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PERVAPORATION DEHYDRATION OF ISOPROPANOL/WATER USING POLY(HEMA)/POLY ACRYLIC ACID COMPOSITE MEMBRANES

BY

Anas El-Anani

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Abstract

Dehydration of alcohols by pervaporation is a growing industry which has many advantages over the high energy consuming and polluting distillation. Pervaporation is a unique membrane separation process that involves phase change.

Poly (2-hydroxyethylmethacrylate) and polyacrylic acid were used to form a selective layer on top of polyacrylonitrile and polyethersulfone porous substrate membranes, to perform dehydration of isopropyl alcohol by pervaporation. In order to achieve the best performance, membranes were prepared under many casting variables including casting solution compositions, number of layers, curing temperatures and curing times. The fluxes of composite membranes based on polyethersulfone substrate were higher than those based on polyacrylonitrile substrate when the membranes were prepared under the same preparation conditions. On the other hand, selectivities of polyethersulfone based membranes were lower. Therefore, attempts were made to increase the flux of polyacrylonitrile composite membranes. The best flux and separation factor of polyethersulfone composite membranes were 0.126 kg/hr.m^2 and 183.12, respectively, while for polyacrylonitrile composite membranes they were 0.038 kg/hr.m^2 and 1925, respectively.

Cross-linking was necessary to prevent the swelling of the coated layer of poly (2-hydroxyethylmethacrylate), which was done by adding polyacrylic acid as a cross-linking agent. It was found that the pores of the substrate membrane shrunk during the cross-linking process.

Abstrait

La déshydratation des alcools par pervaporation est une industrie croissante qui a beaucoup d'avantages. Par exemple, celle-ci utilise moins d'énergie et est moins polluante que la distillation. La pervaporation est un procédé de séparation par membrane qui implique un changement de phase.

Le poly (2-hydroxyethylméthacrylate) et l`acide polyacrylique ont été employés pour former une couche sélective sur les membranes poreuses composées de polyacrylonitrile et de polyéthersulfone6 de pour exécuter la déshydratation de l'alcool de isopropyle par la pervaporation. Afin de réaliser des performances optimales, les membranes ont été préparées par differentes façons comprenant des changements dans les compositions de solutions, le nombre de couches utiliser dans la fabrication, les températures de traitement et les périodes de traitement. Les flux de la membrane composée basée sur le substrat de polyéthersulfone était plus haut que ceux basés sur le substrat de polyacrylonitrile quand les membranes ont été préparées dans les mêmes conditions. Cependant; la sélectivité du premier était moins élevée. Par conséquent, des tentatives ont été faites pour augmenter le flux des membranes composées de polyacrylonitrile. Le meilleur facteur de flux et de séparation des membranes composées de polyéthersulfone étaient de 0,126 kg/hr.m^2 et 183,12 respectivement, alors que pour les membranes composées polyacrylonitrile ils étaient de 0,038 kg/hr.m^2, 1925 respectivement.

Pour empêcher le gonflement de la couche enduite de poly (2-ydroxyéthylmethacrylate), l'édition absolue était nécessaire en ajoutant l'acide polyacrylique comme agent suivit d`un traitement à température élevée dans un four de convection d'air. On a constaté que le substrat polyacrylonitrile est plus sensible à la chaleur que le polyéthersulfone. Pendant l'étape d'édition absolue, le rétrécissement des pores du substrat polyacrylonitrile a été remarqué.

Acknowledgements

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Table of Contents

List of Figures

List of Tables

Nomenclature

a	Einstein-Stokes radius, (cm)
A	A constant related to the liquid transport defined by Equation (16), (mol/m s Pa)
A_o	Intercept of linear regression on log-normal probability paper (dimensionless)
A_1	Slope of linear regression on log-normal probability paper, (m^{-1})
B	A constant related to vapor transport, (mol/m s Pa)
C_A	Weight concentration of the fast permeant (A) in the feed (dimensionless)
C'_A	Weight concentration of the fast permeant (A) in the permeate (dimensionless)
C_B	Weight concentration of the slow permeant (B) in the feed (dimensionless)
C'_B	Weight concentration of the slow permeant (B) in the permeate (dimensionless)
c_{Bm}	Concentration of the solvent in the membrane, (mol/m^3)
C_f	Solute concentration in the feed solution, (ppm)
C_p	Solute concentration in the permeate, (ppm)
D_{AB}	Diffusivity of solute, (cm^2/s)
D_{Bm}	Diffusion coefficient of solvent in the membrane, (m^2/s)
d_s	Solute size, (nm)
E_p	Activation energy of pervaporation, (J/mol)
f	Solute separation, (%)

J	Permeate flux, (g/hr.m^2)
J	Molar permeation flux, (mol/m^2 s)
J$_o$	Permeate flux of pure component, (g/hr.m^2)
J_B	Solvent molar flux, (mol/m^2 s)
J_L	J for liquid transport, (mol/m^2 s)
J_V	J for vapor transport, (mol/m^2 s)
k	Boltzmann's constant (dimensionless)
M	Molecular weight, (g/mol)
P_2	Upstream pressure, (Pa)
P_3	Downstream pressure, (Pa)
P^*	Saturation vapor pressure, (Pa)
R	Gas constant, 8.314 (J/mol K)
T	Absolute temperature, (K)
W	Weight permeation flux, (kg/m^2 s)
Y	Mole fraction (dimensionless)
Y_3	Mole fraction in the permeate vapor (dimensionless)
Y^*	Mole fraction in the saturated vapor (dimensionless)

Greek letters

α	Separation factor (dimensionless)
β	Enrichment factor (dimensionless)
δ	The total pore length, (m)
δ_L	The length of the pore where liquid transport dominates, (m)

δ_V	The length of the pore where vapor transport dominates, (m)
η	Solvent (water) viscosity, (Pa. s)
$[\eta]$	Intrinsic viscosity of PEG/PEO, (dl/g)
μ_s	Geometric mean pore size of the membrane, (nm)
σ_g	Geometric standard deviation of solute size (dimensionless)
v_B	Molar volume of the solvent, (m^3/mol)

Subscripts

i	i th component of the mixture
j	j th component of the mixture

Abbreviations

AA	Acetic acid
MWCO	Molecular weight cut off
PAA	Poly(acrylic acid)
PAN	Polyacrylonitrile
PEG	Polyethylene Glycol
PEO	Polyethylene oxide
PES	Polyethersulfone
pHEMA	Poly (2-hydroxy ethyl) methacrylate
PVA	Poly(vinyl alcohol)
PWP	Pure water permeation

SD	Standard deviation
TFC	Thin film composite

1 Introduction

Pervaporation is a membrane separation process that can be used to separate liquid mixtures whose separation is very often difficult by conventional distillation. The liquid feed is brought into contact with a semipermeable membrane, the permeate is removed as a vapor from the permeate side by applying a vacuum or a sweeping gas stream, but is usually condensed afterwards to obtain a permeate in liquid form. A schematic diagram of this process is shown in Figure 1. Recently, it has been realized that the process is the most efficient separation process for neutral substances such as organic liquid mixtures. It is currently best identified with dehydration of liquid organics to yield high-purity products, most notably ethanol, isopropyl alcohol, and ethylene glycol (Scott, 1995).

The permselectivity of the pervaporation process is determined by the membrane material. The selection of these polymers is a key task in the development of pervaporation membranes. Membranes used for pervaporation separation processes are generally dense (non-porous), homogeneous thin polymer films, or membranes that have a dense polymer top-layer (composite membranes).

Hydrophilic-hydrophobic balance should be maintained because the introduction of hydrophilic groups swells the membranes under aqueous mixture, which results in poor selectivity. Several techniques have been attempted to control the hydrophilic-hydrophobic balance such as: blending, cross-linking, grafting and more (Mulder, 1996).

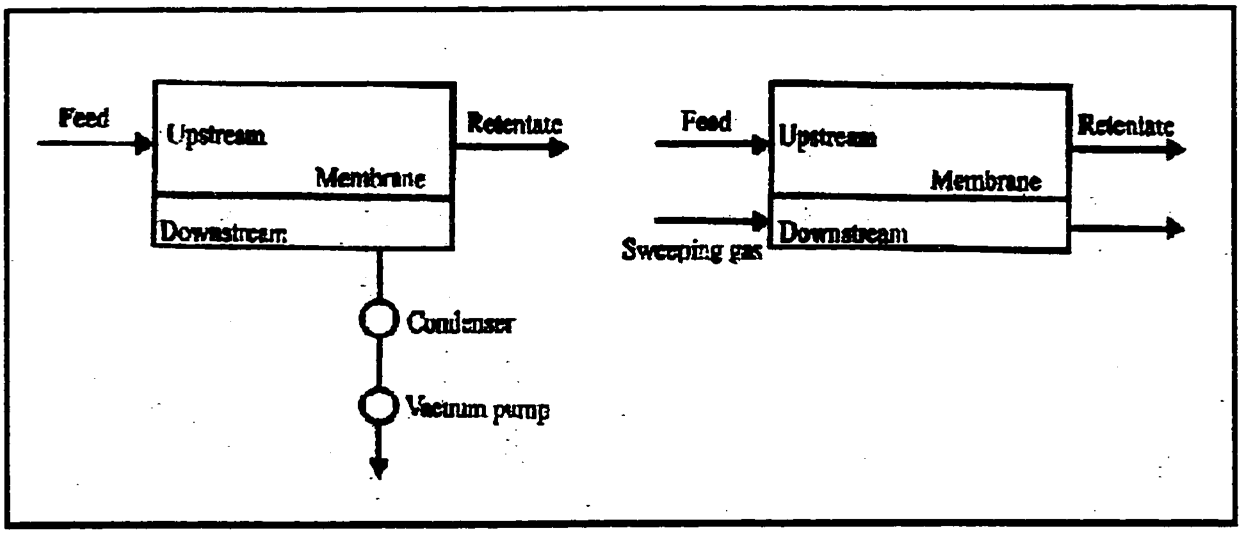


Figure (1) **Schematic diagram of pervaporation process (Tsang, 1998).**

1.1 Objectives of the Thesis

The objective of this work is to develop composite membranes with a thin film of poly(2-hydroxy ethyl) methacrylate for dehydration of solvents by pervaporation. For this purpose, the following tasks are accomplished.

- To study the pervaporation dehydration of isopropanol using polyacrylonitrile (PAN) and polyethersulfone (PES) substrate membranes coated with a thin film of poly (2-hydroxy ethyl) methacrylate (pHEMA) and poly(acrylic acid) (PAA) mixture.
- To find the optimum coating solution composition, curing time, curing temperature and number of coating layers to achieve the best performance.
- To find the relation between the porous substrate membrane and the dense top layer.

2 Literature Survey

2.1 The History of Pervaporation

The history of pervaporation started in the year 1906. Kahlenberg reported some qualitative observations about the selective transport of hydrocarbon/ alcohol mixtures through a thin rubber sheet. The first one to use the pervaporation term was Kober in 1917. He was the first to observe the selective water permeation from an albumin/toluene solution through a collodion bag (cellulose nitrate)(Kober, 1917). Eighteen years later Farber did some studies about the applications of pervaporation.

Heisler and co-workers studied dehydration of aqueous ethanol solutions using cellulose membrane (Heisler et al., 1956). Binning and coworkers focused on the commercial potential of separating azeotropic mixtures by pervaporation separation; e.g. separation of hydrocarbon mixtures by a non-porous film of polyethylene. However, they were not successful in obtaining an industrial process because of low permeation and selectivity (Binning et al., 1961).

A German company called (G.F.T.) made the first breakthrough in the early 1980s by developing a composite membrane with a thin layer of cross-linked poly (vinyl alcohol) supported on a porous poly (acrylonitrile) substrate. Currently, two applications using pervaporation have been commercialized: dehydration of alcohols and other solvents, and removal of small amounts of organic compounds from contaminated water. (Baker et al. 1991; Mulder, 1996; Shieh. 1996; Feng and Huang, 1997; Nawawi, 1997).

2.2 Pervaporation

Pervaporation is a unique membrane technique because it involves a phase change from a liquid in the feed side to a vapor in the permeate side. The feed mixture diffuses through a nonporous permselective membrane and evaporates on the permeate side due to a vacuum maintained by a vacuum pump or a stream of carrier gas. Permeate is then condensed and collected. Swelling of the membrane is common in pervaporation and it is more on the feed side than on the permeate side (Néel, 1995).

Any pervaporation process must consist of three steps:

- Selective sorption of the feed into the membrane.
- Selective diffusion through the membrane.
- Vapor phase desorption on the permeate side (Heinzelmann, 1991; Mulder, 1996).

The driving force for pervaporation is achieved by lowering the activity of the permeate side due to the vacuum (Matsuura, 1993). The evaporation of the permeate means that the energy consumption of this process is higher than for other membrane processes (Colman et al., 1996).

2.3 Performance Parameters of Pervaporation

Pervaporation performance is specified by two experimental parameters:

Firstly, the permeate flux (J), expressed in kg/hr.m^2 which means the weight of permeate that goes through the membrane area of 1 m^2 during 1 hour. Secondly, the membrane selectivity, expressed either by (β) or (α) defined as:

$$\beta = \frac{C'_A}{C_A} \tag{1}$$

$$\alpha = \frac{C'_A / C'_B}{C_A / C_B} \tag{2}$$

where C'_A is the weight concentration of the fast permeant (A) in the permeate, C_A is the weight concentration of the fast permeant (A) in the feed, while C'_B, C_B are the weight concentration of the slow permeant (B) in the permeate and the weight concentration of the slow permeant (B) in the feed, respectively. According to the terminology commission of the European Society of Membrane Science and Technology (α) is called the separation factor and (β) is called the enrichment factor (Néel, 1991).

2.4 Advantages and Disadvantages of Pervaporation

The possibility of separating azeotropic and close boiling point mixtures is one of the most important advantages of pervaporation, because in some cases, it is the only way to separate azeotropic mixtures. Pervaporation can also save pollution caused by entrainers and chemicals used to break the azeotropes. Moreover, removing a minor component from a mixture can save energy wasted by evaporating a large quantity of solvent such as in the case of distillation. Even though the performance would be better at relatively high temperatures, pervaporation can be operated at any temperature, enabling its applications in treating temperature sensitive substances. Finally, it is a very flexible operation; it can be economical with small installations and with low or high loadings (Krug, 1989; Lorrain, 1991; Minnery, 1995).

Despite all of these advantages, it has some disadvantages. Pervaporation is more energy consuming than any other membrane separation process due to the need for heat to evaporate the permeate (Colman, 1996). Large industrial scale applications of pervaporation have been realized. However they are limited due to the high price, limited availability, poor chemical or thermal resistances and poor durability of membranes (Krug, 1989; Minnery, 1995).

2.5 Applications of Pervaporation

There are three applications of pervaporation; i.e. dehydration of organic compounds, water purification and separation of organic mixtures (Baker, 1991; Scott, 1995; Mulder, 1996). Pervaporation is considered to be attractive when the mixture to be treated has an azeotropic composition, which means that the liquid and the vapor above it have the same composition and regular distillation does not work any more.

Pervaporation can be used alone if the azeotropic composition is close to the composition of a pure component. However, a hybrid system of distillation and pervaporation should be used when the azeotropic compositions are far from that of the pure components (Mulder, 1996). Table 1 shows some azeotropic mixtures (Mulder, 1996).

Table (1) The compositions of different azeotropic mixtures

Mixture	Azeotropic composition (weight %)
Water/ethanol	4.4/95.6
Water/isopropanol	12.2/87.8
Water/t-butanol	11.8/88.2
Water/tetrahydrofuran	5.9/94.1
Water/dioxane	18.4/81.6
Methanol/acetone	12/88
Ethanol/hexane	21/79
n-propanol/cyclohexane	20/80

Shah and Bartels (1991) found that it is also economically possible to use pervaporation with non-azeotropic mixtures such as ethylene glycol/water system, because it can be performed at a much lower temperature than distillation. Some examples of industrial applications of pervaporation are discussed below.

2.5.1 Dehydration of organic compounds as solvents

Dehydration by pervaporation is widely applied in the industry. Examples are dehydration of ethyl alcohol, cleaning agents, isopropyl alcohol, dichloroethene, ethylenedichloride, esters, solvents, ketones, acetic acid, and organic amines (Lorrain, 1991; Matsuura, 1993; Scott, 1995).

2.5.2 Purification of water

When an organophilic membrane is used, water can be purified from organic contaminants such as benzene, hydrocarbons, esters, ketones, ethers, alcohols, phenolics, and aromatic compounds. Therefore, pervaporation can be used for pollution control (Baker, 1991; Matsuura, 1993; Scott, 1995; Mulder, 1996).

2.5.3 Separation of organic-organic mixtures

When an organic mixture contains two or more compounds with a similar boiling point and relative volatility, the separation is costly and difficult to do by distillation. Therefore, a good pervaporation membrane has a very good chance of being substituted for distillation in the petroleum and chemical processing industries. Examples are mixtures of alcohols and aromatic compounds, alcohols and aliphatic compounds, alcohols and ethers, aromatic and aliphatic compounds, saturated and unsaturated compounds, and isomers (Baker, 1991; Scott, 1995; Mulder, 1996).

2.6 Polymeric Materials for Pervaporation Membranes

There are many kinds of polymeric materials which may be called glassy polymers, rubbery polymers, and ionic polymers. A polymer is considered as a glassy polymer if it is in a glassy state at room temperature. On the other hand, a polymer is considered as a rubbery polymer if it is in an amorphous state at room temperature. A polymer is considered as an ionic polymer when it carries ionic groups. Ionic polymers can be either glassy or rubbery.

