

# Pervaporation Separation of Water–Isopropyl Alcohol Mixtures with Blend Membranes of Sodium Alginate and Poly(acrylamide)-Grafted Guar Gum

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**ABSTRACT:** The blend membranes of sodium alginate (Na-Alg) and poly(acrylamide)-grafted guar gum (PAAm-g-GG) in the ratios of 3:1 and 1:1 were prepared and studied for the pervaporation separation of water–isopropyl alcohol mixtures over the entire range of mixture composition at 30°C. Membranes prepared from neat Na-Alg (M-1) and the 1:1 blend of Na-Alg and PAAm-g-GG (M-3) showed the highest separation selectivity for 10 mass % water in the feed mixture, whereas membranes prepared with the 3:1 blend ratio of Na-Alg to PAAm-g-GG showed the highest separation selectivity of 20 mass % water in the feed. Selectivity decreased with increasing amount of water in the feed for all the membranes, but these values show an increase with increasing amount of grafted copolymer in the blend mixture. Flux increased with increasing amount of water in the mixture, but the flux values did not change markedly with the PAAm-g-GG content in the blend membrane at the lower mass % water. At higher mass % of water, the flux values of the blends increase systematically with increasing amount of PAAm-g-GG in the blend polymer. For the 10 mass %-containing binary mixtures, the pervaporation separation experiments were performed at 30, 40, and 50°C, and the resulting data were used to calculate the Arrhenius activation parameters. These data indicated activated pore-type diffusion of the permeants in the membranes. Dynamic sorption studies were also performed on up to 40 mass % water–isopropyl alcohol mixtures at 30°C. These results, when analyzed by the empirical equation, indicated Fickian transport in all the cases. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2014–2024, 2002

**Key words:** pervaporation; water–isopropyl alcohol; sodium alginate; blend membranes; polyacrylamide-grafted guar gum

## INTRODUCTION

Pervaporation separation (PV) of aqueous–organic mixtures with polymeric membranes has been actively studied in our laboratory over the past few years.<sup>1–3</sup> The method is particularly use-

ful to separate liquid mixtures with close boiling points as well as azeotropic mixtures because it is possible to separate the mixture components on the basis of liquid polarity and its interaction with the polymer membranes.<sup>4</sup> The PV technique has been widely used in many industrial areas, such as in the dehydration of alcohols<sup>5–7</sup> and organic acids.<sup>8,9</sup> In addition, PV finds applications in the separation of isomeric compounds,<sup>10</sup> mixtures of saturated hydrocarbons,<sup>11</sup> as well as volatile organic compounds<sup>12</sup> from water.

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Isopropyl alcohol (Iso-OH) is an important organic solvent used in the commercial production of acetone through the catalytic dehydrogenation process. It is also useful in the production of hydrogen peroxide as an anti-icing agent in gasoline and as extracting solvent in fish protein concentration process. In chemical process engineering areas, there is a need to concentrate/purify isopropyl alcohol from water. In such studies, both synthetic<sup>13,14</sup> and natural hydrophilic polymers<sup>15,16</sup> can be used. Among the many natural polymers, alginates (heteropolysaccharides made up of blocks of mannuronic acid and guluronic acid) have gained much importance in recent years in PV separation studies because of their good membrane-forming properties that give the highest flux and separation factor. Earlier, Uragami and Saito<sup>17</sup> separated methanol–water and ethanol–water mixtures with alginic acid membranes.

Over the course of time, several researchers have modified the alginate membranes by blending with different types of hydrophilic polymers or in the form of composite membranes for the separation of water–acetic acid mixtures.<sup>18–21</sup> In our earlier study, we developed polyacrylamide-grafted poly(vinyl alcohol) membranes for the separation of water–acetic acid and water–dimethylformamide mixtures.<sup>1,3</sup> Later, we developed<sup>2</sup> the blend membranes of polyacrylamide-grafted guar gum (PAAm-g-GG) with Na-Alg in different ratios to enhance the hydrophilicity of the membrane for the separation of water–acetic acid mixtures. In continuation of this study, we now present the PV separation characteristics of the same blend membranes for water–isopropyl alcohol mixtures.

## EXPERIMENTAL

### Materials

Sodium alginate was purchased from Luba Chemicals, Mumbai, India. Guar gum was purchased from s.d. Fine Chemicals, Mumbai, India. Acrylamide-grafted guar gum was prepared as per the procedure given earlier.<sup>2</sup> The ceric ammonium nitrate, glutaraldehyde (GA) isopropyl alcohol, and methanol used were of AR grade samples; all these were obtained from s.d. Fine Chemicals, Mumbai, India, and used as received. Double-distilled water was used throughout the research.

### Preparation of Membranes and their Characterization

Synthesis of PAAm-g-GG and its blend membranes with Na-Alg were prepared and cross-linked as described earlier.<sup>2</sup> In brief, PAAm-g-GG was synthesized by reacting guar gum with acrylamide at 60°C, using ceric ammonium nitrate (CAN) as an initiator. To prepare membranes, a 4 mass % solution of Na-Alg was prepared in water, to which 0.00175 mol of GA (0.1 mL of 25 wt % in water) was added, keeping the total volume at 100 mL. The mixture was stirred for 2 h at 25°C and poured uniformly on a glass plate. Membranes were dried at room temperature for ~2–3 days. The casted membranes were cross-linked by immersing in 1% HCl solution taken in an equimolar mixture of methanol and water for 24 h, then washed thoroughly with water and dried. The pure Na-Alg membrane thus prepared was designated as M-1.

