housing membrane)		12033	188.91
3.	Head		12034	81.90
4.	Adapter		13526	21.84
				783.7

Contact Person: Mr. Scott (Technical Service)
Ph: (800)-783-7873
(508)-934-9349

The pervaporation models developed in this study should be applied to predict the experiments performed in this study with Nafion™ (K^+ form) membrane. This can be a challenging task because Nafion™ (K^+ form) is an ionomer membrane with unusual properties and the information regarding its physical properties is also scarcely available.

Although random errors always exist in any measurement, systematic errors can be minimized by improvements in the design of an equipment. For example, a possible systematic error is due to the inability of removing all the permeate from the cold traps because of the adhesive forces between the permeate and the glass walls of the cold traps. This systematic error can be minimized by using some sort of a permeate-repellent material on the inside surface of the glass cold traps. The accomplishment of this task requires a careful study of the technical and economical feasibility of using a permeate-repellent material. Since a study of this nature has not been covered in this study, it is recommended as a future endeavor.

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APPENDIX A

ERROR ANALYSIS

The objective of this analysis is to estimate the error in a calculated quantity which has propagated from the measured quantities due to their uncertainties. The desired quantity is expressed as a function of the measured variables. The uncertainties in each measured variable is expressed in terms of its standard deviation, σ. If y is the desired quantity, then the uncertainty in y due to the measured variables $x_1, x_2, \ldots x_n$ is given by:

$$\sigma^2_y = \sum_{x=i}^{n}[(\partial y/\partial x_i)\ \sigma^2_{x_i}] \qquad \text{(A1)}$$

where $\sigma^2_{x_i}$ represents the uncertainties in the measured variables $x_1, x_2, \ldots x_n$.

Error Propagation in Permeate Collection:

The permeate samples were collected in sampling bottles and the weight of each sample was calculated by the subtracting the weight of the empty bottle from the weight of the bottle containing the sample. If S is the weight of a sample, SB is the weight of the sample plus sampling bottle, and B is the weight of the bottle, then:

$$S = SB - S \qquad \text{(A2)}$$

Since the uncertainty in SB is the same as the uncertainty in B, the uncertainty in the weight of a sample can, be represented by:

$$\sigma^2_S = \sigma^2_{SB} + \sigma^2_B = 2\sigma^2_B \qquad (A3)$$

Using the weights of the samples collected at various times, the cumulative weight of the permeate collected (data point) is calculated by adding the weights of all the samples collected until that time. Hence, the nth data point involves n measurements of SB and n measurements of S. Therefore, the uncertainty in the nth data point can be calculated by:

$$\sigma^2_{Wn} = 2n^2\sigma^2_B \qquad (A4)$$

or

$$\sigma_{Wn} = \pm 1.44n\sigma_B \qquad (A5)$$

In this study, the uncertainty in measuring weights (σ_{SB} and σ_B) is taken as 0.1g.

Error Propagation in Refractive Index:

The plots of refractive index as a function of weight % alcohol in aqueous alcohol mixtures (Figures 9, 11 and 13) were prepared by using samples prepared in sampling bottles. Solutions of 20 gram total weight were prepared in the bottles by adding together appropriate weights of alcohol and water. The uncertainty in the weights of alcohol and water was due to the weight of a drop of any of these components which could be added in excess. It was assumed that the weight of that excess drop was 1 gram. Therefore, the refractive index was influenced by the precision in measuring the weights of alcohol and of water.

Another factor influencing the refractive index was the temperature which could deviate 2 °C from the set-point of 20 °C. The uncertainty in refractive index can, therefore, be written as:

$$\sigma^2_{RI} = (\partial RI/\partial w_a)^2\, \sigma^2_{wa} + (\partial RI/\partial T)^2\, \sigma^2_T \qquad \text{(A6)}$$

where w_a represents the weight percent of alcohol in the mixture. The weight percent of alcohol in the mixture can be related to the weights of the individual components as:

$$w_a = \frac{W_a}{W_a + W_b} \times 100 \qquad \text{(A7)}$$

where W_a is the weight of alcohol and W_b is the weight of water used in making the mixture.

Therefore, uncertainty in w_a can be written as:

$$\sigma^2_{wa} = (\partial w_a/\partial W_a)^2\, \sigma^2_{Wa} + (\partial w_a/\partial W_b)^2\, \sigma^2_{W_b} \qquad \text{(A8)}$$

where σ^2_{Wa} and σ^2_{Wb} are the uncertainties in the weights of alcohol and water respectively and can be quantified as the weight of a drop of these components (taken as 1gram in this study) plus the uncertainty in each weight measurement as given by equation (A3) in the previous section. The partial derivative, $\partial RI/\partial w_a$ can be calculated from a fourth order polynomial relating refractive index and the weight percent alcohol.

Using equation (A6), (A7) and (A8), the final form for the uncertainty in refractive index can be written as:

$$\sigma^2_{RI} = 10^4\,(\partial RI/\partial w_a)^2 \left[\frac{W_b^{\,2}}{(W_a+W_b)^4}\sigma^2_{Wa} + \frac{W_a^{\,2}}{(W_a+W_b)^4}\sigma^2_{Wb}\right] + (\partial RI/\partial T)^2\,\sigma^2_T \qquad \text{(A9)}$$

The value of $\partial RI/\partial T$ is 0.000404 and that of σ_T is 2 °C(Kirk-Othmer Encyclopedia of Chemical Technology, 1984). Since the samples are prepared independently, the error bars are not influenced by the number of data points.

Error Propagation in Gas Chromatography:

As opposed to refractive index, the temperature affects in gas chromatography (GC) are smaller and the uncertainty in the weight percent calculated by GC is assumed to be only due to the uncertainties in sample preparation as discussed earlier in the previous section. Therefore, the uncertainty in the results of GC can be written as:

$$\sigma^2_{w_{GC}} = (\partial w_{GC}/\partial w_a)^2\,\sigma^2_{wa} \qquad \text{(A10)}$$

where w_{GC} is the weight percent of alcohol obtained by the GC. Using equations (A7), (A8) and (A10), the final form of the equation for the uncertainty in GC results is:

$$\sigma^2_{w_{GC}} = 10^4\,(\partial w_{GC}/\partial w_a)^2 \left[\frac{W_b^{\,2}}{(W_a+W_b)^4}\sigma^2_{Wa} + \frac{W_a^{\,2}}{(W_a+W_b)^4}\sigma^2_{Wb}\right] \qquad \text{(A11)}$$

The partial derivative, $\partial w_{GC}/\partial w_a$ can be calculated from a straight line fit relating weight percent alcohol obtained by GC and the weight percent alcohol as prepared in the sampling bottles. Since the samples are prepared independently, the error bars are not influenced by the number of data points.

