

# Pervaporation Separation of Pentane–Alcohol Mixtures Using Nylon 6–Polyacrylic Acid (PAA) Ionically Crosslinked Membranes. II. Experimental Data and Theoretical Interpretation

ROBERT Y. M. HUANG,\* MALINI BALAKRISHNAN, and JI-WON RHIM†

Department of Chemical Engineering, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

## SYNOPSIS

Novel ionically cross-linked blended membranes of nylon 6 and poly(acrylic acid) (PAA) were studied for the pervaporation separation of the binary organic mixture of pentane and methanol. Membranes of composition 25 wt % PAA were used after cross-linking. The experimental data obtained from the pervaporation runs were compared with the theoretical values of the individual permeabilities for binary mixtures predicted by the modified Fels and Huang model. This new model is based on an extension of the free volume theory and the introduction of Flory–Huggins thermodynamics for the calculations of the binary interaction parameters and the diffusion coefficients. The calculated values of permeabilities obtained from this modified model were reasonably close to the experimental values.

## INTRODUCTION

The present paper is concerned with the use of blending and cross-linking techniques to develop highly permselective membranes for the pervaporation separation of pentane–methanol mixtures over the entire range of compositions. It is a continuation of our investigation on the synthesis and preparation of ionically cross-linked nylon 6–poly(acrylic acid) (PAA)-blended membranes that have been successfully used for the separation of acetic acid–water and ethanol–water mixture systems and have been reported.<sup>1–7</sup> The present study deals with the separation of pentane–methanol mixtures that forms an azeotrope at 93% wt % pentane. Part I of this investigation dealt with the preparation of the membrane and its characterization in terms of glass transition temperature, morphology, mechanical properties, and water absorption.<sup>8</sup> Currently, little

data are available for such alkane–alcohol mixtures. Aptel et al.<sup>9</sup> reported a detailed investigation of several constant boiling liquid systems comprising water aprotic solvents, water alcohol, and water alkane mixtures. They have reported data for ethanol–hexane mixtures that are close to the system presently being reported. Another similar system is that of methanol and hexane which has been reported by Cabasso.<sup>10</sup> They used different membranes including ion-exchange membranes (Nafion) and highly cross-linked quaternary poly(phenylene oxide) (PPO) membranes for this purpose. Thompson et al.<sup>11</sup> recently reported experimental results on the hexane–heptane and toluene–ethanol systems. The specific goals of this research are the synthesis and preparation of nylon 6–PAA ionically cross-linked membranes prepared according to the methods described earlier,<sup>1–6</sup> and the subsequent pervaporation separation of the pentane–methanol mixtures in terms of permeabilities and separation factors. The pervaporation results were then compared with the calculated values using the modified Fels–Huang model that recently has been reported.<sup>12,13</sup> This new model is based on an extension of the free-volume theory and the introduction of the Flory–Huggins thermodynamics for the calculation of the binary inter-

\* To whom correspondence should be addressed.

† Present address: Membranes and Separation Laboratory, Korea Research Institute of Chemical Technology (KRICT), P.O. Box 9, Daedeog-Danji, Daejeon 305-606, South Korea.

action parameters and is a modification of the previous Fels-Huang model.<sup>12,13</sup> The diffusion coefficients were determined experimentally by the desorption method and computed using the method as recently described.<sup>14</sup> It was found that the values of the permeabilities using this model were in close agreement with the experimental results from the pervaporation runs. A brief description of the modified Fels and Huang model and the calculation method to obtain the diffusion coefficients are presented in the next section.

## THEORY

From the known diffusion coefficients at zero concentration ( $D_{c=0}$ ), the Fujita's free-volume parameters,  $A_d$  and  $B_d$ , can be determined from the following relationship:

$$D_{c=0} = RTA_d \exp\left[\frac{-B_d}{f(0, T)(1 - \phi_c)}\right] \quad (1)$$

Another parameter  $\beta(T)$  can be obtained from the following expression:

$$f(v_i, T) = f(0, T) + \beta(T)v_i \quad (2)$$

Once the parameters are determined, the thermodynamic diffusion coefficient  $D_T$  that increases the resistance of the diffusing species in the polymer network is given by

$$D_T = RTA_d \exp\left[\frac{-B_d}{f(1 - \phi_c)}\right] \quad (3)$$

Further, the thermodynamic diffusion coefficient can be related to  $D_{i3}$  by

$$(D_T)_i = \frac{D_{i3}}{1 - v_i} \frac{2 \ln v_i}{2 \ln a_i} \quad (4)$$

For a binary system, the term  $(2 \ln v_i)/(2 \ln a_i)$  in the above equation can be expressed as

$$\frac{2 \ln a_i}{2 \ln v_i} = 1 - \left(1 - \frac{V_i}{V_3}\right)v_i - 2\chi_{i3}v_3 \quad (5)$$