To prepare the blend membranes, 4 mass % of the stock solutions of Na-Alg and PAAm-g-GG were respectively mixed in the ratios of 75 : 25 (membrane designated as M-2) and 50 : 50 (membrane designated as M-3) at 60°C for 4 h, and the solution was cooled to room temperature. To this solution, 0.00175 mol of GA (0.1 mL of 25 wt % in water) was added and the mixture was stirred for additional 2 h.

The Fourier transform infrared spectra (FTIR; Nicolet, Model Impact 410) of graft copolymer and the blend membranes were taken to confirm the grafting reaction. Copolymer and its membranes of different blend ratios were crushed under hydraulic pressure of 300 kg to make the KBr pellets, and spectra were taken in the wave number range 400–4000 cm<sup>-1</sup>.

### Sorption Experiments

Dynamic and equilibrium sorption experiments on the membranes were performed in water–isopropyl alcohol mixtures at 30 ± 0.5°C in an electronically controlled oven (WTB Binder, Germany). In these studies, we used circularly cut (~2.00 cm) disk-shaped membranes that were kept in a vacuum oven at 25°C for 48 h before use. The initial mass of these membranes was measured on a top-loading single-pan digital microbalance (model AE 240, Switzerland) sensitive to ±0.01 mg. Samples were placed inside the screw-tight test bottles containing different compositions of water–isopropyl alcohol mixtures. The test bottles were placed in the oven that was

**Table I** Equilibrium Mass Percent Uptake (*S*) and Diffusion Coefficient (*D*) of the Membranes at 30°C

Mass % Water in Feed	<i>S</i> (kg/kg)			<i>D</i> (m <sup>2</sup> /s) × 10 <sup>13</sup> (eq. 2)		
	M-1	M-2	M-3	M-1 <sup>a</sup>	M-2 <sup>a</sup>	M-3 <sup>a</sup>
10	12.88	11.0	9.39	3.27	1.67	0.72
20	19.80	19.5	18.83	5.12	2.78	2.80
30	26.92	26.6	29.22	13.7	7.02	16.3
40	32.93	29.8	35.23	11.2	5.35	8.15
50	38.72	44.5	47.33			
60	40.96	48.7	68.50			
70	45.00	55.6	77.13			
80	51.48	71.3	107.0			
90	58.60	82.2	127.0			
Water	66.78	106.	138.0			

<sup>a</sup> The diffusion process becomes very fast, so the data at higher composition of water were not obtained.

maintained at a constant temperature of 30°C. The mass measurements were done at the suitably selected time intervals by removing the samples from the test bottles, wiping the surface-adhered solvent drops by gently pressing them in between filter paper wraps, weighed the samples immediately, and again placing the samples back into the oven. To minimize the errors due to evaporation losses, this step was completed within 15–20 s.

From the gravimetric data, the mass % uptake by the membrane,  $M_t$ , at time  $t$  was calculated by knowing the initial dry mass of the membrane,  $W_0$ , and by measuring the mass of the membrane at regular intervals of time,  $W_t$ :

$$M_t = \frac{W_t - W_0}{W_0} \times 100 \quad (1)$$

The equilibrium mass % uptake ( $M_\infty$  or  $S$ ) was calculated from the asymptotic region of the sorption curve (i.e., after complete attainment of equilibrium saturation). The diffusion coefficient,  $D$ , was calculated by calculating the slope of the linear portion of the sorption curve before attainment of equilibrium.<sup>22</sup>

$$\frac{M_t}{M_\infty} = \frac{4}{h} \left[ \frac{Dt}{\pi} \right]^{1/2} \quad (2)$$

where  $h$  is thickness of the membrane. The  $S$  and  $D$  results are presented in Table I.

### Sorption Selectivity ( $\alpha_{\text{sorp}}$ )

To compute the sorption selectivity values, the completely equilibrated membranes with different mass % water in the binary mixture were removed from the test bottles by blotting the surface-adhered liquid drops with a filter paper. The membranes were then placed into a glass trap connected to another cold trap that was surrounded by liquid nitrogen and then heated to 120°C (close to the boiling temperature of isopropyl alcohol, 117.5°C). The vapor was condensed in the cold trap surrounded by the liquid nitrogen jar. The composition of the condensed liquid mixture was then calculated by measuring the refractive index (accurate up to  $\pm 0.0002$  units) with an Abbe Refractometer (Atago 3T, Japan). The sorption selectivity was then calculated using eq. 3:

$$\alpha_{\text{sorp}} = \frac{M_{\text{W}}/M_{\text{Iso-OH}}}{F_{\text{W}}/F_{\text{Iso-OH}}} \quad (3)$$

where  $M_{\text{W}}$ ,  $M_{\text{Iso-OH}}$  and  $F_{\text{W}}$ ,  $F_{\text{Iso-OH}}$  are the mass % water and isopropyl alcohol in the membrane and the feed, respectively.

### Pervaporation Experiments

PV experiments were performed with the module designed in-house.<sup>1</sup> The effective surface area of the membrane in contact with the feed mixture was 32.4 cm<sup>2</sup>, and the capacity of PV cell used was  $\sim 250$  cm<sup>3</sup>. The mass % water in its acetic acid mixture was varied from 10 to 80. After taking

150 mL of the mixture in the feed compartment, the test membrane was allowed to equilibrate for 2 h. The downstream side of the PV apparatus was continuously evacuated with a vacuum pump (Toshniwal, India) at a vacuum pressure of 10 Torr. The permeate mixture was condensed in the liquid nitrogen traps. The mass of the permeate mixture collected in the trap was taken, and its composition was determined by measuring its refractive index and by comparing it with a standard graph. The depleted solvent mixture of the feed component was continuously enriched with the fresh solvent mixture.

