Syntheses and Characterization of Blend Membranes of Sodium Alginate and Poly(vinyl alcohol) for the Pervaporation Separation of Water + Isopropanol Mixtures

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ABSTRACT: The blend membranes of sodium alginate and poly(vinyl alcohol) have been prepared by physical mixing in different ratios (75, 50, and 25%) of sodium alginate with poly(vinyl alcohol). The membranes were crosslinked with glutaraldehyde and used in the pervaporation separation of water + isopropanol mixtures at 30°C. The crosslinking reaction was confirmed by Fourier transform infrared spectra. Permeation flux increased with an increase in mass % of water in the feed mixture as well as with an increase in the amount of poly(vinyl alcohol) in the blend, but separation selectivity decreased. Diffusion coefficients of water + isopropanol mixtures have been calculated using the Fick's equation from the sorption data. Arrhenius activation parameters were calculated for 10 mass % of water in the feed mixture using the values of flux and diffusion coefficients obtained at 30, 40, and 50°C. The diffusion and pervaporation results have been explained on the basis of solution-diffusion principles. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 3642–3651, 2002

Key words: pervaporation; blends; crosslinking; hydrophilic polymers; poly(vinyl alcohol)

INTRODUCTION

Pervaporation (PV) separation based on polymeric membranes has been widely used in separating alcohols from their aqueous mixtures.[1–5] A good pervaporation membrane should exhibit high permeation flux and high separation selectivity. The simultaneous enhancement of both these parameters has been a challenge in PV separation industries.[6] For aqueous mixtures, hydrophilic polymers have good separation characteristics due to their strong affinity towards water,[7–10] but the main drawback of such polymers is their excessive swelling due to hydrogen bonding between hydrophilic functional groups of the polymer and the water molecule. Introduction of hydrophilic groups on the membrane results in high swelling and low water selectivity. To suppress this effect three-dimensional crosslinked network polymers have been proposed.[11] Among the hydrophilic polysaccharide polymers, sodium alginate has gained widespread application as a membrane material because it exhibits high separation selectivity and flux when compared to many other hydrophilic polymers.[12,13]

In the present study, blend membranes of sodium alginate (Na-Alg) and poly(vinyl alcohol), (PVA) are prepared and used for the PV separation of isopropanol (Iso-OH) and water mixtures. There have been very few limited studies in the previous literature on the PV separation of blend membranes derived from Na-Alg and PVA. For instance, Moon et al.[14] have prepared the sodium alginate and chitosan two-ply membranes and used in the PV dehydration of Iso-OH. Recently, the Na-Alg membranes have been studied for the PV separation of aqueous–organic mixtures.[15–18] In continuation of our ongoing program of research in developing newer membranes,[18–21] we now extend our study on the pervaporation separation of water + Iso-OH mixtures using the blend membranes of Na-Alg and PVA. It is hoped that the use of a more flexible PVA will enhance the overall membrane flexibility of the otherwise rigid Na-Alg membrane. This would make the blend membrane more suitable for the PV separation of polar molecules such as water from water + isopropanol mixture. The important PV separation parameters, viz., sorption, diffusion, sorption selectivity, pervaporation separation index, enrichment factor, and flux have been studied. Activation parameters for the solvent flux and diffusion have been computed from the Arrhenius relationship. The results are discussed in terms of the diffusion anomalies.[22]

EXPERIMENTAL

Materials

Sodium alginate (LR grade) and poly(vinyl alcohol), M.W. 1,25,000, isopropanol (AR grade), glutaralde-

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hyde (25% aqueous solution) (LR grade), and acetone (AR grade) were all purchased from s.d. fine Chemicals, Mumbai, India. These chemicals were used without further purification. Doubly distilled deionized water was used throughout this study.

Preparation of membranes

Different blend membranes of sodium alginate and poly(vinyl alcohol) in the mass % ratios of 75/25, 50/50, and 25/75 were taken in separate beakers and dissolved in 100 mL of deionized water. After uniform mixing, 0.15 mL of glutaraldehyde was added and the mixture was stirred overnight to achieve a more uniform mixing of the polymers. The solution was filtered to remove any undissolved solids as well as impurities. The solution was then casted onto a clean glass plate and the casted membrane was dried at room temperature in a dust free atmosphere. The dried membrane was peeled off from the glass plate and treated for crosslinking and insolubilization.

The membranes prepared as above were immersed in acetone containing 2% HCl at room temperature for 24 h. The membranes were removed from acetone and transferred to deionized water for 15 min to attain the equilibrium swelling. These were then immersed in the same solution of acetone containing 2% HCl for 30 min to attain uniform crosslinking. Later they were transferred to the fresh deionized water for 30 min to remove the unreacted glutaraldehyde. The membranes thus formed were dried at room temperature and used in the pervaporation experiments.

Fourier transform infrared spectra (FTIR)

FTIR spectral measurements were performed using a Nicolet (Model, Impact 410, USA) spectrophotometer to confirm the crosslinking of the membranes. Crosslinked and uncrosslinked membranes were finely ground with KBr and pellets were made. The spectra were scanned between 400 and 4000 cm^{-1}. The 2% HCl in acetone was used as a catalyst along with glutaraldehyde as the crosslinking agent. Crosslinking reaction between the hydroxyl groups of Na-Alg and PVA with the aldehydic groups of glutaraldehyde is confirmed in view of the increase in the peak intensity at 1097 cm^{-1} from the uncrosslinked polymer to the crosslinked matrix due to the formation of an acetal ring and ether linkage.[23] FTIR spectra of the crosslinked and the uncrosslinked blend membranes are presented respectively as A and B in Figure 1.