The Gibbs free energy of mixing of a ternary system can be given by

$$\begin{aligned} \frac{\Delta G_{\text{mix}}}{RT} = & n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 \\ & + \chi_{12}(u_1)n_1\chi_2 + \chi_{13}n_1\phi_3 + \chi_{23}n_2\phi_3 \quad (6) \end{aligned}$$

Differentiation of the above equation with respect to  $n_1$  and  $n_2$ , respectively, gives the activity of each component in the membrane, and another differentiation of this resulting equation for activities with respect to  $\ln \phi_1$  and  $\ln \phi_2$ , respectively, yields the  $2 \ln a_1/2 \ln a_1'$  and  $2 \ln a_2/2 \ln a_2'$ .

## Determination of Binary Interaction Parameter

(i)  $\chi_{12}$  parameter.

The  $\chi_{12}$  parameter can be determined from the excess free-energy data,  $\Delta G^E$ , by using Flory-Huggins thermodynamics. This relationship can be given:

(ii)  $\chi_{12}$  and  $\chi_{13}$  parameter:

$$\chi_{12} = \frac{1}{x_1 u_2} \left[ v_1 \ln \frac{x_2}{u_2} + \frac{\Delta G^E}{RT} \right] \quad (7)$$

At swelling equilibrium,  $\Delta G^E$ , thus:

$$\begin{aligned} \ln(1 - v_p) + v_p + x v_p^2 \\ + \frac{V_1}{M_c v_p} \left( V_p^{1/3} - \frac{1}{2} v_p \right) = 0 \quad (8) \end{aligned}$$

Since the cross-linking densities of the nylon 6-PAA membrane are quite low, the last term in the above equation could go to 0 and, as a result, can be reduced to a simpler form as follows:

$$x = - \frac{\ln(1 - v_p) + v_p}{v_p^2} \quad (9)$$

## Determination of the Individual Permeability

The permeabilities and separation factors at various compositions and temperatures can be predictably calculated by using the Flick equation:

$$\int_0^{C_i} \frac{D_{i3}}{1 - v_i} dC_i = N_{iL} \quad (10)$$

For more information about the theoretical background, one can refer to Refs. 13-16.

## EXPERIMENTAL

### Materials

#### Polymers

Both polymers were supplied by Polyscience Inc. The nylon 6 had an intrinsic viscosity ( $\eta$ ) of 1.4 determined in 90% formic acid. This corresponds to an  $\bar{M}_v$  of approximately 42,000. The poly(acrylic acid) was an aqueous solution of 25% solids in water with a molecular weight of 90,000.

#### Chemicals

Formic acid (88% and 90%) was obtained from Fisher Scientific. Aluminum nitrate crystals,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , were obtained from Mallinckrodt Chemicals. Methyl alcohol was from BDH chemicals; ethyl alcohol, from Commercial Alcohols, and propyl alcohol, from Mallinckrodt Chemicals. Pentane was supplied by J. T. Baker Chemical Co. All the chemicals were reagent grade and used without further purification.

#### Preparation of the 25% Wt PAA Blended Nylon 6-PAA Membrane

Twenty-five percent aqueous PAA and 10 wt % nylon 6 in 88% formic acid were mixed together in