From the PV data, the membrane performance was studied by calculating the total flux,  $J_p$ , separation selectivity,  $\alpha_{sep}$ , pervaporation separation index, PSI, and enrichment factor,  $\beta$ , using the following relations:

$$J_p = \frac{W_p}{At} \quad (4)$$

$$\alpha_{sep} = \frac{P_w/P_{Iso-OH}}{F_w/F_{Iso-OH}} \quad (5)$$

$$PSI = J_p (\alpha_{sep} - 1) \quad (6)$$

$$\beta = \frac{C_w^P}{C_w^F} \quad (7)$$

In these equations,  $W_p$  is mass of the permeate;  $A$  is area of the membrane in contact with the feed mixture;  $t$  is time;  $P_w$  and  $P_{Iso-OH}$  are the mass %

**Table II Pervaporation Flux and Separation Selectivity at Different Mass Percent Water in the Feed Mixture at 30°C**

Mass % Water in Feed	$J_p \times 10^2$ (kg/m <sup>2</sup> h), eq. 4			$\alpha_{sep}$ , eq. 5		
	M-1	M-2	M-3	M-1	M-2	M-3
10	5.8	6.2	4.3	441	711	891
20	10.6	12.3	10.8	396	796	796
30	13.6	16.4	15.7	101	153	184
40	20.2	22.0	24.7	74	65	153
50	23.9	30.8	31.6	43	35	53
60	30.8	33.1	36.9	24	13	30
70	35.0	41.8	42.6	14	10	14
80	38.1	47.3	54.9	8	7	7
90	57.6	69.7	74.7	5	5	5

**Table III Pervaporation Flux and Separation Selectivity at Different Temperatures for 10 Mass % Water in the Feed Mixture**

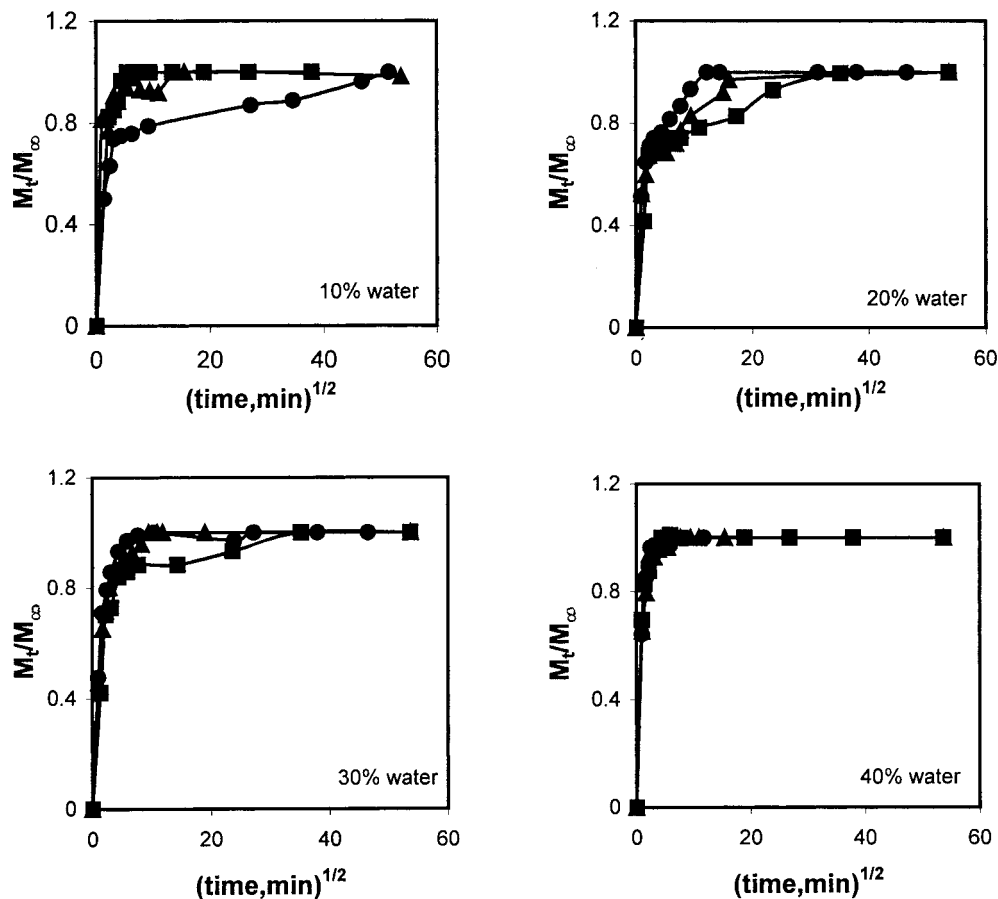
Temp (°C)	$J_p \times 10^2$ (kg/m <sup>2</sup> h), eq. 4			$\alpha_{sep}$ , eq. 5		
	M-1	M-2	M-3	M-1	M-2	M-3
30	5.7	6.2	4.3	441	711	891
40	6.6	6.8	5.1	349	591	711
50	6.5	7.3	5.6	318	554	634

water and isopropyl alcohol respectively, in the permeate;  $F_w$  and  $F_{Iso-OH}$  are the mass % water and isopropyl alcohol in the feed, respectively; and  $C_w^P$  and  $C_w^F$  are concentrations of permeate and feed, respectively. The pervaporation flux and  $\alpha_{sep}$  data are presented in Tables II and III. However, the results of PSI and  $\beta$  are only displayed graphically and discussed subsequently.