The choice of the polymer depends strongly on the type of application. Glassy polymers with hydrophilic functional groups are suitable for making water-selective membranes used for solvent dehydration, and rubbery polymer membranes normally do not contain hydrophilic fuctional groups. Therefore, they are favorable for the removal of organic compounds from water. However, there are some exceptions. For the separation of organic mixtures, it is not yet very clear whether glassy or rubbery polymers are more appropriate, and both types of polymers show some pervaporation selectivity. Ionic polymers contain ionic groups that are neutralized by counter ions. They may be viewed as cross-linked polyelectrolytes. Ionic membranes, which can be subdivided into cationic and anionic, are normally water selective due to their affinity to water. Ionic polysaccharides have been shown to be potential materials for making dehydration membranes.

A membrane with low hydrophilicity generally exhibits a low water flux in dehydration, but some membranes made of polymers with very high hydrophilicity such as poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAA) need cross-linking for improved stability and selectivity. The polymer materials for dehydration membranes should maintain a proper balance of hydrophilicity and hydrophobicity.

Polymers with high selectivity and low permeability are often preferred for further study over membranes with low selectivity and high permeability, since the disadvantage associated with low permeability can be partly overcome by introducing asymmetricity to the membrane structure.

Improvement in membrane performance can often be achieved by polymer modification, for which several techniques have been developed, including cross-linking, grafting, blending, copolymerization, and incorporation of adsorbent materials.

For making dehydration membranes, PVA- and PAA-based polymers are the most widely used materials, while chitosan and aromatic polyimide materials are attracting great interest. PVA is a 1,3-diglycol polymer whose hydroxyl groups have strong interactions with water through hydrogen bonding. It is one of the very few high-molecular-weight water-soluble resins and can easily be cross-linked either chemically or thermally. Of all the membranes for pervaporation separation of aqueous organic mixtures, PVA-based membranes have been studied most intensively. Most of the research is centered on the modification of PVA for improved permselectivity and stability and performance testing for various perspective applications. The commercial membrane of G.F.T. Co. for solvent dehydration is made from chemically cross-linked PVA. PAA is another polymer suitable for preparing water selective membranes. It has a high charge density based on the carboxyl groups, which are available for cross-linking. Inorganic materials such as ceramics, metals and glasses are also potentially useful for the development of pervaporation membranes. Solubility parameter, polarity parameter, surface thermodynamics, contact angle and liquid chromatography are examples of the theoretical approaches developed to select a suitable material for a given system. (Koops and Smolders, 1991; Tyagi, 1993; Feng, 1994; Mahmud, 1996; Mulder, 1996; Shieh, 1996; Nawawi, 1997; Tsang, 1998).

2.7 Preparation of Synthetic Membranes for Pervaporation

Several techniques are used to prepare membranes to be used in different kinds of separation. These techniques are sintering, stretching, track-etching, sol-gel process, vapor deposition, phase inversion and solution coating (Mulder, 1996).

2.8 Polymer Modification

Since pervaporation depends largely on the properties of the membrane material and it is hard to find a single polymer with all the desirable properties, modification and copolymerization are the logical answer to this problem. Modification of polymers can be done by crosslinking, blending and introduction of ionic charges.

2.8.1 Crosslinking

Crosslinking is a way of improving some properties of polymers such as mechanical strength, resistance to chemicals and swelling, and dissolution in feed solutions. There are three ways of crosslinking: chemical reaction to connect two polymer chains, irradiation, and physical crosslinking (Koops and Smolders, 1991). Sun et al.(1997) studied the effects of crosslinking, molecular weight, and the membrane thickness on the degree of swelling of poly(2- hydroxyethyl methacrylate) (pHEMA) membrane. They found that increasing the concentration of the crosslinking agent decreases the degree of swelling because it causes the network chain to bundle together and become more difficult to stretch and dilate. They also found that the degree of swelling increases with an increase in molecular weight of the polymer because, shorter chains are more mobile within the solution, which makes them easier to collide and form intermolecular linkages or smaller network holes. It is exactly the opposite when it comes to larger chains, (see Figure 2).

Huang et al. (1999) ionically crosslinked sodium alginate membrane using various divalent and trivalent ions to control the water solubility and mechanical weakness. They found that crosslinking sodium alginate with Ca^{2+} ion produced the highest performance in separating ethanol/water and isopropanol/water mixtures. Huang et al. (1999) attempted dehydration of isopropanol using chitosan/polysulfone composite membranes. Chitosan layer was crosslinked using glutaraldehyde with sulfuric acid. Immersing polysulfone substrate membrane in dilute PVA solution was done to improve the poor wettability, structural stability, and to reduce the hydrophobicity of the substrate membrane.

2.8.2 Blending

Polymer blending is a very convenient method to obtain desirable polymer properties (David et al., 1992). A polymer blend is a mixture of two or more polymers, which are not covalently bonded. There are two kinds of blends. The first one is a homogeneous blend which occurs when the polymers are miscible on the molecular scale for all compositions, and the second is a heterogeneous blend, which is exactly the opposite. Blending polymers is a way of controlling and balancing hydrophilicity and

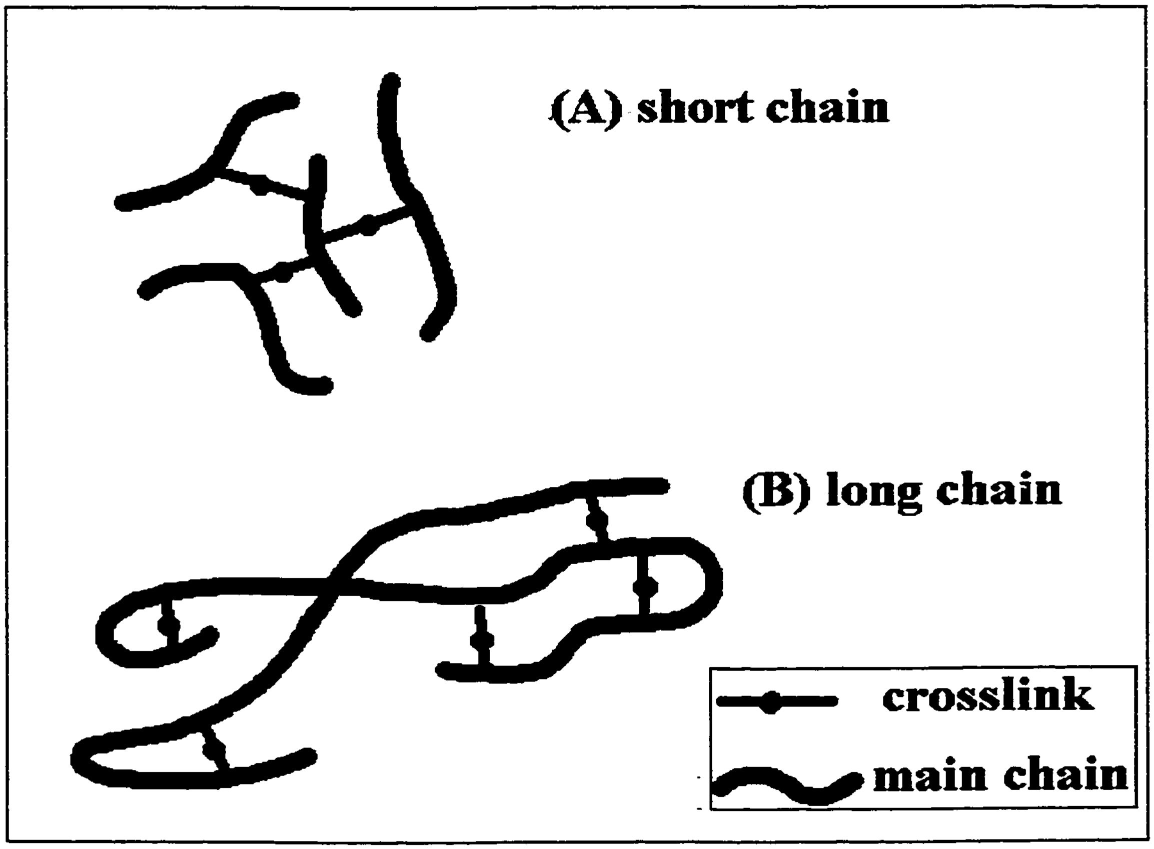


Figure (2) **Cross-linking of short and long chain polymers (Sun et al., 1997).**

hydrophobicity by mixing hydrophobic and hydrophilic polymers in different ratios (Koops and Smolders, 1991). Despite the good potential for polymer blend membranes, some membranes suffered from losing some of its components during operation due to the solubility of that component in the feed solution. This problem can be overcome by chemical crosslinking (David et al., 1992).

Homogeneity in the structure of a polymer blend is not required all the time to obtain a good pervaporation membrane. An example of that is the heterogeneous nafion membrane, which performed very well in many processes (David et al., 1992).

Wu et al., (1994) found that strength, stability, and resistance to water of poly(vinyl alcohol) membranes were enhanced by cross-linking and blending with chitosan.

2.8.3 Copolymerization

Copolymerization is used for the same reason as blending, but the main difference between them is that copolymers have covalent bonds, which give more stability to the membrane. There are many kinds of copolymers like block copolymer, random copolymer, and graft copolymer.

When the monomers are distributed in blocks throughout a polymer chain the polymer is called block copolymer, while the polymer is called random copolymer when the monomers are completely irregularly distributed. Grafted copolymer contains irregularly distributed side chains of different monomer blocks connected to a regular main chain (Koops and Smolders, 1991; Shieh, 1996; Nawawi, 1997).

2.8.4 Introduction of Ionic Charges

Ionic groups such as $-COO^-$, $-SO_3^-$, $-NH_3^+$ are introduced to polymer chains mainly to increase the hydrophilicity of membranes due to the ion/dipole interaction between ionic groups and water (Koops and Smolders, 1991).

2.9 Poly(2- hydroxyethyl methacrylate) and Poly(acrylic acid)

Poly(2-hydroxyethyl methacrylate) (pHEMA) is a polymer well known in the industry. It is used in contact lenses and artificial crystalline lenses due to its softness and ultraviolet absorption behavior (Chirila, 1993). It has a long tradition in biomedical applications as a temporary cover for the treatment of skin defects (Pvořánková et al., 1996). The high biocompatibility is due to low irritant and toxic effect of the monomer, high resistance to polymeric chain dehydration, the ability of water to ensure polymer plasticisation, and the high solubility of gases and metabolites within the macromolecular matrix. This is why it is used as hydrogels, prosthetic materials, contact lenses and controlled drug delivery systems (Sun et al., 1997; Barbieri et al., 1998).

Narayani and Rao (1996) studied collagen-poly(HEMA) composites and found the possibility of using it as an anticancer drug delivery. It was found that the copolymer ethyleneglycoldimethacrylate-poly(HEMA) is used as microbeads sorbent for removal of heavy metal ions (Salih et al. 1995; Denizli et al. 1996; Salhi et al. 1996; Denizli et al. 1997; Kocakulak et al. 1997). According to Sun et al. (1997), a cross-linked poly(HEMA) swells in water and becomes soft hydrogel, while, dry poly(HEMA) is inflexible and brittle at ambient temperature due to its high glass temperature which is more than 100°C.

Poly acrylic acid (PAA) is a very hydrophilic polymer that has many applications in the membrane industry. According to Lee et al. (1999), it was doped with polyaniline to make a pervaporation membrane that can dehydrate aqueous isopropanol. Polyethersulfone (PES) and polyacrylonitrile (PAN) nonporous membranes can be used by themselves as pervaporation membranes for dehydration of organic compounds (Scott, 1995). They are also used as materials for the preparation of ultrafiltration membranes (Nawawi,1997). The chemical formula of pHEMA, PAA, PES and PAN are given in Figure (3).

2.10 Effect of Process Conditions on Pervaporation Performance

2.10.1 Feed concentration

Pervaporation process is highly concentration dependent. It is concentration dependent more than any other membrane separation processes. Changing the feed concentration can affect sorption and diffusion of permeants in the membrane, coupling phenomena in the membrane transport, membrane swelling or shrinking, and concentration polarization (Huang and Rhim, 1991; Tyagi, 1993; Shieh, 1996; Nawawi, 1997).

In their attempt to separate ethanol from water using cross linked chitosan composite membrane, Lee et al. (1997) found that both permeate flux and the water content in the permeate decreased drastically at feed ethanol concentration above 97% by weight.

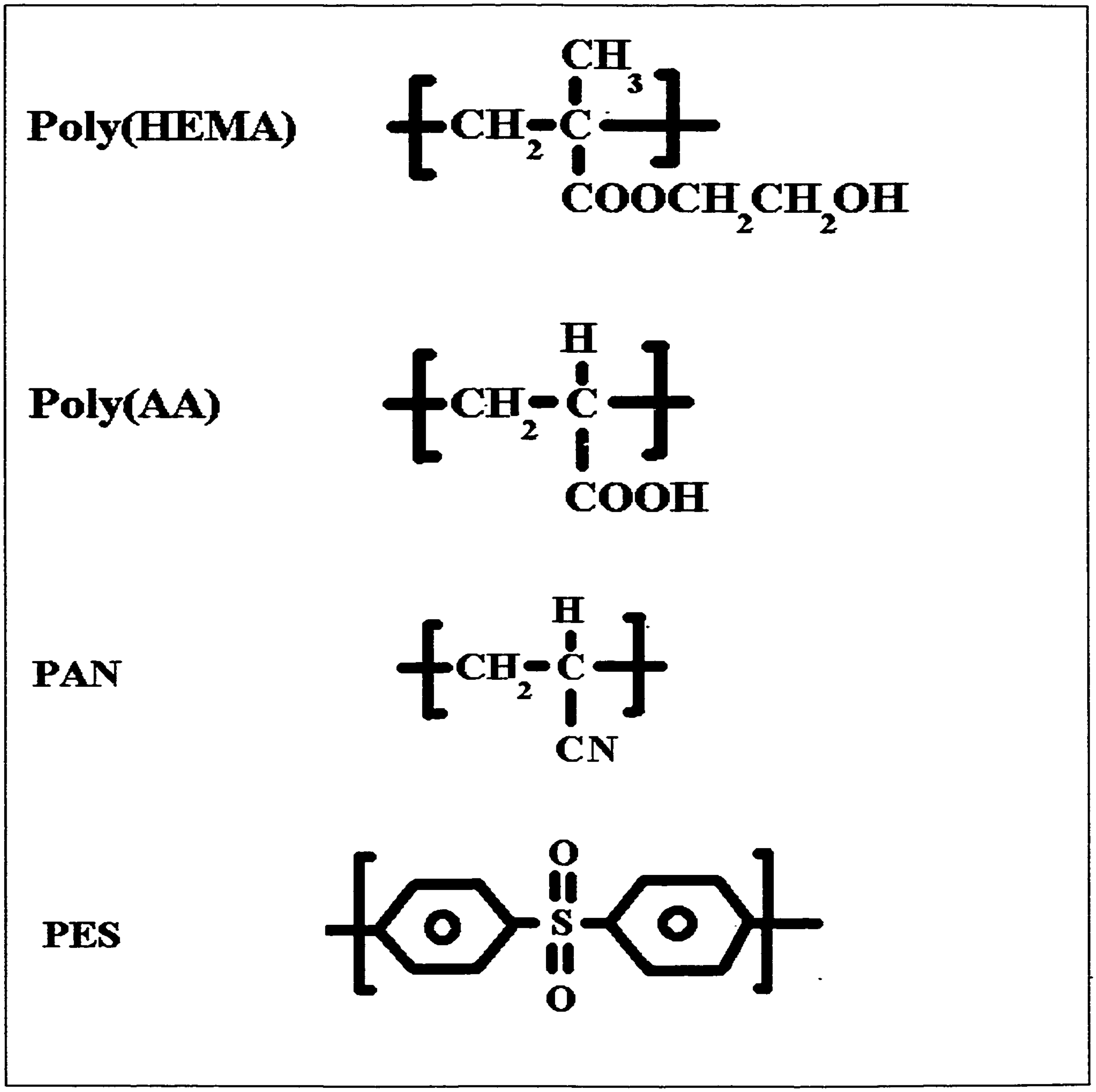


Figure (3) Chemical formula for Poly(2- hydroxyethyl methacrylate) (pHEMA), Poly acrylic acid (PAA), Polyacrylonitrile (PAN) and Polyethersulfone (PES).

2.10.2 Feed and permeate pressure

The maximum in permeation rate occurs when the permeate pressure is close to zero and the minimum in permeation rate occurs when the permeate pressure reaches the saturation vapor pressure (Huang and Rhim, 1991; Tyagi, 1993; Shieh, 1996; Nawawi, 1997).

2.10.3 Temperature

Permeation rate depends on the temperature, because solubility and diffusivity of permeants are dependent on the temperature. Generally, the permeation rate follows Arrhenius-type equation

$$J = J_o \exp(-E_p/RT) \qquad (3)$$

Sometimes the permeation rates increase several folds for each 10°C temperature increment. On the other hand, selectivity is not a strong function of temperature; it may increase or decrease with increasing temperature. In most cases, it decreases with increasing temperature due to the increase of the thermal motion of the polymer chains, which results in larger diffusional holes (Huang and Rhim, 1991; Tyagi, 1993; Shieh, 1996; Nawawi, 1997).

Lee et al. (1997) studied the separation of ethanol-water and isopropanol-water mixtures by pervaporation using cross-linked chitosan composite membranes. They noticed that the separation is less temperature dependent compared to poly(vinyl alcohol) membranes. Shieh and Huang (1997) found that, with increasing temperature, the permeability and separation factor increased dramatically when the water content was higher than 30% by weight. While studying chitosan and polyacrylic acid blends membrane to dehydrate ethanol, Hollein et al. (1993) indicated that the increase in temperature increased the flux exponentially, but had little effect on selectivity in the concentration of dilute acetone-water solution using pervaporation. Qunhui et al. (1995) studied chitosan membranes and discovered that the partial fluxes of water and ethanol increased with temperature. They also found that the total permeant solubility increased and the sorption selectivity of the membrane decreased with increasing temperature.