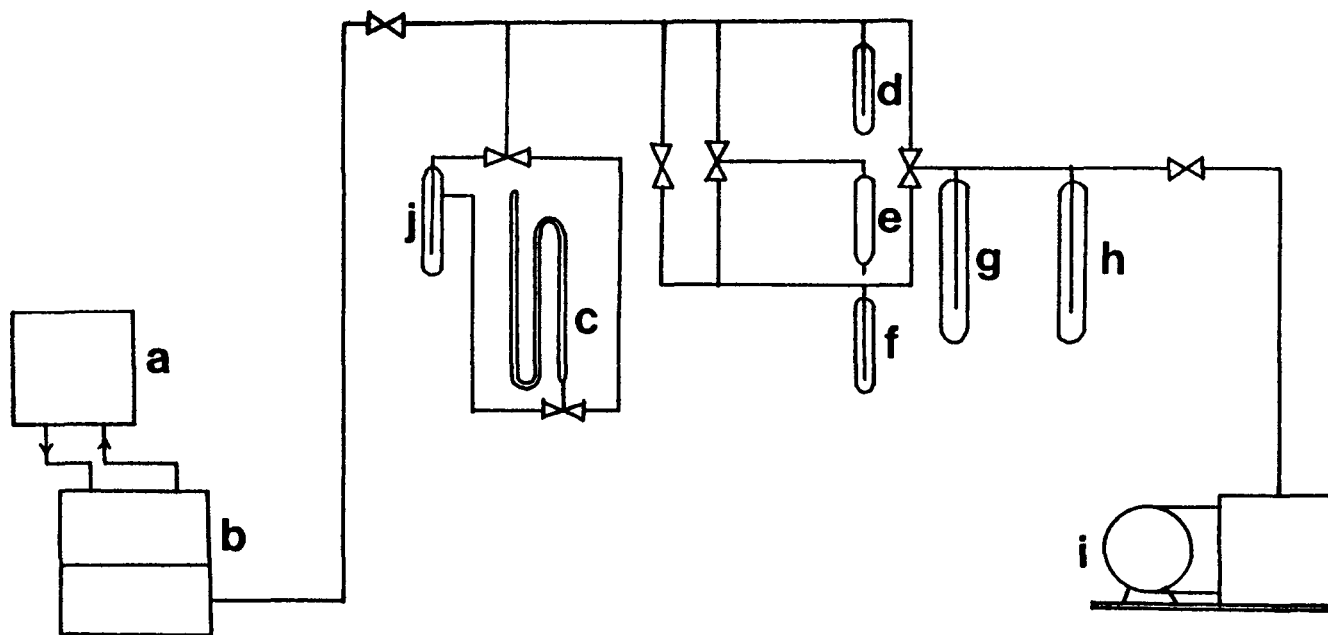
various proportions and blended for at least 48 h to form a homogeneous casting solution. This solution was cast onto a smooth glass plate with the aid of a Gardner casting knife adjusted to appropriate thickness. The membrane was then dried at room temperature for 5 min before drying in an oven at 55°C for 50 min. This was followed by cross-linking in a 10 wt % aluminum nitrate aqueous solution at room temperature for about 30 h. It was subsequently removed from the cross-linking bath, rinsed, and immersed in deionized water for at least 24 h before use. The thickness of the films was measured with a precision micrometer and was in the range of 27–75  $\mu\text{m}$  (1–3 mils).

## TRANSPORT PROPERTIES

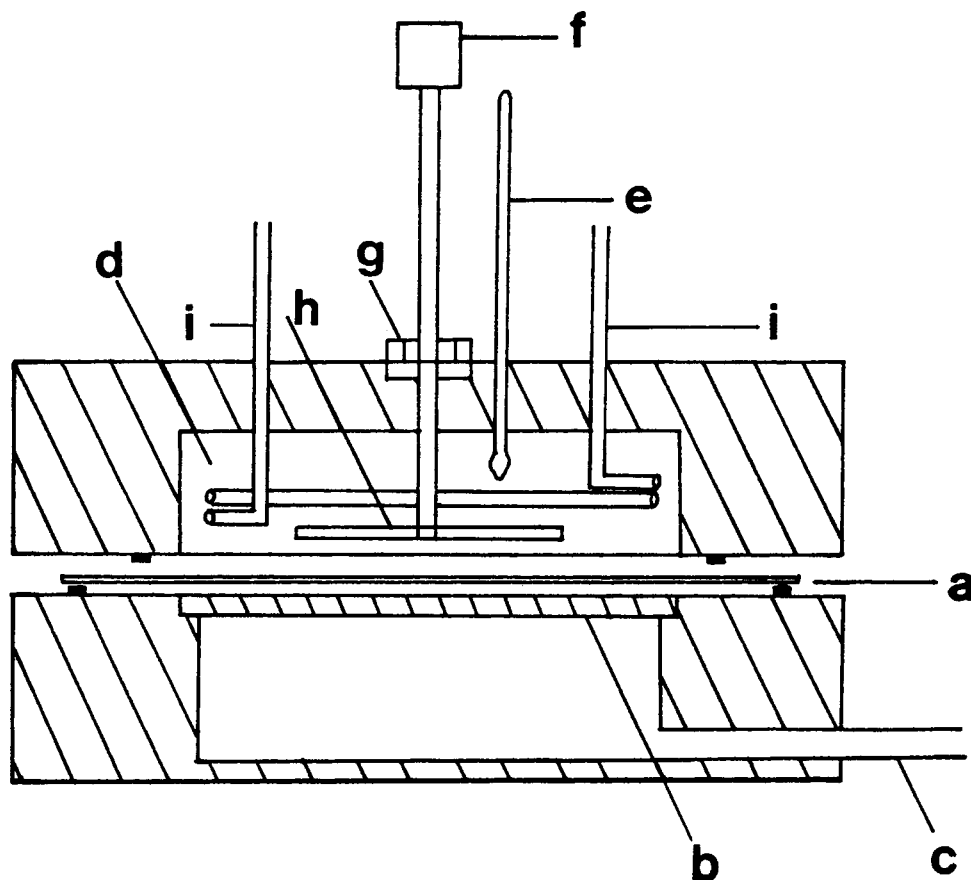
### Apparatus

The apparatus consisted of a permeation cell that holds the membrane and the liquid to be permeated, a means of condensing and collecting the permeant vapor that is evaporated at the downstream side, and a vacuum pump. A schematic diagram is shown in Figure 1.

