

# Synthesis and Characterization of Polyacrylamide-Grafted Sodium Alginate Copolymeric Membranes and Their Use in Pervaporation Separation of Water and Tetrahydrofuran Mixtures

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**ABSTRACT:** Polyacrylamide-grafted sodium alginate (PAAm-g-Na-Alg) copolymeric membranes have been prepared, characterized, and used in the pervaporation separation of 10–80 mass % water-containing tetrahydrofuran mixtures. Totally three membranes were prepared: (1) neat Na-Alg with 10 mass % of polyethylene glycol (PEG) and 5 mass % of polyvinyl alcohol (PVA), (2) 46 % grafted PAAm-g-Na-Alg membrane containing 10 mass % of PEG and 5 mass % of PVA, and (3) 93 % grafted PAAm-g-Na-Alg membrane containing 10 mass % of PEG and 5 mass % of PVA. Using the transport data, important parameters like permeation flux, selectivity, pervaporation separation index, swelling index, and diffusion coefficient have been calculated at 30°C. Diffusion coefficients were

also calculated from sorption gravimetric data of water-tetrahydrofuran mixtures using Fick's equation. Arrhenius activation parameters for the transport processes were calculated for 10 mass % of water in the feed mixture using flux and diffusion data obtained at 30, 35, and 40°C. The separation selectivity of the membranes ranged between 216 and 591. The highest permeation flux of 0.677 kg/m<sup>2</sup> h was observed for 93% grafted membrane at 80 mass % of water in the feed mixture. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 272–281, 2002

**Key words:** pervaporation; tetrahydrofuran; sodium alginate; polyacrylamide; polyethylene glycol

## INTRODUCTION

Pervaporation (PV) is a membrane-based separation technique used extensively in the separation of aqueous-organic mixtures.<sup>1–4</sup> The method is relatively inexpensive and eco-friendly, yet its commercial exploitation has not yet been achieved satisfactorily. In earlier studies,<sup>5,6</sup> several hydrophilic membranes (e.g., polyvinyl alcohol) have been used in separating the aqueous-organic mixtures. However, the use of a natural polymer like sodium alginate (Na-Alg) along with a synthetic polymer like polyacrylamide (PAAm) may be advantageous, particularly to increase the flux.<sup>6–10</sup> In our earlier study,<sup>6</sup> we found that when Na-Alg was blended with polyvinyl alcohol (PVA), flux of the blend membrane was increased with increasing amount of PVA. In continuation of this study and as a part of our ongoing research program on membrane-based processes, we present here the synthesis of grafted copolymeric membranes of PAAm and Na-Alg for PV separation of water and tetrahydrofuran (THF) mixtures. Water and THF form azeotrope at 6.7 mass % of water,<sup>11</sup> and hence it is difficult

to separate the components by the so-called conventional techniques like distillation, etc. Even though some reports have already been published in the literature on the PV separation of water and THF mixtures,<sup>12–17</sup> the present paper reports on the improved selectivity to water by the use of new membranes developed.

## EXPERIMENTAL

### Materials

Sodium alginate (LR) and poly(vinyl alcohol) (molecular weight, 1,25,000), glutaraldehyde (25 mass % aqueous solution) (LR), and acetone were obtained from S. D. Fine Chem. Ltd., Mumbai, India. The A. R. grade tetrahydrofuran (anhydrous) was supplied by Spectrochem Pvt. Ltd., Mumbai, India. Polyethylene glycol (PEG-200) and potassium persulfate were respectively procured from Merck and Sisco-Chem Industries, Mumbai, India. All these chemicals were used as such and solutions were prepared from double distilled water.

### Preparation of grafted copolymers

About 10 g of Na-Alg was dissolved in 100 mL of distilled water at 60°C with constant stirring under nitrogen atmosphere in a three-necked round-bottom

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flask fitted with a condenser, a gas inlet, and a thermometer. The resulting solution was cooled and a 0.12 mol of acrylamide (AAm) was added to Na-Alg solution by stirring. To this, 10 mL of 0.1M potassium persulfate was added, and the reaction mixture was maintained between 50 and 60°C for 4 h. The polymer was precipitated by the addition of excess amount of methanol, filtered under suction, and dried in a vacuum oven maintained at 60°C. The polymer was then dissolved in water and filtered to remove the undissolved acrylamide homopolymer. The filtrate was concentrated and the dissolved graft copolymer was again precipitated using an excess amount of methanol. Two copolymers with the percentage grafting of 46 and 93 (designated respectively as Copoly-1 and Copoly-2) were prepared respectively, by using 5 and 10 g of acrylamide monomer; 100% grafting efficiency was obtained with 92% conversion of acrylamide.

### Characterization of copolymers

The copolymers were characterized for grafting by Fourier transform infrared (FTIR) spectra scanned between 4000 and 400  $\text{cm}^{-1}$  using KBr pellets on a Nicolet spectrometer (Model Impact 410, USA).

Differential scanning calorimetric (DSC) analyses were performed using duPont-2000 microcalorimeter at the heating rate of 10°C/min from -50 to 250°C under a constant flow of argon gas.

### Membrane preparation

Membranes were prepared with pure Na-Alg as well as with the grafted copolymers (Copoly-1 and Copoly-2). The polymers were dissolved separately in 100 mL of distilled water at 50°C under constant stirring in nitrogen atmosphere and the mixture was cooled to room temperature. To each of the three polymer solutions, 10 mass % of PEG was added to plasticize the membranes. Simultaneously, 15 mass % of polyvinyl alcohol (PVA) solution dissolved in 30 mL distilled water was prepared under constant stirring and a 10 mL (5 mass %) of this solution was added to each of the previous solution. The solutions were spread on a clean glass plate and the casted membrane was allowed to dry at room temperature in a dust-free atmosphere. The dried membranes were further crosslinked by immersing the membranes in a acetone:water (7:3 ratio) mixture containing 0.0062 mol of glutaraldehyde (GA) and 2 mL of HCl at room temperature for about 12 h. The membranes were repeatedly washed with distilled water to remove excess GA and HCl, and then dried at room temperature for 24 h before being used in PV experiments.