3 Theory

3.1 Mean Pore Size and Pore Size Distribution of Ultrafiltration Membranes

There are several techniques used to measure pore and pore size distribution. Some of them are bubble point technique, microscopic technique, mercury porosimetry, permporometry, thermoporometry, and solute transport (Singh et al., 1998). Molecular weight cut-off (MWCO) is used in the solute transport technique, it is defined as the molecular weight of a solute, that corresponds to 90% rejection by a membrane (Mulder, 1996). It was found by many researchers that the relation between the sieving coefficient and the solute size in many ultrafiltration and microfiltration membranes could be fitted to a log-normal probability distribution curve (Singh et al., 1998).

According to Singh et al. (1998), in order to establish that curve, the solute separation (f) needs to be calculated. (f) is defined as

$$f = (1 - C_p/C_f) * 100\% \tag{4}$$

where C_p is the solute concentration in the product and C_f is the solute concentration in the feed. According to Michaels (1980), when a solute separation of an ultrafiltration membrane is plotted vs. the solute diameter on a log-normal probability paper, a straight line is formed. Because it is a log-normal probability function, the relationship can be expressed as

$$f = erf(z) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{z} e^{-\frac{u^2}{2}} du \tag{5}$$

Where

$$Z = \frac{\ln d_s - \ln \mu_s}{\ln \sigma_g} \tag{6}$$

d_s is the solute diameter, μ_s is the geometric mean diameter of the solute and σ_g is the geometric standard deviation about the mean diameter.

According to equation (5) and (6) a straight line in the form of

$$F(f) = A_o + A_1\,(\ln d_s) \tag{7}$$

is obtained. f can be calculated from equation (4) and d_s can be found using Stokes radius, which can be obtained from the diffusivity equation

$$D_{AB} = \frac{2.5\times 10^6 kT}{\left\{\eta\left(M[\eta]\right)^{1/3}\right\}} \tag{8}$$

where D_{AB} is the diffusivity, k is Boltzmann's constant, M is the molecular weight of the polymer and $[\eta]$ is the intrinsic viscosity of the polymer,

and from Stokes-Einstein equation

$$D_{AB} = \frac{kT}{6\pi\eta a} \tag{9}$$

where a is the Stokes radius, D_{AB} is the diffusivity, k is Boltzmann's constant, and η is the viscosity of the solvent (in this case water).

By combining these two equations we obtain

$$a = 2.122\times 10^{-8}\left(M[\eta]\right)^{1/3} \tag{10}$$

For the intrinsic viscosity values of PEG, Meireles et al.(1995) found that

$$[\eta] = 4.9\times 10^{-4}\, M^{0.672} \tag{11}$$

And for PEO, Nabi (1968) found that

$$[\eta] = 1.192\times 10^{-4}\, M^{0.76} \tag{12}$$

Then the Stokes radius of PEG is

$$a = 16.73\times 10^{-10}\, M^{0.557} \tag{13}$$

And for PEO is

$$a = 10.44 \times 10^{-10} M^{0.587} \tag{14}$$

μ_s can be determined from d_s which is ($2a$) corresponding to f=50% and σ_g can be determined from the ratio of d_s at f=84.13% and at 50%.

3.2 Pervaporation Transport Models

In pervaporation, the driving force for the transport is the gradient of the chemical potential between the liquid in the feed and the vapor in permeate (Nawawi, 1997). Shieh (1996) indicated that there are three different models of pervaporation: the nonequilibrium thermodynamic model, the pore flow model, and the solution diffusion model. Tyagi (1993) added a fourth model, which is the free volume model. According to the solution diffusion model, pervaporation consists of three consecutive steps: sorption of the permeant from the liquid feed to the membrane, diffusion of the permeant through the membrane, and desorption of the permeant to the vapor phase on the downstream side of the membrane (Feng and Huang, 1997). Desorption is rapid and non-selective, but diffusion through the membrane is the rate-determining step (Néel, 1991). Many researchers studied pervaporation models. Shieh and Huang (1998) studied the pseudophase-change solution diffusion model for pervaporation. Soltanieh and Zaare-asl (1996) suggested a modification to the solution diffusion model and Huang and Feng (1993) discussed the resistance model approach for pervaporation. They found that in asymmetric membranes, the selectivity is influenced by relative resistance of the skin layer, the substrate layer, by the relative resistance of both, the polymer matrix and the pores in the substrate.

3.2.1 The pore model for pervaporation

According to Matsuura (1993), this model is based on the assumption that the membrane consists of straight cylindrical pores of length (δ) perpendicular to the membrane surface (see Figure (4)). The second assumption suggests an isothermal behavior of the membrane. Thirdly, the pores are filled with liquid from the inlet to a distance δ_L and filled with vapor from the distance δ_L to the end of the cross section of the membrane, which is called δ_V. Therefore, there should be a liquid-vapor boundary which is under saturation vapor pressure P^* somewhere in the pore. The pressure of the feed is P_2 and that of the permeate P_3. When $P_3 \leq P^*$ there are both vapor and liquid phases in the pore and when $P_3 > P^*$, the pore is filled with liquid. For a single component system and for $P_3 \leq P^*$, according to Matsuura, (1993), the equation applied to the molar liquid flux J_B of the liquid filled portion of the pore, is expressed as

$$J_B = \frac{c_{Bm} D_{Bm} v_B}{RT\delta_L}\left(P_2 - P^*\right) \tag{15}$$

As in reverse osmosis, the pressure in the liquid phase drops from P_2 to P^* and the distance of the liquid in the pore is δ_L. By defining the liquid transport parameter as:

$$A = \frac{c_{Bm} D_{Bm} v_B}{RT} \tag{16}$$

Then the molar permeation flux of the liquid through the pore becomes

$$J_L = \frac{A}{\delta_L}\left(P_2 - P^*\right) \tag{17}$$

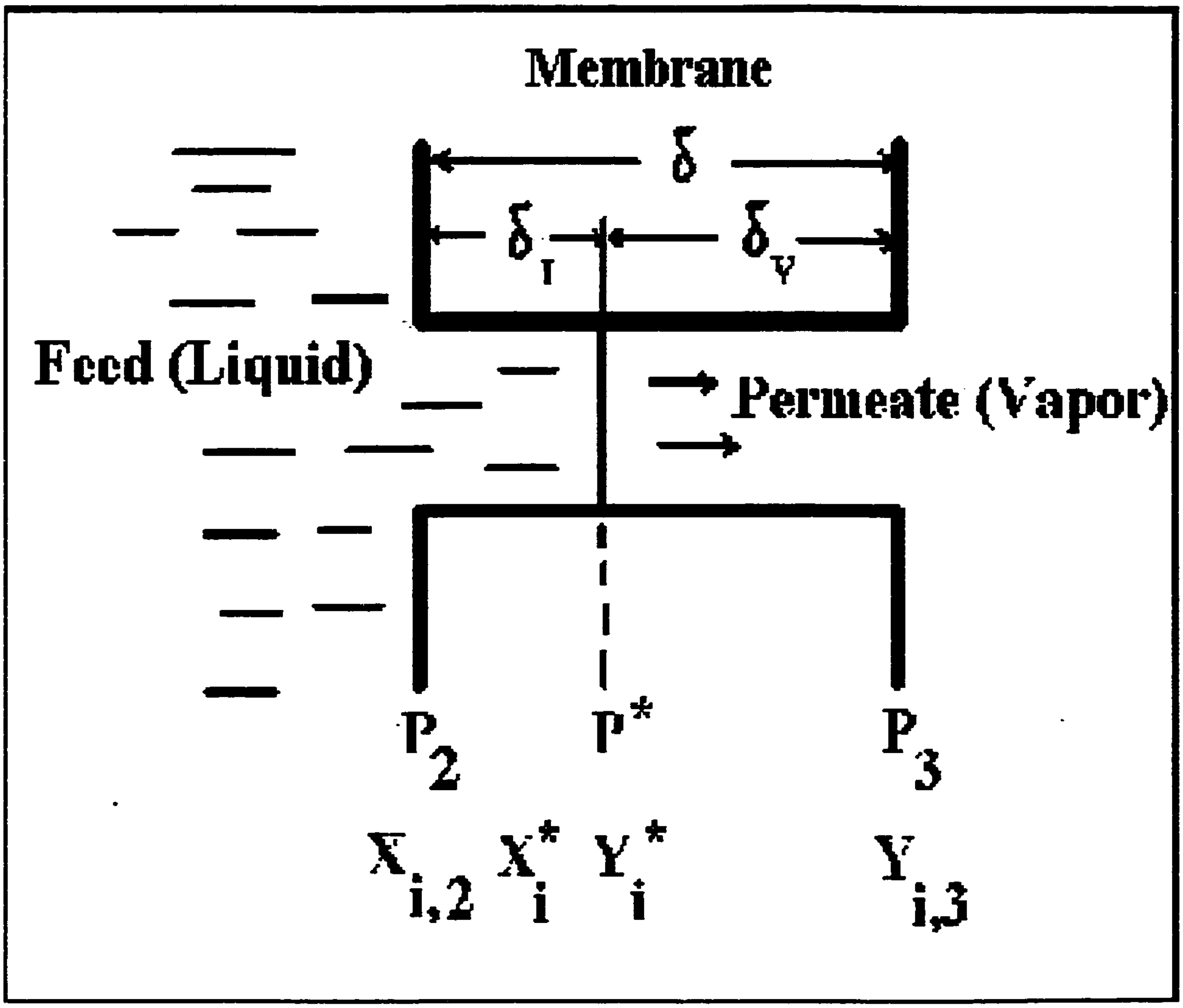


Figure (4) Schematic representation of pervaporation occurring in a membrane pore (Matsuura, 1993).

As for the transport of the vapor in the pore, the surface flow is assumed, so the molar permeation flux is proportional to the difference in the squares of the pressures at both ends of the vapor-filled pore, which is demonstrated as

$$J_V = \frac{B}{\delta_V}\left(P^{*2} - P_3^2\right) \tag{18}$$

At steady state

$$J = J_L = J_V \tag{19}$$

And

$$\delta = \delta_L + \delta_V \tag{20}$$

By combining equations (17), (18), (19) and (20) we obtain

$$J = \frac{B}{\delta}\left(P^{*2} - P_3^2\right) + \frac{A}{\delta}\left(P_2 - P^*\right) \tag{21}$$

By multiplying the last equation with the molecular weight of the component, we obtain the weight flux of the membrane

$$W = \frac{BM}{\delta}\left(P^{*2} - P_3^2\right) + \frac{AM}{\delta}\left(P_2 - P^*\right) \tag{22}$$

while, for the condition when $P_3>P^*$, the entire pore is filled with liquid which means that

$$J = \frac{A}{\delta}\left(P_2 - P_3\right) \tag{23}$$

and the weight flux is

$$W = \frac{AM}{\delta}\left(P_2 - P_3\right) \tag{24}$$

In the binary system that includes (i)th and (j)th components, the following approach is adopted. Since pervaporation is carried out under a very low permeate pressure, much lower than the saturation pressure, it is safe to assume that the pore is filled only with vapor. Then, ignoring the second term (contribution of liquid-filled portion) in equation (21), the equation is written down for each component as,

$$J_i = \frac{B_i}{\delta}\left(P_i^{*2} - P_{i,3}^2\right) \tag{25}$$

$$J_j = \frac{B_j}{\delta}\left(P_j^{*2} - P_{j,3}^2\right) \tag{26}$$

Since

$$Y_{i,3} = \frac{J_i}{J_i + J_j} \tag{27}$$

$$Y_{j,3} = 1 - Y_{i,3} \tag{28}$$

$$P_i^* = P^* Y_i^* \tag{29}$$

$$P_j^* = P^* Y_j^* \tag{30}$$

$$P_{i,3} = P_3 Y_{i,3} \tag{31}$$

$$P_{j,3} = P_3 Y_{j,3} \tag{32}$$

Combination of equations (25), (26), and (27) yields

$$Y_{i,3} = \frac{\left(P_i^{*2} - P_{i,3}^2\right)}{\left(P_i^{*2} - P_{i,3}^2\right) + \left(B_j / B_i\right)\left(P_j^{*2} - P_{j,3}^2\right)} \quad . \tag{33}$$

And since

$$J = J_i + J_j \tag{34}$$

The total molar permeation flux can be written as

$$J = \frac{B_i}{\delta}\left(P_i^{*2} - P_{i,3}^2\right) + \frac{B_j}{\delta}\left(P_j^{*2} - P_{j,3}^2\right). \tag{35}$$

The total weight flux of the membrane is

$$W = \left[\frac{B_i}{\delta}\left(P_i^{*2} - P_{i,3}^2\right) + \frac{B_j}{\delta}\left(P_j^{*2} - P_{j,3}^2\right)\right]\left(M_i Y_{i,3} + M_j Y_{j,3}\right). \tag{36}$$

4 Experimental Methods

4.1 Materials

The materials used in the experiments are discussed below.

4.1.1 Materials for composite p-HEMA/PAA/PES membrane

- Polyethersulfone (PES) ultrafiltration membrane (S-12185) was generously supplied by Osmonics, MN.
- Poly (2-hydroxy ethyl methacrylate) (pHEMA) with molecular weight of 1,000,000 was supplied by Prof. C. J.Kim of Temple University.
- Poly(acrylic acid) (PAA) with molecular weight of 90,000 as an aqueous solution of 25%by weight was supplied by Polysciences Inc.
- Acetic acid (AA) 99.7% was supplied by BDH Inc.
- Distilled water.

4.1.2 Materials for composite p-HEMA/PAA/PAN membrane

- Polyacrylonitrile (PAN) membrane was supplied by Mr.F.Baig of Fielding Chemicals Technologies Inc.
- Poly (2-hydroxy ethyl methacrylate) (pHEMA)with molecular weight of 1,000,000 was supplied by Prof. C. J.Kim of Temple University.
- Poly(acrylic acid) (PAA) with molecular weight of 90,000 as an aqueous solution of 25% was supplied by Polysciences Inc.
- Acetic acid (AA) 99.7% was supplied by BDH Inc.
- Distilled water

4.1.3 Materials for ultrafiltration experiments

- Polyethylene glycol (PEG) with molecular weights of 4,000 and 8,000 were supplied by Aldrich Chemical Company Inc.
- PEG with molecular weight of 10,000 was supplied by Sigma Chemical Company.
- PEGs with molecular weights of 12,000, 20,000 and 35,000 were supplied by Fluka Chemika.
- Poly(ethylene oxide) (PEO) with molecular weights of 100,000 and 200,000 were supplied by Aldrich Chemical Company Inc.

4.1.4 Materials for pervaporation experiments

- Isopropyl alcohol (99.5%) was supplied by BDH Inc.
- Distilled water.

4.2 Membrane Preparation

After some preliminary experiments membranes were prepared according to 15 methods outlined below and explained in Table (2). The molar ratio signifies the number of repeat units of poly(2-hydroxy ethyl methacrylate) to the number of repeat units of poly(acrylic acid). The procedure of composite membrane preparation using PES substrate membrane consists of five steps as described for PES.A, unless otherwise stated. Similarly, the procedure of composite membrane preparation using PAN substrate membrane consists of five steps as described for PAN.A, unless otherwise stated. The number of coated layers and curing time are given in tables together with experimental results.

PES.A

- Step 1: A coating solution was made by blending 3 wt.% pHEMA solution in 30wt.% AA aqueous solution with aqueous 25wt.% PAA solution according to a molar ratio of (1 : 0.5).
- Step 2: The coating solution was poured onto the surface of a (PES) substrate membrane, which was placed on top of a coating glass jar.
- Step 3: The excess solution was drained by holding the glass jar vertically for two minutes after waiting for one minute.
- Step 4: The coated substrate membrane was placed in an oven with forced air circulation for curing. The oven temperature was maintained at 70°C.
- Step 5: Steps 2-4 were repeated three times.

PES.B

- Step 1: A coating solution was made by blending 3 wt.% pHEMA solution in 30wt.% AA aqueous solution with aqueous 25wt.% PAA solution according to a molar ratio of (1 : 1).
- Steps 2, 3, 4 and 5 were the same as PES.A.

PES.C

- Step 1: A coating solution was made by blending 3 wt.% pHEMA solution in 30wt.% AA aqueous solution with aqueous 25wt.% PAA solution according to a molar ratio of (1 : 2).
- Steps 2, 3, 4 and 5 were the same as PES.A.

PES.D

- Step 1: A coating solution was made by blending 3 wt.% pHEMA solution in 30wt.% AA aqueous solution with aqueous 25wt.% PAA solution according to a molar ratio of (1 : 3).
- Steps 2, 3, 4 and 5 were the same as PES.A.

PES.E

- Step 1: A coating solution was made by blending 6 wt.% pHEMA solution in 30wt.% AA aqueous solution with aqueous 25wt.% PAA solution according to a molar ratio of (2 : 1).
- Steps 2, 3, 4 and 5 were the same as PES.A.

PAN.A

The procedure of composite membrane preparation using PAN substrate membranes consists of five steps as described for PES.A, unless otherwise stated.

- Step 1: A coating solution was made by blending 3 wt.% pHEMA solution in 30wt.% AA aqueous solution with aqueous 25wt.% PAA solution according to a molar ratio of (1 : 0.5).
- Step 2: The coating solution was poured onto the surface of PAN substrate membrane instead of PES membrane, which was placed on top of a coating glass jar.
- Step 3: The excess solution was drained by holding the glass jar vertically for two minutes after waiting for one minute.
- Step 4: The coated substrate membrane was placed in an oven with forced air circulation for curing. The oven temperature was maintained at 70°C.
- Step 5: Steps 2-4 were repeated three times for some membranes (three layers coating) and not repeated for other membranes (one layer coating).