Error Propagation in Permeate Flux:

The permeate flux is calculated by dividing the amount of permeate collected in a unit time by the area of the membrane used by pervaporation:

$$j_i = \frac{W_i}{At} = \frac{4W_i}{\pi t D^2} \qquad \text{(A12)}$$

The uncertainty in flux can be written as:

$$\sigma^2 j_i = \left(\frac{4}{\pi t D^2}\right)^2 \sigma^2 W_i + \left(\frac{4W_i}{\pi t^2 D^2}\right)^2 \sigma^2 W_i + \left(\frac{8W_i}{\pi t D^3}\right)^2 \sigma^2 W_i \qquad \text{(A13)}$$

Error Propagation in Selectivity:

Selectivity of the membrane for component i is defined as:

$$\alpha_{i/j} = \frac{y_i/y_j}{x_i/x_j} = \frac{y_i x_j}{x_i y_j} \qquad \text{(A14)}$$

where y_i, y_j are the weight fractions of components i and j, respectively, in the permeate and x_i, x_j are their weight fractions in the feed. The uncertainty in selectivity propagates due to the uncertainties in y_i, y_j, x_i, and x_j and can, therefore, be represented by:

$$\sigma^2_\alpha = \left(\frac{x_j}{x_i y_j}\right)^2 \sigma^2_{y_i} + \left(\frac{y_i x_j}{x_i y_j^2}\right)^2 \sigma^2_{y_j} + \left(\frac{y_i x_j}{x_i^2 y_j}\right)^2 \sigma^2_{x_i} + \left(\frac{y_i}{x_i y_j}\right)^2 \sigma^2_{y_j} \qquad \text{(A15)}$$

Error Propagation in Effective Permeation Coefficient:

The effective permeation coefficient is defined as:

$$Q_{eff} = \frac{jl}{\Delta P} \qquad \text{(A16)}$$

where j is the total flux, l is the thickness of the membrane, and ΔP is the pressure drop across the membrane. The uncertainty in Q_{eff} can, therefore, be represented by:

$$\sigma^2_{Q_{eff}} = \left(\frac{l}{\Delta P}\right)^2 \sigma^2_{j_i} + \left(\frac{j}{\Delta P}\right)^2 \sigma^2_l + \left(\frac{jl}{(\Delta P)^2}\right)^2 \sigma^2_{\Delta P} \qquad \text{(A17)}$$

Error Propagation in Component Flux:

The component flux can be calculated by:

$$j_i = w_i j/100 \qquad \text{(A18)}$$

where j is the total flux and w_i is the weight percent of the component i. The uncertainty in the component flux can, therefore, be estimated by:

$$\sigma^2_{j_i} = 10^{-4}[w_i^2 \sigma^2_{j_i} + j^2 \sigma^2_{w_i}] \qquad \text{(A19)}$$

Sample Calculation of Overall Uncertainty:

This section shows an example of how an error in a measurable quantity, x, is propagated as an error in the dependent quatity, y. For instance, the case of the cumulative weight of permeate collected (y) as a function of the weight of the sample collected (x) at a particular time, t during pervaporation of 21.5 % aqueous ethanol through Nafion is presented below:

t	x	y	σ_y	σ_y /y
6	7.96	7.96	±0.1414	±0.0178
12	7.28	15.24	±0.2828	±0.0186
18	7.12	22.36	±0.4243	±0.0190
24	7.10	29.46	±0.5657	±0.0192
32	7.92	37.38	±0.7071	±0.0189
37	5.47	42.85	±0.8485	±0.0198
43	7.90	50.75	±0.9899	±0.0195

The above table shows that the uncertainty is higher for the later data points than the initial data points. However, the relative error does not change significantly.