## RESULTS AND DISCUSSION

### Dynamic Swelling

When liquids permeate through the swollen polymeric membrane, there will be a coupling of fluxes, leading to permeation and molecular transport, which in turn will affect the membrane performance. When the polymers are used below their glass transition temperatures, thermal segmental motions will be restricted; under this situation, when the polymer chains come in contact with the low molecular weight liquid components, their interactions will further increase the chain mobility. Both the mixtures used in the present study are polar in nature, which may have an effect on inducing the polymer chain segmental motion. Because PV is mainly governed by the molecular transport of liquids as embodied due to the interactions between the liquid molecules and the polymer chain and because the water is more polar in nature, the present membranes will have more affinity for water molecules than isopropyl alcohol. The PV is also governed by the coupling phenomenon due to sorption and diffusion of liquids.<sup>23</sup> Even though numerous theories have been proposed, none of them is completely satisfactory in explaining the molecular transport of polar liquids and/or their mixtures through the membrane polymers containing hydrophilic groups.<sup>24</sup>



**Figure 1** Plot of  $M_t/M_\infty$  versus square root of time for different mass % water in feed for (●) neat Na-Alg membrane (M-1), (■) 75 : 25 blend of Na-Alg and PAAm-g-GG (M-2), and (▲) 50 : 50 blend of Na-Alg and PAAm-g-GG (M-3).

The results in Table I indicate that the equilibrium % mass uptake of the membranes and diffusion coefficients increase with increasing water content of the feed mixture, but not with the blend composition of the membrane. Due to experimental difficulties, diffusion coefficients were calculated for only up to 40 mass % water in the feed mixture.

The variation of mass % uptake versus square root of time for all the membranes in 10, 20, 30, and 40 mass % water-isopropyl alcohol feed mixtures at 30°C is shown in Figure 1. The sorption tendencies depend on the water content of the feed mixture. For instance, with an increasing amount of water in the feed mixture, sorption also increases, indicating the increased hydrophilic interactions between the water molecules and the membrane materials. In general, the mass % uptake by the Na-Alg membrane (M-1) is considerably lower than those of the blend membranes

(M-2 or M-3). Shapes of the curves vary depending on the composition of the mixture. For instance, with the feed mixture containing 10 mass % water, the increase in mass uptake by the Na-Alg membrane (M-1) is much slower than those observed for M-2 and M-3 membranes. For the 20 mass % water in the feed mixture, the increase in uptake for M-3 membrane is quite dramatic when compared with both M-1 and M-2 membranes. Also, diffusion follows a non-Fickian trend, as evidenced by the sigmoidal curves observed at the higher amount of PAAm-g-GG in the blend membrane (M-3). When 30 or 40 mass % water in the feed was used, considerable differences between the uptake values were noted. With 30 mass % water in the feed mixture, M-3 membrane exhibits a more sigmoidal trend compared with M-1 and M-2 membranes. However, at 40 mass % water in the feed mixture, the attainment of equilibrium uptake is very fast. In general, the attain-



ment of equilibrium sorption becomes faster as the amount of water in the feed increases.

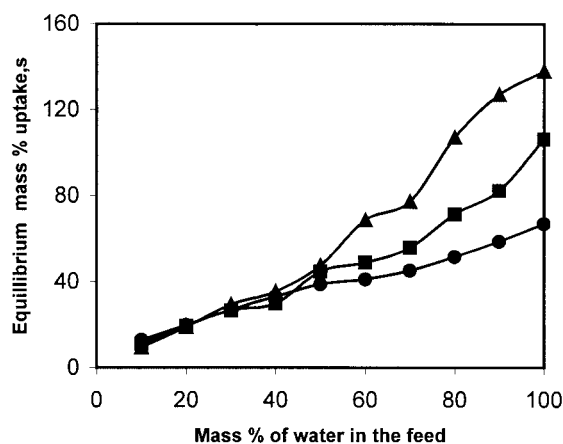
To find the types of diffusion anomalies, the experimental uptake data (i.e.,  $M_t/M_\infty$ ) were fitted to the following empirical relation:<sup>25</sup>

$$\frac{M_t}{M_\infty} = kt^n \quad (8)$$

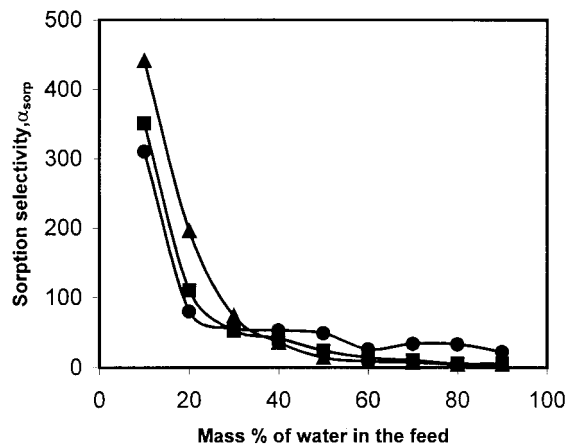
where  $M_\infty$  is the equilibrium sorption value calculated from the asymptotic region of the sorption curve and  $k$  and  $n$  are the empirical parameters ( $k$  represents the polymer–solvent interactions;  $n$  indicates the type of transport). For Fickian transport,  $n$  is  $\sim 0.50$ , and for diffusion that is of the anomalous transport type,  $n$  varies between 0.50 and 1.0. The values of  $k$  and  $n$  were obtained by the least squares method at the 95% confidence limit before the completion of 60% equilibrium. The values of  $n$  vary from 0.03 to 0.29, which is a much smaller range than those expected for Fickian transport. The values of  $k$  vary between 0.378 to 0.717. It appears that the polymer chain relaxation plays an important role in controlling the molecular transport of liquids through the membrane materials.

### Equilibrium Mass Uptake ( $S$ ) and Sorption Selectivity ( $\alpha_{\text{sorp}}$ )

The phenomenon of pervaporation has been well studied in terms of solution–diffusion concepts. Hence, the knowledge of sorption and diffusion



**Figure 2** Plot of equilibrium mass % uptake versus mass % water in feed for (●) neat Na-Alg membrane (M-1), (■) 75 : 25 blend of Na-Alg and PAAm-g-GG (M-2), and (▲) 50 : 50 blend of Na-Alg and PAAm-g-GG (M-3).