PAN.B

- Step 1: A coating solution was made by blending 3 wt.% pHEMA solution in 30wt.% AA aqueous solution with aqueous 25wt.% PAA solution according to a molar ratio of (1 : 1).
- Steps 2, 3, 4 and 5 were the same as PAN.A.

PAN.C

- Step 1: A coating solution was made by blending 3 wt.% pHEMA solution in 30wt.% AA aqueous solution with aqueous 25wt.% PAA solution according to a molar ratio of (1 : 1). The solution was used after storage for six months.

- Steps 2, 3, 4 and 5 were the same as PAN.A.

PAN.D

- Step 1: A coating solution was made by blending 3 wt.% pHEMA solution in 30wt.% AA aqueous solution with aqueous 25wt.% PAA solution according to a molar ratio of (1 : 2).
- Steps 2, 3, 4 and 5 were the same as PAN.A.

PAN.E

- Step 1: A coating solution was made by blending 3 wt.% pHEMA solution in 30wt.% AA aqueous solution with aqueous 25wt.% PAA solution according to a molar ratio of (1 : 3).
- Steps 2, 3, 4 and 5 were the same as PAN.A.

PAN.F

- Step 1: A coating solution was made by blending 3 wt.% pHEMA solution in 30wt.% AA aqueous solution with aqueous 25wt.% PAA solution according to a molar ratio of (1 : 1).
- Step 2 was the same as step 2 in PAN.A
- Step 3: The excess solution was drained by holding the glass jar vertically for **15-20 minutes** after waiting for one minute.

- Step 4: The coated substrate membrane was placed in an oven with forced air circulation for curing. The oven temperature was maintained at room temperature, 50, 60, 70, 80, 90, 100, 110, 120 or 130°C as indicated in Tables (7) and (8).
- Step 5: Steps 2-4 were repeated three or two times for some membranes (tree or two layers coating), and not repeated for other membranes (one layer coating).

PAN.G

- Step 1: A coating solution was made by blending 3 wt.% pHEMA solution in 30wt.% AA aqueous solution with aqueous 25wt.% PAA solution according to a molar ratio of (1 : 1). The solution prepared was further diluted using 30wt.% AA aqueous solution to 75% of the original concentration by weight.
- Steps 2 and 3 were the same as steps 2 and 3 in PAN.F
- Step 4 was the same as step 4 in PAN.A
- Step 5: Steps 2-4 were repeated three or two times for some membranes (tree or two layers coating), and not repeated for other membranes (one layer coating).

PAN.H

- Step 1: A coating solution was made by blending 3 wt.% pHEMA solution in 30wt.% AA aqueous solution with aqueous 25wt.% PAA solution according to a molar ratio of (1 : 1). The solution prepared was further diluted using 30wt.% AA aqueous solution to 50% of the original concentration by weight.
- Steps 2 – 5 were the same as PAN.G.

PAN.I

- Step 1: A coating solution was made by blending 3 wt.% pHEMA solution in 30wt.% AA aqueous solution with aqueous 25wt.% PAA solution according to a molar ratio of (1 : 1). The solution prepared was further diluted using 30wt.% AA aqueous solution to 25% of the original concentration by weight.
- Steps 2 – 5 were the same as PAN.G

PAN.best

- Step 1: A coating solution was made by blending 3 wt.% pHEMA solution in 30wt.% AA aqueous solution with aqueous 25wt.% PAA solution according to a molar ratio of (1 : 1).
- Steps 2 and 3 were the same as PAN.F
- Step 4: The coated membrane was placed in an oven with forced air circulation for curing for one hour at 70°C.
- Step 5: steps 2 and 3 were repeated.
- Step 6: steps 2-4 were repeated after step 5.

The coating solution compositions are summarized in Table (2).

Table (2) Composition of coating solutions used for the preparation of pHEMA TFC membranes for pervaporation.

Membrane	PHEMA wt.%	PAA wt.%	AA wt.%	Water wt.%
PES.A	2.89	0.86	28.1	68.14
PES.B	2.8	1.66	27.16	68.38
PES.C	2.63	3.12	25.46	68.79
PES.D	2.47	4.4	23.97	69.16
PES.E	5.45	1.62	26.42	66.51
PAN.A	2.89	0.86	28.1	68.14
PAN.B	2.8	1.66	27.16	68.38
PAN.C	2.8	1.66	27.16	68.38
PAN.D	2.63	3.12	25.46	68.79
PAN.E	2.47	4.4	23.97	69.16
PAN.F	2.8	1.66	27.16	68.38
PAN.G	2.10	1.25	27.86	68.79
PAN.H	1.40	0.83	28.58	69.19
PAN.I	0.70	0.42	29.28	69.6
PAN.best	2.8	1.66	27.16	68.38

4.3 Pervaporation Experiment

Pervaporation experiments were carried out to test the performance of the composite membranes prepared according to the method described in section (4.2). All membranes were tested by a system illustrated in Figure (5) for dehydration of 95 wt.% aqueous isopropanol solution at 1.2 torr on the permeate side while the feed pressure was maintained at one atmospheric pressure. Temperature was ambient. A membrane was placed in a pervaporation cell, illustrated in Figure (6). After 250 ml of the feed solution (95 wt.% isopropanol) was loaded in the cell, a vacuum was applied to the permeate side of the membrane. The permeate was condensed in the first cold trap cooled by liquid nitrogen. Then, the line was switched to the second cold trap after one hour, during which steady state was reached. The permeate sample collected for a predetermined period was weighed and analyzed by gas chromatography.

4.4 Ultrafiltration Experiment

Ultrafiltration experiment was carried out to find the molecular weight cut off of the substrate membranes (PES and PAN). The membranes were cut into circular coupons with an effective area of 10.2 cm^2, and were loaded into the ultrafiltration test cells. An ultrafiltration test cell and a continuous flow testing system are shown schematically in Figures (7) and (8). The membranes were then compacted using distilled water as a feed. Compaction serves to minimize mechanical deformation of a polymeric membrane matrix that occurs in pressure-driven membrane operations. During the compaction process, the feed distilled water was flowing in the feed chamber of the UF test cells at 2 L/min

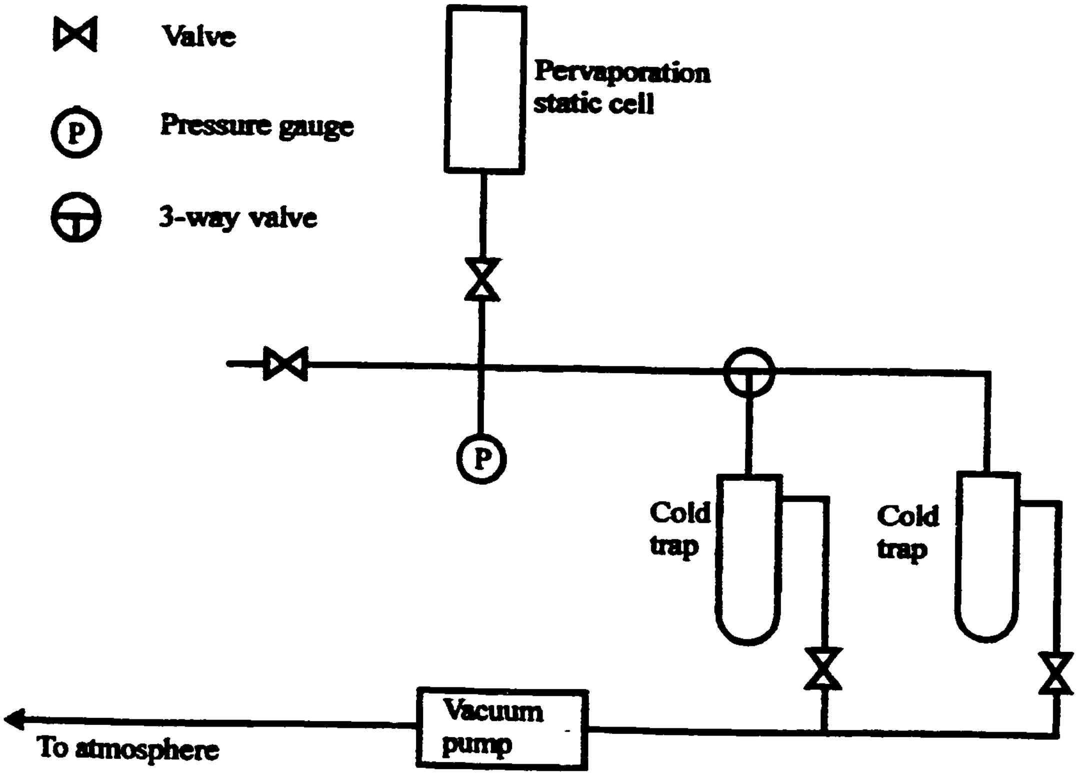


Figure (5) Schematic diagram for the pervaporation system.

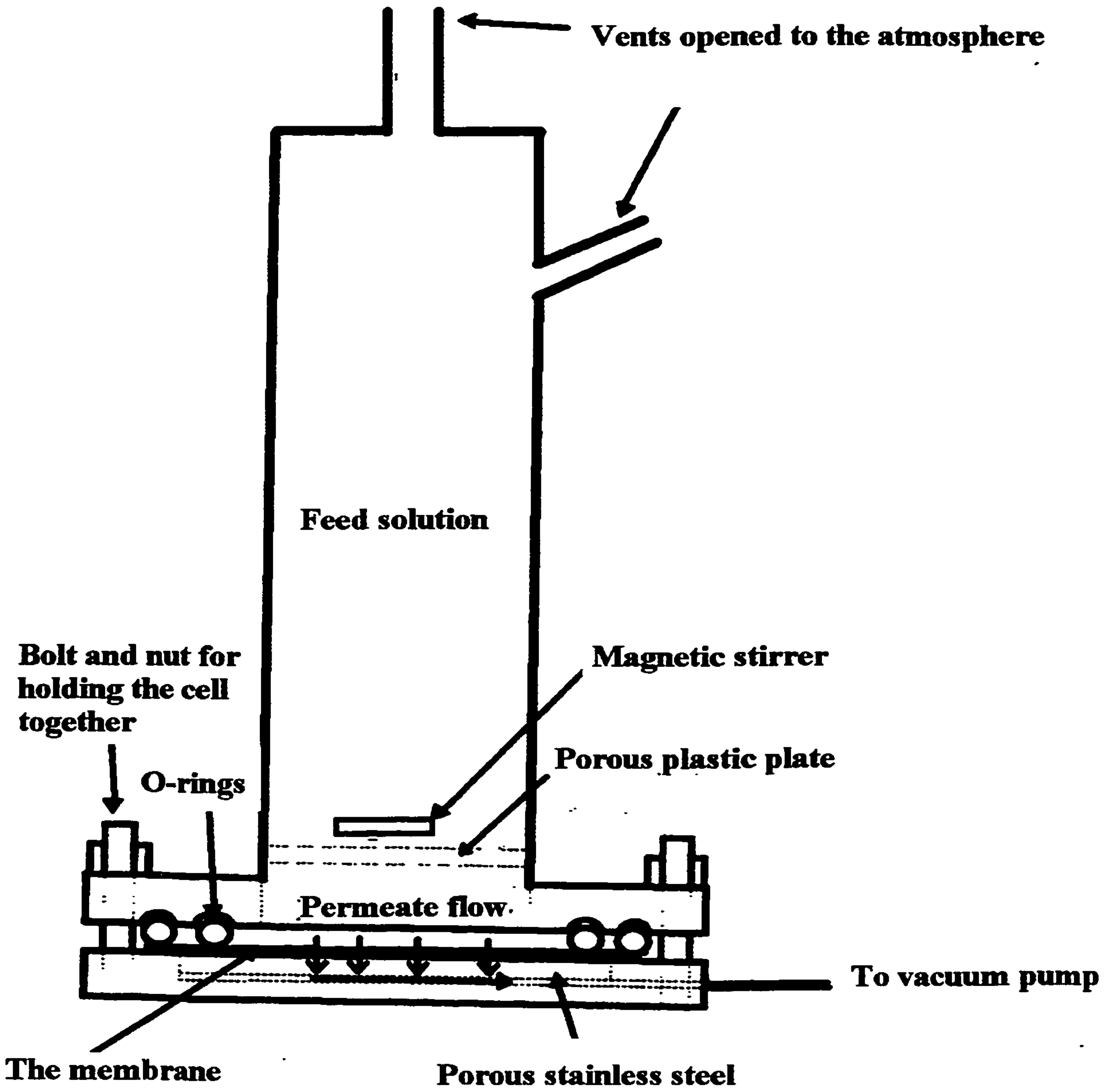


Figure (6) **Schematic diagram for the pervaporation static cell.**

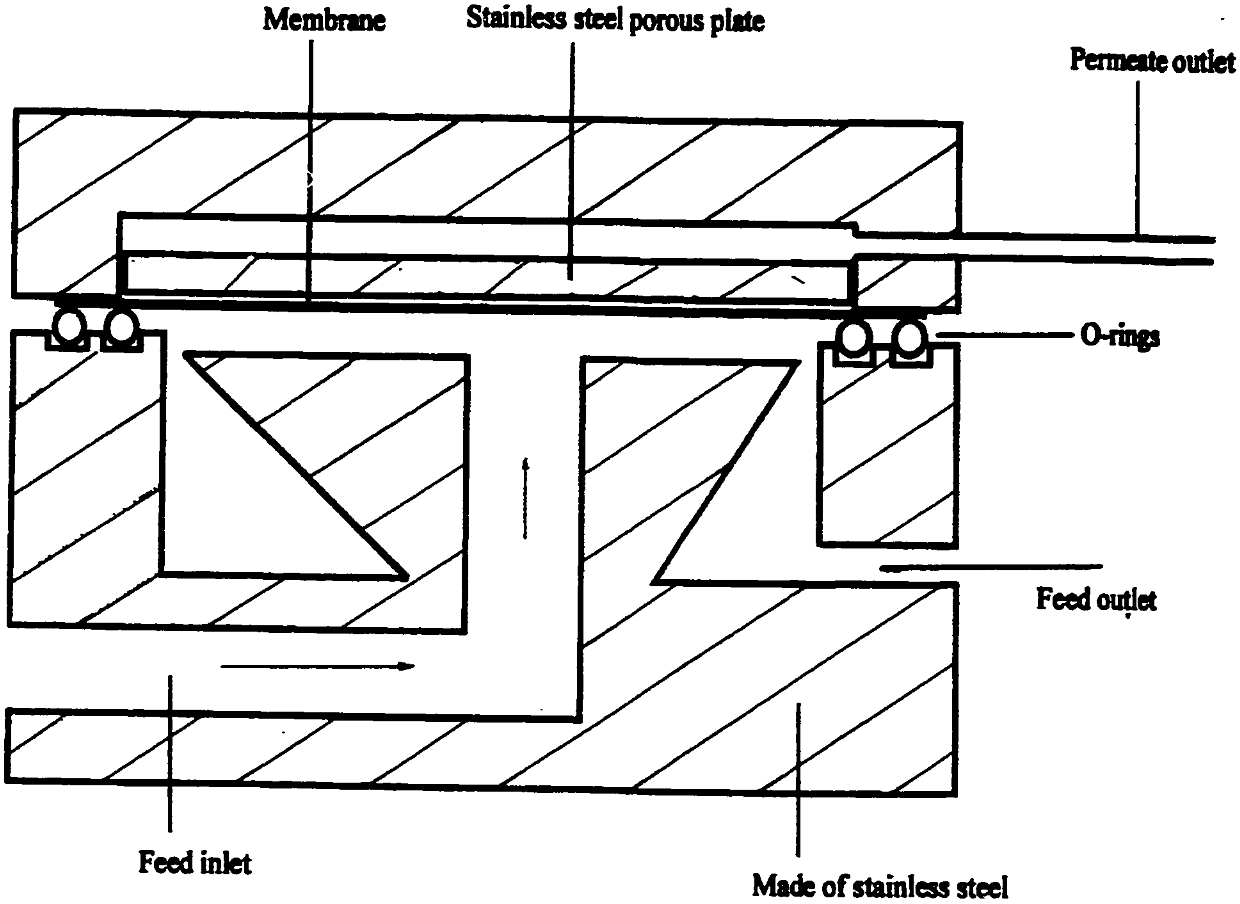
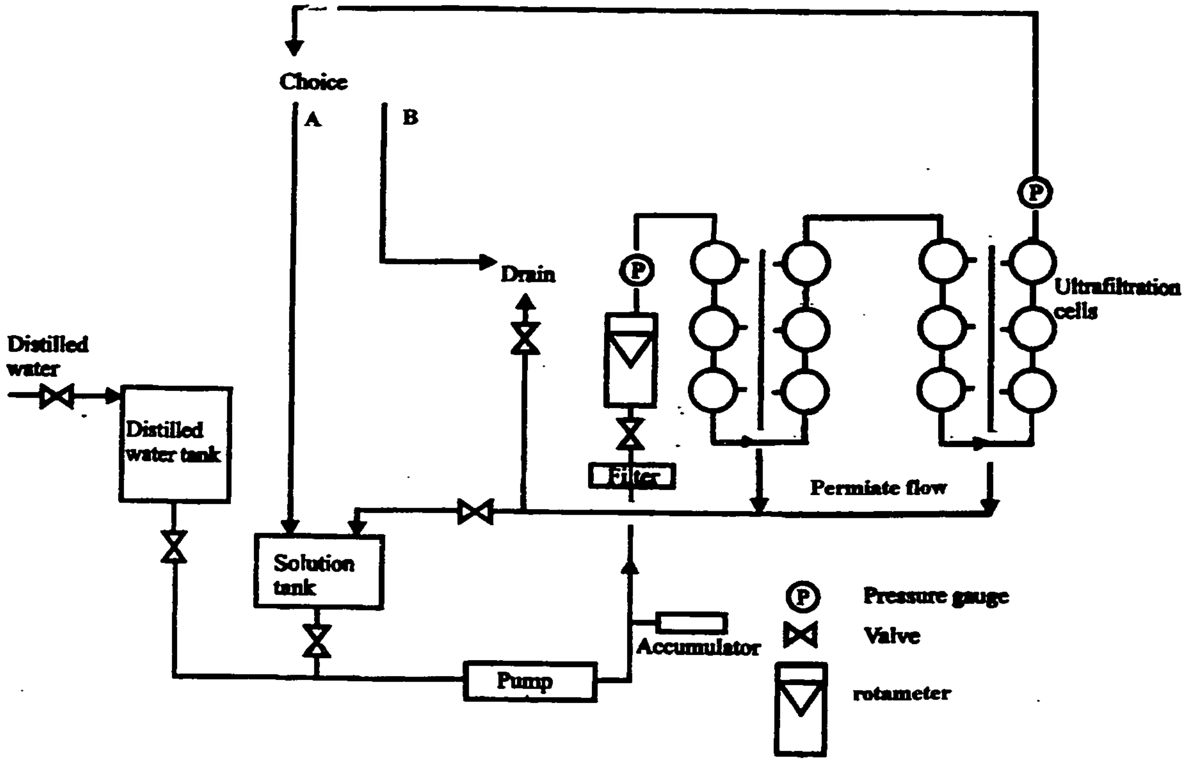


Figure (7) Schematic diagram for the ultrafiltration cell.