The permeation cell (Fig. 2) was constructed of two 16-cm-diameter stainless-steel disks. The bottom disk was fitted with a sintered steel plate, 9 cm



**Figure 1** Schematic diagram of the pervaporation setup. (a) Haake circulator; (b) permeation cell; (c) Bennert-type vacuum manometer; (d, f) cold traps for collecting samples; (e) drying tube; (g, h) cold traps; (i) vacuum pump; (j) trap.



**Figure 2** Schematic diagram of the permeation cell. (a) Polymer membrane; (b) sintered steel support plate; (c) stainless-steel vapor removal tube; (d) liquid reservoir; (e) thermometer; (f) variable-speed stirring motor; (g) packing gland; (h) paddle wheel stirrer; (i) circulation coil.

in diameter, to support the membrane. To attach the downstream side to the vacuum glassware, a stainless-steel tube was cemented to the side of the lower disk. Both the top and the bottom disks had grooves for Teflon "O" rings needed for sealing the membrane. The liquid reservoir, 9 cm in diameter and 1.5 cm deep, was machined into the upper disk. A small amount of silicone vacuum grease was spread on those surfaces of the cell that came into contact with the membrane. The membrane was placed on a filter paper on the lower disk and the two halves of the cell were then bolted tightly together by six bolts. To maintain the feed temperature, water at a constant temperature from a Haake circulator was pumped continuously through a steel coil in the feed compartment. To ensure adequate mixing of the liquid feed so as to eliminate any concentration and temperature gradients, provision was made for stirring the liquid by means of a four-blade paddle wheel in the upper chamber. The stirring rod

was attached to a variable speed motor. A thermometer was placed in the cell to constantly monitor the temperature of the feed.

To collect and condense the vapors, cold traps immersed in liquid nitrogen were used on the vacuum side of the equipment. The traps were arranged in such a way as to enable one trap to be removed with the permeant while the other was being used. In this way, samples could be withdrawn at any time without interrupting the permeation run. Liquid nitrogen was used because it solidified the permeant, thus reducing errors that could be caused by evaporation in the collection traps. The traps themselves consisted of test tubes with a ground joint and had mating glass stoppers that were used when the traps were weighed.

The necessary vacuum in the downstream side was maintained by a two-stage Edwards high-vacuum pump. The vacuum was measured by a Fisher brand, closed-end, Bennert-type vacuum manometer

**Table I Flux and Separation Factors for the Pervaporation of Pentane–Methanol Mixtures through 25 Wt % PAA Membrane at 20°C; Membrane Thickness = 31.5  $\mu\text{m}$  (1.24 mils)**

Weight Fraction Methanol in		Flux ( $\text{g}/\text{m}^2 \text{ h}$ )	Separation Factor
Feed	Permeate		
1	1	278.32	—
0.7599	0.9998	165.53	1388.5
0.4896	0.9998	120.25	6857.4
0.2472	0.9998	105.72	20,031.9
0.0932	0.9888	75.01	64,000.9

in the vacuum line near the permeation cell and was always kept below 4 mmHg.

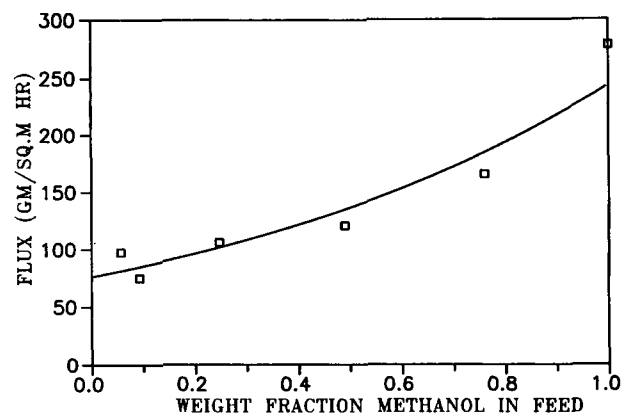
The analysis of the feed was done using an Anton-Paar DMA60 digital density meter. A calibration curve of density vs. composition of methanol–pentane mixtures was prepared using known quantities of the two components that had a linear relation over the entire range of composition. Permeate samples containing very small amounts of pentane were analyzed using an HP5880A gas chromatograph with a flame ionization detector, as the density meter was found to be incapable of detecting less than 1% pentane in the methanol–pentane mixtures.