### Sorption experiments

Dynamic and equilibrium sorption experiments on the membranes were performed in water and THF mix-

tures at  $30 \pm 0.5^\circ\text{C}$  using an electronically controlled oven (WTB Binder, model BD-53, Germany) following the procedure published earlier.<sup>18</sup> Circularly cut (surface area = 9.08  $\text{cm}^2$ ) disk-shaped membrane samples were stored in a desiccator over anhydrous calcium chloride maintained at 25°C for at least 48 h before use. The initial mass of the membranes was taken on a single pan digital microbalance (model AE 240, Switzerland) sensitive to  $\pm 0.01$  mg. Polymer samples were placed inside the air-tight test bottles containing mixtures of water and THF. The test bottles were placed inside the oven maintained at a constant temperature of 30°C. The mass of the samples was determined at the selected time intervals by removing the samples from the test bottles, wiping the surface to remove the adhered solvent droplets by gently pressing them between filter papers, and again placed back into the oven. This step was completed within 15–20 s in order to minimize solvent evaporation.

Using the sorption data at different time intervals, mass % uptake,  $M_t$ , values were calculated by knowing the dry initial mass,  $W_o$  of the membrane using the relation,

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

Here,  $W_t$  is mass of the membrane at different time intervals. Equilibrium degree of swelling,  $DS$  of the membranes was calculated using the relation,

$$DS = \frac{W_\infty}{W_o} \quad (2)$$

Here,  $W_\infty$  is equilibrium mass uptake of the membrane. The concentration-independent diffusion coefficient,  $D$ , was calculated from the modified Fick's relation,<sup>19</sup>

$$\frac{M_t}{M_\infty} = \frac{4}{\pi} \left[ \frac{Dt}{h^2} \right]^{1/2} \quad (3)$$

where  $h$  is thickness of the membrane. The detailed procedure to determine the values of  $D$  using eq. (3) was published earlier.<sup>18</sup>

The results of equilibrium mass uptake, degree of swelling and diffusion coefficient are summarized in Table I.

### PV Experiments

PV experiments were carried out for water and THF mixtures using the apparatus designed indigenously. The composition of THF was varied from 20 to 80 mass % and the temperature of the feed mixture in the PV apparatus was monitored by a thermometer. The

**TABLE I**  
Equilibrium Mass % Uptake, (*S*), Degree of Swelling, (*DS*), and Diffusion Coefficient (*D*)

Mass % water	Equilibrium sorption, <i>S</i> (kg/kg)		
	Na-Alg	Copoly-1	Copoly-2
10	16.09	33.35	42.23
20	26.84	39.55	65.74
30	30.82	47.95	83.98
40	35.35	59.05	102.5
50	33.32	86.28	125.1
60	56.09	89.94	154.1
70	65.57	102.6	191.6
80	68.25	117.1	195.8
Mass % water	Degree of swelling, <i>DS</i> (kg/kg)		
	Na-Alg	Copoly-1	Copoly-2
10	1.16	1.33	1.42
20	1.27	1.40	1.66
30	1.31	1.48	1.84
40	1.35	1.59	2.03
50	1.33	1.86	2.25
60	1.56	1.89	2.54
70	1.66	2.03	2.92
80	1.68	2.17	2.96
Mass % water	Diffusion coefficient, <i>D</i> × 10 <sup>11</sup> (m <sup>2</sup> /s)		
	Na-Alg	Copoly-1	Copoly-2
10	3.41	3.62	5.59
20	5.90	9.87	1.24
30	8.33	1.09	1.34

membrane was placed on the porous stainless steel support of the PV apparatus and then secured firmly with the aid of bolts and nuts. After pouring the mixture in the feed compartment, nearly 30 min was allowed to attain the equilibrium. The solution in the PV cell is kept continuously stirred. The effective surface area of the membrane in contact with the feed mixture was 32 cm<sup>2</sup>. Water was circulated around the PV cell outer jacket to maintain a constant temperature. Vacuum (10 torr) was applied on the permeate side using a vacuum pump (Toshniwal, India). Permeate was collected in glass ampules (traps) immersed in liquid nitrogen. Permeate in the cold trap

was cooled at room temperature, removed, and weighed to determine the flux. The permeate composition was calculated by measuring the refractive index for sodium-D line at 30°C using an Abbe refractometer (Model, Atago 3T, Japan); and these data were used to compute the separation selectivity.

Permeation flux,  $J_p$ , separation selectivity,  $\alpha_{sep}$ , pervaporation separation index, *PSI*, and enrichment factor,  $\beta$ , were respectively calculated as

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

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

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

$$\beta = \frac{C_w^p}{C_w^f} \quad (7)$$

where  $W_p$  is mass of permeate,  $A$  is area of the membrane in contact with feed mixture, and  $t$  is time;  $P_w$  and  $P_{THF}$  are the mass % of water and THF, respectively, in the permeate;  $F_w$  and  $F_{THF}$  are, respectively, mass % of water and THF in the feed;  $C_w^p$  and  $C_w^f$  are concentrations of water at permeate and feed side, respectively. Total pervaporation flux,  $J_p$ , and separation selectivity,  $\alpha_{sep}$ , are presented in Table II. Similar data at different temperatures for 10 mass % water-containing mixtures are presented in Table III. The results of *PSI* and  $\beta$  are displayed graphically.

