

Synthesis and Characterization of PolyAcrylamideGrafted Sodium Alginate Membranes for Pervaporation Separation of Water + Isopropanol Mixtures

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ABSTRACT: Polyacrylamide-grafted-sodium alginate copolymers were prepared by persulfate-induced radical polymerization by using polymer-to-monomer ratios of 2 : 1 and 1 : 1. Polymers were characterized by Fourier transform infrared spectroscopy, differential thermal analysis, and viscosity. Membranes were prepared from the polymers, crosslinked with glutaraldehyde, and used in the pervaporation separation of water + isopropanol mixtures at 30°C. Equilibrium swelling experiments were performed for mixtures containing 10 to 80 mass % of water in the feed. Both the grafted copolymer membranes were ruptured while separating 10 mass % of water in the feed mixture. However,

beyond 20 mass % of water in the feed mixture, flux increased with increasing grafting ratio, while selectivity decreased. Pervaporation separation experiments were carried out at 30, 40, and 50°C for 20 mass % of water in the feed mixture. By increasing the temperature, flux increased, whereas selectivity decreased. Arrhenius activation parameters for pervaporation and diffusion decreased with increasing grafting ratio of the membranes. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2030–2037, 2004

Key words: pervaporation; selectivity; diffusion; graft copolymers; membrane

INTRODUCTION

Simplicity and relatively better efficiency in terms of energy consumption and cleanliness when compared to other conventional methods of separation made pervaporation (PV) separation a viable technique to separate water–organic mixtures.^{1–5} Despite the successful commercialization of poly(vinyl alcohol) (PVA)-based membranes,^{6,7} researchers have attempted to develop other polymer membranes having good permeation flux and separation selectivity. These include blends,^{8,9} composites,^{10,11} charged membranes,^{12,13} polyion complex membranes,¹⁴ copolymer,¹⁵ and grafted copolymer¹⁶ membranes, etc. However, due to their abundant availability and commercial viability, natural polymers are also used in PV separation studies.^{17–20} Among these, membranes prepared from sodium alginate (NaAlg) have shown outstanding PV separation characteristics for water + methanol or water + ethanol mixtures.²¹ However,

they suffer from mechanical stability, which can be improved by crosslinking,²² blending with other polymers,²³ or by developing composite films.²⁴ On top of these, polymer grafting can also be helpful in imparting mechanical strength to the membranes.

In the previous literature, we are not aware of the grafted copolymer membranes of NaAlg with acrylamide (AAM) used in the PV separation of water–organic mixtures. The present study deals with the synthesis of grafted copolymers of NaAlg in different ratios with AAM. Copolymers formed were characterized by FTIR, DTA, and solution viscosity. Membranes were prepared by crosslinking with glutaraldehyde (GA) and used in the PV separation of water + isopropanol mixtures containing 10 to 80 mass % of water in the feed. Swelling experiments were also performed to understand the stability of the membranes in the chosen fluid environment. Temperature dependency of PV separation at 20 mass % of water in the feed mixture was studied to estimate the Arrhenius parameters.

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EXPERIMENTAL

Materials

Sodium alginate, potassium persulfate, isopropanol, hydrochloric acid, glutaraldehyde, polyethylene glycol (PEG-200), PVA, acetone, and methanol used were of analytical reagent grade samples purchased from

TABLE I
Synthetic Details of Polyacrylamide-grafted-Sodium Alginate Copolymers

Sample code	Mass of polymer (g)	Mass of AAm (g)	Mass of initiator (g/g of polymer)	% Grafting	Grafting efficiency	% Conversion of AAm
NaAlg	0	0	0	0	0	0
NaAlg-1	10	5	0.03	44 ± 1	96 ± 1	89 ± 1
NaAlg-2	10	10	0.03	94 ± 1	98 ± 1	95 ± 1

s. d. fine Chemicals (Mumbai, India). Double-distilled water was used throughout the study.

Synthesis of graft copolymers

Polyacrylamide-grafted-sodium alginate was prepared by persulfate-induced radical polymerization in polymer-to-monomer ratios of 2 : 1 and 1 : 1. First, a 10 mass % of aqueous solution of NaAlg was taken in a three-necked 500 mL round-bottom flask. To this, different amounts of acrylamide monomer were added and the mixture was stirred vigorously for 1 h at 70°C. Then, a 100 mL of solution containing potassium persulfate initiator at a concentration of 10^{-3} mol (0.03 g/L of the initiator per gram of the polymer) was added. Stirring was further continued for 10 h at 70°C under inert nitrogen gas atmosphere. Polymer mass obtained was precipitated in acetone and washed with water : methanol (7 : 3) mixture to remove the homopolymer formed. The solid polymer formed was dried in the incubator at 40°C, weighed, and stored in a desiccator before being used to make the membranes. Synthetic details are given in Table I.