Sorption experiments

Dynamic and equilibrium sorption experiments were performed in water + Iso-OH mixtures at 30 ± 0.5°C by using an electronically controlled oven (WTB Binder, model BD 53, Germany) as per the procedure published earlier.[22] Circularly cut (surface area = 9.08 cm^2) disk-shaped membranes were kept in the desiccator over anhydrous calcium chloride maintained at 25°C for 48 h before use. The initial mass of the membranes was measured using a single pan digital microbalance (model AE 240, Switzerland) sensitive to ±0.01 mg. Polymer samples were placed inside the screw-tight test bottles containing different mixtures of water and Iso-OH. The test bottles were placed inside the oven maintained at the 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 droplets by pressing them slowly in between filter paper wraps, weighed immediately, and again placed back into the oven. This step was completed within 15–20 s to minimize the evaporation losses due to solvent evaporation. The equilibrium sorption data collected at 30°C are presented in Table I.

From the sorption data measured at different time intervals, we have calculated the mass % uptake, M_t, by knowing the dry initial mass, W_o, of the membranes using the relation:

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

The equilibrium swelling was calculated by taking the ratio of the equilibrium mass, W_∞, to that of the dry mass of the membrane using:

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

The concentration independent diffusion coefficient, D was calculated using[24]

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

where h is the thickness of the membrane. A detailed procedure to determine the values of D using eq. (3) has been published elsewhere.[22] The results of degree of swelling and diffusion coefficients are given in Table I.

Pervaporation experiments

Pervaporation experiments were carried out for water + Iso-OH mixtures using the apparatus designed indigenously. The composition of Iso-OH was varied from 50 to 90 mass %, and the feed solution temperature in the PV apparatus was measured at the desired value by inserting a thermometer with a continuous stirring by means of a stirrer. The properly cut mem-
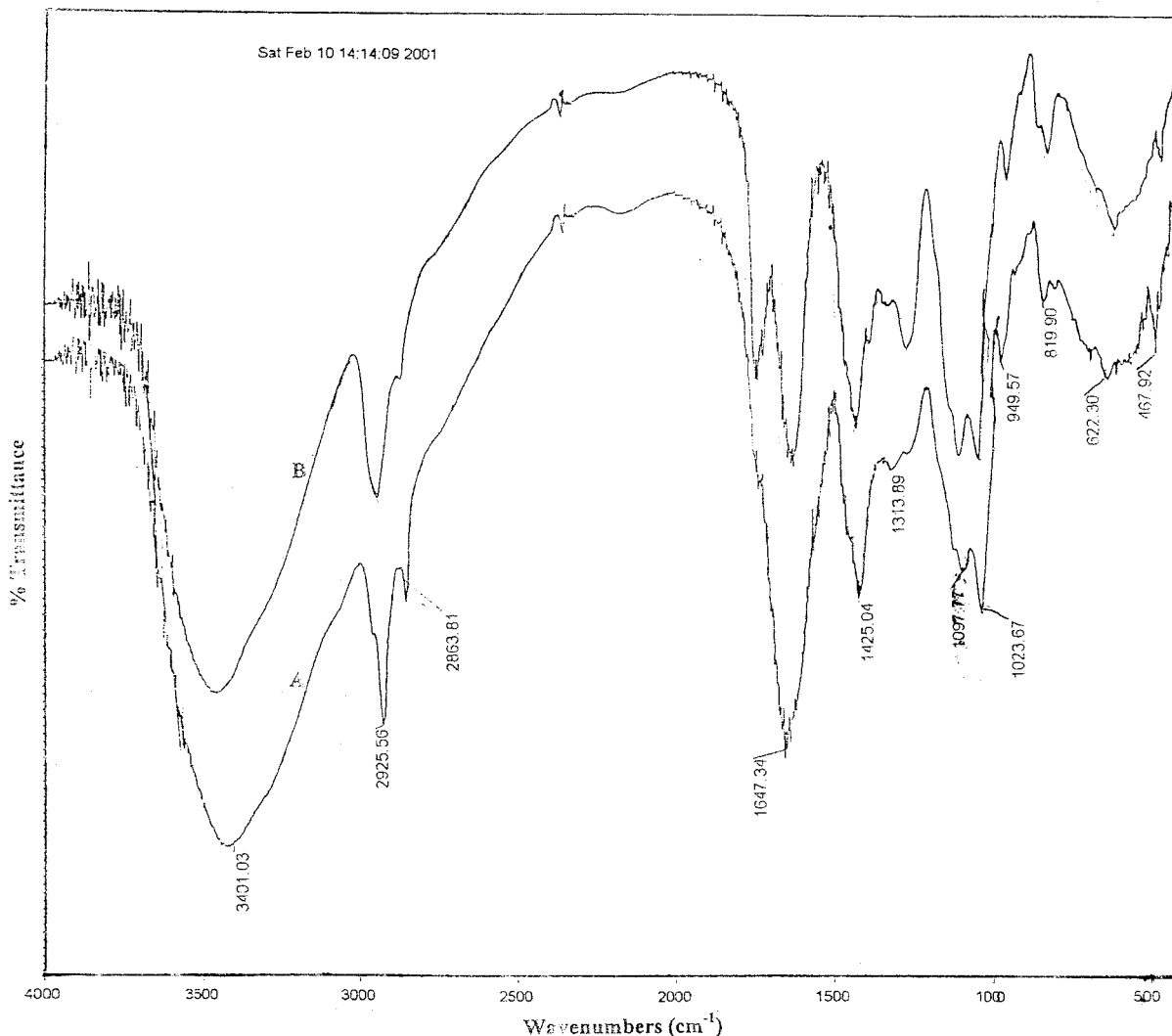
Figure 1 FTIR spectra of (A) uncrosslinked membrane and (B) crosslinked membrane.