## RESULTS AND DISCUSSION

FTIR spectra of pure Na-Alg and the grafted copolymers (PAAm-g-Na-Alg) are shown in Figure 1. FTIR spectral analyses confirmed the presence of grafting between PAAm and Na-Alg. A broad band appearing at ~3400 cm<sup>-1</sup> corresponds to the associated -OH stretching vibrations of the hydroxyl groups; the peak appearing at 1610 cm<sup>-1</sup> corresponds to the deforma-

**TABLE II**  
Total Pervaporation Flux and Separation Selectivity Data for Different Mass % of Water in the Feed at 30°C

Mass % water	$J_p \cdot 10^2$ (kg/m <sup>2</sup> h)			$\alpha_{sep}$		
	Na-Alg	Copoly-1	Copoly-2	Na-Alg	Copoly-1	Copoly-2
10	9.11	9.38	13.1	591	303	216
20	10.4	11.0	13.2	36.0	29.3	25.6
30	13.2	13.9	16.3	20.8	18.0	13.2
40	26.7	28.3	39.4	9.6	9.2	7.9
50	24.4	31.9	47.0	7.0	2.3	1.8
60	29.4	38.1	55.6	7.7	2.0	1.2
70	33.4	39.4	63.8	2.3	1.2	0.4
80	34.9	40.6	67.7	1.2	0.6	0.3

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

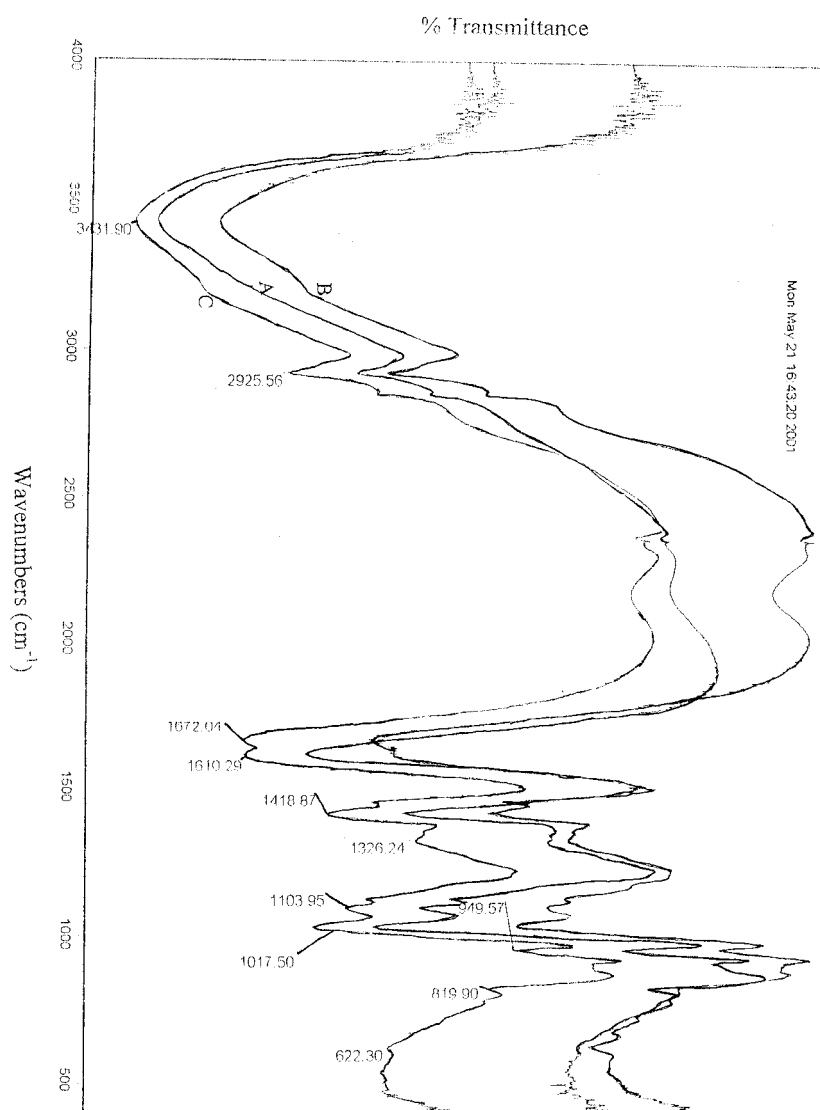
Temp. (°C)	$J_p \cdot 10^2$ (kg/m <sup>2</sup> h)			$\alpha_{sep}$		
	Na-Alg	Copoly-1	Copoly-2	Na-Alg	Copoly-1	Copoly-2
30	9.11	9.38	13.08	591.00	301.34	216.00
35	9.14	9.42	13.09	441.00	191.00	129.50
40	9.16	9.47	13.12	441.00	171.00	119.60

tion of carbonyl group of Na-Alg. In the spectra of the copolymer, a new peak appearing at 3200 cm<sup>-1</sup> corresponds to the bonded —NH stretching vibrations while antisymmetric —NH bending appears at 1672 cm<sup>-1</sup> due to the primary amide group. The relatively high intense peak obtained at 2925 cm<sup>-1</sup> corresponds to aliphatic —CH stretching vibration in the grafted copolymers, thus confirming the grafting reaction.

DSC scans (see Fig. 2) on the plain Na-Alg, Copoly-1 (46% grafted), and Copoly-2 (93% grafted) membranes

show the glass transition temperature ( $T_g$ ) values at 56, 61, and 65°C, respectively. It is observed that with an increase in grafting of PAAm onto Na-Alg, there is a gradual increase in  $T_g$  from 61 to 65°C. This supports that there is modification of Na-Alg by grafting with PAAm, rendering the Na-Alg polymer thermally more stable. This also confirms that the copolymer with higher % of grafting is thermally more stable.