Polymer characterization

FTIR spectra of the polymers in KBr pellets were taken on a Nicolet, Model Impact 410 (Milwaukee, WI), in the wavelength range of 4000 to 400 cm^{-1} . DTA thermograms were taken by using SICKO, Model TG/TDA-320 (Tokyo, Japan) in an inert atmosphere in the temperature range from 0 to 300°C. Viscosity measurements were done on the aqueous solutions of NaAlg in 0.25 mass % concentration and grafted copolymers (NaAlg-1 and NaAlg-2), both prepared in 1 mass % concentration at 30°C by using a Schott-Gerate Viscometer, Model AVS 350 (Hofheim, Germany). Details of these measurements were given earlier.²⁵

Membrane preparation

A 5 mass % solution of the copolymer was prepared in 100 mL of distilled water. To this, a 25-mL mixture of 10 mass % polyethylene glycol (PEG) and 5 mass % PVA were added and stirred for 12 h at room temperature. The solution was filtered through a cotton plug;

membranes (30 μm thickness) were cast on a leveled glass plate and dried at room temperature. Membranes obtained were peeled off uniformly from the glass plate and crosslinked in acidic (25 : 75) water : methanol mixture containing 1.0 vol % of GA for 24 h. The membranes were designated, respectively, as NaAlg, NaAlg-1, and NaAlg-2 for the pure sodium alginate, 1 : 0.5 grafted copolymer, and 1 : 1 grafted copolymer. Membranes were first stored in a dry and dust-free atmosphere at room temperature before being used in PV experiments.

Equilibrium swelling

Equilibrium swelling of the membranes was done in water + isopropanol mixtures at $30 \pm 0.5^\circ\text{C}$ in an electronically controlled oven, Model WTB Binder (Tuttlingen, Germany). The circularly cut (≈ 4.00 cm diameter) disk-shaped membranes were kept in a vacuum oven at 30°C for 48 h before use. Initial mass of the membranes was measured on a top-loading single-pan digital Mettler microbalance, Model AE 240 (Greifensee, Switzerland) sensitive to ± 0.01 mg. Samples were placed inside the air-tight test bottles containing different compositions of water + isopropanol mixtures.

Test bottles were placed in an oven maintained at a constant temperature of 30°C. Mass measurements were done at the suitably selected time intervals by removing the samples from test bottles, wiping the surface-adhered solvent drops by gently pressing them in between filter-paper wraps, weighing immediately, and again placing them back into the oven. To minimize errors due to evaporation losses, this step was completed within 15–20 s. From the gravimetric solvent uptake data, equilibrium swelling (S) of the membrane was calculated by using the initial dry mass, W_0 , and equilibrium-swollen mass, W_∞ (after ~ 48 h), of the membrane by using the equation

$$S = \left(\frac{W_\infty - W_0}{W_0} \right) \times 100 \quad (1)$$

Pervaporation experiments

Pervaporation experiments were performed by using the module designed indigenously.²⁶ Effective surface

TABLE II
Pervaporation Flux, Separation Selectivity, and Diffusion Coefficients of Water and Isopropanol at Different Mass % of Water in the Feed Mixture at 30°C

Mass % of water in the feed	$J_p \times 10^2$ (kg/m ² h) [eq. (2)]			α_{sep} [eq. (3)]		
	NaAlg	NaAlg-1	NaAlg-2	NaAlg	NaAlg-1	NaAlg-2
10	5.0	a	a	3591	a	a
20	13.8	14.7	17.6	96.0	96.0	53.1
30	22.6	23.2	32.5	49.5	44.3	36.6
40	31.8	46.1	56.6	28.5	23.5	19.9
50	44.0	58.5	76.8	14.4	13.3	11.5
60	51.1	68.6	84.3	11.1	12.0	7.5
70	b	112.2	a	b	10.9	a

Mass % of water in the feed	$D_w \times 10^{13}$ (m ² /s) [eq.(4)]			$D_{\text{ISO-OH-OH}} \times 10^{13}$ (m ² /s) [eq.(4)]		
	NaAlg	NaAlg-1	NaAlg-2	NaAlg	NaAlg-1	NaAlg-2
10	4.5	a	a	0.01	a	a
20	15.0	15.0	18.2	0.80	0.80	1.75
30	26.0	26.8	37.7	1.58	1.80	3.08
40	42.4	62.0	76.9	2.86	5.06	7.41
50	71.4	95.7	128	6.35	9.23	14.2
60	106	141.1	188	10.2	12.6	26.8
70	b	203	a	b	13.7	a

^a Membrane ruptured.

^b Data not obtained; data for 80 mass % of water in feed are not included here.

area of the membrane in contact with the feed mixture was 32.4 cm² and the capacity of the PV cell used was about 250 cm³. Mass % of water in the binary mixture 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 evacuated continuously by using a vacuum pump (Toshniwal, Mumbai, India) at a vacuum pressure of 10 Torr and the permeate mixture was condensed in liquid nitrogen traps. 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 the previously established standard graph. Adding the required amount of fresh solvent mixture continuously enriched the depleted solvent mixture in the feed compartment.