APPENDIX B

PROGRAM FOR CALCULATING THE EQUILIBRIUM SORPTION OF PERMEANTS IN A POLYMER MEMBRANE

```
$debug
C*********************************  ABSTRACT  *********************************
C
C       THIS PROGRAM CALCULATES THE COMPOSITION OF THE PENETRANTS IN THAT
C       LAYER OF THE MEMBRANE WHICH IS JUST ADJACENT TO THE LIQUID FEED.  AT
C       EQUILIBRIUM, THE CHEMICAL POTENTIAL OF THE PENETRANTS IN THE LIQUID
C       FEED IS EQUAL TO THEIR CHEMICAL POTENTIAL IN THE FIRST LAYER OF THE
C       MEMBRANE.  THE CHEMICAL POTENTIAL AT BOTH THESE POSITIONS IS DERIVED
C       BY USING THE FLORY-HUGGINS THERMODYNAMICS.  FOR A BINARY MIXTURE
C       OF ETHANOL AND WATER,  TWO NON-LINEAR EQUATIONS IN TWO UNKNOWNS
C       (VOLUME FRACTIONS) ARE OBTAINED.  THIS SYSTEM OF EQUATIONS IS SOLVED
C       USING THE NEWTON METHOD.
C
C       NOTE: THE ORIGINAL IDEA OF THIS PROGRAM IS FROM RIGGS (1988)
C
C               CODED BY:               NADIR KAMAL
C                                 OKLAHOMA STATE UNIVERSITY
C                                          6 - 18 - 93
C
C************************************* CONVENTION *****************************
C       1 - SOLVENT (FASTER PERMEANT)
C       2 - SOLUTE (SLOWER PERMEANT).  ALSO KNOWN AS NON-
C           SOLVENT.
C       3 - POLYMER
C******************************* NOMENCLATURE ******************************
C
C ERLIM-        ERROR CRITERIA
C FX(I)-        THE VALUE OF THE NONLINEAR EQUATIONS WHERE I
C               INDICATES THE NUMBER OF EQUATION
C N-            THE NUMBER OF NONLINEAR EQUATIONS
C X(I)-         THE INDEPENDENT VARIABLES OF THE PROBLEM  I=1
C               (CONC OF A), I=2 (CONC OF B), AND I=3 (CONC OF C).
C
C****************************  INPUT DESCRIPTION  ****************************
C
C       THE INITIAL GUESSES ARE SPECIFIED IN THE MAIN PROGRAM AS WELL AS THE
C       ERROR CRITERIA AND THE NUMBER OF NONLINEAR EQUATIONS.  THE
C       FUNCTIONS ARE SPECIFIED IN SUBROUTINE FUNC AND THE PARTIAL
C       DERIVATIVES OF THE FUNCTION WITH RESPECT TO THE INDEPENDENT
C       VARIABLES ARE SPECIFIED IN SUBROUTINE DER.
C
C*****************************************************************************

        DIMENSION X(10),FX(10)
        COMMON /ONE/V2,R12,R13,R23,R21,CHI13,CHI23
C
C MAKE INITIAL GUESSES
```

```
C
            X(1)=.1
            X(2)=.2
            X(3)=.7
            N = 3
            ERLIM=1.E-3
C
C     INTERACTIVELY ENTER THE VALUES OF MOLAR VOLUMES
C
      WRITE(*,*) 'ENTER THE VOLUME FRACTION OF SOLUTE, V2'
      READ(*,*) V2
      WRITE(*,*) 'IF MOLAR VOLUMES ARE TO BE USED AS INPUT, '
      WRITE(*,*) 'ENTER 1'
      WRITE(*,*) 'IF RATIOS, V1/V2, ETC., ARE AVAILABLE, ENTER 0'
      READ(*,*) FLAG
      IF (FLAG .NE. 1) GO TO 10
      WRITE(*,*) 'ENTER THE MOLAR VOLUME OF SOLVENT, VBAR1'
      READ(*,*) VBAR1
      WRITE(*,*) 'ENTER THE MOLAR VOLUME OF SOLUTE, VBAR2'
      READ(*,*) VBAR2
      WRITE(*,*) 'ENTER THE MOLAR VOLUME OF POLYMER, VBAR3'
      READ(*,*) VBAR3
      R12 = VBAR1/VBAR2
      R13 = VBAR1/VBAR3
      R23 = VBAR2/VBAR3

      GO TO 11
 10   WRITE(*,*) 'ENTER THE MOLAR VOLUME RATIO, V1/V2'
      READ(*,*) R12
      WRITE(*,*) 'ENTER THE MOLAR VOLUME RATIO, V1/V3'
      READ(*,*) R13
      WRITE(*,*) 'ENTER THE MOLAR VOLUME RATIO, V2/V3'
      READ(*,*) R23
 11   R21 = 1./R12
      WRITE(*,*) 'ENTER THE SOLVENT-POLYMER INTERACTION'
      WRITE(*,*) 'PARAMETER, X13'
      READ(*,*) CHI13
      WRITE(*,*)'ENTER THE SLUTE-POLYMER INTERACTION'
      WRITE(*,*) 'PARAMETER, X23'
      READ(*,*) CHI23
C
C     PRINT OUT THE INPUT PARAMETERS
C

      WRITE(8,101) CHI13, CHI23
      WRITE(8,103) R12, R13, R23
      V1 = 1. - V2
      WRITE(8,110) V1,V2
C
C  CALL NEWTON METHOD
C
      CALL NEWTN(N,X,FX,ERLIM)
C
C  PRINT OUT RESULTS
```

```
C
      DO 6 I=1,N
  6   WRITE(8,7)I,X(I)
C
C  FORMAT STATEMENTS
C
101   FORMAT(5X,'INTERACTION PARAMETERS: CHI13=',F7.5,3X,'CHI23=',F7.5)
103   FORMAT(5X,'RATIOS: R12=',F7.5,3X,'R13=',F7.5,3X,'R23=',F7.5)
110   FORMAT(5X,'THE FEED CONCENTRATION (VOL %) IS:',/,
  &       5X, 'V1=',F7.5,3X,'V2=',F7.5)
  7   FORMAT( 3H I=,I3,5X,3H X=,E14.7)
      STOP
      END
C
C********************************* ABSTRACT *********************************
C
C     THIS SUBROUTINE CALCULATES THE PARTIAL DERIVATIVES THE THE
C     FUNCTIONS WITH RESPECT TO THE INDEPENDENT VARIABLES.  A(I,J)
C     REPRESENTS THE PARTIAL OF THE ITH FUNCTION WITH RESPECT TO THE JTH
C     VARIABLE.
C
C**************************** INPUT DESCRIPTION ******************************
C