Transport mechanism in PV separation can be understood in terms of molecular transport of liquids



**Figure 1** FTIR spectra of pure Na-Alg (A), Copoly-1 (B), and Copoly-2 (C).

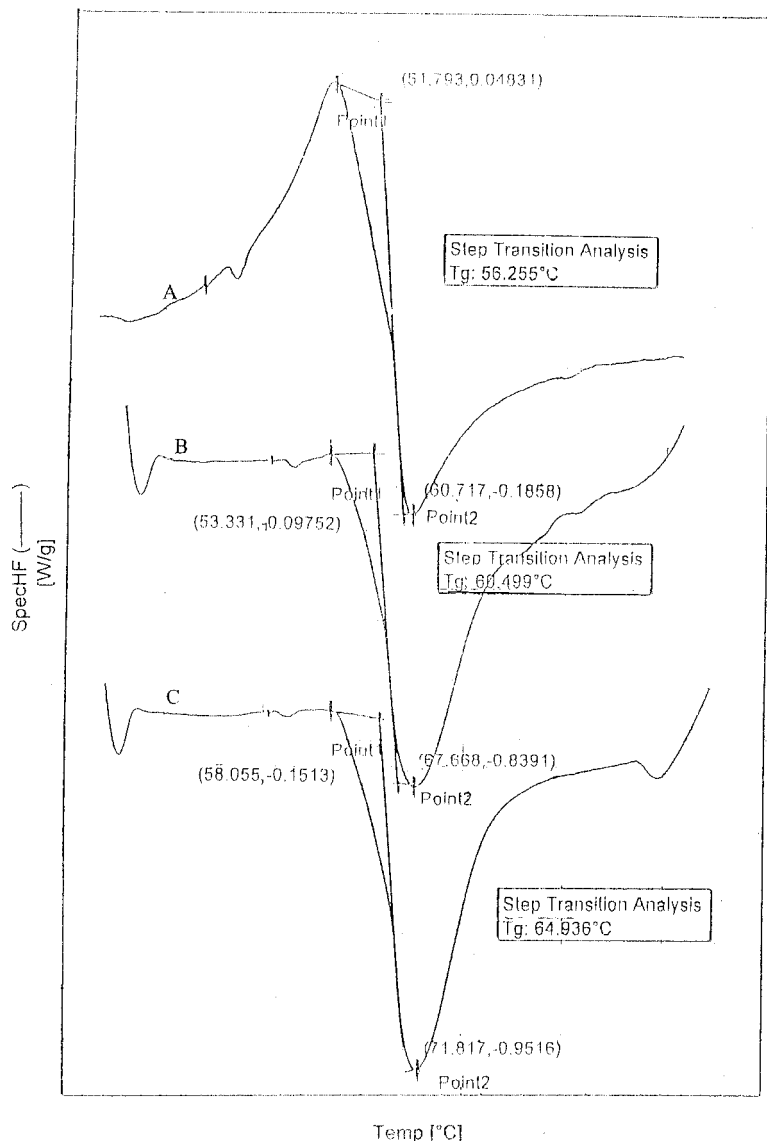
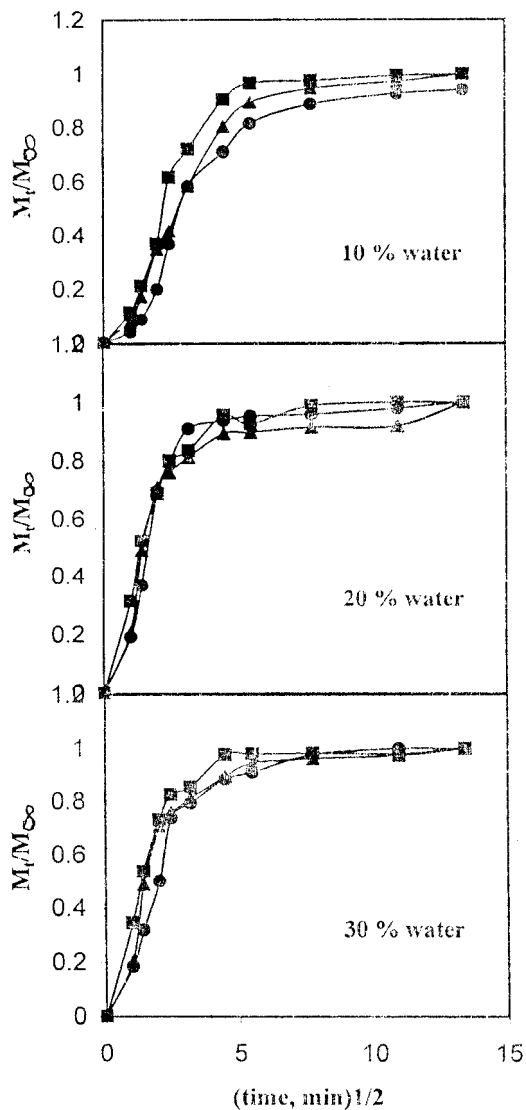


Figure 2 DSC analysis of pure Na-Alg (A), Copoly-1 (B), and Copoly-2 (C).

through the membrane and the phenomenon can be described by a combination of sorption and diffusion processes.<sup>20</sup> When liquids permeate through the swollen polymeric membrane, there will be a coupling of fluxes leading to the permeation, which in turn affects the membrane performance. Polymers below their  $T_g$  have a restricted chain movement, but when in contact with low molecular weight liquids, due to molecular level interactions between the polymer and the solvent molecules, chain mobility increases.<sup>21</sup> From the data presented in Table I, it is found that degree of swelling, equilibrium mass % uptake, and diffusion coefficients increase with increasing water content of the feed mixtures. This suggests the increased interactions of water molecules (since membranes are water selective). In view of the experimental difficulties, we could not compute diffusion coefficients beyond 30 mass % of water for the feed mixture.