### Pervaporation Runs

Permeation runs for methanol–pentane mixtures were carried out using different ionically cross-linked nylon 6–PAA blended membranes with 25% PAA content. To start an experimental run, the required membrane was first conditioned in methanol–water mixtures with increasing methanol concentration for

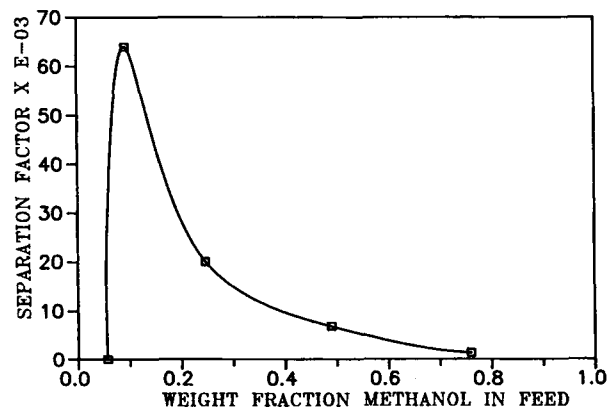
**Table II Flux and Separation Factors for the Pervaporation of Pentane–Methanol Mixtures through 25 Wt % PAA Membrane at 25°C; Membrane Thickness = 37.6  $\mu\text{m}$  (1.48 mils)**

Weight Fraction Methanol in		Flux ( $\text{g}/\text{m}^2 \text{ h}$ )	Separation Factor
Feed	Permeate		
1	1	278.95	—
0.7582	0.9992	172.95	382.53
0.4706	0.9997	126.19	894.53
0.2370	0.9984	126.29	2053.91
0.0998	0.9802	91.28	447.27

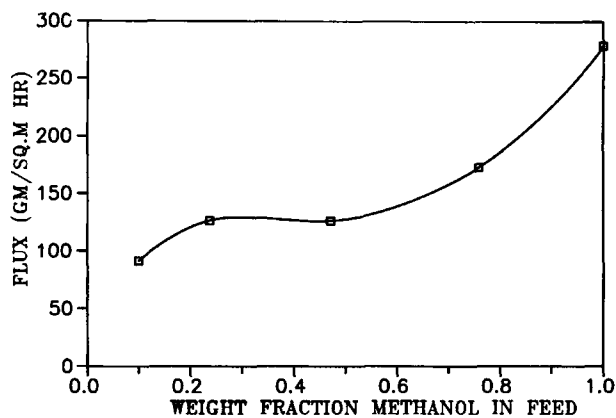


**Figure 3** Permeation rate of methanol–pentane mixtures through 25 wt % PAA membrane at 20°C. Membrane thickness = 31.5  $\mu\text{m}$  (1.24 mils).

about 24 h, which is sufficient to achieve quasi-equilibrium. The membrane was then placed in the cell and the cell was bolted together. Pure methanol was introduced in the top half of the cell and the traps were placed in Dewar flasks containing liquid nitrogen. Water was circulated through the cooling coil and the feed temperature was allowed to reach 20°C before evacuating the system and starting the permeation run. When the permeation rate became constant, the permeant was collected over a known period of time. It was then weighed to determine the permeation rate. For every feed concentration, the permeation was measured at least twice. When the run with pure methanol was finished, the feed was replaced by the pentane–methanol mixture. Runs were carried out for feed mixtures with 75, 50, 25, 7, and 2 wt % methanol. After the last run, the cell was dismantled. The entire procedure was repeated at 25°C with a fresh membrane.



**Figure 4** Separation factor of methanol–pentane mixtures through 25 wt % PAA membrane at 20°C. Membrane thickness = 31.5  $\mu\text{m}$  (1.24 mils).

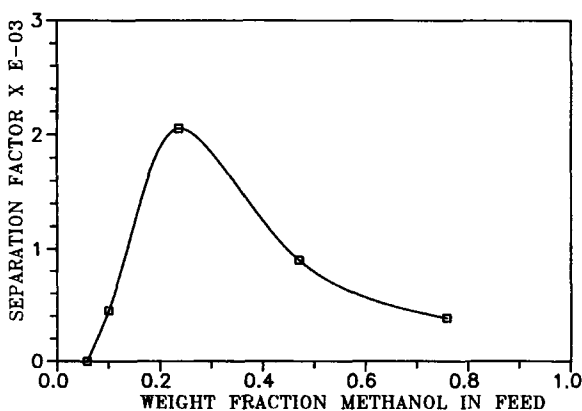


**Figure 5** Permeation rate of methanol-pentane mixtures through 25 wt % PAA membrane at 25°C. Membrane thickness = 37.6  $\mu\text{m}$  (1.48 mils).