C     THE VALUE OF N AND X(I) ARE SUPPLIED TO DER BY
C     SUBROUTINE NEWTON THROUGH THE CALLING STATEMENT.
C
C     NOTE: THE ORIGINAL IDEA OF THIS PROGRAM IS FROM RIGGS
C           (1988)
C
C*****************************************************************************
C
C
      SUBROUTINE DER(N,X,A)
      DIMENSION A(10,10),X(10),FXB(10),FXD(10)
      DELTA=.01
C  CALCULATE FUNCTION VALUE AT X(I)
      CALL FUNC(N,X,FXB)
C  CALCULATE NUMERICAL DERIVATIVES USING FINITE
C  DIFFERENCE  EQUATIONS
      DO 1 I=1,N
         X(I)=X(I)*(1.+DELTA)
         CALL FUNC(N,X,FXD)
         X(I)=X(I)/(1.+DELTA)
         DO 2 J=1,N
  2      A(J,I)=(FXD(J)-FXB(J))/X(I)/DELTA
  1   CONTINUE
      RETURN
      END

C
C**************************** ABSTRACT **********************
C
C     THIS SUBROUTINE CALCULATES THE VALUES OF EACH NONLINEAR EQUATION
C     GIVEN THE VALUE OF X(I) AND N.  THESE VALUES ARE SUPPLIED TO THIS
```

```
C       SUBROUTINE WHEN IT IS CALLED BY NEWTN
C
C       NOTE: THE ORIGINAL IDEA OF THIS PROGRAM IS FROM RIGGS (1988)
C
C*****************************************************************************
C
        SUBROUTINE FUNC(N,X,FX)
        DIMENSION X(10),FX(10)
        COMMON /ONE/V2,R12,R13,R23,R21,CHI13,CHI23
        DO 10 I = 1,N
                IF(X(I) .LT. 0.0) X(I) = 1.E-6
 10     CONTINUE
        U2 = X(2)/(X(1) + X(2))
C
C       CHI12 POLYNOMIAL FOR ETOH/WATER SYSTEM IS PROVIDED
C       BY MULDER AND SMOLDER (1984).  CALL IT FROM THE
C       SUBROUTINE ETWATER
C
        CALL ETWATER(A,B,C,D,E)
        CHI12 =A + B * U2 + C * U2**2. + D * U2**3. + E * U2**4.
        E1 = 1. - X(1) - X(2) * R12 - X(3) * R13
  &       + CHI12 * ( X(2)**2 + X(2) * X(3) - V2**2)
  &     + CHI13 * (X(2) * X(3) + X(3)**2)
  &       - CHI23 * R12 * X(2) * X(3)
  &       - V2 * (1. - R12)
        E2 = 1. - X(2) - X(1) * R21 - X(3) * R23
  &       + CHI12 * R21 * ( X(1)**2 + X(1) * X(3) - (1. - V2)**2)
  &     + CHI23 * (X(1) * X(3) + X(3)**2)
  &       - CHI13 * R21 * X(1) * X(3)
  &       - (1. - V2) * (1. - R21)
        FX(1) = X(1) * EXP(E1) /(1. - V2) - 1.
        FX(2) = X(2) * EXP(E2) /V2 - 1.
        FX(3)= X(1) + X(2) + X(3) - 1.
        RETURN
        END
C
C********************************** ABSTRACT **********************************
C
C       THIS SUBROUTINE EMPLOYES NEWTON'S METHOD IN ORDER TO SOLVE A SET OF
C       N NONLINEAR EQUATIONS CONTAINING N UNKNOWNS.  THIS SUBROUTINE IS
C       CALLED BY THE MAIN PROGRAM AND IS SUPPLIED THE VALUES OF THE INITIAL
C       GUESS FOR X(I)'S AS WELL AS THE VALUE OF N.  THIS SUBROUTINE USES THE
C       VALUES OF THE FUNCTION FROM FUNC AND THE VALUES OF THE PARTIAL
C       DERIVATIVES OFTHE FUNCTION IN ORDER TO DETERMINE THE SOLUTION. THIS
C       METHOD USES THE LIBRARY ROUTINE LINPAC TO SOLVE THE SYSTEM OF
C       LINEAR EQUATION USED BY NEWTON'S METHOD.
C
C       NOTE: THE ORIGINAL IDEA OF THIS PROGRAM IS FROM RIGGS (1988)
C*********************************************************************************
C
C
        SUBROUTINE NEWTN(N,X,FX,ERLIM)
        DIMENSION A(10,10),X(10),FX(10),B(10),RAT(10)
C
```

```
C***************************************************************
C  NOTE THAT AA,BB,XX,IPVT 'MUST BE' DIMENSIONED BY N
C***************************************************************
C
      DOUBLE PRECISION AA(3,3),BB(3),XX(3),IPVT(3)
C
C     AVOID ENDLESS RUNNING OF THIS SUBROUTINE
C
      COUNT = 0.0
  1   CONTINUE
      COUNT = COUNT + 1.0
      IF(COUNT .EQ. 25.0) STOP
C
      ITEST=0
C
C  MAKE FUNCTION EVALUATIONS
C
      CALL FUNC(N,X,FX)
      DO 3 I=1,N
  3   B(I)=-FX(I)
C
C  EVALUATE JACOBIAN MATRIX
C
      CALL DER(N,X,A)
      DO 32 I=1,N
      DO 32 J=1,N
 32   AA(I,J)=A(I,J)
      DO 35 I=1,N
 35   BB(I)=B(I)
C
C  CALL LINEAR EQUATION SOLVER
C
      CALL LINPAC(N,AA,BB,XX,IPVT)
C
C  MAKE AN IMPROVED VALUE FOR X(I)
C
      DO 5 I=1,N
            RAT(I)=XX(I)/X(I)
  5   X(I)=X(I)+XX(I)
C
C  CHECK FOR CONVERGENCE
C
      DO 125 I=1,N
125   IF(ABS(RAT(I)).GT.ERLIM)ITEST=ITEST+1
      WRITE(8,10)(X(I),FX(I),I=1,N)
 10   FORMAT( 3H X=,E14.7,5X,3H F=,E14.7)
      WRITE(8,11)
 11   FORMAT(//)
      IF(ITEST.NE.0)GO TO 1
      RETURN
      END

C
C     THIS SUBROUTINE PROVIDES THE SOLVENT-SOLUTE BINARY
```

```
C       INTERACTION PARAMETER, X12, AS A POLYNOMIAL IN
C       CONCENTRATION.  X12 FOR WATER/ETHANOL MIXTURE IS
C       PROVIDED BY MULDER AND SMOLDERS (1984)
C
        SUBROUTINE ETWATER(A,B,C,D,E)
        A = 0.98
        B = -1.35
        C = 4.15
        D = -3.31
        E = 0.89
        RETURN
        END
```