. Figure (8) Schematic diagram for the ultrafiltration system.

under the pressure of 80 psig (552 kPa gauge). The feed temperature was approximately 25°C. After 12 hours of compaction the ultrafiltration experiment began. The operating pressure was lowered to 50 psig (345 kPa gauge) with the flow-rate of the feed kept constant at 2 L/min for another 1 hour. The pure water permeation rate (PWP) was measured by collecting the permeate for a predetermined period. The feed was then switched to either aqueous polyethylene glycol or polyethylene oxide solution. The solute concentration in the feed was 200ppm. After a steady state was reached in about one hour, the permeation rate was determined by collecting the permeate for a predetermined period. The feed and permeate samples were subjected to total organic carbon analysis. Throughout the experiments the temperature was kept ambient. For each experiment the solute separation defined as solute separation = (feed solute concentration – permeate solute concentration) / (feed solute concentration) was determined. After each ultrafiltration test, the system was flushed with distilled water. Then, the system continued to operate using distilled water until the pure water permeation was approximately restored before applying another fresh feed.

4.5 Analysis

4.5.1 Gas chromatography

The gas chromatographic method was used to find the composition of the isopropanol and water mixtures collected from pervaporation experiments. Two analyzers were used for this purpose; the first one was a Varian 3400 with Varian 4400 integrator and the second one was Varian 1400 with a Hewlett Packard 3390 integrator.

The temperature of the detector was set at 200°C and the filament at 250°C. Helium was used as a carrier gas. A calibration curve was generated using isopropanol/water mixtures of concentrations 0, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 wt.%. (see Appendix B).

4.5.2 Total organic carbon analyzer

A Rosemount Analytical Inc. (DC-190) high temperature total organic carbon analyzer was used to analyze the total organic carbon content in the ultrafiltration samples.

5 Results and Discussion

5.1 Effect of the Composition of Coating Solution on the Performance of pHEMA/PAA Thin Film Composite (TFC) Membranes With PES and PAN Membranes as Substrates.

As mentioned before in section 4.2, the composition of the coating solution was systematically changed; i.e. the molar ratio of pHEMA:PAA was changed to 1:0.5, 1:1, 1:2 and 1:3.

5.1.1 pHEMA/PAA thin film composite (TFC) membranes with PES membrane as substrate.

Generally, it was found that the flux decreased with an increase in the content of PAA in the coating solution as shown in Figure (9), probably because the top layer thickness increased due to the increase in the viscosity of the coating solution. Figure (10) shows the change of separation factor with the change in the molar ratio pHEMA:PAA. Separation factor showed a maximum at the molar ratio of 1:1. It is believed that cross-linking is occurring between pHEMA and PAA by the reaction between carboxyl group of PAA and hydroxyl group of pHEMA to form ester linkage between PAA and pHEMA in the presence of an acidic environment provided by acetic acid (see Figure (2)). It is also known that PAA and pHEMA are extremely hydrophilic because of the presence of (COOH), (OH) and (COO) groups. The results show that the maximum separation factor at 1:1 molar ratio corresponds to the optimum combination of cross-linking and hydrophilicity. In order to test the occurrence of cross-linking, a piece

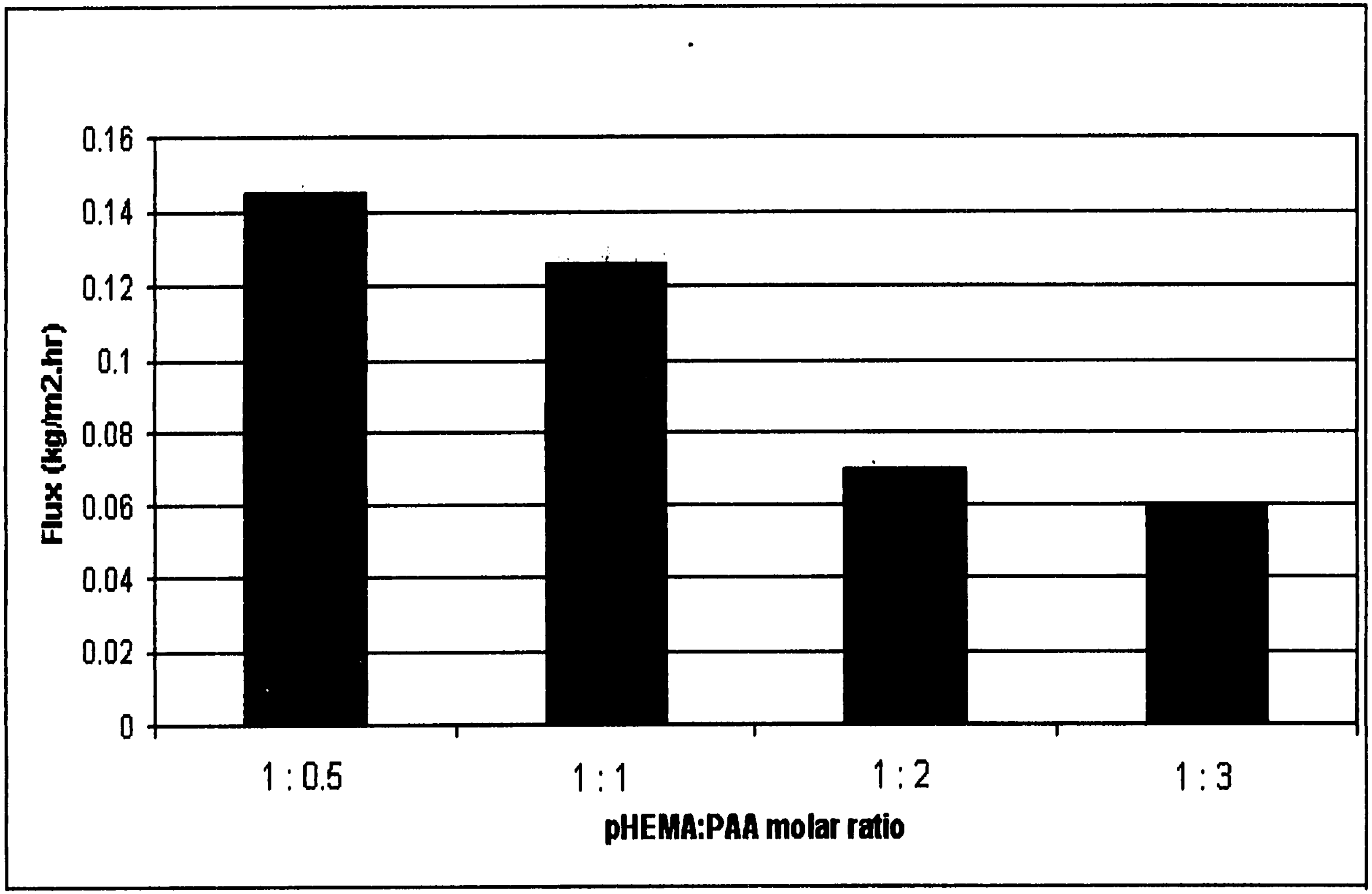


Figure (9) **The effect of composition change on the flux of pHEMA/PAA thin film composite (TFC) membranes with PES membrane as substrate.**

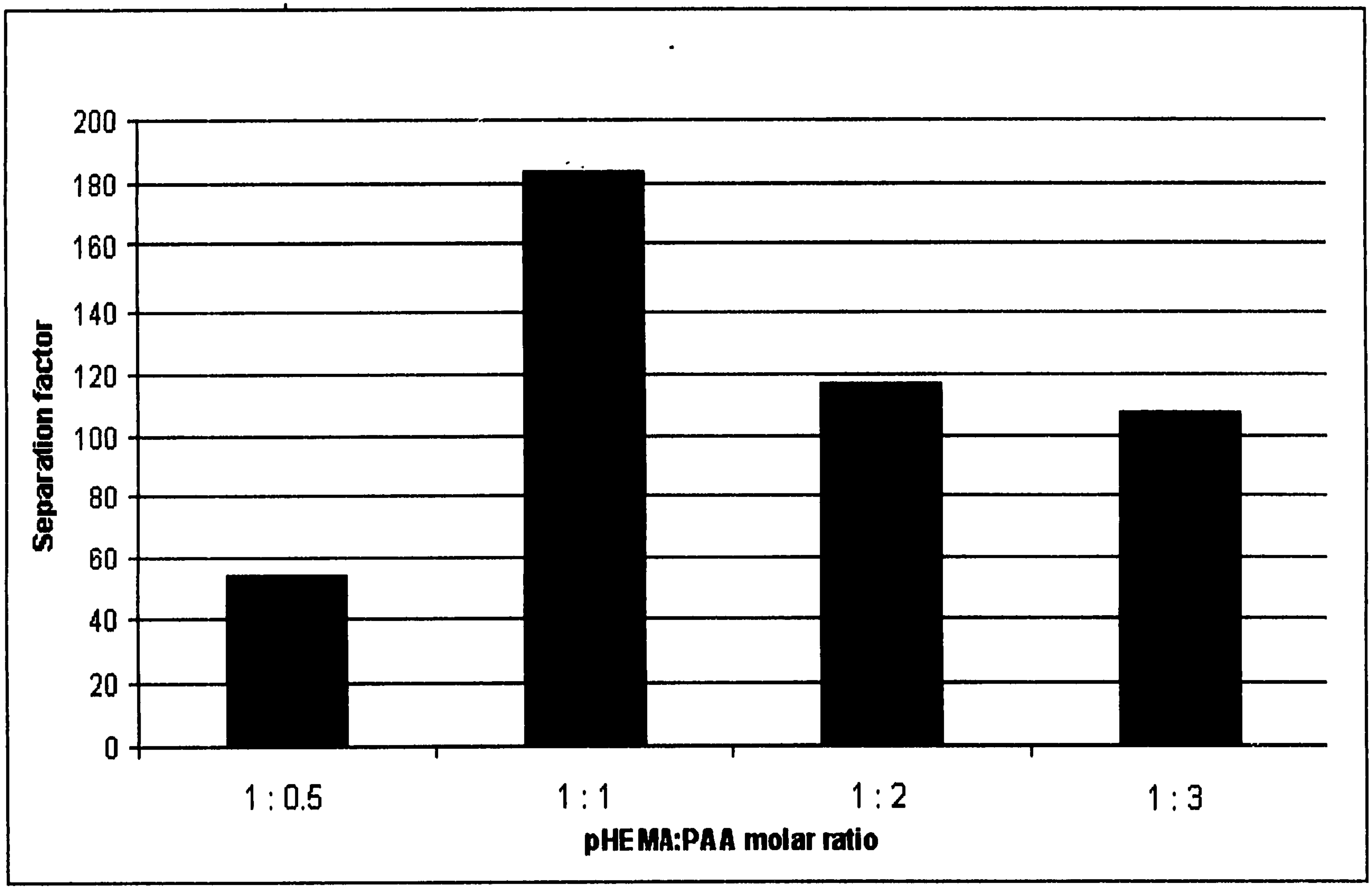


Figure (10) The effect of composition change on the separation factor of pHEMA/PAA thin film composite (TFC) membranes with PES membrane as substrate of pHEMA/PAA film that was cured under the same condition as that of PES.B TFC membrane was immersed in boiling water and kept there for one hour. A similar treatment in boiling water was made for a piece of pHEMA film that was heat treated under the same condition as that of PES.B TFC membrane. Whereas pHEMA film dissolved in boiling water, pHEMA/PAA film did not. This proves that cross-linking took place between pHEMA and PAA. The experimental results are also given in Table (3).

Table (3) Results of pervaporation experiments for pHEMA/PAA TFC membranes (substrate :PES membrane)[a].

Membrane preparation method	Number of layers	Curing time(hr)	PHEMA:PAA ratio	Flux (Kg/m^2.hr)	Separation factor
PES.A	3	6	1:0.5	0.15	54
PES.B	3	6	1:1	0.13	183
PES.C	3	6	1:2	0.07	117
PES.D	3	6	1:3	0.06	108

a. Downstream pressure, 160 Pa; operating temperature, 25°C; Isopropanol concentration in feed, 95 wt.%.

5.1.2 pHEMA/PAA thin film composite (TFC) membranes with PAN membrane as substrate.

The fluxes were an order of magnitude lower than those of pHEMA/PAA TFC membranes with PES substrate membranes. The reason behind that is because PAN substrate membrane is more heat sensitive than PES substrate membrane witch resulted in more pore shrinkage. (See section 5.8 for more discussion). The flux decreased with

PAA content and became zero when pHEMA:PAA ratio became 1:3 for the same reason as discussed in the previous section. The separation factor also decreased as PAA content increased. The results are shown in Table (4).

Table (4) Results of pervaporation experiments for pHEMA/PAA TFC membranes (substrate :PAN membrane)[a] .

Membrane preparation method	Number of layers	Curing time (hr)	PHEMA:PAA ratio	Flux ($kg/m^2.hr$)	Separation factor
PAN.A	3	6	1:0.5	0.0158	929
PAN.B	3	6	1:1	0.013	395
PAN.D	3	6	1:2	0.005	133
PAN.E	3	6	1:3	0	-

a. Downstream pressure, 160 Pa; operating temperature, 25°C; Isopropanol concentration in feed, 95 wt.%.

5.2 The Effect of the Number of Coated Layers and the Curing Time on the Performance of Composite Membranes

5.2.1 PES membrane as substrate

The number of coatings was three and the curing time was 6 hours. When PES membrane was used for substrate, it was found by the preliminary experiments that number of coating layers less than three and coating time less than six hours were not sufficient to achieve desirable separation factors.

5.2.2 PAN membrane as substrate

Table (5) shows the results for the PAN substrate membranes. From the table it is clear that the flux decreased when the number of the coating layers increased from one to three. The separation factor increased from one to three coating layers except for PAN.D with curing time of three hours. Three layers of coating is absolutely necessary to achieve any practically meaningful separation factor.

Table (5) **Results of pervaporation experiments for pHEMA/PAA TFC membranes (substrate PAN membrane)[a].**

		One layer		Three layers	
Membrane preparation method	**Curing time (hr)**	**Flux ($kg/m^2.hr$)**	**Separation factor**	**Flux ($kg/m^2.hr$)**	**Separation factor**
PAN.A	0.33	0.704	1.94	0.0228	48.5
PAN.A	1	0.537	2.09	0.0347	133.3
PAN.A	3	0.0465	54.7	0.027	86.4
PAN.B	0.33	0.834	1.83	0.044	32.3
PAN.B	1	0.454	3.65	0.0107	672.8
PAN.B	3	0.076	19.0	0.0123	67.9
PAN.D	0.33	0.26	2.12	0.0081	33.9
PAN.D	1	0.068	6.27	0.0075	4850
PAN.D	3	0.112	6.57	0.028	2.32

a. Downstream pressure, 160 Pa; operating temperature, 25°C; Isopropanol concentration in feed, 95 wt.%.

5.3 Effect of the Method of Draining the Coating Layer on the Performance of pHEMA/PAA TFC Membranes

Effect of the method to drain coating solution from the surface of the substrate membrane was examined by changing the method described in section 4.2 under PES.A and PAN.A to a newly discovered one. According to the latter method a substrate membrane was held vertically for 20 minutes after coating to make the coated layer as thin as possible. The new method was applied to PAN.F. Improvement in pervaporation performance was remarkable. By comparing PAN.B and PAN.F with one hour of curing time and three layers of coating, the flux increased from 0.0107 kg/m^2.hr to 0.021 kg/m^2.hr and the separation factor increased from 672.8 to 824 (see Tables (5)and (7)).

5.4 The Effect of Coating Solution Storage Time on the Performance of pHEMA/PAA TFC Membranes (Substrate:PAN Membrane)

A thick gel was formed in the solution container when pHEMA/PAA molar ratios of the solutions were 1:2 and 1:3, after the solution was stored for nearly one month. This was not the case when the ratios were 1:0.5 and 1:1. The formation of gel-like material is considered to be caused by excessive cross-linking of the polymers (see section 5.1.1).