**Figure 3** Plot of sorption selectivity vs mass % water in feed for (●) neat Na-Alg membrane (M-1), (■) 75 : 25 blend of Na-Alg and PAAm-g-GG (M-2), and (▲) 50 : 50 blend of Na-Alg and PAAm-g-GG (M-3).

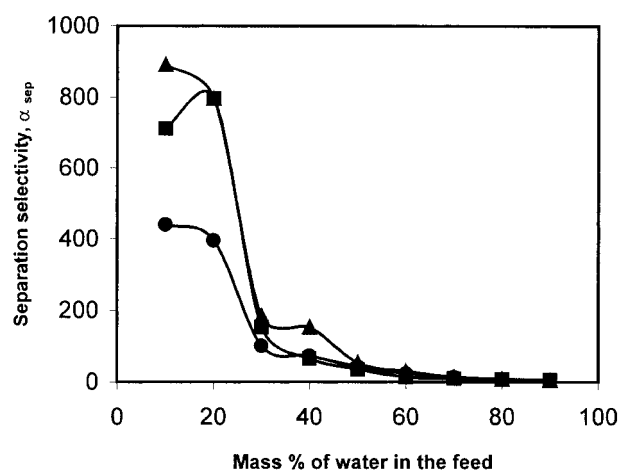
coefficients of the permeating molecules through the membrane materials is important to understand the molecular transport phenomenon. The variation of equilibrium % mass uptake at 30°C as a function of mass % water in the feed mixture is displayed in Figure 2. Up to 40 mass % water in the feed mixture, the equilibrium mass % uptake values of all the three membranes vary almost identically. However, beyond 40 mass % water in the feed mixture, a wide variation in the equilibrium mass % uptake values are observed. The equilibrium mass % uptake of the membranes increases with an increasing amount of water in the feed mixture. Also, with increasing amount of PAAm-g-GG in the blend membranes, from 25 % (M-2) to 50 % (M-3), equilibrium mass % uptake varies according to the sequence M-1 > M-2 > M-3. This result supports the fact that blend membrane M-3 is more hydrophilic than M-2, which in turn exhibits higher hydrophilicity than the neat Na-Alg membrane. The wide disparity in the water uptake properties of the membranes at higher water contents of the feed mixture may be due to stronger specific interactions between water molecules and membrane polymers.

Sorption selectivity is an assessment of membrane permselectivity because it describes how selective the membrane would be towards a particular component of the mixture. These data for M-1, M-2, and M-3 membranes are presented in Figure 3. In all the cases, sorption selectivity decreases with increasing amount of water in the feed mixture. This decrease is quite considerable at lower water content of the feed mixture, which

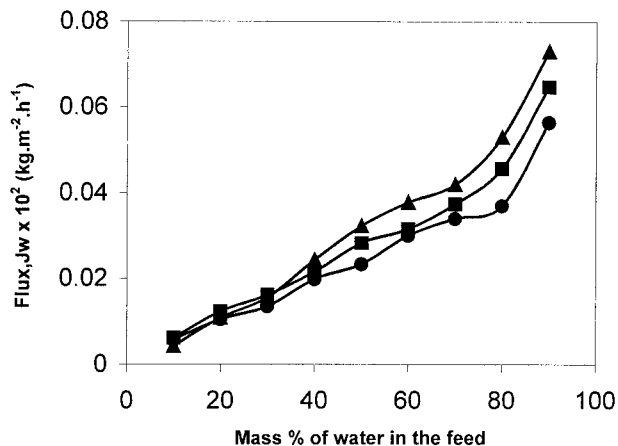
may be due to the insignificant swelling of the membranes. At higher amount of water in the feed mixture (i.e., > 40 %), sorption selectivity levels off. Sorption selectivity for pure Na-Alg membrane (M-1) is lower than those of the blend membranes M-2 and M-3 at lower composition of water but is higher at higher composition of water in the feed mixture.

### Membrane Performance

In PV separation studies, the membrane performance was studied by calculating the separation selectivity, flux, and permeation separation index. These parameters depend on the nature of the membrane material, liquid permeant molecules, feed composition, and the operating temperature.<sup>26</sup> The graph of separation selectivity versus mass % water in the feed mixture is displayed in Figure 4. Separation selectivity in all the membranes decreases drastically beyond 30 mass % water in the feed mixture and then this decreasing tendency slows down. It should be noted that the blend membranes exhibited almost a twofold increase in separation selectivity compared with the pure Na-Alg membrane. The increased selectivity of M-1 and M-2 membranes suggests the increased hydrophilicity of the blend membranes compared with the neat Na-Alg membrane. The flux data for water, presented in Figure 5, increase continuously with increasing amount of water in the feed mixture. Different



**Figure 4** Plot of separation selectivity versus mass % of water in the feed for (●) neat Na-Alg membrane (M-1), (■) 75 : 25 blend of Na-Alg and PAAm-g-GG (M-2), and (▲) 50 : 50 blend of Na-Alg and PAAm-g-GG (M-3).