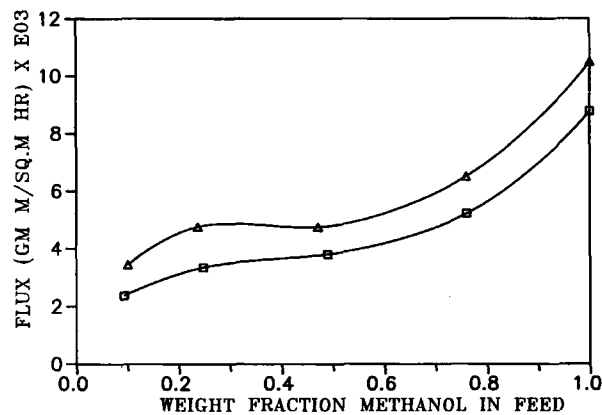
## RESULTS AND DISCUSSION

### Study of Transport Properties

The ionically cross-linked nylon 6-PAA blended membranes were investigated for the pervaporation separation of pentane-methanol mixtures. Of the different membranes prepared, it was found by scanning electron microscopy studies<sup>8</sup> that only the ones with 25 and 30 wt % PAA are truly dense. Thus, only these membranes were used for the pervaporation runs since the others were porous and thus not suitable for pervaporation use. Prior to starting the pervaporation runs, the membranes were annealed in pure ethanol for 50 days. Absence of the pretreatment step was found to result in very low permeation rates. The experimental results are summarized in Tables I and II and the separation factors and permeation rates for the various feed compositions at



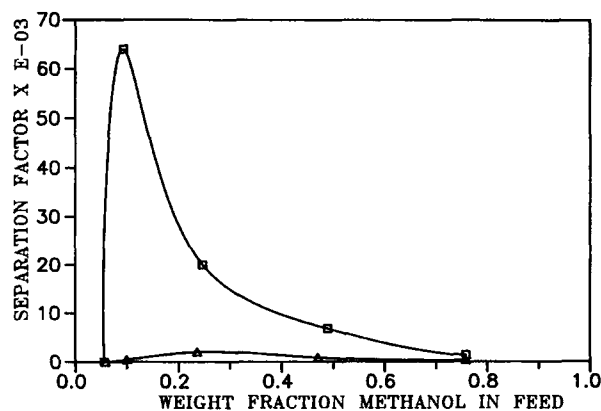
**Figure 6** Separation factor of methanol-pentane mixtures through 25 wt % PAA membrane at 25°C. Membrane thickness = 37.6  $\mu\text{m}$  (1.48 mils).



**Figure 7** Effect of feed temperature on the permeation rate for 25 wt % PAA membrane: ( $\square$ ) 20°C; ( $\triangle$ ) 25°C.

20 and 25°C, respectively, for the 25% PAA blended membranes are shown in Figures 3-6. The separation factors for the various feed compositions (Figs. 4 and 6) show a large increase with decreasing methanol concentration. At high methanol concentrations, the membrane would be comparatively more swollen that at low concentrations, and this would enable the nonpreferential component pentane to enter the polymer matrix and diffuse through the membrane. In spite of this, the separation factor at 20°C for a feed mixture of approximately 75% methanol is determined to be more than 1000, indicating that methanol is highly favored as opposed to pentane. For the permeation runs at 25°C, the maximum separation factor is reached at 25 wt % methanol in the feed.

The effect of temperature on the separation factor is shown in Figures 7 and 8. As the temperature increases, there is an increase in the flux, but the separation efficiency is adversely affected. A change in the feed temperature from 20 to 25°C caused the



**Figure 8** Effect of feed temperature on the separation factor for 25 wt % PAA membrane: ( $\square$ ) 20°C; ( $\triangle$ ) 25°C.

**Table III Binary Interaction Parameter for Pentane(1) and Methanol(2) Mixture at 20 and 25°C**

Volume Fraction of Pentane	$\Delta G^E$ (cal/mol)		$\chi_{12}$	
	Temperatures (°C)		Temperatures (°C)	
	20	25	20	25
0.127	72.89	73.70	1.3261	1.3207
0.193	110.26	111.54	1.3589	1.3538
0.516	292.093	285.81	1.6163	1.6116
0.758	355.56	360.57	2.0478	2.0422
0.893	298.04	302.23	2.6303	2.6217
0.993	45.83	46.13	4.4232	4.3765

permeation rate to increase by a factor of 1.2. The lower separation factors can be explained by the increase in agitational energy or motions of the polymer chains at higher temperatures. According to Eyring's hole theory of diffusion, the formation of "holes" in the polymer requires enough energy to break down a number of secondary valence bonds. At low temperatures, there are more smaller than larger holes in the amorphous regions. These holes allow methanol to go through because of its smaller molecular size. At higher temperatures, larger holes are produced as a result of the higher agitational energy of the polymer chains. More pentane molecules can diffuse through the larger holes and thus the separation factor decreases at elevated temperatures.

### Study of Theoretical Transport Properties

The binary interaction parameter,  $\chi_{12}$ , between pentane (1) and methanol (2) with varying composition at 20 and 25°C was determined from eq. (7), which is known as the Flory-Huggins thermodynamics equation. The excess Gibbs free energy,  $\Delta G^E$ ,

in eq. (7) was calculated from the Wilson equation for the system in question. Table III shows the calculated  $\Delta G^E$  and  $\chi_{12}$  for pentane-methanol mixtures at 20 and 25°C.