APPENDIX C1

PROGRAM FOR CALCULATING THE SOLVENT FREE VOLUME PARAMETERS FOR WATER

```
$debug
C       FILE: H2OGEN.FOR
C***************************** ABSTRACT *******************************
C
C       THIS PROGRAM DETERMINES THE SOLVENT PARAMETERS, Do, K11/GAMA AND
C       (K21 - Tg1) FOR WATER USING NON-LINEAR REGRESSION BY THE NELDER-
C       MEAD PATTERN SEARCH OPTIMIZATION METHOD.
C
C           .       CODED BY:      NADIR KAMAL
C                           OKLAHOMA STATE UNIVERSITY
C                                   5 - 08 - 94
C
C**************************** NOMENCLATURE ****************************
C
C  C(1)  -      THE CONSTANT WHICH RELATES TO Do
C  C(2)  -      THE CONSTANT WHICH RELATES TO k11/GAMA
C  C(3)  -      THE CONSTANT (K21 - Tg1)
C  DEGREE -     THE DEGREE OF ASSOCIATION OF WATER MOLECULES
C  H     -      THE INITIAL SIMPLEX SIZE
C  N     -      THE NUMBER OF DATA POINTS USED
C  P(I)  -      THE PARAMETER, .124E-16 * Vc**(2/3.) *R*T/(VIS*WM*DEGREE*V1)
C  T(I) -       THE ITH TEMPERATURE (K)
C  VIS(I) -     VISCOSITY (POISE)
C  V1STAR -     CRITICAL SPECIFIC HOLE FREE VOLUME (cm3/g)
C  RHOC  -      CRITICAL DENSITY (g/cm3)
C  TC    -      CRITICAL TEMPERATURE (K)
C  SV(J) -      SPECIFIC VOLUME (cm3/g)
C  WM -         MOLECULAR WEIGHT
C  VC -         CRITICAL MOLAR VOLUME (cm3/mol)
C  R -          GAS CONSTANT (g.cm2/gmol.s2.K)
C
C********************************************************************
C
C
        REAL C(10)
        COMMON /DATA/T(200),P(200),N
        DIMENSION VIS(200), SV(200), D(10)
        N = 94

C
C  SET THE INITIAL SIMPLEX SIZE AND SELECT PRINT OPTION
C
        H=.5
        IPRINT=0
C
C  GENERATE THE TEMPERATURE (K)
C
```

```
        T(1) = 273.15
        T(2) = 276.73
        T(3) = 280.13
        T(4) = 283.00
        DO 10 I = 4, N-1
                T(I+1) = T(I) + 1.0
 10     CONTINUE

C
C  NOW GENERATE THE CORRESPONDING LIQUID VISCOSITIES IN mN.s/m2 USING
C  THE EMPIRICAL EQUATION BY SINNOTT (1991).   THE UNITS ARE CONVERTED
C  TO g/(cm.s) (POISE) BY MULTIPLICATION WITH 0.01
C
        VISA = 658.25
        VISB = 283.16
        DO 20 I = 1, N
                VISLOG = VISA * (1.0 / T(I) - 1.0 / VISB)
                VIS(I) = 10.**VISLOG
                VIS(I) = VIS(I) * 0.01
 20     CONTINUE
C
C       INPUT THE SPECIFIC VOLUMES FOR THE FIRST THREE TEMPERATURES AS
C       PROVIDED BY SADIK KAKAC IN THE BOOK, BOILERS, EVAPORATORS, AND
C       CONDENSORS, PUBLISHED BY JOHN WILEY & SONS, INC., IN NEW YORK
C       IN 1991.  THE UNUSUAL BEHAVIOR OF WATER IS THAT WHEN HEATED FROM
C       273.15 K, ITS SPECIFIC VOLUME FIRST DECREASES SLIGHTLY AND THEN
C       INCREASES CONTINUOUSLY.
C
        SV(1) = 1.0002
        SV(2) = 1.0001
        SV(3) = 1.0001
C
C       NOW GENERATE THE CORRESPONDING SPECIFIC VOLUMES IN CM3/G FOR THE
C       REST OF THE TEMPERATUES STARTING FROM 283 K AND ENDING AT 373 K.
C       THE SPECIFIC VOLUME OF WATER CAN BE CALCULATED BY THE EMPIRICAL
C       EQUATION BY W.C. RENOLDS (1979).  FOR REFERENCE, SEE PAGES
C       126 AND 154 OF HIS BOOK, "THERMODYNAMIC PROPERTIES IN SI",
C       PUBLISHED BY THE DEPARTMENT OF MECHANICAL ENGINEERING, STANFORD
C       UNIVERSITY, STANFORD, CA 94305
C
        RHOC = 0.317
        TC   = 647.286
        D(1) =    3.6711257
        D(2) =  -28.512396
        D(3) =  222.6524
        D(4) = -882.43852
        D(5) =  2000.2765
        D(6) = -2612.2557
        D(7) =  1829.7674
        D(8) =  -533.5052
        DO 40 J = 4, N
                COEFF = 1.0
                DO 30 I = 1, 8
                        AI = I
```

```
                    COEFF = COEFF + D(I) * (1 - T(J)/TC)**(AI/3.)
 30             CONTINUE
                RHO1 = RHOC * COEFF
                SV(J) = 1.0/RHO1
 40     CONTINUE
        OPEN(6,FILE='H2OGEN.CON',STATUS='UNKNOWN')
        WRITE(6,*) '  THE INPUT DATA FOR WATER ARE: '
        WRITE(6,*) '   T (K)    VISCOSITY (POISE)    SP. VOL. (CM3/G) '
        DO 17 I = 1, N
              WRITE(6,31) T(I), VIS(I), SV(I)
 17     CONTINUE
C
C  INPUT INITIAL GUESSES FOR THE CONSTANTS
C
        WRITE(*,*) 'C(1)?', '       C(2)?', ' C(3)?'
        READ(*,*) C(1), C(2), C(3)
C
C  CALCULATE THE DEPENDENT VARIABLE
C
        WM = 18.016
        VC = 1. / RHOC * WM
        R  = 8.314E+07
  7     WRITE(*,*) 'ENTER THE DEGREE OF ASSOCIATION OF WATER MOLECULES'
        WRITE(*,*) 'IN THE LIQUID STATE INSIDE THE MEMBRANE'
        READ(*,*) DEGREE
        DO 50 I = 1, N
        P(I) = .124E-16 * VC**(2./3.) * R * T(I) /
    &                    (WM * DEGREE * VIS(I) * SV(I))
 50     CONTINUE
C
C  CALL NELDER-MEAD OPTIMIZER
C
        CALL NMEAD(C,3,H,IPRINT)
C
C       V1STAR BY SUDGEN'S APPROXIMATION (1927) IS 1.072 CM3/G
C
        V1STAR = 1.072
        Do = DEXP(C(1))
        AK11GAMA = - V1STAR / C(2)
        AK21TG1 = C(3)
C
C  PRINT OUT RESULTS
C
        WRITE(6,*) 'THE DEGREE OF ASSOCIATION OF WATER MOLECULES'
        WRITE(6,*) 'IN THE LIQUID STATE INSIDE THE MEMBRANE=', DEGREE
        WRITE(6,22)
        WRITE(6,23)  Do, AK11GAMA, AK21TG1
C
C       V1STAR BY BILTZ'S APPROXIMATION (1934) IS 0.942 CM3/G
C
        V1STAR = 0.942
        AK11GAMA = - V1STAR / C(2)
        WRITE(6,24)
        WRITE(6,23)  Do, AK11GAMA, AK21TG1
```

```
      WRITE(*,*) 'IF YOU WANT TO CALCULATE THE FREE-VOLUME PARAMETERS'
      WRITE(*,*) 'FOR DIFFERENT DEGREE OF ASSOCIATION OF WATER'
      WRITE(*,*) 'MOLECULES, PRESS 1'
      READ(*,*) FLAG
      IF (FLAG .EQ. 1) GO TO 7

 22   FORMAT(//, 'THE FREE VOLUME PARAMETERS BASED ON SUDGEN METHOD:')
 23   FORMAT(3X, 'Do=',F12.6,3X,'K11/GAMA=',E12.5,3X,'K21-Tg1 =',F12.3)
 24   FORMAT(//, 'THE FREE VOLUME PARAMETERS BASED ON BILTZ METHOD:')
 31   FORMAT(2X,F12.3, 2X, F12.5, 2X, F12.5)
      STOP
      END
C
C
C***************************** ABSTRACT *******************************
C
C     THIS SUBROUTINE CALCULATES THE SUM OF THE SQUARES OF THE ERROR
C     GIVEN THE ANTOINE-TYPE CONSTANTS, C(I).
C
C*********************************************************************
C
      SUBROUTINE NSOLV(X,F)
      REAL X(3),DP(200)
      COMMON /DATA/T(200),P(200),N
      F = 0.0
      DO 10 I = 1, N
C           NOTE THE EXPONENTIAL FORM OF THE EQUATION IS USED HERE
            DP(I) = P(I) - EXP( X(1) +  X(2) / (T(I) + X(3)) )
 10   F = F + DP(I) * DP(I)
      RETURN
      END
```