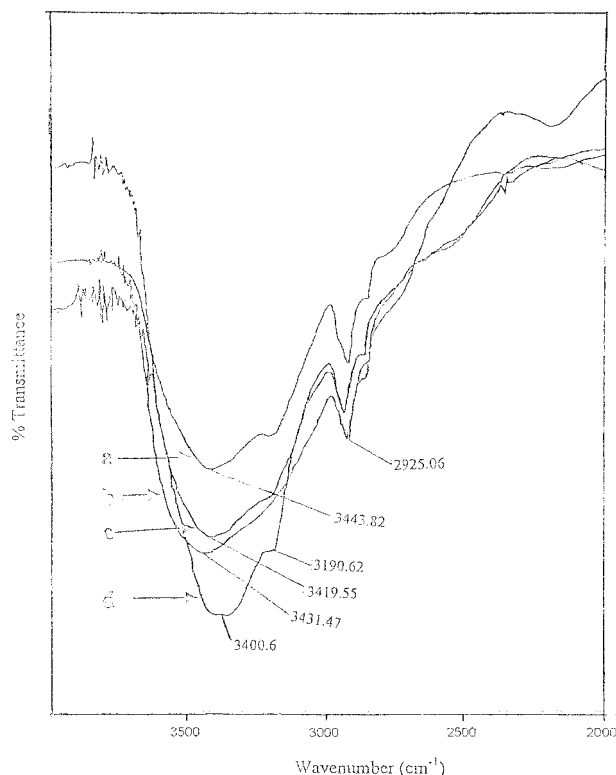


**Figure 5** Plot of water flux versus mass % water in feed for (●) neat Na-Alg membrane (M-1), (■) 75 : 25 blend of Na-Alg and PAAm-g-GG (M-2), and (▲) 50 : 50 blend of Na-Alg and PAAm-g-GG (M-3).

membranes exhibit varying dependencies; that is, the flux for the Na-Alg membrane is lower than those of the blend membranes, but the variation in flux curves are almost identical in all the membranes. In general, a decrease in selectivity and an increase in flux are operative.

The flux and separation selectivity results at 30°C are presented in Table II. In the lower content region of the mixture,  $\alpha_{sep}$  increases from pure Na-Alg membranes to the blend membranes, but quite contrarily, the flux data of the membranes increase in the order M-1 > M-2 > M-3 beyond 30 mass % water in the feed. The increase in selectivity at lower composition of water for M-1 and M-2 membranes may be attributed to the hydrogen bonding interactions between —OH and —COOH groups of Na-Alg with the —CONH<sub>2</sub> group of the grafted copolymer. Equilibrium mass % uptake as well as the FTIR spectra shown in Figure 6 support such hydrogen bond interactions. The —OH stretching of the hydroxyl group appeared at 3443 cm<sup>-1</sup> for PAAm-g-GG (curve A) and at 3431 cm<sup>-1</sup> for the Na-Alg polymer (curve B). For the blend membranes of Na-Alg and PAAm-g-GG, this peak appears at 3419 cm<sup>-1</sup> for M-2 (curve C), and at 3400 cm<sup>-1</sup> for M-3 (curve D). These results confirm the formation of inter-/intramolecular hydrogen bonding. Huang et al.<sup>18</sup> reported a similar decrease in equilibrium mass uptake due to the hydrogen bond interactions.

Results of separation selectivity and pervaporation flux obtained at three temperatures (30, 40, and 50°C) for 10 mass % water-containing feed mixture are presented in Table III. With



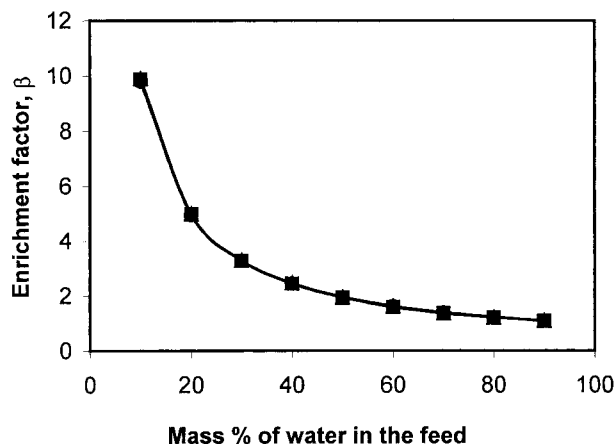
**Figure 6** FTIR spectra of (a) PAAm-g-GG, (b) neat Na-Alg, (c) 75 : 25 blend (M-1), and (d) 50 : 50 blend (M-2).

increasing temperature,  $J_p$  values increase, whereas  $\alpha_{sep}$  values decrease. However, with regard to temperature variation, there is no systematic trend of  $J_p$  values for different types of membranes.

To study the membrane performance, two other parameters (i.e., enrichment factor,  $\beta$ , and permeation separation index, PSI) were used.<sup>1–3</sup> These data are presented respectively in Figures 7 and 8. The  $\beta$  value for different membranes remains the same and hence its dependence is shown by a single curve for all the membranes. The PSI values (Figure 8) show a decreasing tendency with increasing amount of water in the feed mixture. At 20 mass % water in the feed mixture, the PSI showed a maximum for all the membranes, suggesting the separation efficiency of the membranes for this particular composition.

#### Determination of Diffusion Coefficients

Transport in PV experiments can be explained by the solution–diffusion model.<sup>27</sup> Diffusion generally occurs because of the presence of a concen-

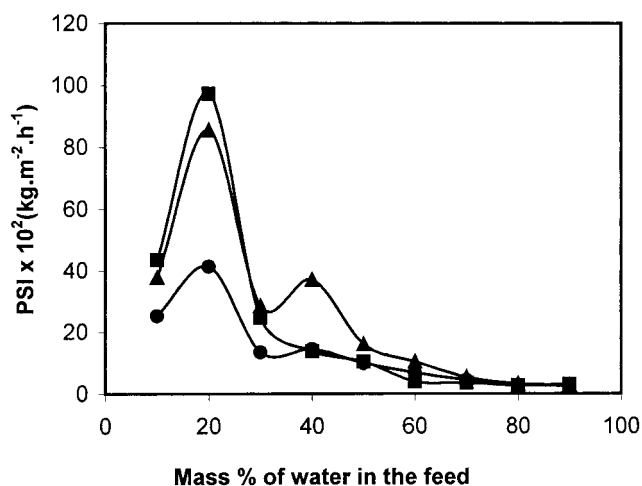


**Figure 7** Plot of enrichment factor versus mass % water in feed for (●) neat Na-Alg membrane (M-1), (■) 75 : 25 blend of Na-Alg and PAAm-g-GG (M-2), and (▲) 50 : 50 blend of Na-Alg and PAAm-g-GG (M-3).