brane was placed on the porous stainless steel support and fixed with the help of nuts. At least about 30 min was allowed for the feed mixture to be in contact with the membrane so as to attain the equilibrium. The effective surface area of the membrane in contact with the feed mixture was 32 cm². Water was circulated around the PV cell to maintain a constant temperature and the vacuum pump (Toshniwal, India) was used at permeate side by applying a vacuum pressure of 10 Torr.

The pervaporation experiment was run for 1 h, and permeate was collected in glass tubes (trappers) immersed in liquid nitrogen. The cold trap containing permeate was allowed to cool at room temperature, then removed, and weighed to determine the flux. Permeate composition was measured at 30°C using an Abbe-type refractometer (Model, Attago 3T, Japan), and these data were used to compute the separation selectivity. The required parameters viz. permeation flux, J_p, separation selectivity, α_{sep}, pervaporation sep-

aration index, *PSI*, and enrichment factor, β were calculated using the following relations

$$J_p = \frac{W_p}{At} \tag{4}$$

$$\alpha_{\text{sep}} = \frac{P_W/P_{\text{Iso-OH}}}{F_W/F_{\text{Iso-OH}}} \tag{5}$$

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

$$\beta = \frac{C_W^P}{C_W^F} \tag{7}$$

In the above equations, W_p is mass of the permeate, A is area of the membrane in contact with the feed mixture and t is time; P_w and $P_{\text{Iso-OH}}$ are the mass % of water and Iso-OH respectively, in the permeate; F_w and $F_{\text{Iso-OH}}$ are the mass % of water and Iso-OH in the

TABLE I
Equilibrium Mass % Uptake, (S), Degree of Swelling, (DS), and Diffusion Coefficient, (D) at 30°C

% Water content	Equilibrium sorption, S (kg/kg)				
	Na-Alg	75/25	50/50	25/75	PVA
10	5.85	7.65	20.4	22.6	32.4
20	11.9	18.6	31.9	44.2	53.8
30	16.8	31.5	41.1	58.0	63.7
40	20.1	39.8	51.2	61.7	64.1
50	21.2	40.8	51.5	62.8	65.1
	Degree of swelling, DS (kg/kg)				
10	1.06	1.14	1.29	1.29	1.48
20	1.14	1.31	1.47	1.79	2.17
30	1.20	1.48	1.72	2.38	2.75
40	1.31	1.66	2.05	2.61	3.12
50	1.50	1.69	2.06	3.37	3.72
	Diffusion coefficient, D 10^{11} (m²/s)				
10	3.97	4.92	9.08	9.94	22.5
20	8.08	24.9	30.8	41.4	44.2
30	37.5	40.5	42.2	48.9	126

feed, respectively; C_W^P and C_W^F are respectively permeate concentration of water and feed concentration of water. The pervaporation flux and α_{sep} data are presented in Tables II. However, the pervaporation flux and separation selectivity data for the 10 mass % of water in the feed at different temperatures are given in Table III. The results of PSI and β are displayed only graphically and discussed subsequently.

RESULTS AND DISCUSSION

The molecular transport occurring in pervaporation separation processes can be described simultaneously by the sorption and diffusion processes.[25] When liquids permeate through the swollen polymeric membrane, there will be a variation in the fluxes leading to permeation of molecules, which controls the membrane performance. When polymers are used below their glass transition temperatures (as is the case with the presently used polymers), thermal motion of the chain segments will be restricted. When such polymers come in contact with the low molecular weight liquid components, interactions between the polymer chain segments and the solvent molecules will increase, thereby leading to an increase in polymer chain mobility. Even though numerous theories have been proposed to understand the molecular transport phenomenon, yet none of them are completely satisfactory in explaining the molecular transport of liquids/or their mixtures through the membranes prepared from hydrophilic polymers.[26,27]

The results of equilibrium sorption, degree of swelling and diffusion coefficients at 30°C are presented in Table I. These data show an increase with the increasing amount of PVA in the blend membrane as well as with the increasing amount of water in the binary

TABLE II
Total Pervaporation Flux, J_p and Separation Selectivity, α_{sep} of Water at Different Mass % of Water in the Feed Mixture at 30°C

Mass % of water in the feed	Flux, $J_p \times 10^2$ (kg/m²h)				
	Na-Alg	75/25	50/50	25/75	PVA
10	1.24	2.36	3.38	3.90	4.09
20	4.57	7.15	11.50	12.06	12.90
30	7.81	10.50	12.70	19.45	23.78
40	13.71	10.33	13.30	24.40	26.00
50	13.16	18.80	21.30	24.00	25.50
	Separation selectivity, α_{sep}				
10	356.0	195.5	119.6	91.0	21.0
20	62.7	23.2	23.3	6.7	3.87
30	15.2	8.6	2.7	1.8	1.65
40	15.8	2.7	1.2	1.5	1.20
50	8.1	1.5	0.96	0.82	0.80

TABLE III
Pervaporation Flux and Separation Selectivity at Different Temperature for 10 Mass % of Water in the Feed Mixtures