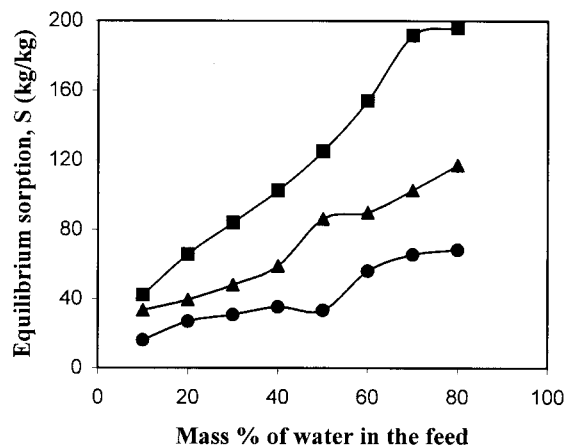
Figure 3 displays  $M_t/M_\infty$  vs  $t^{1/2}$  plots of the three membranes (sorption curves) for 10, 20, and 30 mass % of water in the feed mixture. In all three cases, the time required to attain equilibrium sorption is almost the same, but equilibrium sorption values do not seem to vary widely with respect to water content in the feed mixture. However, a closer inspection reveals that sorption curves for the 10 mass % water-containing mixture vary depending upon the type of the membrane employed, but this effect is not so significant for 30 mass % water-containing mixtures. In all the cases, sigmoidal shapes of the sorption curves are observed, indicating a deviation of molecular transport from Fickian trend.<sup>22,23</sup> Also, equilibrium sorption curves of all the membranes at longer times merge into a single curve for 20 mass % and 30 mass % water-containing feed mixtures. With increasing % grafting of PAAm onto Na-Alg, mass % uptake values also increase,



**Figure 3** Plot of  $M_t/M_\infty$  vs square root of time at different mass % of water in the feed for (●) Na-Alg, (▲) Copoly-1, and (■) Copoly-2.

suggesting increased hydrophilic interactions between water molecules and the membranes.

Sigmoidal nature of the sorption curves prompted us to probe further the details of transport mechanism. To investigate this, we have fitted the experimental uptake data,  $M_t/M_\infty$ , to an empirical relationship<sup>24</sup>:



**Figure 4** Plot of equilibrium % mass uptake vs mass % of water in the feed. Symbols are the same as in Figure 3.

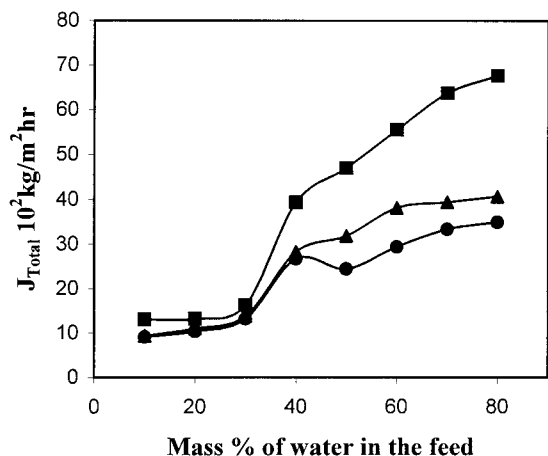
$$\frac{M_t}{M_\infty} = kt^n \tag{8}$$

where  $M_\infty$ , equilibrium % mass uptake by the membrane, was calculated from the asymptotic (saturation) region of the curve;  $k$  and  $n$  are the empirical parameters, of which  $k$  represents polymer-solvent interaction, whereas the values of  $n$  indicate the type or nature of transport mechanism. For a Fickian transport,  $n = 0.5$ , while  $n = 1.0$  for the non-Fickian transport. The values of  $n$  ranging between 0.5 and 1.0 suggest the anomalous transport.<sup>22-24</sup> The values of  $n$  and  $k$  have been calculated from the least squares method by fitting the sorption results to eq. (8), and these data are presented in Table IV. The values of  $n$  vary widely from a lowest of 0.49 for Copoly-2 in case of 30 mass % of water to a highest of 1.27 for Na-Alg for 10 mass % of water-containing binary mixture; those of  $k$  range between 0.002 and 0.006.

Figure 4 shows the dependency of equilibrium sorption on mass % of water in the feed mixture. Equilibrium sorption increases with an increasing amount of water in the feed mixture for all the three membranes. However, equilibrium sorption is higher for Copoly-1 and Copoly-2, whereas Na-Alg membrane shows the least equilibrium values. Thus, there is a systematic increase in equilibrium sorption with increasing amount of grafting. These trends can also be com-

**TABLE IV**  
The Estimated Values of  $n$  and  $k$  calculated from Eq. eight

Membrane	10 mass % water		20 mass % water		30 mass % water	
	$n$	$k \times 10^2$	$n$	$k \times 10^2$	$n$	$k \times 10^2$
Na-Alg	1.27	0.19	0.82	0.62	0.75	0.42
Copoly-1	0.92	0.24	0.72	0.46	0.72	0.41
Copoly-2	0.90	0.26	0.51	0.55	0.50	0.41



**Figure 5** Plot of total flux vs mass % of water in the feed. Symbols are the same as in Figure 3.

pared with the total flux values presented in Figure 5. For all the membranes total flux increases with increasing amount of water in the feed mixture, probably because of the hydrogen-bond-type interactions between water and polymer chain segments. For all the membranes, total flux increases slightly for 10 up to 30 mass % of water, but beyond that, i.e., at higher amounts of water (40–80 mass %), the flux values increase considerably, indicating higher preferential interactions of water molecules. This may be due to the higher amount of PAAm present in the grafted membrane, making it more hydrophilic to have a favorable interaction with water molecules, thereby resulting in higher total flux values with increasing amount of water in the feed. Lower flux values observed for Copoly-1 than Copoly-2 membrane may be because at lower grafting there is an increase in the number of branches on the polymer backbone.<sup>25</sup>