The effect of the polymer solution storage was studied for pHEMA:PAA ratio of 1:1.The number of coating layers and curing time were changed. The data from PAN.B (fresh solution) and PAN.C (after six months storage) are compared in Table (6). It is difficult to conclude that there was an effect of solution storage on the membrane performance.

Table (6) Effect of coating solution storage on the performance of pHEMA/PAA TFC membranes (substrate:PAN membrane).

		Fresh solution (PAN.B)[a]	Fresh solution (PAN.B)[a]	Old solution (PAN.C)[b]	Old solution (PAN.C)[b]
Number of coating layers	**Curing time per layer (hr)**	**Flux ($kg/m^2.hr$)**	**Separation factor**	**Flux ($kg/m^2.hr$)**	**Separation factor**
3	0.33	0.044	32.33	0.008	69.26
3	1	0.011	672.79	0.016	30.17
3	3	0.0 12	67.87	0.013	61.9
3	6	0.013	394.59	0.008	2121

a. Coating solution was used soon after its preparation.

b. Coating solution was used after six months of storage.

5.5 The Effect of Curing Temperature on the Performance of pHEMA/PAA TFC Membranes (Substrate:PAN Membrane)

The effect of curing temperature was studied by adopting the membrane preparation procedure PAN.F. Either one or two layers of coating was applied and the coated layers were cured at different temperatures. The curing time was one hour. Table (7) summarizes the experimental results. The table also includes the data without curing. It was found that more than one layer of coating and 70°C of curing temperature was necessary to obtain sufficiently high separation factors.

The effect of curing temperatures equal to and greater than 70°C was further studied using membranes prepared according to the procedure PAN.F. After single coating was applied, the membrane was cured at various temperatures for 5 min (0.083 hr). The experimental results are summarized in Table (8), Figures (11) and (12). From the figures it is obvious that flux decreases whereas separation factor increases with an increase in curing temperature. The standard deviations were calculated and reported after gathering data from three membranes. They are reported in Table (8) and are given as bars in Figures (11) and (12).

To make sure that the shrinkage of PES and PAN pores is not so severe to make them responsible by themselves for the pervaporation, PES and PAN were heated under the same conditions as the best performance composite membrane, and tested using the pervaporation setup. It was found that no separation was achieved by both of them and they had very high fluxes.

Table (7) The effect of curing temperature on the pervaporation performance of pHEMA/PAA TFC membranes (substrate:PAN membrane)[a].

Membrane preparation procedure	Number of layers	Curing temp. (°C)	Curing time per layer (hr)	Flux (kg/m^2. hr)	Separation factor
PAN.F[b]	1	25	24	1.86	1.46
PAN.F[b]	2	25	24	1.54	2.35
PAN.F	1	50	1	0.81	2.16
PAN.F	2	50	1	0.72	3.36
PAN.F	3	50	1	0.25	3.87
PAN.F	1	60	1	0.7	2.06
PAN.F	2	60	1	0.36	6.07
PAN.F	3	60	1	0.14	18.44
PAN.F	1	70	1	0.45	3.65
PAN.F	2	70	1	0.06	307.5
PAN.F	3	70	1	0.02	824.7

a. Downstream pressure, 160 Pa; operating temperature, 25°C; Isopropanol concentration in feed, 95 wt.%.

b. Pervaporation experiment was performed after coating the substrate membrane and leaving it for 24 h without curing.

Table (8) **Effect of curing temperature on the pervaporation performance of pHEMA/PAA TFC membranes[a].**

Membrane preparation procedure	Number of coated layers	Curing time (hr)	Curing Temp. (^{o}C)	Flux ($kg/m^2.hr$)	Flux SD[b] ($kg/m^2.hr$)	Separation factor	Separation factor SD[b]
PAN.F	1	0.083	70	1.626	0.115	1.277	0.0914
PAN.F	1	0.083	80	1.32	0.506	1.457	0.2985
PAN.F	1	0.083	90	0.925	0.318	2.040	0.6349
PAN.F	1	0.083	100	0.55	0.051	10.06	7.4892
PAN.F	1	0.083	110	0.399	0.0004	12.89	10.05
PAN.F	1	0.083	120	0.013	0.0005	17.02	4.3642
PAN.F	1	0.083	130	0	-	-	-

a. Downstream pressure, 160 Pa; operating temperature, 25°C; Isopropanol concentration in feed, 95 wt.%.

b. SD = standard deviation.

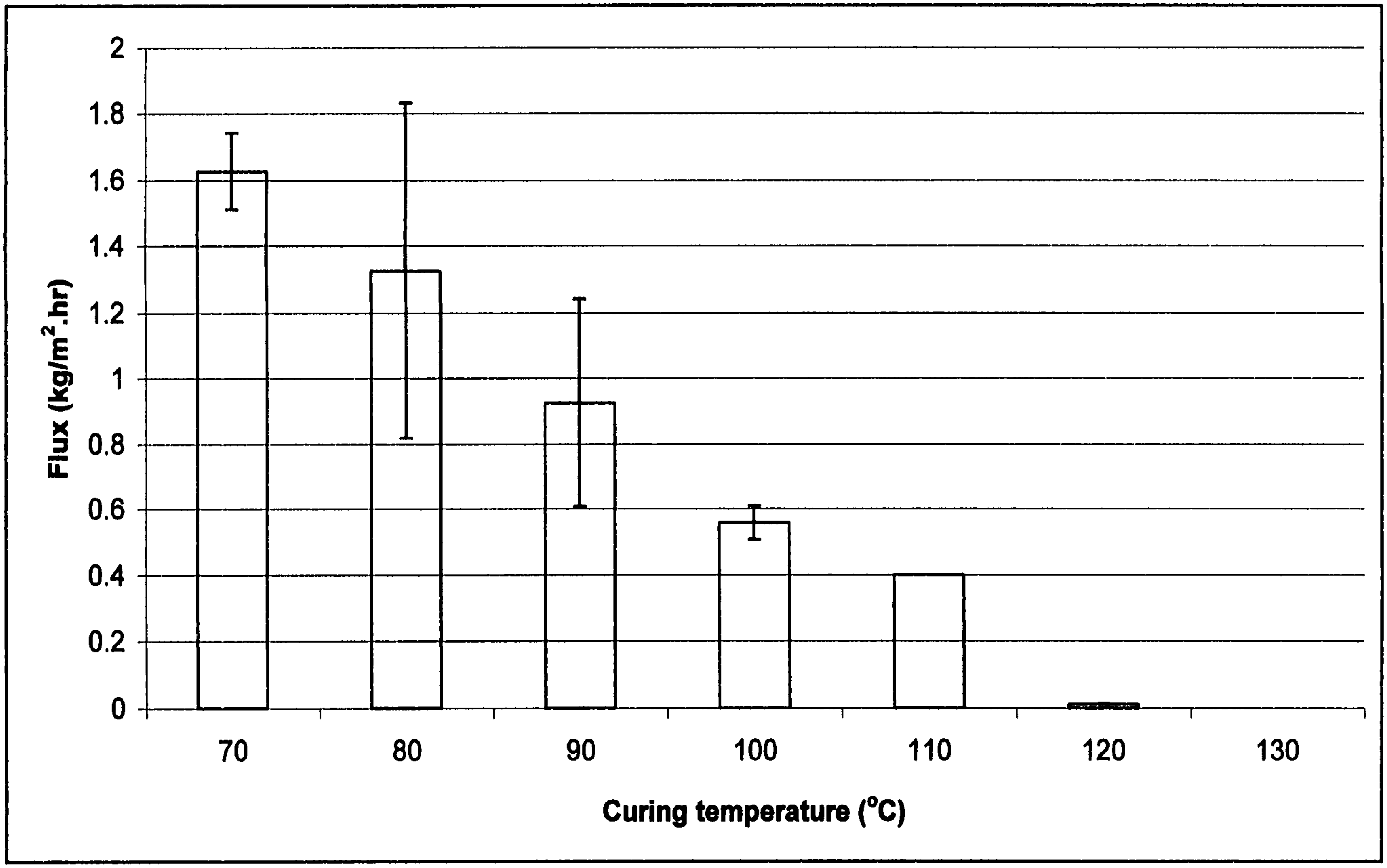


Figure (11) **The effect of curing temperature on the flux of pHEMA/PAA TFC membranes [a].**

a. Membranes and preparation conditions, same as those listed in table (8).

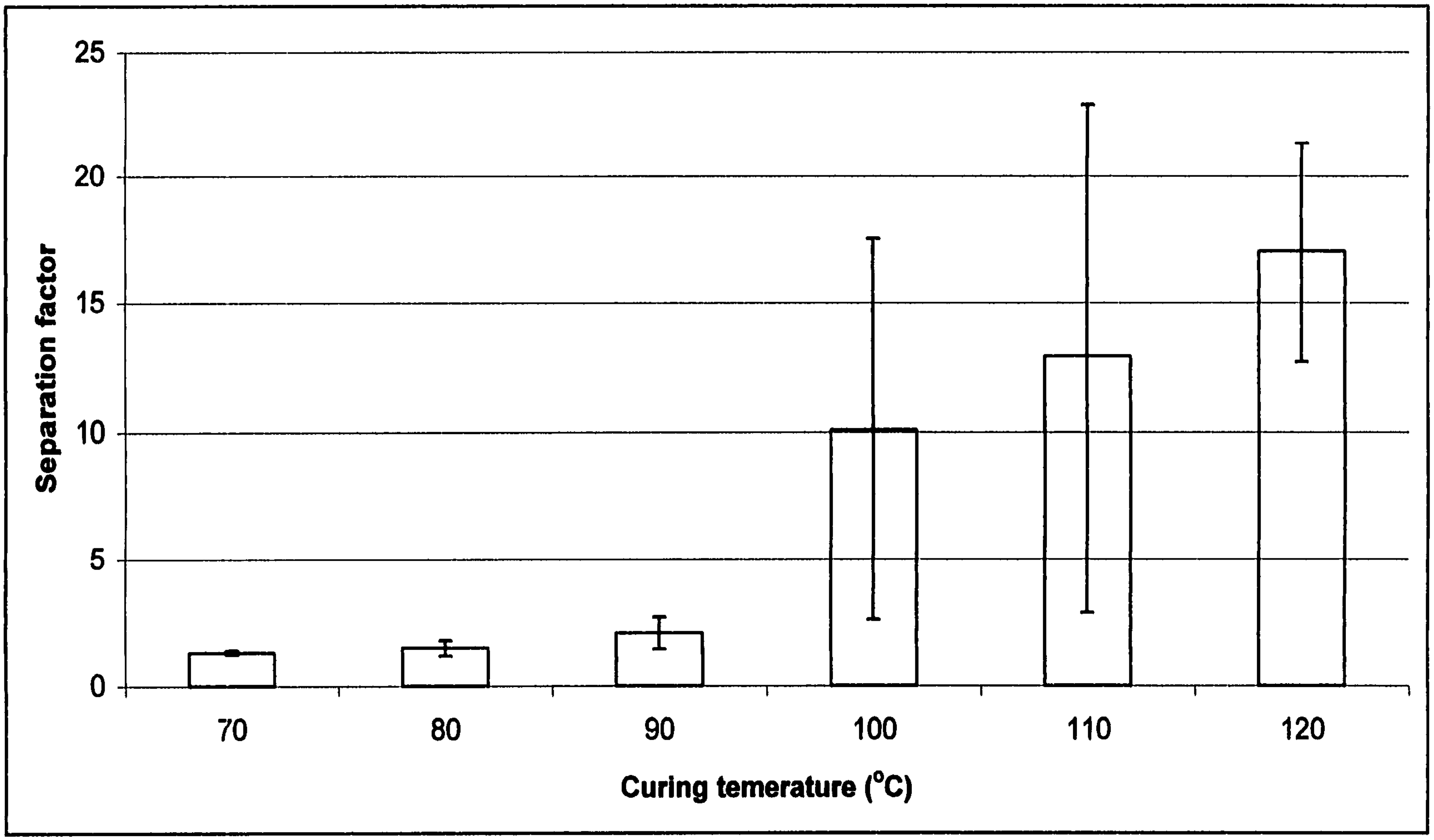


Figure (12) The effect of curing temperature on the separation factor of pHEMA/PAA TFC membranes [a].

a. Membranes and preparation conditions, same as those listed in table (8).

5.6 The Effect of the Dilution of Coating Solution on the Performance pHEMA/PAA TFC Membranes (Substrate:PAN Membrane)

It was found in section 5.1.2 that the molar ratio of pHEMA:PAA =1 gave a good result, in terms of flux and separation factor, when pHEMA:PAA TFC membranes were prepared based on a PAN substrate membrane. It was also found that the flux was an order of magnitude lower when the TFC membranes were prepared based on the PAN substrate membrane as compared to TFC membranes based on the PES membrane.

Hence, attempts were made to make the coated layer thinner by lowering the polymer concentration in the coating solution by dilution. In coating procedures PAN.G, PAN.H and PAN.I, the polymer concentration was diluted to 75%, 50% and 25% of the original value of polymer concentration, respectively, by adding 30wt.% AA aqueous solution. The original polymer concentration was the same as that of PAN.F. The number of the coated layers was either 2 or 3. Coating temperature was 70°C and the coating time was 1 hour. The experimental results for pervaporation are summarized in Table (9). The flux increased while the separation factor decreased with a decrease in polymer concentration for membranes prepared by two coating layers. No trend was observed with three coating layers.

Table (9) The effect of dilution of coating solution on the performance of pHEMA/PAA TFC membranes (substrate:PAN membrane).

Membrane preparation prosedure	Number of layers	Curing time per layer (hr)	Polymer concentration[b], (% of the original value)	Flux (kg/m^2.hr)	Flux SD[c]	Separation factor	Separation factor SD[c]
PAN.G	2	1	75	0.046	0.017	136.30	39.1
PAN.G	3	1	75	0.051	0.021	160.35	21.8
PAN.H	2	1	50	0.046	0.009	114.41	116.7
PAN.H	3	1	50	0.043	0.002	864.82	1105.6
PAN.I	2	1	25	0.096	0.040	91.93	133.7
PAN.I	3	1	25	0.047	0.005	80.20	56.36

a. Downstream pressure, 160 Pa; operating temperature, 25°C; Isopropanol concentration in feed, 95 wt.%.

b. The original concentration of pHEMA and PAA is 2.8wt.% and 1.66wt.% respectively.

c. SD = standard deviation.

5.7 The Best Pervaporation Performance of pHEMA/PAA TFC Membranes (Substrate:PAN Membrane)

The membrane with the best performance was obtained when it was prepared based on PAN substrate membrane under the following conditions: coating procedure, according to PAN.best; number of coating layers, 3; curing temperature, 70°C; curing time, 2 hrs. (see Table (2) for PAN.best).

The membrane was tested for different isopropanol concentrations in feed. The results of pervaporation experiments are summarized in Figures (13) and (14). Figure 13 shows that the flux decreased as isopropanol concentration increased. The high fluxes at high water contents in feed solutions are due to swelling of hydrophilic membrane in water. There was one exception when a relatively low flux was obtained at isopropanol concentration of 25 wt.%.

The flux is almost an order of magnitude lower than the commercially available pervaporation membranes based on polyvinyl alcohol (PVA). The isopropanol contents in the permeate are given in Figure (14) as a fraction of isopropanol contents in feed. Isopropanol concentration in the permeate was lower than in feed for the entire range of feed isopropanol concentration indicating its superior selectivity.