APPENDIX C2

PROGRAM FOR CALCULATING THE SOLVENT FREE VOLUME PARAMETERS FOR ETHANOL

```
$debug
C
C***************************** ABSTRACT *******************************
C
C        THIS PROGRAM DETERMINES THE SOLVENT PARAMETERS, Do, K11/GAMMA AND
C        (K21 - Tg1) FOR ETHANOL USING NON-LINEAR REGRESSION BY THE NELDER-
C        MEAD PATTERN SEARCH OPTIMIZATION METHOD.
C
C                 CODED BY:     NADIR KAMAL
C                           OKLAHOMA STATE UNIVERSITY
C                                   5 - 17 - 94
C
C**************************** NOMENCLATURE ***************************
C
C  C(1)  -       THE CONSTANT WHICH RELATES TO Do
C  C(2)  -       THE CONSTANT WHICH RELATES TO k11/GAMA
C  C(3)  -       THE CONSTANT (K21 - Tg1)
C  H     -       THE INITIAL SIMPLEX SIZE
C  N     -       THE NUMBER OF DATA POINTS USED
C  P(I)  -       THE PARAMETER, .124E-16 * Vc**(2/3.) *R*T/(VIS*WM*V1)
C  T(I) -        THE ITH TEMPERATURE (K)
C  VIS(I) -      VISCOSITY (POISE)
C  V1STAR -      CRITICAL SPECIFIC HOLE FREE VOLUME (cm3/g)
C  RHOC  -       CRITICAL DENSITY (g/cm3)
C  TC    -       CRITICAL TEMPERATURE (K)
C  SV(J)  -      SPECIFIC VOLUME (cm3/g)
C  WM -          MOLECULAR WEIGHT
C  VC -          CRITICAL MOLAR VOLUME (cm3/mol)
C  R -           GAS CONSTANT (g.cm2/gmol.s2.K)
C
C*********************************************************************
C
C
   REAL C(10)
   COMMON /DATA/T(200),P(200),N
   DIMENSION VIS(200), SPVL(200), D(10)
       N = 193
C
C  SET THE INITIAL SIMPLEX SIZE AND SELECT PRINT OPTION
C
   H=.5
   IPRINT=0
C
C  GENERATE THE TEMPERATURE (K)
C
       T(1) = 159.0
       DO 10 I = 1, N-1
```

```
                T(I+1) = T(I) + 1.0
 10     CONTINUE
C
C  NOW GENERATE THE CORRESPONDING LIQUID VISCOSITIES IN mN.s/m2 USING
C  THE EMPIRICAL EQUATION BY SINNOTT (1991).  THE UNITS ARE CONVERTED
C  TO g/(cm.s) (POISE) BY MULTIPLICATION WITH 0.01
C
        VISA = 686.64
        VISB = 300.88
        DO 20 I = 1, N
                VISLOG = VISA * (1.0 / T(I) - 1.0 / VISB)
                VIS(I) = 10.0**VISLOG
                VIS(I) = VIS(I) * 0.01
 20     CONTINUE
C
C       NOW GENERATE THE CORRESPONDING SPECIFIC VOLUMES IN CM3/G.
C       THE SPECIFIC VOLUME OF ETHANOL CAN BE CALCULATED BY THE
C       EMPIRICAL EQUATION BY I CIBULKA (1993).
C       REF: CIBULKA, I., FLUID PHASE EQUILIBRIA, 89 (1993) 1-18.
C
        RHOC = 1. / .167 / 1000. * 46
        TC   = 243.1 + 273.0
        D(1) =   -0.9926399
        D(2) =   38.02867
        D(3) = -181.1172
        D(4) =  445.9045
        D(5) = -588.5184
        D(6) =  393.9196
        D(7) = -104.3443
        D(8) =    0.0
        DO 40 J = 1, N
                COEFF = 1.0
                DO 30 I = 1, 8
                        AI = I
                        COEFF = COEFF + D(I) * (1 - T(J)/TC)**(AI/3.)
 30             CONTINUE
                RHO1 = RHOC * COEFF
                SPVL(J) = 1.0/RHO1
 40     CONTINUE
        OPEN(6,FILE='ETOHGEN.CON',STATUS='UNKNOWN')
        WRITE(6,*) '  THE INPUT DATA FOR ETHANOL ARE: '
        WRITE(6,*) '   T (K)    VISCOSITY (POISE)    SP. VOL. (CM3/G) '
        DO 17 I = 1, N
                WRITE(6,31) T(I), VIS(I), SPVL(I)
 17   CONTINUE

C
C  CALCULATE THE DEPENDENT VARIABLE
C
        WM = 46.0
        VC = 1. / RHOC * WM
        R  = 8.314E+07
        DO 50 I = 1, N
      P(I) = .124E-16 * VC**(2./3.) * R * T(I) /
```

```
     &                    (WM * VIS(I) * SPVL(I))
  50     CONTINUE
C
C  INPUT INITIAL GUESSES FOR THE ANTOINE-TYPE CONSTANTS
C
         WRITE(*,*) 'ENTER THE INITIAL GUESSES FOR THE ANTOINE-TYPE'
         WRITE(*,*) 'CONSTANTS:'
         WRITE(*,*) 'C(1)?', '       C(2)?', ' C(3)?'
         READ(*,*) C(1), C(2), C(3)
C
C  CALL NELDER-MEAD OPTIMIZER
C
    CALL NMEAD(C,3,H,IPRINT)
C
C        V1STAR BY SUDGEN'S APPROXIMATION (1934) IS .987 CM3/G
C
         V1STAR = 0.987
         Do = EXP(C(1))
         AK11GAMA = - V1STAR / C(2)
         AK21TG1 = C(3)
C
C  PRINT OUT RESULTS
C
    WRITE(6,22)
    WRITE(6,60)
    WRITE(6,21) C(1),C(2),C(3)
    WRITE(6,23)  Do, AK11GAMA, AK21TG1
C
C        V1STAR BY BILTZ'S APPROXIMATION (1934) IS .963 CM3/G
C
         V1STAR = 0.963
         AK11GAMA = - V1STAR / C(2)
         WRITE(6,24)
         WRITE(6,23)  Do, AK11GAMA, AK21TG1
  60 FORMAT( 3X, 'THE CONSTANTS ARE:')
  21 FORMAT( 3H A=,E12.5,4X,3H B=,E12.5,4X,3H C=,E12.5)
  22 FORMAT( //,'THE FREE VOLUME PARAMETERS BASED ON SUDGEN METHOD:')
  23 FORMAT(3X, 'Do=',F12.6,3X,'K11/GAMA=',E12.5,3X,'K21-Tg1 =',F12.3)
  24 FORMAT( //,'THE FREE VOLUME PARAMETERS BASED ON BILTZ METHOD:')
  31 FORMAT(2X,F12.3, 2X, F12.5, 2X, F12.5)
    STOP
    END
C
C
C*************************** ABSTRACT ******************************
C
C   THIS SUBROUTINE CALCULATES THE SUM OF THE SQUARES OF THE ERROR
C  GIVEN THE ANTOINE CONSTANTS, C(I).
C
C*******************************************************************
C
    SUBROUTINE NSOLV(X,F)
    REAL X(3),DP(200)
    COMMON /DATA/T(200),P(200),N
```

```
      F = 0.0
      DO 10 I = 1, N
C           NOTE THE EXPONENTIAL FORM OF THE ANTOINE EQUATION IS USED HERE
            DP(I) = P(I) - EXP(X(1) + X(2) / (T(I) + X(3)))
   10 F = F + DP(I) * DP(I)
      RETURN
      END
```