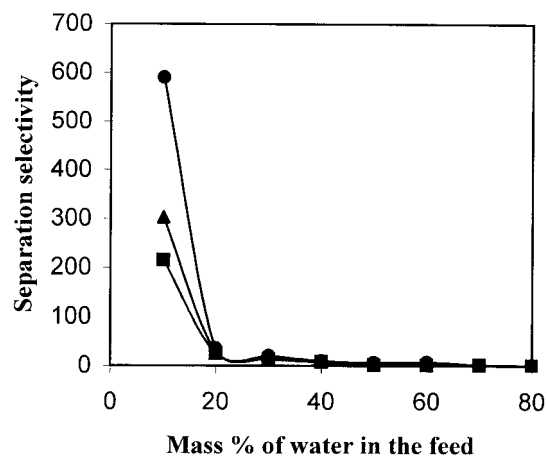
The results of separation selectivity of the three membranes displayed in Figure 6 show the highest value for 10 mass % water-containing THF mixture. However, with increasing water content in the feed mixture, separation selectivity decreases quite drastically and remains constant between 20 and 80 mass % of water in the feed for all the three membranes, indicating that at higher water content in the feed mixture, membrane affinity toward water remains the same.

It appears important to compare our selectivity data with those of the published reports. See Table V. For instance, poly(vinylpyrrolidone)-grafted polytetrafluoroethylene membrane used by Aptel et al.<sup>12</sup> gave the separation selectivity of 8.5 with a flux of 0.3 kg/m<sup>2</sup> h for 5.9 mass % of water in the feed containing THF. Neel et al.<sup>13</sup> used the polytetrafluoroethylene-poly(vinylpyrrolidone) membrane to improve the separation selectivity up to 18.4 and the flux of 0.94 kg/m<sup>2</sup> h respectively at 5.7 mass % of water in the feed. On the other hand, the polyacrylonitrile-poly(vi-

nylpyrrolidone) membrane developed by Nguyen et al.<sup>14</sup> gave a selectivity 10.4 and a flux of 0.4 kg/m<sup>2</sup> h at 5.9 mass % of water in the feed. The poly(vinyl alcohol)-based composite membrane used by Mencarini et al.<sup>15</sup> gave a higher separation selectivity of 28, sacrificing the flux value of 0.2 kg/m<sup>2</sup> h for the 6 mass % of water in the feed. Oikawa et al.<sup>16</sup> used a poly(vinylpyrrolidone) membrane containing pyridine moieties to get the highest separation selectivity of 1518, again at the cost of lowest flux of 0.125 kg/m<sup>2</sup> h for 6.7 mass % of water in the feed. Li et al.<sup>17</sup> used the Y-type zeolite membrane to obtain a better balance between separation selectivity of 360 and flux of 2.1 kg/m<sup>2</sup> h at 5 mass % of water in the feed.

In the present research, for the Na-Alg membrane, the separation selectivity of 591 is higher than many of the earlier membranes discussed before, but the flux is very low, i.e., 0.091 kg/m<sup>2</sup> h. On the other hand, for the Copoly-1 membrane, separation selectivity of 303 and flux of 0.094 kg/m<sup>2</sup> h are obtained, showing not much improvement. For the Copoly-2 membrane, a separation selectivity of 216 and a slight increase in the flux value of 0.131 kg/m<sup>2</sup> h are obtained for the 10 mass % of water in the feed. Therefore, at the best, the present membranes have better selectivity than many other membranes cited in the literature (see Table V), but there is a need to improve their flux values. There are several reasons for this anomaly.

Neel et al.<sup>26</sup> suggested that selective diffusion in the dry region of the membrane at the downstream side plays an important role in determining the overall selectivity. Mulder et al.<sup>27</sup> argues that selectivity is controlled by preferential sorption of one of the components of the mixture toward the swollen membrane at the upstream side. The present results suggest that affinity of the membranes toward water is higher at the downstream side when compared with THF, and thus the membranes of the present study are water



**Figure 6** Plot of separation selectivity vs mass % of water in the feed. Symbols are the same as in Figure 3.

**TABLE V**  
Comparison of Our Data for Water/THF Mixtures in the Literature Findings

Membrane <sup>a</sup>	Mass % of water in the feed	Temp. (°C)	Total flux (kg/m <sup>2</sup> h)	Water/THF separation selectivity	Reference
PVP-g-PFTE	5.9	25	0.3	8.5	Aptel et al. (1976) <sup>12</sup>
PTFE-PVP	5.7	25	0.94	18.4	Neel et al. (1983) <sup>13</sup>
PAN-PVP	5.9	20	0.4	10.4	Nguyen et al. (1985) <sup>14</sup>
Composite PVA	6	50	0.2	28	Mencarini et al. (1994) <sup>15</sup>
PMCP	6.7	25	0.125	1518	Oikawa et al. (1995) <sup>16</sup>
Y-type zeolite	5	60	2.1	360	Li et al. (2001) <sup>17</sup>
Na-Alg	10	30	0.091	591	This study
Copoly-1	10	30	0.094	303	This study
Copoly-2	10	30	0.131	216	This study

<sup>a</sup>PVP-g-PTFE: polyvinyl pyrrolidone grafted polytetrafluoroethylene; PTFE-PVPD: polytetrafluoroethylene-polyvinyl pyrrolidone; PAN-PVPD: polyacrylonitrile-polyvinyl pyrrolidone; PVA; poly(vinyl alcohol); PMCP; pyridine moieties containing poly(vinylpyrrolidone); Y-type zeolite: Si/Al containing membrane with Al<sub>2</sub>O<sub>3</sub> support.

selective. However, the mechanism of transport through such membranes is not yet very clear at the phenomenological level. At any rate, membrane performance in PV separation can be influenced by several process parameters like feed composition and temperature in addition to the chain relaxation process in relation to diffusion as well as the morphology of the membranes. Relaxation involves the configurational rearrangements of the polymer chains, thereby resulting in a decrease of flux as by suggested by Yeom et al.<sup>28</sup> Again, relaxation can be complicated by the liquid transport and their interactions with the polymer chain segments. Therefore, it is a complicated process and many efforts are still underway to increase the membrane selectivity and flux simultaneously to achieve the optimum separation in PV experiments.