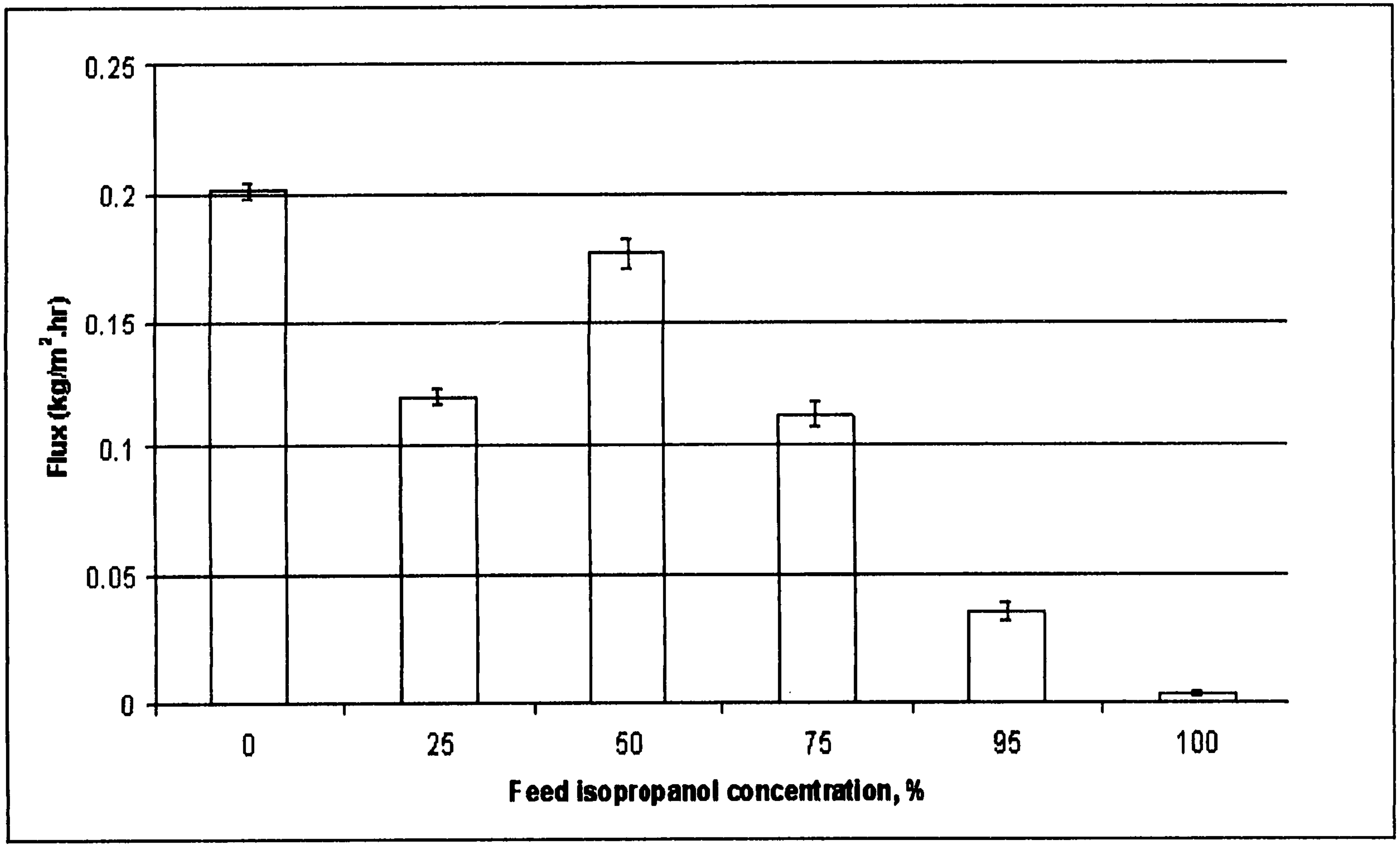


Figure (13) The permeate flux of different feed compositions using pHEMA/PAA TFC membrane of the best performance (Substrate:PAN membrane)

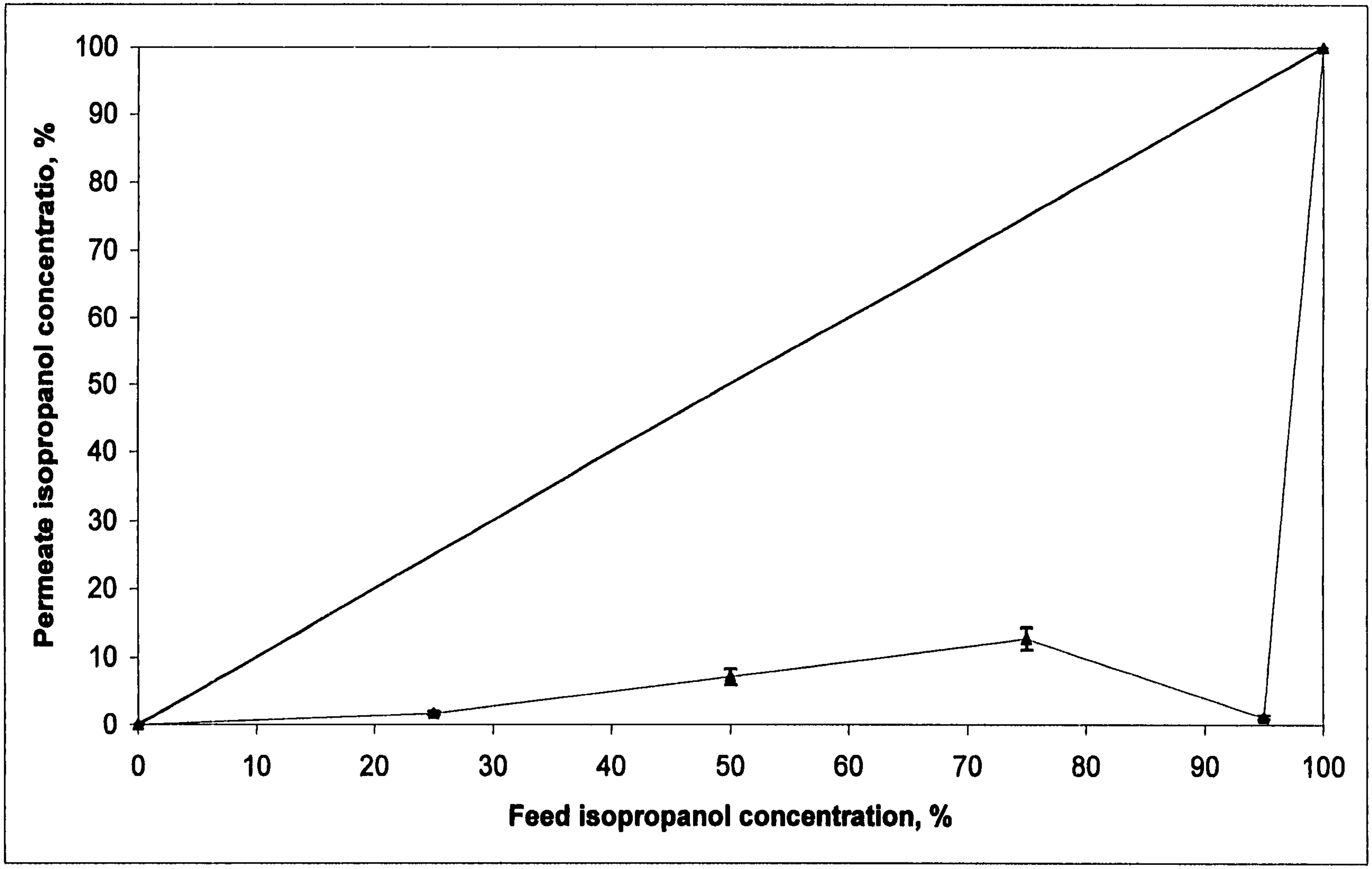


Figure (14) The concentration of isopropanol in the feed vs. the concentration of isopropanol in the permeate using pHEMA/PAA TFC membrane of the best performance (Substrate:PAN Membrane).

5.8 Characterization of the Substrate Membranes

Ultrafiltration experiments were conducted to characterize PES and PAN membranes used as substrates in preparation of the pHEMA/PAA TFC membranes. Polyethylene glycol (PEG) and polyethylene oxide (PEO) of different molecular weights were used as solutes. Using the separation data of the solutes, the molecular weight cut off (MWCO) values of the membranes were determined in the following way:

The solute separation and the Einstein-Stokes radius, a (cm), were plotted on a log-normal scale. A straight line relationship is expected between solute rejection and the Einstein-Stokes radius when the pore size is distributed according to the log-normal distribution. Einstein-Stokes radius, a, can be calculated from the molecular weight of solute by

$$a = 16.73 \times 10^{-10} M^{0.557} \qquad \text{for PEG} \qquad (13)$$

$$a = 10.44 \times 10^{-10} M^{0.587} \qquad \text{for PEO} \qquad (14)$$

The Einstein-Stokes radius which corresponds to 90% solute separation was obtained from linear interpolation. MWCO was obtained as the molecular weight that corresponds to the above Einstein-Stokes radius. MWCO obtained can be used as a measure of the pore size. The pure water permeation flux was also determined experimentally at an operation pressure of 50 psig.

Table (10) summarizes the results of ultrafiltration experiments. Comparing PES membrane and PAN membrane unheated, MWCO of the latter membrane is far greater than the former, whereas the pure water permeation fluxes are not different from each other. This means larger size and smaller number of pores on the PAN membrane.

Dipping the PAN membrane in acetic acid for 18 hours did not change either pure water permeation flux or MWCO very much. This means the pore size of the membrane did not change very much in aqueous acetic acid solution.

The heat treatment of the PAN membrane reduced both pure water permeation flux and MWCO, significantly. This is because of the shrinkage of the membrane pore at 70°C. Recall that the latter temperature was necessary to cross-link the polymers.
From the large pore size of the PAN substrate membrane and the shrinkage of the pore during the curing process, it is understood that both pHEMA and PAA polymers penetrate into the pore of the substrate membrane during the coating procedure. During the subsequent curing procedure, the polymers are more compactly packed in more ordered fashion in the membrane pore, thus resulting in very high selectivity, however, in low flux of the membrane.

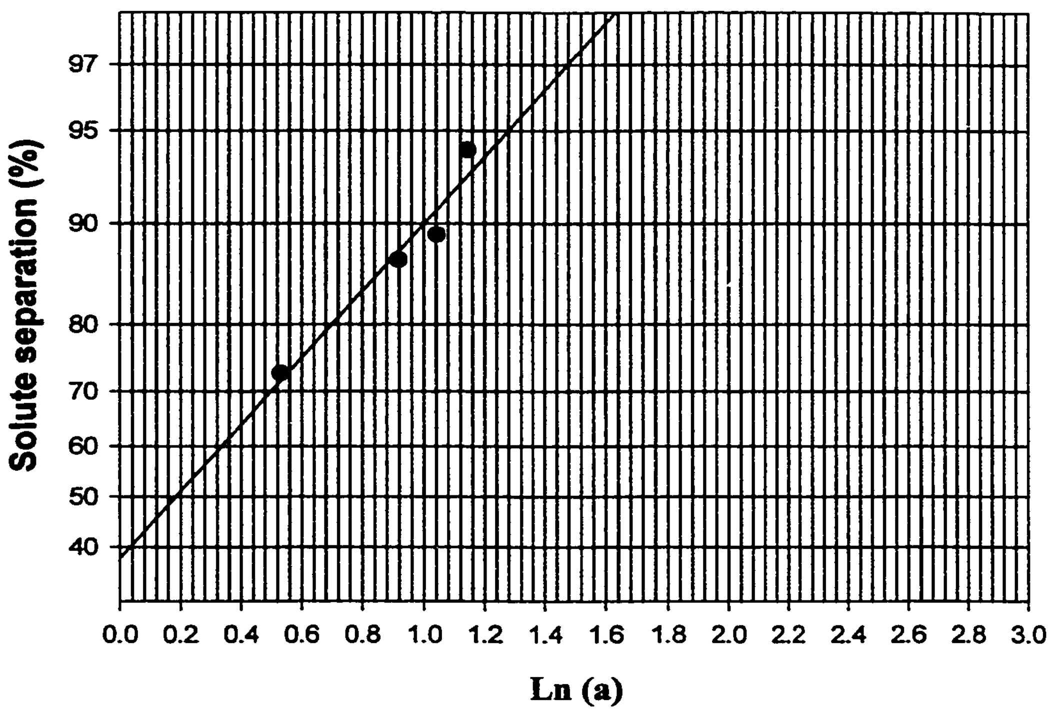


Figure (15) **Log-normal plot of solute separation versus stokes radius, a, for PES substrate membrane[a].**

a. Operating pressure, 50 psig, PEG or PEO concentration in the feed, 200 ppm.

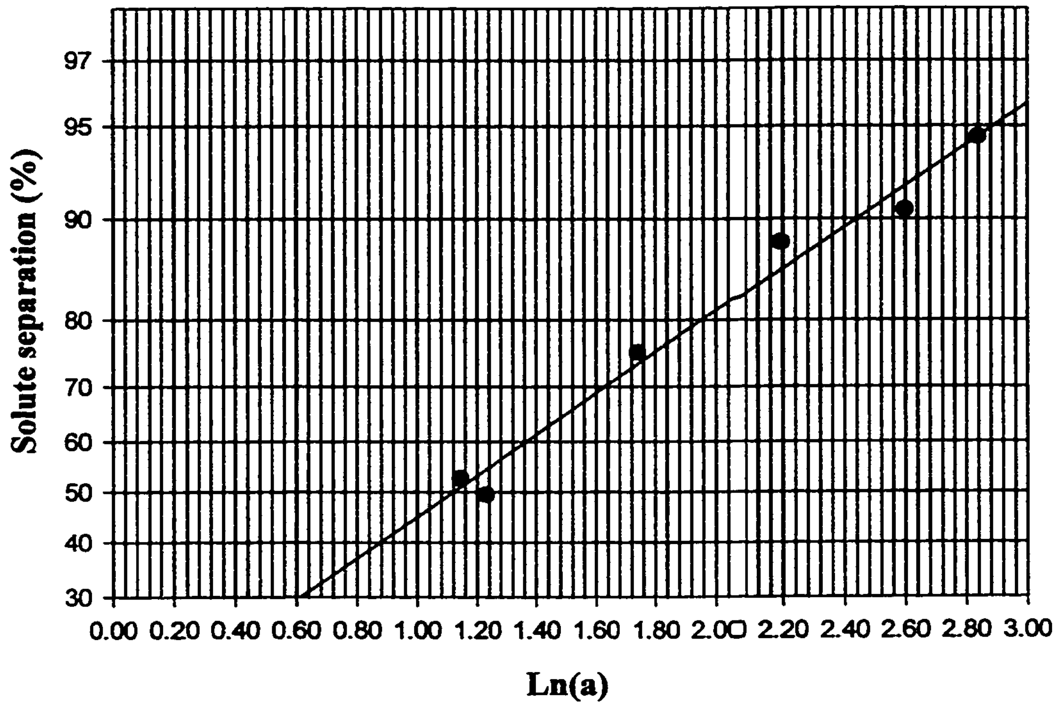


Figure (16) **Log-normal plot of solute separation versus stokes radius, a, for PAN substrate membrane**[a]**.**

a. Operating pressure, 50 psig, PEG or PEO concentration in the feed, 200 ppm.

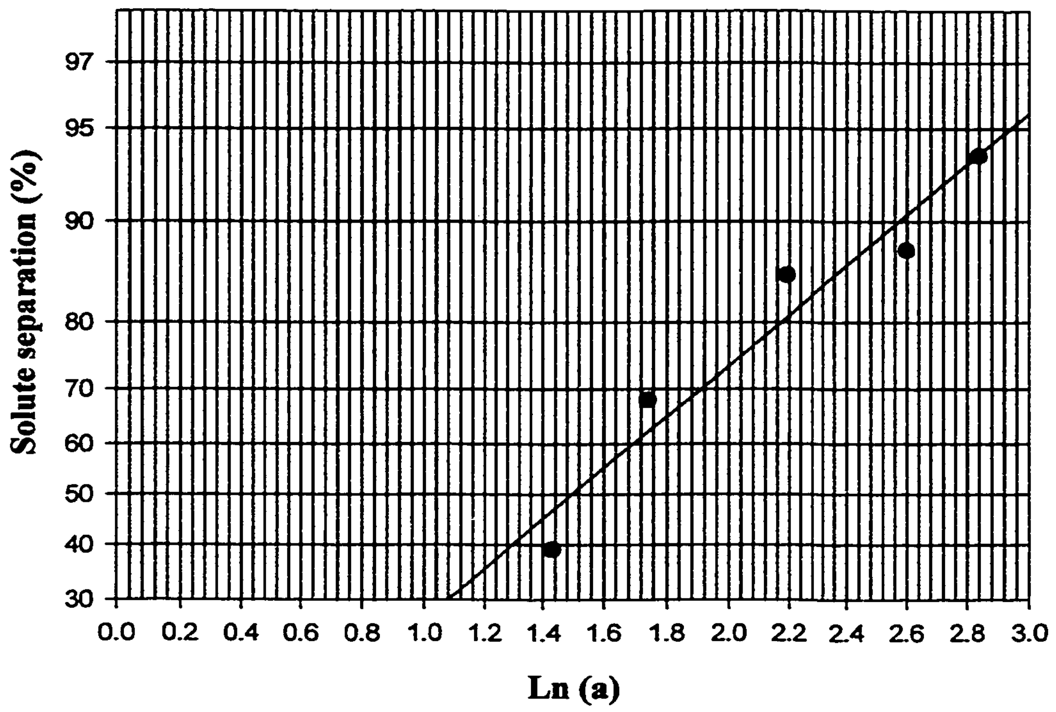


Figure (17) **Log-normal plot of solute separation versus stokes radius, a, for PAN substrate membrane after dipping in 30 wt.% aqueous acetic acid solution for 18 hours at room temperature [a].**

a. Operating pressure, 50 psig, PEG or PEO concentration in the feed, 200 ppm.

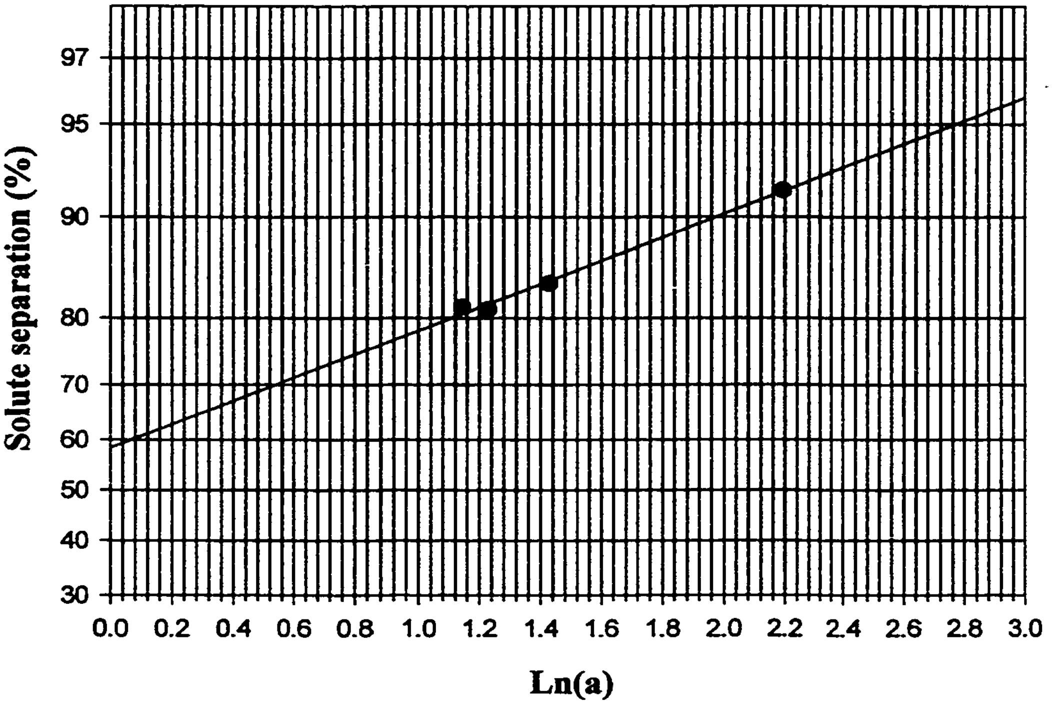


Figure (18) **Log-normal plot of solute separation versus stokes radius, a, for PAN substrate membrane after dipping in 30 wt.% aqueous acetic acid solution and then heating for 18 hours under 70°C [a].**

a. Operating pressure, 50 psig, PEG or PEO concentration in the feed, 200 ppm.