Also, the binary interaction parameters  $\chi_{12}$  and  $\chi_{13}$  between a pure liquid and a membrane were calculated from eq. (9). Table IV shows the solubility and the interaction parameters. The binary interaction parameters increase with the decrease of the affinity of a polymer with methanol, as can be seen in Table IV, whereas there is no difference of solubility and binary interaction parameter for pentane for two temperatures.

Table V shows the diffusion coefficients at zero concentration ( $D_{c=0}$ ) determined by the desorption method using a Cahn balance setup. The results were analyzed and computed by the method and procedures described in a separate paper by Rhim and Huang.<sup>16</sup> The free-volume parameters,  $A_d$  and  $B_d$ , in eq. (1) can be determined; then the thermodynamic diffusion coefficients of pentane and methanol can be obtained from eq. (3). Finally, the diffusion coefficients can be calculated from eq. (4). If the diffusion coefficients that are considered independent on the concentration in this system are known,

**Table IV Solubility Data and Binary Interaction Parameters between Each Liquid and Membrane at 20 and 25°C**

System	Temp (°C)	Solubility <sup>a</sup>	Volume Fraction of Polymer	$\chi_{13}^b$ <i>i</i> = 1, 2
Pentane(1)-nylon 6-PAA(3)	20	0.01335	0.98665	3.4203
	25	0.01345	0.98655	3.4134
Methanol(2)-nylon 6-PAA(3)	20	0.1559	0.8441	1.4238
	25	0.1631	0.8369	1.3942

<sup>a</sup> Solubility: liquid cc/(liquid cc + polymer cc).

<sup>b</sup> Binary interaction parameter.

**Table V Diffusion Coefficients of Zero Concentration of Pentane and Methanol at 20 and 25°C for Nylon 6–PAA Blended Membranes**

Diffusing Species	$D_{c=0}$ (cm <sup>2</sup> /s)	
	20°C	25°C
Pentane	$8.4064 \times 10^{-10}$	$8.5498 \times 10^{-10}$
Methanol	$1.1173 \times 10^{-7}$	$1.1364 \times 10^{-7}$

the individual permeabilities for pentane–methanol mixtures and also separation factors can be predicted from eq. (10). Tables VI and VII show the comparisons of experimental and calculated permeabilities of each component at 20 and 25°C, respectively. In the case of methanol, the calculated permeabilities are close to the experimental values. When the pen-

tane permeabilities at both temperatures are compared to each other, the pentane permeation rate at 20°C is decreasing with increasing pentane concentration in the feed mixture, whereas the pentane permeation rate at 25°C is increasing gradually. Some pentane can also enter the polymer network, once the membranes are swollen and comparatively looser. From the solubility data in Table IV, the transport of pentane across the membrane would not be favored owing to its much larger molecular size as compared to that of methanol. However, once the polymer network is loosened by absorbing the methanol in the feed mixture, the pentane can also be absorbed depending on the pentane concentration in the feed. In other words, there could be more chances to absorb the pentane in higher pentane concentration than in lower pentane concentration. This could be the reason why the ratio of the calculated and experimental permeabilities becomes

**Table VI Calculated and Experimental Permeabilities of Each Component for Pentane–Methanol Mixture at 20°C**

Wt % Pentane in Feed	Permeabilities <sup>a</sup>			
	Experimental		Calculated	
	$p^b$	$M^c$	$P$	$M$
0.2401	0.0353	166.49	0.0467	287.15
0.5104	0.0183	120.23	0.118	247.52
0.7528	0.0161	105.70	0.217	175.88
0.9068	0.0114	97.60	0.298	87.71

<sup>a</sup> g/m<sup>2</sup> h.

<sup>b</sup> Pentane.

<sup>c</sup> Methanol.

**Table VII Calculated and Experimental Permeabilities of Each Component for Pentane–Methanol Mixture at 25°C**

Wt % Pentane in Feed	Permeabilities <sup>a</sup>			
	Experimental		Calculated	
	$p^b$	$M^c$	$P$	$M$
0.2418	0.144	172.806	0.063	288.36
0.5294	0.158	126.032	0.166	245.09
0.7630	0.198	126.092	0.295	173.08
0.9002	1.804	89.476	0.394	93.81

<sup>a</sup> g/m<sup>2</sup> h.

<sup>b</sup> Pentane.

<sup>c</sup> Methanol.



higher with increasing pentane concentration in the feed mixture. At 25°C, the ratio for the pentane shows reasonably good agreement except for the pentane concentration at both ends.