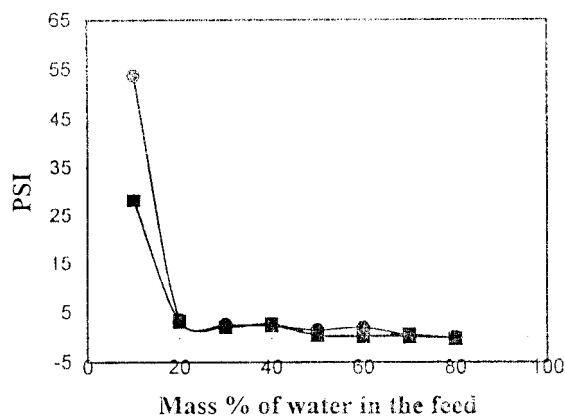
The results of the permeation separation index, *PSI*, and enrichment factor,  $\beta$ , are displayed, respectively, in Figures 7 and 8. Both parameters show a decrease with an increasing amount of water in the feed mixture. However, the  $\beta$  values show a more systematic decreasing trend for all the membranes with increas-

ing composition of water in the feed mixture, whereas *PSI* values do not exhibit any systematic trend.

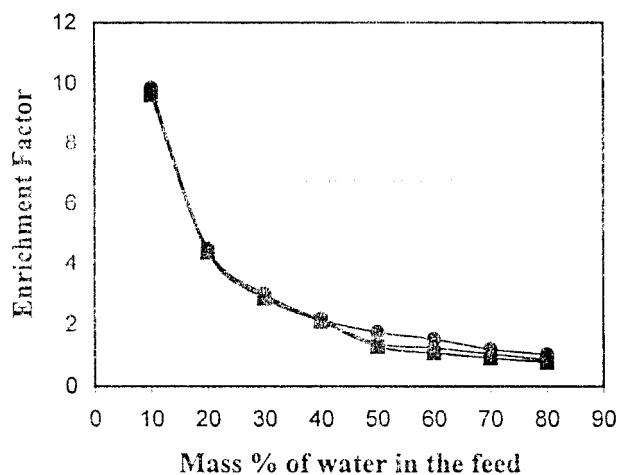
The diffusion coefficient,  $D_i$  of the liquid through the membranes was calculated from PV results using

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

where  $D_i$  is assumed to be constant across the effective membrane thickness,  $h$ ;  $C_i(\text{feed})$  and  $C_i(\text{permeate})$  are the mixture compositions in the feed and the permeate, respectively. The computed values of  $D_i$  (where the subscript  $i$  stands for either water or THF) at 30°C presented in Table VI for water are lower than those observed for THF by an order of magnitude over the entire mixture compositions. Diffusion coefficients vary according to the sequence: Na-Alg > Copoly-1 > Copoly-2. Diffusion coefficients also tend to increase with an increasing amount of water in the feed mixture. Values of diffusion coefficients of water-THF mixtures given Table I cannot be compared with the



**Figure 7** Plot of pervaporation separation index vs mass % of water in the feed. Symbols are the same as in Figure 3.



**Figure 8** Plot of enrichment factor vs mass % of water in the feed. Symbols are the same as in Figure 3.



TABLE VI  
Diffusion Coefficients of Water and THF Calculated from Eq. (9) at 30°C

Mass % water	$D_W \times 10^9$ (m <sup>2</sup> /s)			$D_{THF} \times 10^{10}$ (m <sup>2</sup> /s)		
	Na-Alg	Copoly-1	Copoly-2	Na-Alg	Copoly-1	Copoly-2
10	3.94	4.06	5.67	0.6	1.21	2.37
20	5.19	5.56	6.67	5.75	7.56	10.4
30	7.72	8.14	9.78	8.67	10.6	17.3
40	19.3	20.6	29.2	30.3	33.3	55.6
50	22.2	43.3	81.4	31.7	186	447
60	32.8	74.2	281.0	28.6	247	1510
70	75.6	322	47.5	139	1160	558
80	486	111	2.59	1040	475	725

values given for individual components (water or THF) in Table VI.

The effect of temperature on flux as well as diffusion has been very systematic as expected, i.e., an increase in feed temperature increases thermal mobility of the polymer chains, thereby increasing the diffusion rate. The results of total flux and separation selectivity for 10 mass % water in the feed at 30, 35, and 40°C are presented in Table III. It is observed that flux values increase, but those of separation selectivity decrease with increasing temperature. Temperature dependency of flux and diffusion was analyzed by Arrhenius relationships,