Table (10) Characterization of PES and PAN substrate membranes by ultrafiltration experiments [a].

Membrane	Treatment	Pure water permeation flux kg/m^2.hr	MWCO
PES	No treatment	0.94	9300
PAN	No treatment	1.3	152,000
PAN	Dipped in acetic acid for 18hours	1.2	186,000
PAN	Dipped in acetic acid then heated in 70°C oven for 18hours	0.093	52,000

a. Operating pressure, 50 psig, PEG or PEO concentration in the feed, 200 ppm.

6 Conclusions

1. The best performance of the coating solution was obtained from membranes prepared from polymer solutions with one to one molar ratio between pHEMA and PAA witch indicates that this ratio has the optimum viscosity and composition for coating and cross-linking.
2. Mixing more than one mole of PAA per mole of PHEMA will make the solution unstable and shorten the storage time before becoming very viscous due to severe cross-linking.
3. Diluting the coating solution does not drastically affect the performance.
4. The average pore size of the PAN substrate membrane is larger than the PES substrate membrane. The PAN substrate membrane is, however, less porous than the PES substrate membrane.
5. Curing at temperatures higher than 70°C causes substrate membrane pores to shrink. The pores in the PAN substrate membrane shrank more than the PES substrate membrane due to PAN's lower glass transition temperature.
6. The best performance of pHEMA/PAN TFC membrane was achieved by two hours of curing time and three coating layers. Two hours of curing time seem to be long enough for cross-linking to take place to a degree that allows sufficiently high selectivity of the membrane. Three coating layers seem to be a minimum skin layer thickness to prevent the formation of defective pores.
7. Three coating layers and eighteen hours of curing time resulted in the best performance of pHEMA/PES TFC membrane. A much longer curing time was allowed for pHEMA/PES TFC membrane than for pHEMA/PAN TFC membrane

due to the fact that the PES substrate membrane is less heat sensitive than the PAN substrate membrane.

8. The curing temperature should not be less than 70°C because cross-linking does not take place to a sufficient degree when the curing temperature is lower than 70°C.

7 Recommendations

1. It is recommended to use PAN and PES substrate membranes of different average pore sizes to observe the effect of different pore sizes on the performance of the TFC membrane.

2. It is recommended to prepare coating solutions using different molecular weights of pHEMA and PAA to study the effect of defferent degrees of cross-linking.

3. It is recommended to use a substrate membrane with deffirent heat resistances than PES and PAN membranes to study the effect of deffirent degrees of pore shrinkage.

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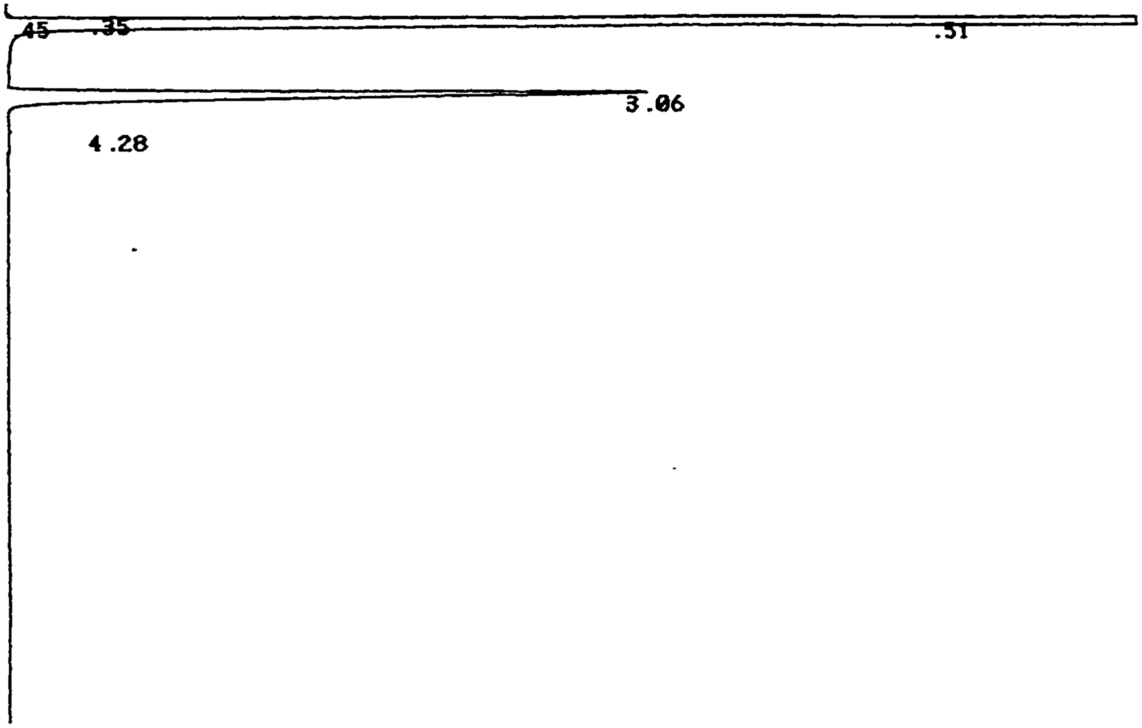
Appendices

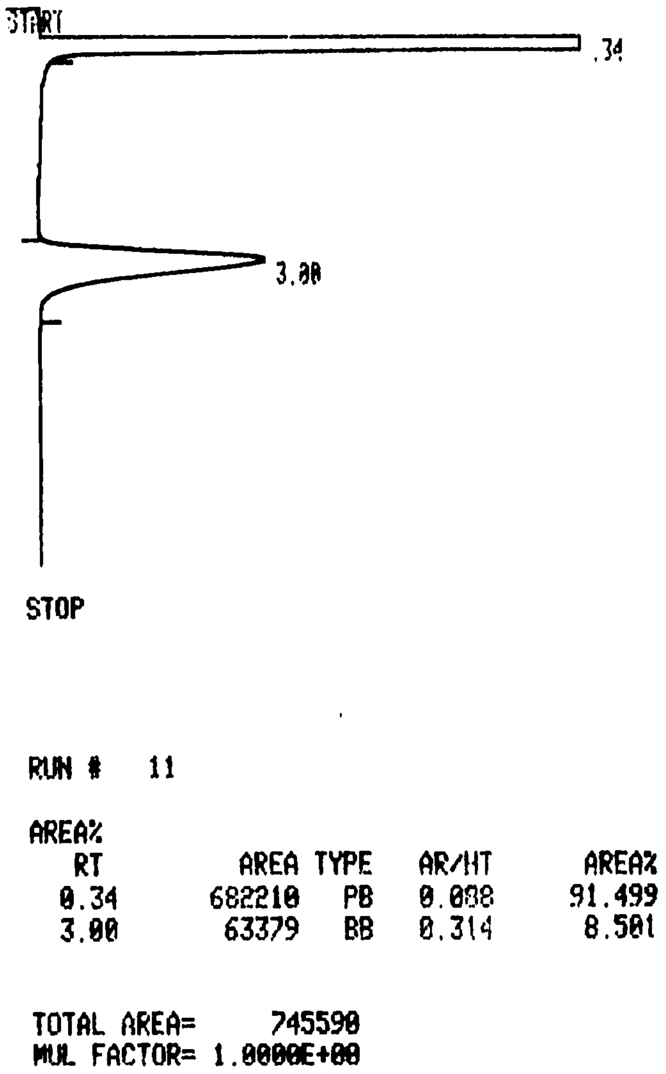
Appendix A **Gas Chromatography integrator reports.**

```
CHANNEL A      INJECT  06/09/98 11:43:39   STORED TO BIN #  40
```



```
DATA SAVED TO BIN #  40


                              06/09/98  11:43:39     CH= "A"  PS=  1.

FILE  1.     METHOD  0.     RUN  42      INDEX  42            BIN  40

PEAK#       AREA%        RT       AREA BC



     1         0.003      0.35         144 02
     2         0.002      0.45         107 02
     3        87.061      0.51     3792357 03
     4        12.902      3.06      562018 01
     5         0.031      4.28        1370 01

TOTAL       100.                   4355996
```

Figure (19) (Varian 3400) Gas Chromatography integrator report.



```
RUN #   11

AREA%
   RT          AREA TYPE   AR/HT       AREA%
  0.34       682210   PB   0.088      91.499
  3.00        63379   BB   0.314       8.501

TOTAL AREA=     745590
MUL FACTOR= 1.0000E+00
```

Figure (20) (Varian 1400) Gas Chromatography integrator report.

Appendix B Calibration for the gas chromatography.

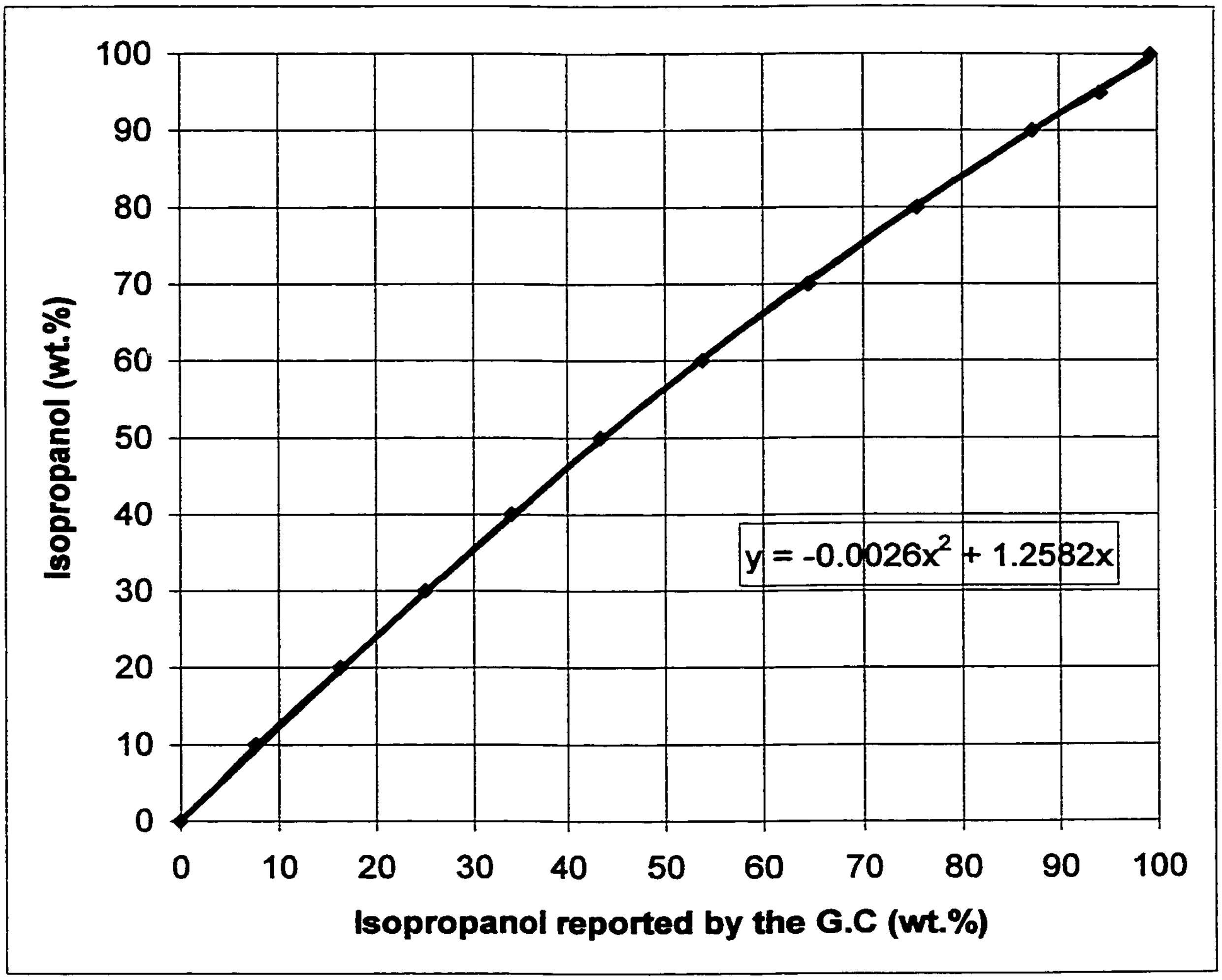


Figure (21) Calibration for the gas chromatography.

Appendix C Pervaporation experiment results.

Membrane preparation procedure	**Number of coated layers**	**Curing time (hr)**	**Curing Temp. (^{0}C)**	**Concentration of isopropanol in the feed (%)**	**Flux (kg/m^2.hr)**	**Separation factor**
PES.A	3	6	70	95	0.145	54.07
PES.B	3	0.33	70	95	0.575	4.17
PES.B	3	1	70	95	0.400	5.05
PES.B	3	3	70	95	0.260	13.75
PES.B	3	6	70	95	0.126	183.12
PES.C	3	0.33	70	95	0.259	7.2
PES.C	3	1	70	95	0.147	17.89
PES.C	3	3	70	95	0.090	133
PES.C	3	6	70	95	0.069	116.7
PES.D	3	0.33	70	95	0.130	19
PES.D	3	1	70	95	0.150	7.2

PES.D	3	3	70	95	0.080	78.43
PES.D	3	6	70	95	0.060	107.66
PES.E	3	6	70	95	0.108	51.37
PAN.A	3	0.33	70	95	0.023	48.49
PAN.A	3	1	70	95	0.0347	133.3
PAN.A	3	3	70	95	0.027	86.36
PAN.A	3	6	70	95	0.016	928.93
PAN.B	3	0.33	70	95	0.044	32.33
PAN.B	3	1	70	95	0.011	672.79
PAN.B	3	3	70	95	0.012	67.86
PAN.B	3	6	70	95	0.013	394.59
PAN.C	3	0.33	70	95	0.008	69.26
PAN.C	3	1	70	95	0.016	30.17
PAN.C	3	3	70	95	0.013	61.9
PAN.C	3	6	70	95	0.008	2121

PAN.D	3	0.33	70	95	0.008	33.89
PAN.D	3	1	70	95	0.007	4850.1
PAN.D	3	3	70	95	0.028	2.31
PAN.D	3	6	70	95	0.005	133.37
PAN.E	3	0.33	70	95	0.009	43.96
PAN.E	3	1	70	95	0	-
PAN.E	3	3	70	95	0	-
PAN.E	3	6	70	95	0	-
PAN.A	1	0.33	70	95	0.704	1.93
PAN.A	1	1	70	95	0.537	2.08
PAN.A	1	3	70	95	0.046	54.72
PAN.B	1	0.33	70	95	0.834	1.827
PAN.B	1	1	70	95	0.454	3.64
PAN.B	1	3	70	95	0.076	18.98
PAN.C	1	0.33	70	95	0.726	1.55

PAN.C	1	1	70	95	0.522	2.09
PAN.C	1	3	70	95	0.098	12.54
PAN.D	1	0.33	70	95	0.260	2.12
PAN.D	1	1	70	95	0.068	6.27
PAN.D	1	3	70	95	0.112	6.57
PAN.E	1	0.33	70	95	0.094	3.33
PAN.E	1	1	70	95	-	-
PAN.E	1	3	70	95	0.012	15.1
PAN.F	1	24	25	95	1.86	1.46
PAN.F	2	24	25	95	1.54	2.35
PAN.F	1	1	50	95	0.810	2.16
PAN.F	2	1	50	95	0.720	3.36
PAN.F	3	1	50	95	0.250	3.87
PAN.F	1	1	60	95	0.700	2.06
PAN.F	2	1	60	95	0.360	6.07

PAN.F	3	1	60	95	0.135	18.44
PAN.F	1	1	70	95	0.450	3.65
PAN.F	2	1	70	95	0.060	307.5
PAN.F	3	1	70	95	0.020	824.7
PAN.F	1	1	70,60,50	95	0.590	2.81
PAN.F	2	1	70,60,50	95	0.110	27.88
PAN.F	3	1	70,60,50	95	0.020	298.75
PAN.F	1	0.083	70	95	1.63	1.27
PAN.F	1	0.083	80	95	1.33	1.45
PAN.F	1	0.083	90	95	0.925	2.04
PAN.F	1	0.083	100	95	0.261	10.06
PAN.F	1	0.083	110	95	0.150	12.89
PAN.F	1	0.083	120	95	0.013	17.02
PAN.F	1	0.083	130	95	0	-

PAN.G	2	1	70	95	0.046	136.30
PAN.G	3	1	70	95	0.051	160.35
PAN.H	2	1	70	95	0.046	114.41
PAN.H	3	1	70	95	0.043	864.82
PAN.I	2	1	70	95	0.096	91.93
PAN.I	3	1	70	95	0.047	80.20
PAN.best	3	1, 0.33	70, 25	100	0.004	-
PAN.best	3	1 ,0.33	70, 25	75	0.112	16.65
PAN.best	3	1 ,0.33	70, 25	50	0.177	10.59
PAN.best	3	1 ,0.33	70, 25	25	0.120	16
PAN.best	3	1 ,0.33	70, 25	0	0.201	-
PAN.best	3	1 ,0.33	70, 25	95	0.038	1925