tration gradient, and hence, it is useful to calculate the diffusion coefficient,  $D_i$ , of the solvent mixtures through the membrane materials from the actual permeation data. Thus, using the PV results, we have calculated the values of  $D_i$  from the following equation:<sup>28</sup>

$$J_i = P_i [p_{i(\text{feed})} - p_{i(\text{permeate})}] = \frac{D_i}{h} [C_{i(\text{feed})} - C_{i(\text{permeate})}] \quad (9)$$

where  $D_i$  is assumed to be constant across the effective membrane thickness,  $h$ , and  $C_{i(\text{feed})}$  and



**Figure 8** Plot of permeation separation index versus mass % water in for (●) neat Na-Alg membrane (M-1), (■) 75 : 25 blend of Na-Alg and PAAm-g-GG (M-2), and (▲) 50 : 50 blend of Na-Alg and PAAm-g-GG (M-3).



**Table IV** Diffusion Coefficients of Water and Isopropyl Alcohol Calculated with Equation 9 at 30°C

Mass % Water in Feed	$D_w \times 10^{10}$ (m <sup>2</sup> /s)			$D_{\text{Iso-OH}} \times 10^{10}$ (m <sup>2</sup> /s)		
	M-1	M-2	M-3	M-1	M-2	M-3
10	5.42	5.74	3.97	0.111	0.073	0.040
20	11.0	12.8	11.28	0.111	0.064	0.057
30	16.3	19.6	18.81	0.249	0.300	0.238
40	28.5	31.1	34.60	0.581	0.714	0.527
50	40.7	50.9	56.77	0.936	1.573	1.605
60	67.0	74.5	85.56	1.895	3.717	2.874
70	104.8	120.9	138.32	3.240	5.364	6.898
80	180.2	230.6	267.6	5.380	8.363	9.705
90	588.1	674.8	785.1	12.00	13.771	18.07

$C_{i(\text{permeate})}$  are the composition of the species in the feed and in the permeate, respectively. The computed values of  $D_i$  (where the subscript  $i$  stands for water or isopropyl alcohol) at 30°C are presented in Table IV. As expected, diffusion coefficients of water increase considerably with increasing amount of water in the feed mixture, suggesting that the membranes are water selective. Such increases are quite dramatic at higher compositions of water in the feed, and the increase in  $D_i$  with increasing amount of water in the feed mixture is attributed to the creation of extra free volume in the membrane matrix. Similarly, the diffusion coefficients of isopropyl alcohol, although quite smaller in magnitude than those observed for water, show slight increases with increasing water in the feed. As regards the nature of the membranes, diffusion values show a systematic trend for all the membranes beyond 40 mass % water in the feed mixture; that is, with increasing mass % water in the feed,  $D_i$  values also increase systematically from membrane M-1 to M-3. A similar trend is also observed for isopropyl alcohol, but the diffusion values for isopropyl alcohol are quite smaller because the membranes are less selective to isopropyl alcohol. It may be noted that the  $D_i$  values calculated with eq. 9 are quite different than those computed with eq. 2. This difference is possibly because the diffusion values calculated with eq. 2 are concentration-independent quantities and are based on the Fickian transport mode. On the other hand, the diffusion values calculated with eq. 9 represent phenomenological quantities.

### Effect of Temperature

The temperature-dependent PV parameters (per-vaporation flux and diffusivity) for the feed mix-

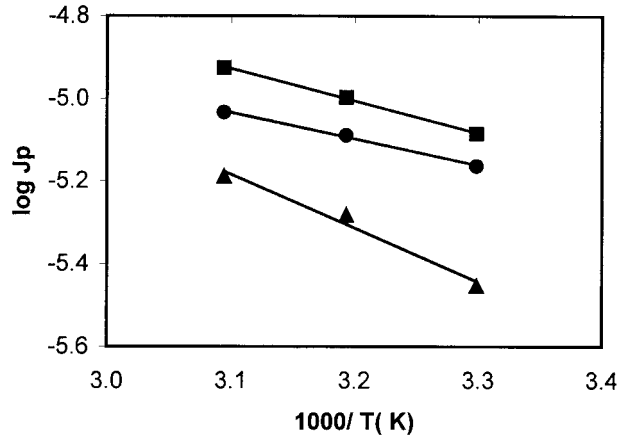
ture containing 10 mass % water were fitted to the Arrhenius equation to estimate the activation parameters. Thus,

$$J_P = J_{P0} \exp(-E_P/RT) \quad (10)$$

where  $E_P$  is the activation energy for permeation,  $J_{P0}$ , is the permeation rate constant,  $R$  is the gas constant, and  $T$  is temperature in Kelvin. If activation energy is positive, then permeation flux increases with increasing temperature, which has usually been observed in many PV experiments.<sup>29,30</sup> Apart from the enhanced liquid permeation flux, the driving force for mass transport also increases with increasing temperature. This driving force represents the concentration gradient resulting from a difference in the partial vapor pressure of the permeants between the feed and the permeate. As the feed temperature increases, the vapor pressure in the feed compartment also increases, but the vapor pressure at the permeate side will not be affected, resulting in an increase of the driving force at higher temperatures. The Arrhenius plots of  $\log J_P$  versus  $1000/T$  shown in Figure 9 are linear, signifying that the temperature dependence of total permeation flux follows Arrhenius behavior. The apparent activation energy for permeation,  $E_P$ , calculated from the slopes of the straight lines of the Arrhenius plots by the least squares method, are presented in Table V. The  $E_P$  values show the sequence M-1 < M-2 < M-3.