$$J_p = J_{p0} \exp(-E_p/RT) \quad (10)$$

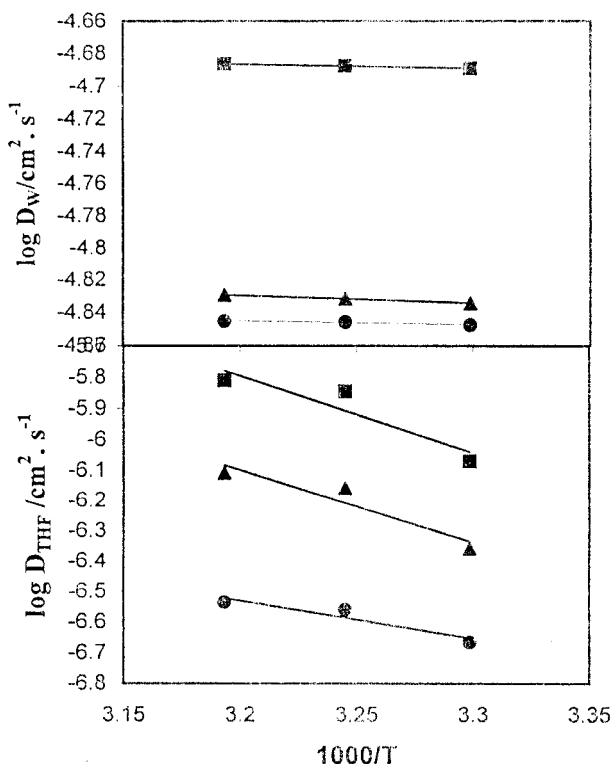


Figure 9 Arrhenius plot of  $\log D_W$  and  $\log D_{THF}$  vs  $1000/T$  at 10 mass % of water in the feed. Symbols are the same as in Figure 3.

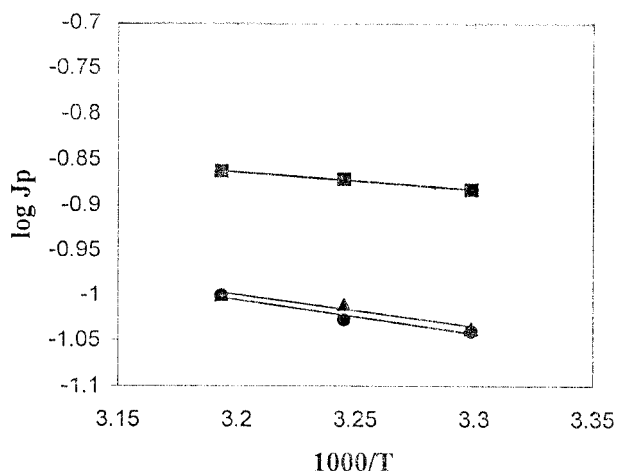
$$D_i = D_{i0} \exp(-E_D/RT) \quad (11)$$

where  $E_D$  and  $E_p$  are the energy of activation for diffusion and permeation, respectively,  $J_{PO}$  is the permeation rate constant,  $R$  is the gas constant, and  $T$  is the temperature in Kelvin. The Arrhenius plots of  $\log D_i$  vs  $1000/T$  are presented in Figure 9. The  $E_D$  values estimated by the method of least squares are included in Table VII. If activation energy is positive, then permeation flux increases with increasing temperature, a phenomenon that is most common in PV separation. This further increases the driving force for mass transport since it represents the concentration gradient due to differential vapor pressure of the permeant molecules between feed and permeate. As the feed temperature increases, vapor pressure in the feed compartment also increases, but vapor pressure at the permeate side is not affected. Thus, with increasing temperature the driving force for molecular transport also increases.

In the Arrhenius plots of  $\log J_p$  vs  $1000/T$  shown in Figure 10, it can be observed that the temperature dependency of total permeation flux follows the Arrhenius trend, i.e., these plots exhibit a linear behavior. The apparent activation energy values ( $E_p$  or  $E_D$ ) calculated from the slopes of the straight lines of the Arrhenius plots of  $\log E_p$  vs  $1000/T$  or  $\log E_D$  vs  $1000/T$  by the least squares method are presented in Table VII. By taking the  $E_p$  and  $E_D$  values for water, the heat of sorption,  $\Delta H_S$  for water permeation were calculated using  $\Delta H_S = E_p - E_D$ , and these data are also included in Table VII. The  $\Delta H_S$  values are nega-

TABLE VII  
Permeation and Diffusion Activation Energies, Heat of Sorption for Water, and Energy Difference Values

Parameter	Na-Alg	Copoly-1	Copoly-2
$E_p$ (kJ/mol), Eq. (9)	6.87	3.34	2.02
$E_D$ (kJ/mol), Eq. (10)	7.29	5.27	3.88
$\Delta H_S$ (kJ/mol)	-0.42	-1.93	-1.86
$(E_{THF} - E_W)$ (kJ/mol)	23.24	44.86	33.78



**Figure 10** Arrhenius plot of  $\log J_p$  vs  $1000/T$  at 10 mass % of water in the feed.

tive in all the cases, suggesting an endothermic mode of sorption.

Temperature dependency of separation selectivity was also studied by employing the equation proposed by Ping et al.<sup>29</sup>

$$Y_w = \frac{1}{1 + \left(\frac{J_{\text{THF}}}{J_w}\right) \exp\{[-E_{\text{THF}} + E_w]/RT\}} \quad (12)$$

where  $Y_w$  is water composition in the permeate,  $J_w$  and  $J_{\text{THF}}$  are permeation fluxes;  $E_w$  and  $E_{\text{THF}}$  are Arrhenius activation energies of water and THF, respectively, at the average energy level. The positive values of  $(E_{\text{THF}} - E_w)$  indicate that separation selectivity decreases with an increase in temperature, but negative values indicate that separation selectivity increases with increasing temperature.<sup>30</sup> In the present study, the difference  $(E_{\text{THF}} - E_w)$  is positive, indicating that separation selectivity decreases with increasing temperature. Results presented in Table III also support that selectivity decreases with increasing temperature between 30 and 40°C.

## CONCLUSIONS

Polyacrylamide-grafted sodium alginate polymeric membranes were prepared by free radical polymerization and their membrane properties were investigated in relation to neat sodium alginate membrane for the pervaporation separation of water and THF mixtures. Diffusion, selectivity, flux, and sorption data of the membranes tend to indicate that the membranes of the present study are water selective. An increase in % grafting resulted in the membranes with higher flux than the neat sodium alginate membrane. In the

present membranes, it was possible to improve the selectivity toward water, but not the flux. However, more research efforts are in progress to develop thin film composite membranes having a good balance between flux and selectivity.

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