APPENDIX D

NUMERICAL TECHNIQUE USING MATHCAD SOFTWARE

Pervaporation Of 73% Aqueous Ethanol Through Cellulose Acetate

$t := 299.7$ $L := 786$ $f1 := .27$ $f2 := .73$

Cellulose Acetate

$tg := 312$ $mwru := 257.57$ $v3 := \frac{1.3 \cdot 97}{mwru}$ $v3bar := 0.6224 \cdot tg - 86.95$

$r3 := 1.3$ $k13 := \frac{v3}{2.303 \cdot 17.44 \cdot 51.6}$ $k13 = 2.362 \cdot 10^{-4}$ $v3bar = 107.239$

$v3 = 0.49$

$k23 := 51.6 - tg$ $p := k13 \cdot (k23 + t)$ $p = 0.009$

$k23 = -260.4$

Cellulose Acetate and Water

$v1 := 1.072$ $zeta13 := 18 \cdot 2 \cdot \frac{v1}{v3bar}$ $zeta13 = 0.36$ $p1 := v3 \cdot zeta13$ $p1 = 0.176$

Cellulose Acetate and Ethanol

$v2 := 0.987$ $zeta23 := 46 \cdot \frac{v2}{v3bar}$ $zeta23 = 0.423$ $p2 := v3 \cdot zeta23$ $p2 = 0.207$

Water

$r1 := \frac{1}{1.00368}$ $r1 = 0.996$ $b1 := \frac{zeta13}{zeta23} \cdot v2$ $c := 0.00060644 \cdot (-2.104 + t)$

$d01 := 0.006448$ $a1 := v1$ $b1 = 0.839$ $c = 0.18$

Ethanol

$r2 := \frac{1}{1.27733}$ $r2 = 0.783$ $b2 := \frac{zeta23}{zeta13} \cdot v1$ $e := 0.00054213 \cdot (3.517 + t)$

$d02 := 0.006332$ $a2 := v2$ $b2 = 1.261$ $e = 0.164$

$s := b1 \cdot c - e \cdot a1$ $t := p1 \cdot c - p \cdot a1$ $u := b2 \cdot e - c \cdot a2$ $v := p2 \cdot e - p \cdot a2$

$s = -0.025$ $t = 0.022$ $u = 0.029$ $v = 0.025$

$q1 := p1 \cdot e - b1 \cdot p$ $stq1 := s - t + q1$ $q2 := p2 \cdot c - b2 \cdot p$ $uvq2 := u - v + q2$

$q1 = 0.021$ $stq1 = -0.025$ $q2 = 0.026$ $uvq2 = 0.03$

$cp := c - p$ $ep := e - p$ $cp = 0.171$ $ep = 0.155$

$$y := \begin{bmatrix} 0.116 \\ -0.040503 \\ 0.159 \\ -0.0386 \end{bmatrix}$$

$$D(x,y) := \begin{bmatrix} y_1 \\ -\left[\frac{(r2-r3)\cdot y_3+(r1-r3)\cdot y_1}{r1\cdot y_0+r2\cdot y_2+r3\cdot(1-y_0-y_2)}+\frac{q1\cdot y_3+t\cdot y_1+stq1\cdot(y_1\cdot y_2-y_0\cdot y_3)}{(cp\cdot y_0+ep\cdot y_2+p)^2}\right]\cdot y_1 \\ y_3 \\ -\left[\frac{(r2-r3)\cdot y_3+(r1-r3)\cdot y_1}{r1\cdot y_0+r2\cdot y_2+r3\cdot(1-y_0-y_2)}+\frac{q2\cdot y_1+v\cdot y_3+uvq2\cdot(y_0\cdot y_3-y_2\cdot y_1)}{(cp\cdot y_0+ep\cdot y_2+p)^2}\right]\cdot y_3 \end{bmatrix}$$