Temp. (°C)	Flux, $J_p \times 10^2$ (kg/m^{2}h)				
	Na-Alg	75/25	50/50	25/75	PVA
30	1.24	2.36	3.38	3.90	4.09
40	1.89	3.65	5.87	6.18	6.19
50	2.11	4.12	6.28	7.14	9.48
	Separation selectivity, α_{sep}				
30	356.0	195.5	119.6	91.0	21.0
40	355.4	67.3	51.0	41.0	19.1
50	81.1	55.8	47.3	36.0	16.7

mixture, indicating increased hydrophilic interactions between the mixture components and the polymeric chains. PVA is more hydrophilic than Na-Alg, and hence, it exhibits higher equilibrium sorption, degree of swelling and diffusion coefficients when compared to Na-Alg. The blend membranes exhibit a systematic trend of increase in equilibrium sorption, diffusion coefficient, and degree of swelling with the increasing hydrophilicity of the membranes from pure Na-Alg to pure PVA (i.e., with increasing amount of PVA in the blend). The diffusion coefficients at 40 and 50 mass % of water in the feed mixture are not presented in Table I, because these data were not obtained due to the experimental difficulties involved due to the immediate swelling of the membranes in these mixtures.

Figure 2 displays the sorption curves, i.e., M_t/M_∞ vs. $t^{1/2}$ plots for 10, 20, and 30 mass % of water in the feed mixture. At 10 mass % of water, sorption takes a longer time to approach equilibrium saturation when compared to 20 and 30 mass % water-containing mixtures. Moreover, the curves for 10 mass % water-containing mixture show wide deviations between Na-Alg and PVA membranes. On the other hand, for 20 and 30 mass % water-containing feed mixture, sorption curves follow quite regular pattern. For all the membranes, sigmoidal shapes are observed for the sorption curves, suggesting that the molecular transport in these systems deviates from Fickian trend.[28,29] Also, the equilibrium sorption curves for all the membranes at a longer time merge together into a single curve for the 20 and 30 mass % water-containing feed mixtures.

In all the cases, mass % uptake by sodium alginate membrane is smaller than the PVA membrane, but the values for blend membranes are in between PVA and Na-Alg membranes. By increasing the amount of PVA in the blend membrane, the mass % uptake also increases, suggesting the increased hydrophilic interactions at higher amounts of PVA. Shapes of the sorption curves also vary depending upon the composition of the feed mixture. For instance, with the feed mixture containing 10 mass % of water, the increase in uptake by Na-Alg membrane is much slower than the
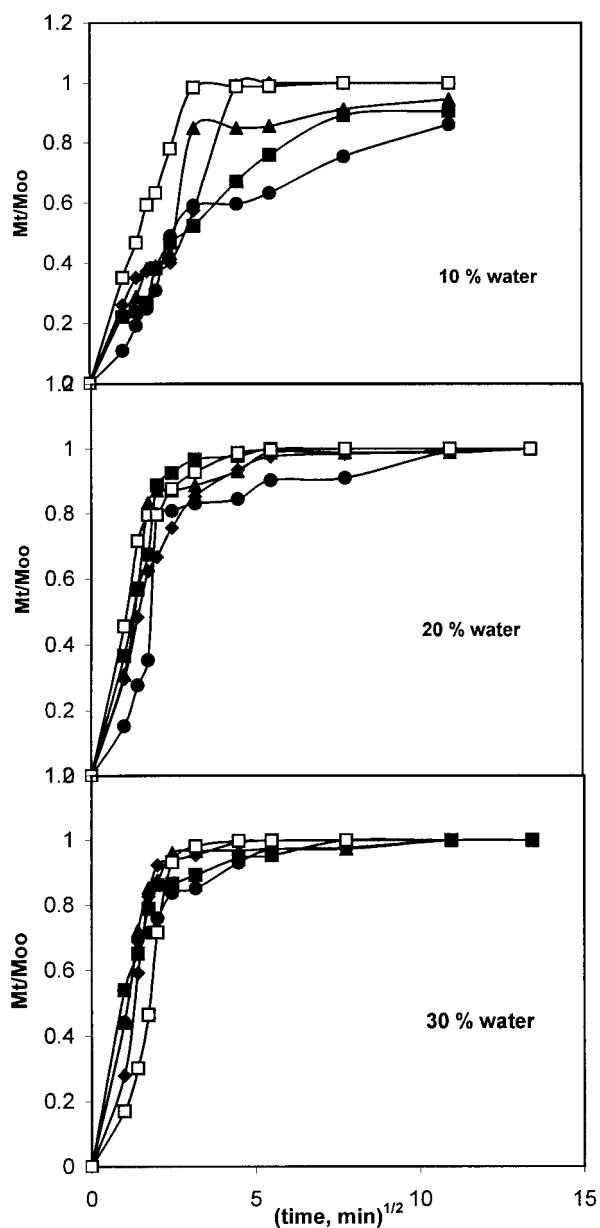

Figure 2 Variation of M_t/M_∞ vs. square root of time at different mass % of water in the feed for (●) pure sodium alginate membrane, (■) 75/25 blend, (▲) 50/50 blend, (◆) 25/75 blend, and (□) pure poly(vinyl alcohol).