## CONCLUSIONS

1. Ionically cross-linked 25 wt % nylon 6-PAA blended membranes of nylon 6 and poly(acrylic acid) (PAA) were prepared by blending the solutions of the two homopolymers in the desired amounts, casting a film, and drying it under controlled conditions before cross-linking in aqueous aluminum nitrate solution for a predetermined time.
2. The pervaporation separation of methanol-pentane mixtures through the ionomeric nylon 6-PAA blended membranes gave quite promising results. Very high separation factors ( $> 1000$ ) were obtained at a feed temperature of 20°C, though the flux rates were not too high (80–280 g/m<sup>2</sup> h through a 31.5 μm-thick membrane).
3. The experimental data obtained from the pervaporation runs were compared with the theoretical values of the individual permeabilities for binary mixtures predicted by the modified Fels and Huang model. This new model is based on an extension of the free-volume theory and the introduction of Flory-Huggins thermodynamics for the calculations of the binary interaction parameters and the diffusion coefficients.
4. The calculated values of the permeabilities obtained from this modified model were reasonably close to the experimental values.

## NOMENCLATURE

$a_i$	activity of the penetrant $i$ in the membrane
$A_d$	proportionality constant
$B_d$	proportionality constant
$C_i$	concentration of the diffusing species in the membrane
$D_{c=0}$	diffusion coefficient at zero concentration
$D_{i3}$	diffusion coefficient of component $i$

$D_T$	thermodynamic diffusion coefficient
$f(v_i, T)$	fractional free volume of the system
$f(0, T)$	fractional free volume of the polymer itself
$\Delta G^E$	excess Gibbs free energy
$\Delta G_{\text{mix}}$	free energy change of mixing
$L$	membrane thickness
$M_c$	average molecular weight between two cross-links
$n_i$	mole fractions of component $i$
$N_i$	mass flux of component $i$ through the membrane
$R$	gas constant
$T$	absolute temperature
$u_i$	volume fraction of component $i$ referred to the liquid part in the ternary system
$v_i$	volume fraction of component $i$ in the membrane
$v_p$	volume fraction of the polymer
$V_i$	molar volume of component $i$
$V_3$	molar volume of polymer
$x_i$	mole fractions of components $i$ in the feed mixture
$\beta(T)$	proportionality constant representing the ability of the penetrant to increase the volume
$\nu_p$	specific volume of the polymer
$\phi_c$	crystallinity of the polymer
$\phi_i$	volume fraction of component $i$
$\chi_{ij}$	Flory-Huggins binary interaction parameter considering concentration independency

The authors wish to thank the National Science and Engineering Council of Canada (NSERC) for their support of this research program.

## REFERENCES

1. R. Y. M. Huang and R. Moreira, R. Notarfonzo, and Y. F. Xu, *J. Appl. Polym. Sci.*, **35**, 191 (1988).
2. R. Y. M. Huang and X. F. Xu, *J. Membrane Sci.*, **43**, 143 (1989).
3. R. Y. M. Huang and Y. F. Xu, in *Proceedings of the Conference on the 25th Anniversary of Membrane Research in Canada*, Ottawa, Canada, September 1986, pp. 313–339.
4. R. Y. M. Huang, Y. F. Xu, Y. Jin, and C. Lipski, in *Proceedings of the Second International Conference on Pervaporation Processes in the Chemical Industry*, San Antonio, Texas, 1987, R. Bakish, Ed., pp. 225–239.

5. Y. F. Xu and R. Y. M. Huang, *J. Appl. Polym. Sci.*, **36**, 1121 (1988).
6. R. Y. M. Huang and X. F. Xu, *Eur. Polym. J.*, **24**(10), 927 (1988).
7. X. P. Zhao and R. Y. M. Huang, *J. Appl. Polym. Sci.*, **41**, 2133 (1990).
8. M. Balakrishnan and R. Y. M. Huang, *Angew. Makromol. Chem.*, **191**, 39 (1991).
9. P. Aptel, N. Challard, J. Cuny, and J. Neel, *J. Membrane Sci.*, **1**, 271 (1975).
10. I. Cabasso, *Ind. Eng. Chem. Prod. Res. Dev.*, **22**, 313 (1983).
11. K. F. Knight, A. Duggal, R. A. Sheldon, and E. V. Thompson, *J. Membrane Sci.*, **25**, 81 (1986).
12. J. W. Rhim and R. Y. M. Huang, *J. Membrane Sci.*, **46**, 335 (1989).
13. J. W. Rhim, PhD Thesis, University of Waterloo, 1989.
14. M. Fels and R. Y. M. Huang, *J. Macromol. Sci. Phys.*, **B5**(1), 89 (1971).
15. M. Fels, PhD Thesis, University of Waterloo, 1968.
16. J. W. Rhim and R. Y. M. Huang, *J. Appl. Polym. Sci.*, **41**, 535 (1990).

Received May 28, 1991

Accepted October 23, 1991