In a similar manner, the mass transport due to activated diffusion was fitted to the Arrhenius equation:

$$D_i = D_{i0} \exp(-E_P/RT) \quad (11)$$



**Figure 9** Arrhenius plot of  $\log J_p$  with  $1000/T$  for 10 mass % water in feed for (●) neat Na-Alg membrane (M-1), (■) 75 : 25 blend of Na-Alg and PAAm-g-GG (M-2), and (▲) 50 : 50 blend of Na-Alg and PAAm-g-GG (M-3).

where  $E_D$  is the energy of activation for diffusion and  $i$  stands for water or isopropyl alcohol. The Arrhenius plots of  $\log D_i$  versus  $1000/T$  are shown in Figure 10A for water and Figure 10B for isopropyl alcohol. These plots are also linear in the temperature interval studied. The heat of sorption values were calculated as  $\Delta H_S (\approx E_P - E_D)$ , and these data are also included in Table V. The  $\Delta H_S$  values are negative in all the cases, suggesting an endothermic sorption process. The  $E_D$  values show the sequence  $M-3 > M-1 > M-2$ .

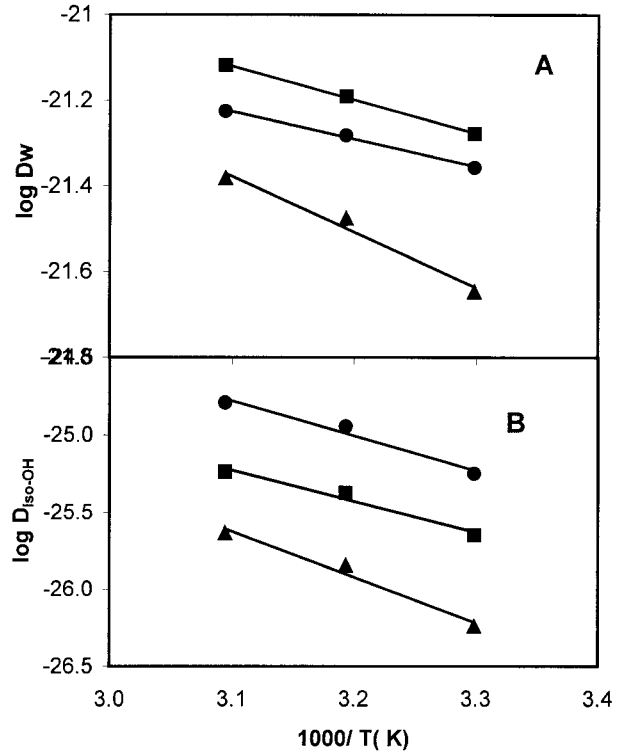
The temperature dependency of  $\alpha_{sep}$  was also investigated by employing the relationship proposed earlier by Ping et al.<sup>31</sup>

$$Y_w = \frac{1}{1 + (J_{Iso-OH}/J_w)\exp(-(E_{Iso-OH} + E_w)/RT)} \quad (12)$$

where  $Y_w$  is water composition in the permeate;  $J_w$  and  $J_{Iso-OH}$  are the permeation fluxes for water

**Table V** Permeation and Diffusion Activation Energies, Heat of Sorption of Water, and Energy Difference Values of the Membranes

Parameter	M-1	M-2	M-3
$E_P$ (kJ/mol) eq. (10)	5.33	6.50	10.84
$E_D$ (kJ/mol) eq. (11)	8.60	6.65	20.57
$\Delta H_S$ (kJ/mol)	-3.27	-0.15	-9.73
$E_{Iso-OH} - E_w$ (kJ/mol)	11.90	10.17	13.55



**Figure 10** Arrhenius plot of (A)  $\log D_w$  and (B)  $\log D_{Iso-OH}$  with  $1000/T$  for 10 mass % water in feed for (●) neat Na-Alg membrane (M-1), (■) 75 : 25 blend of Na-Alg and PAAm-g-GG (M-2), and (▲) 50 : 50 blend of Na-Alg and PAAm-g-GG (M-3).

and isopropyl alcohol, respectively; and  $E_w$  and  $E_{Iso-OH}$  are the Arrhenius activation energies of water and isopropyl alcohol, respectively, at the average energy level. A positive value of  $[E_{Iso-OH} - E_w]$  indicates that  $\alpha_{sep}$  decreases with increasing temperature, and a negative value indicates that  $\alpha_{sep}$  increases with an increase in temperature.<sup>29</sup> In all the membranes, the difference is positive (see Table V), further supporting that  $\alpha_{sep}$  decreases with increasing temperature.

## CONCLUSIONS

Blend membranes of Na-Alg with PAAm-g-GG were prepared and used in the PV separation of water and isopropyl alcohol. All the membranes are water selective. When compared with the neat Na-Alg membrane, the blend membranes have shown better permeation flux with better separation selectivity at lower concentration of water in the feed mixture. This result may be due to the decreased free volume (due to lower swelling) in

the blend membranes as a result of hydrogen-bond-type interactions, a fact that was also supported by the FTIR results. The M-2 membrane is more effective in separating water from the type of mixture used in this research. This result is further evidenced by the highest permeation separation index values of 43.41 and 97.23, respectively, at 10 and 20 mass % water in the feed mixture. On the whole, the PV separation of M-2 membrane is better than the neat Na-Alg membrane as well as that of M-3. The activation parameters for the process of diffusion and permeation follow the solution–diffusion principles.

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