TABLE IV
The Estimated Values of n and k Calculated from Eq. (8)

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	0.56	0.353	0.78	1.674	0.46	3.223
75/25	0.32	2.828	0.56	3.853	0.34	2.194
50/50	0.27	3.112	0.90	1.647	0.61	1.366
25/75	0.18	2.720	0.68	0.805	0.99	0.303
PVA	0.47	7.373	0.52	0.485	0.90	0.117

blend membranes as well as the neat PVA membrane. On the other hand, for the 20 and 30 mass % of water-containing binary mixtures, sorption curves vary almost identically.

To find a relationship between the shapes of the sorption curves and the diffusion anomalies, we have attempted to fit the experimental mass sorption data with the empirical equation used earlier.[30]

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

Here, M_∞ is the equilibrium mass % sorption by the membrane calculated from the asymptotic regions of the equilibrium curves; k and n are the empirical parameters, of which k represents polymer–solvent interactions while the values of n indicate the nature of molecular transport. For a Fickian transport, $n = 0.5$, while $n = 1.0$ is observed for non-Fickian transport. The values of n between 0.5 and 1.0 represent the anomalous transport.[28,29] The values of n and k have been calculated from the least squares method by fitting the sorption results to eq. (8) at 95% confidence limit and these are presented in Table IV. In the present study, the values of n vary widely from the lowest value of 0.18 for 25/75 blend mixture in case of 10 mass % water containing binary mixture to the highest value of 1.0 for the same membrane with 30 mass % of water in the feed mixture. However, it is very unusual to have the values of $n < 0.5$, but there are some instances in the literature[31] where such lower values of n for different membrane geometries have been obtained. Such lower values can be attributed to non-Fickian transport. The results of k vary also widely from the lowest value of 0.003 to the highest value of 0.074.

Figure 3 displays the dependence of equilibrium sorption on mass % of water in the feed mixture. PVA, being more hydrophilic than Na-Alg, shows the highest equilibrium sorption at 30 mass % of water in the binary mixture; however, beyond this composition, it reaches equilibrium sorption. Because Na-Alg is a less hydrophilic polymer than PVA, its equilibrium sorption values increase monotonically with an increasing amount of water, but without actually attaining the

equilibrium sorption even for 50 mass % of water in the feed mixture. All the blend membranes show a very systematic trend, i.e., for 25 and 50% PVA containing blend membranes, the saturation point is reached at 40 mass % of water. Similarly, with 75% PVA containing blend membrane, the sorption equilibrium is reached at 40 mass % of water in the feed mixture.

Membrane performance in PV separation depends upon the flux and selectivity (see Tables II and III), and these are influenced by the process parameters like feed composition and temperature. On top of these effects, the polymer chain relaxation also plays an important role because it involves the conformational rearrangement of the polymeric chains resulting in a decrease of flux with increasing time. A detailed analysis of chain relaxation processes as applied to PV separation has been given by Yeom et al.[2]. The results of flux vs. mass % of water as well as Iso-OH in the feed mixture are displayed graphically in Figure 4. The flux values of both water and Iso-OH increase with increasing mass % of water in the feed mixture. The flux values are higher for PVA in case of both water and Iso-OH, but lower flux values are observed even for Na-Alg membrane when compared to Iso-OH, suggesting the water-selective nature of Na-Alg membrane.
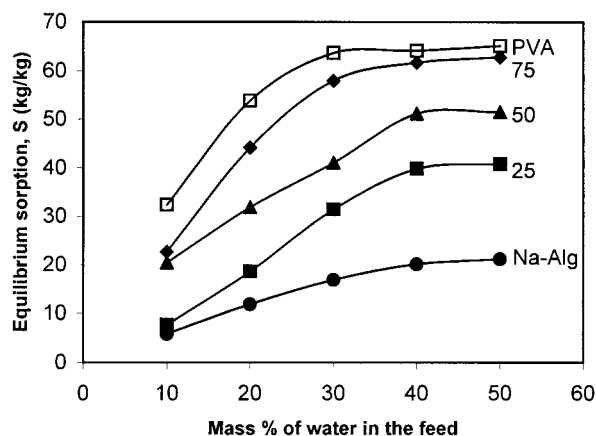

Figure 3 Variation of equilibrium sorption with mass % of water in the feed. Symbols are same as in the Figure 2
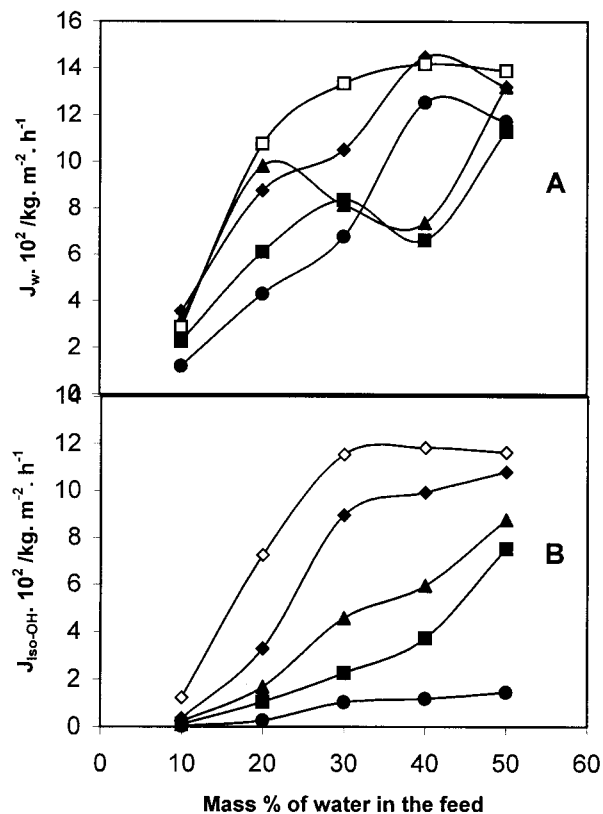
Figure 4 Variation of water flux (A) and isopropanol flux (B) with mass % of water in the feed. Symbols are same as in the Figure 2