$Z := \mathrm{rkfixed}(y,0,1,100,D)$ $\left(Z^T\right)^{\langle 90\rangle T} = (\,0.9 \quad 0.056 \quad -0.162 \quad 0.096 \quad -0.198\,)$

$\left(Z^T\right)^{\langle 100\rangle T} = (\,1 \quad 8.744\cdot 10^{-4} \quad -57.728 \quad 4.617\cdot 10^{-4} \quad -147.008\,)$

$w1 := Z^{\langle 1\rangle}$ $w2 := Z^{\langle 3\rangle}$

$w3 := 1 - w1 - w2$

$Z_{0,1} = 0.116$

$dw1dz := Z^{\langle 2\rangle}$

$dw2dz := Z^{\langle 4\rangle}$

Z =

	0	1	2	3	4
86	0.86	0.062	-0.1301	0.1026	-0.1534
87	0.87	0.0607	-0.1364	0.101	-0.1622
88	0.88	0.0593	-0.1437	0.0994	-0.1724
89	0.89	0.0578	-0.152	0.0976	-0.1843
90	0.9	0.0562	-0.1618	0.0957	-0.1984
91	0.91	0.0546	-0.1735	0.0936	-0.2154
92	0.92	0.0528	-0.1877	0.0913	-0.2363
93	0.93	0.0508	-0.2053	0.0889	-0.2627
94	0.94	0.0486	-0.2281	0.0861	-0.2974
95	0.95	0.0462	-0.2588	0.0829	-0.3452
96	0.96	0.0434	-0.3032	0.0791	-0.4159
97	0.97	0.0401	-0.3741	0.0744	-0.533
98	0.98	0.0357	-0.5116	0.068	-0.7707
99	0.99	0.029	-0.9391	0.0575	-1.5756
100	1	$8.7442\cdot 10^{-4}$	-57.7276	$4.6174\cdot 10^{-4}$	-147.0081

$i := 0, 1 .. 100$

$rho := r1\cdot w1 + r2\cdot w2 + r3\cdot w3$

$d1_i := d01\cdot\exp\left(-\frac{a1\cdot w1_i + b1\cdot w2_i + p1\cdot w3_i}{c\cdot w1_i + e\cdot w2_i + p\cdot w3_i}\right)$ $d2_i := d02\cdot\exp\left(-\frac{b2\cdot w1_i + a2\cdot w2_i + p2\cdot w3_i}{c\cdot w1_i + e\cdot w2_i + p\cdot w3_i}\right)$

$j1_i := -rho_i\cdot d1_i\cdot\frac{dw1dz_i}{L}\cdot 3.6\cdot 10^8$ $j2_i := -rho_i\cdot d2_i\cdot\frac{dw2dz_i}{L}\cdot 3.6\cdot 10^8$

d1 =

	0
0	$4.987 \cdot 10^{-6}$
1	$4.958 \cdot 10^{-6}$
2	$4.93 \cdot 10^{-6}$
3	$4.901 \cdot 10^{-6}$
4	$4.872 \cdot 10^{-6}$
5	$4.843 \cdot 10^{-6}$
6	$4.814 \cdot 10^{-6}$
7	$4.784 \cdot 10^{-6}$
8	$4.754 \cdot 10^{-6}$
9	$4.725 \cdot 10^{-6}$
10	$4.695 \cdot 10^{-6}$

d2 =

	0
0	$1.383 \cdot 10^{-6}$
1	$1.374 \cdot 10^{-6}$
2	$1.365 \cdot 10^{-6}$
3	$1.355 \cdot 10^{-6}$
4	$1.346 \cdot 10^{-6}$
5	$1.336 \cdot 10^{-6}$
6	$1.327 \cdot 10^{-6}$
7	$1.317 \cdot 10^{-6}$
8	$1.308 \cdot 10^{-6}$
9	$1.298 \cdot 10^{-6}$
10	$1.288 \cdot 10^{-6}$

rho =

	0
0	1.183
1	1.183
2	1.183
3	1.184
4	1.184
5	1.184
6	1.185
7	1.185
8	1.185
9	1.186
10	1.186
11	1.186
12	1.187
13	1.187
14	1.187
15	1.188

j1 =

	0
0	0.109
1	0.109
2	0.109
3	0.109
4	0.109
5	0.109
6	0.109
7	0.109
8	0.109
9	0.109
10	0.109
11	0.109
12	0.109
13	0.109
14	0.109
15	0.109

j2 =

	0
0	0.029
1	0.029
2	0.029
3	0.029
4	0.029
5	0.029
6	0.029
7	0.029
8	0.029
9	0.029
10	0.029
11	0.029
12	0.029
13	0.029
14	0.029
15	0.029

$$\mathrm{d1avg} := \frac{\sum_{j=0}^{99} \mathrm{d1}_j}{100} \qquad \mathrm{d2avg} := \frac{\sum_{j=0}^{99} \mathrm{d2}_j}{100} \qquad \mathrm{j1avg} := \frac{\sum_{j=0}^{99} \mathrm{j1}_j}{100} \qquad \mathrm{j2avg} := \frac{\sum_{j=0}^{99} \mathrm{j2}_j}{100}$$

$\mathrm{d1avg} = 3.146 \cdot 10^{-6}$ cm²/s

$\mathrm{j1avg} = 0.109$ kg/m²s

$$\mathrm{rhoavg} := \frac{\sum_{j=0}^{99} \mathrm{rho}_j}{100}$$

$\mathrm{d2avg} = 8.2 \cdot 10^{-7}$ cm²/s

$\mathrm{j2avg} = 0.029$ kg/m²s

$\mathrm{rhoavg} = 1.206$ g/cm³

$$\alpha := \frac{\left(\frac{\mathrm{j1avg}}{\mathrm{j2avg}}\right)}{\left(\frac{\mathrm{f1}}{\mathrm{f2}}\right)} \qquad \alpha = 10.229$$

VITA

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NADIR KAMAL

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Doctor of Philosophy

Thesis: MODELING AND EXPERIMENTS OF AQUEOUS ALCOHOL SEPARATION VIA PERVAPORATION

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