The results of separation selectivity of water for all the membranes are displayed in Figure 5. It is observed that PVA exhibits the least selectivity and is almost independent of the feed mixture composition over the entire range. However, sodium alginate membrane shows a drastic reduction in separation selectivity between 10 and 20 mass % of water in the
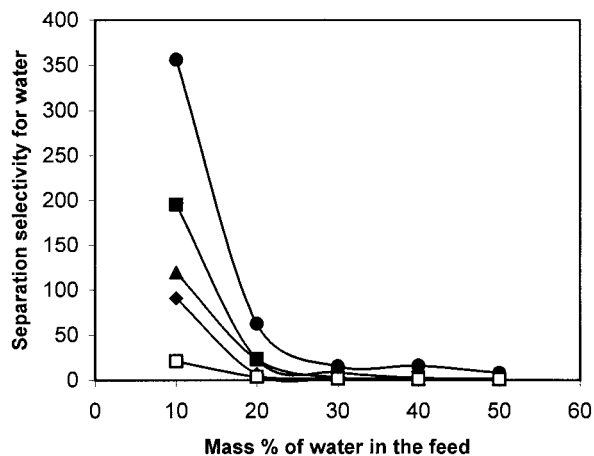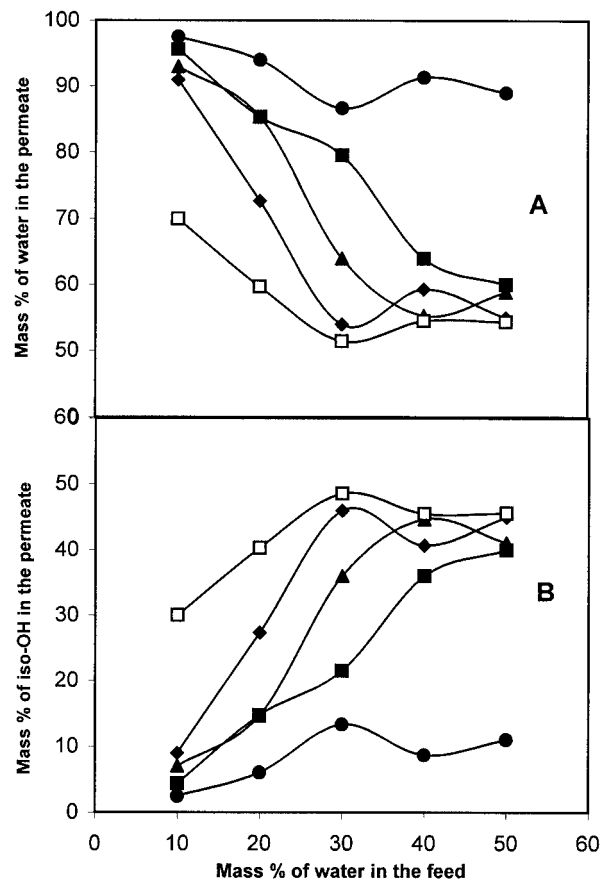

Figure 6 Variation of mass % of water (A) and isopropanol (B) in the permeate mixture with mass % of water in the feed. Symbols are same as in the Figure 2

feed mixture. On the other hand, the blend membranes exhibit the same trends, but their dependencies fall systematically in between those of PVA and Na-Alg membranes. At any rate, all the membranes studied show the highest selectivity values at 10 mass % of
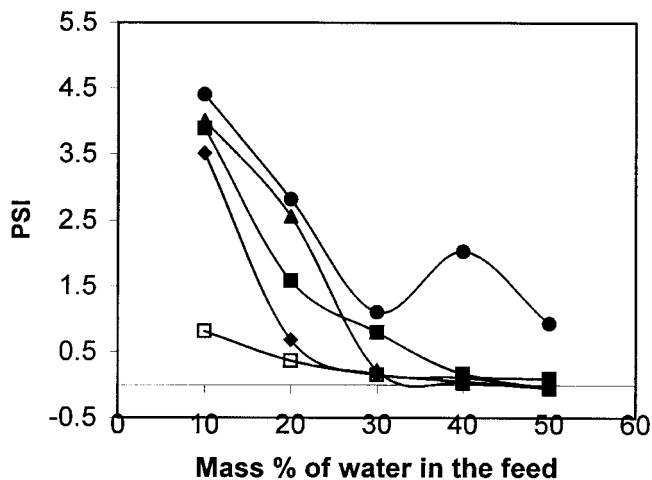

Figure 5 Variation of separation selectivity for water with mass % of water in the feed. Symbols are same as in the Figure 2

Figure 7 Variation of permeation separation index with mass % of water in the feed. Symbols are same as in the Figure 2
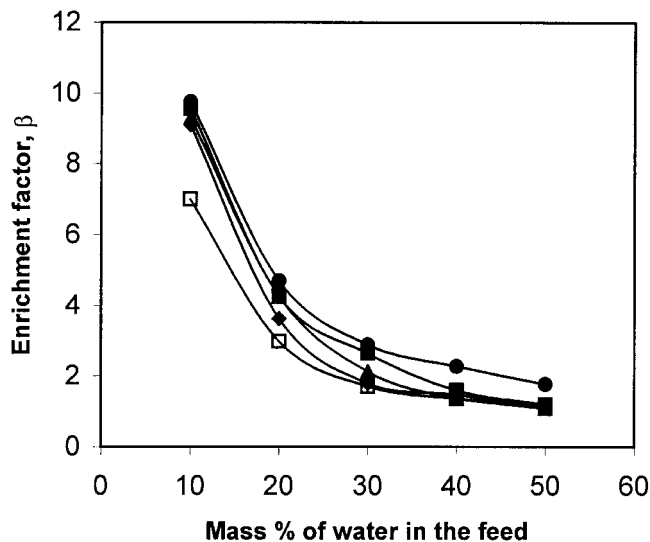
Figure 8 Variation of enrichment factor with mass % of water in the feed. Symbols are same as in the Figure 2

water in the feed mixture, suggesting that the membranes of the present study will have useful applications in separating water from its mixture containing 10 mass % of water.

The dependencies of mass % of water as well as Iso-OH on permeate side as a function of mass % of water in the feed mixture are presented in Figure 6. It is observed that for PVA membrane, the mass % of water in permeate is lowest, whereas a reverse trend is observed for the mass % of Iso-OH in the mixture for the same membrane. Similarly, Na-Alg membrane exhibits the highest mass % value of water in permeate side, but the same membrane shows the lowest values for Iso-OH, but the blend membranes show intermediary trends.

Permeation separation index, PSI and enrichment factor, β are displayed, respectively, in Figures 7 and 8. Both PSI and β curves decrease with increasing amount of water in the feed mixture. Also, these data

decrease with increasing amount of PVA in the blend membranes. The β values show a more systematic decreasing trend for all the membranes with increasing composition of water in the mixture whereas PSI values, even though do not exhibit a very systematic trend, show wide fluctuations.

Transport in PV experiments has been explained by the solution–diffusion model. Diffusion occurs as a result of concentration gradient and, therefore, it is important to estimate the diffusion coefficient, D_i of solvent molecules to understand the transport mechanism. From the PV results, we have calculated D_i using the equation:[32]

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

(9)

Here, D_i is assumed to be constant across the effective membrane thickness, h; C_i (feed) and C_i (permeate) are, respectively, the mixture concentrations in the feed and the permeate. The computed values of D_i (where the subscript i stands for water or Iso-OH) at 30°C are presented in Table V.

In the majority of membrane processes, an increase in feed temperature results in a linear increase of permeation flux, probably due to the increased thermal mobility of the polymeric chains. This facilitates an increase in diffusion coefficients of the permeating molecules. Because the 10 mass % water containing feed mixture exhibits the optimum characteristics, we have decided to investigate in depth the PV characteristics of the membranes for this mixture. The results of pervaporation flux and separation selectivity for the 10 mass % water in the feed mixture at 30, 40, and 50°C are presented in Table III. It is observed that the permeation flux values increase, but separation selectivity values decrease with increasing temperature.

The temperature dependency of flux was analyzed by the Arrhenius relationship

TABLE V
Diffusion Coefficients of Water and Iso-OH Calculated from Eq. (9) at 30°C

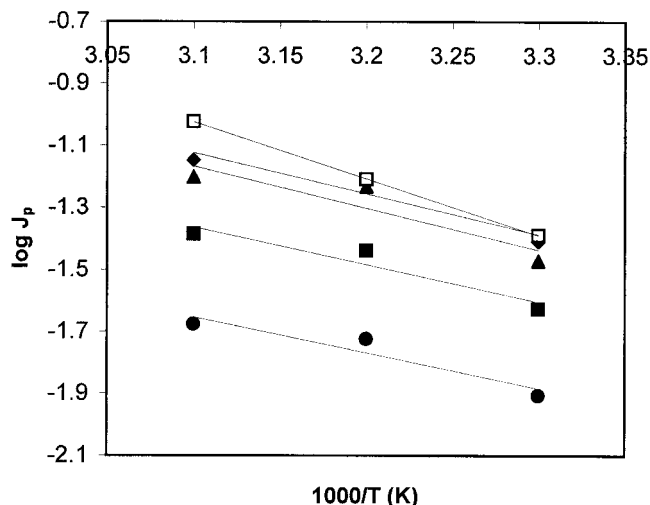| Mass % of water in the feed	D_w (m²/s) 10^9				
	Na-Alg	75/25	50/50	25/75	PVA
10	0.54	1.03	1.47	1.70	1.86
20	2.25	3.63	5.84	6.47	10.5
30	4.63	6.56	9.30	17.0	24.2
40	9.5	10.7	18.7	29.1	38.0
50	11.7	4.39	57.7	103	123
	$D_{\text{Iso-OH}}$ (m²/s) 10^{10}				
10	0.14	0.47	1.11	1.69	7.95
20	1.44	6.26	10.0	24.3	71.0
30	7.14	17.7	52.3	145	210
40	9.00	60.2	151	200	317
50	14.4	292	383	1010	1030

Figure 9 Variation log J_P with $1000/T$ at 10 mass % of water in the feed. Symbols are same as in the Figure 2

$$J_p = J_{po} \exp\left(\frac{-E_p}{RT}\right) \qquad (10)$$

Here, E_p is the activation energy for permeation, J_{PO} is the permeation rate constant (equivalent to Arrhenius frequency factor), R is gas constant, and T is temperature in Kelvin. If activation energy is positive, then permeation flux increases with increasing temperature, and this has been observed in majority of PV experiments.[33–35] 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 mixtures. As the feed temperature increases, the vapor pressure in the feed compartment also increases, but the vapor pressure at the permeate side is not affected. This results in an increase of driving force with an increase in temperature. In the Arrhenius plots of log J_p vs. $1000/T$ represented in Figure 9 it is observed that the temperature dependency of total permeation flux follows the Arrhenius behavior in the studied temperature interval. The apparent activation energy values, E_p for permeation calculated from the slopes of the straight lines of Arrhenius plots by the least squares method are presented in Table VI.
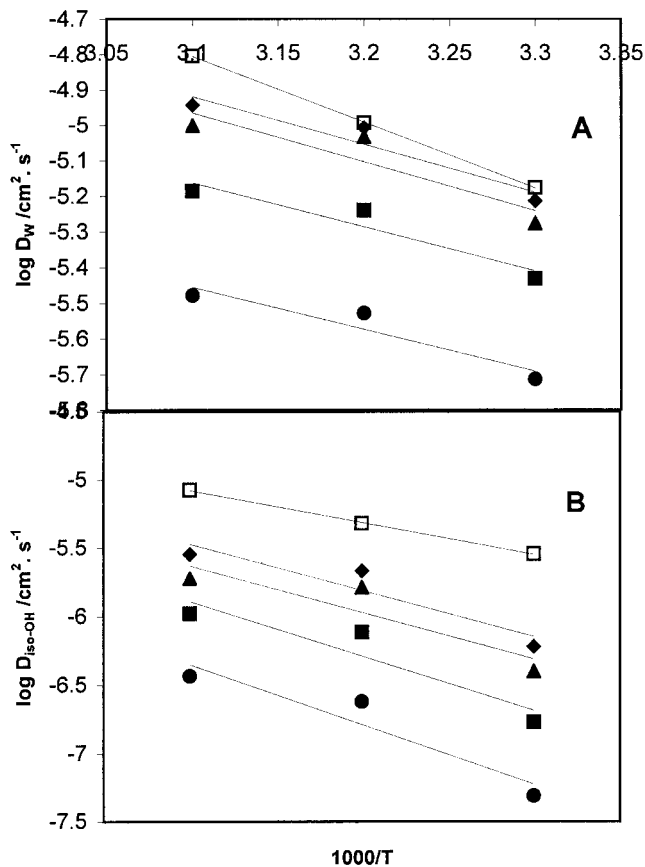

Figure 10 Variation log D_W and log D_{Iso-OH} with $1000/T$ at 10 mass % of water in the feed. Symbols are same as in the Figure 2

In a similar manner, the mass transport secured by diffusion process is given by the Arrhenius relationship

$$D_i = D_{io} \exp\left(\frac{-E_D}{RT}\right) \qquad (11)$$

where E_D is the energy of activation for diffusion and i stands for water or Iso-OH. The Arrhenius plots of log D_i vs. $1000/T$ are shown in Figure 10. The E_D values estimated by the method of least squares are also included in Table VI. The E_D values increase with an increase in PVA content of the blend membranes.

By taking the E_P and E_D values for water, we have computed the heat of sorption, ΔH_S for water perme-

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

Parameter	Na-Alg	75/25	50/50	25/75	PVA
E_P (kJ/mol) eq. (10)	21.78	22.78	25.44	24.74	34.22
E_D (kJ/mol) eq. (11)	22.17	23.31	25.97	25.45	34.75
ΔH_S (kJ/mol)	−0.39	−0.53	−0.53	−0.71	−0.53
E_{Iso-OH}-E_W (kJ/mol)	60.56	51.46	38.14	38.04	9.28

ation using the relation, $\Delta H_S = E_P - E_D$, and these values are also included in Table VI. The ΔH_S values are negative in all the cases, suggesting an endothermic mode of sorption.

The temperature dependency of separation was further studied by employing the equation suggested by Ping et al.[34]

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

where Y_w is water composition in the permeate, J_w and $J_{\text{Iso-OH}}$ are the permeation fluxes; E_w and $E_{\text{Iso-OH}}$ are the Arrhenius activation energies of water and Iso-OH, respectively, at the average energy level. A positive value of $(E_{\text{Iso-OH}} - E_W)$ indicates that the α_{sep} decreases with an increase in temperature; negative values indicate that α_{sep} increases with an increase in temperature.[35] In the present study, in all the cases, the values of $(E_{\text{Iso-OH}} - E_W)$ are positive, indicating a decrease in α_{sep} with increasing temperature (Table VI). Accordingly, the selectivity values decrease with increasing temperature from 30 to 50°C.

CONCLUSIONS

In conclusion, the blend membranes prepared in this study are selective to water molecules. Fluxes of sodium alginate membrane in the pervaporation separation of water + Iso-OH mixture was enhanced by blending it with poly(vinyl alcohol). Pure sodium alginate, poly(vinyl alcohol) and the blend membranes were all good for the PV separation of water from Iso-OH + water mixtures. Permeation flux of the membranes showed an increase with increasing amount of PVA in the blend membranes, while separation selectivity decreased. Highest separation selectivity of 356 was observed for the neat Na-Alg membrane for 10 mass % of water in the feed. The highest flux value of 26×10^{-2} kg/m²h was observed for the neat PVA membrane for the 40 mass % of water in the feed. An increase in flux was due to the enhanced hydrophilicity of the blend membranes. The membranes of this study were found to be more water-selective than isopropanol.

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