From the PV data, membrane performance was studied by calculating the total flux, J_p , and separation selectivity, α_{sep} , as

$$J_p = \frac{W_p}{At} \quad (2)$$

$$\alpha_{\text{sep}} = \frac{P_w/P_{\text{ISO-OH}}}{F_w/F_{\text{ISO-OH}}} \quad (3)$$

In the above equations, W_p is mass of 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 isopropanol, respectively, in the permeate; and F_w and $F_{\text{ISO-OH}}$ are the mass % of water and isopropanol, respectively, in the feed.

Diffusion coefficients, D_i , of the solvent mixtures through the membrane was computed at 30°C by using the relation²⁷:

$$D_i = \frac{J_i h}{[C_{i(\text{feed})} - C_{i(\text{permeate})}]} \quad (4)$$

Here, subscript i stands for water or isopropanol; h is the effective membrane thickness; $C_{i(\text{feed})}$ and $C_{i(\text{permeate})}$ are, respectively, the composition of liquids present in the feed and in the permeate sides. Results of J_p , α_{sep} , and D_i are presented in Table II.

RESULTS AND DISCUSSION

Synthesis and characterization of graft copolymers

Grafting reaction was carried out by using potassium persulfate induced solution polymerization. Initiator concentration of 10⁻³ mol/L was found to be optimum for persulfate-induced grafting reaction.²⁸ Generation of free-radical site by abstracting hydrogen from the —OH group of the polymer facilitates grafting of acrylamide onto NaAlg. Monomer conversion was up to 90% for both the copolymers (see Table I) and more than 95% of the grafting sites were reacted.

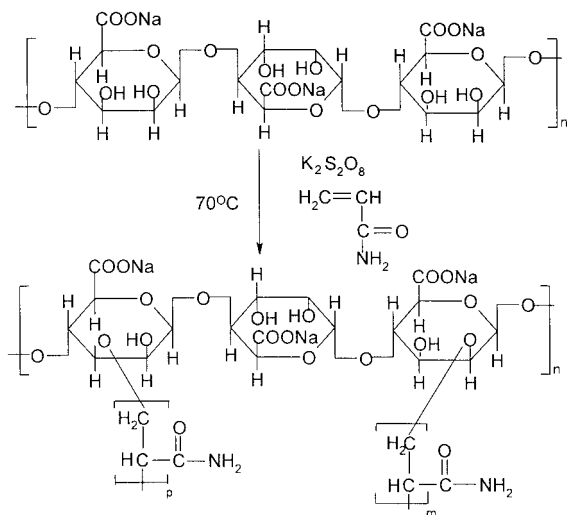


Figure 1 Scheme of reaction for graft copolymerization.

A reaction scheme for the graft copolymerization is presented in Figure 1.

FTIR spectra of NaAlg and sodium alginate-*grafted*-polyacrylamide (NaAlg-*g*-pAAm) polymer are presented in Figure 2. In the case of pure NaAlg, a characteristic broad band appearing at $\sim 3420\text{ cm}^{-1}$ corresponds to O—H stretching vibrations of NaAlg backbone. A sharp peak observed at $\sim 1616\text{ cm}^{-1}$ corresponds to C=O stretching of the carboxylic group of NaAlg. In the spectra of grafted copolymers, a shoulder peak appearing at $\sim 3190\text{ cm}^{-1}$ and a sharp peak at $\sim 1672\text{ cm}^{-1}$ corresponding, respectively, to N—H stretching and C=O stretching vibrations confirm grafting reaction. In addition, a new peak appearing at $\sim 1450\text{ cm}^{-1}$ for NaAlg-1 and NaAlg-2 membranes correspond to C—N bending vibrations, thereby supporting the complete grafting reaction.

DTA thermograms of the pure NaAlg and grafted copolymers (NaAlg-1 and NaAlg-2) are displayed in Figure 3. Characteristic endothermic peak observed at 59.1°C for NaAlg [see Fig. 3(A)] is shifted to 61.5 and 70.5°C , respectively [see Fig. 3(B, C)] for NaAlg-1 and NaAlg-2 polymers. The exothermic peak observed for NaAlg at 255°C is due to the oxidative degradation of NaAlg. The endothermic peak observed at the same temperature for grafted copolymers is due to the loss of water molecules from amide and carboxylic groups present in the grafted copolymers. The energy required at this temperature increases with increasing grafting ratio. These variations in DTA thermograms support the successful grafting of acrylamide onto NaAlg backbone.

Observed kinematic viscosity of 0.25 mass % solution of NaAlg was 1.65 St, whereas for 1 mass % solution of NaAlg-1 and NaAlg-2 polymers, these values were 2.11 and 2.96 St, respectively. An increase in viscosity of NaAlg-1 and NaAlg-2 solutions confirms

the successful grafting. Higher viscosity observed for NaAlg-2 when compared to NaAlg-1 is due to increased chain length as well as increased entanglement of the polymer chain.

Membrane preparation

Solution-casting method was employed to prepare membranes, which were crosslinked by glutaraldehyde in an acidic methanol : water (75 : 25) mixture. Methanol acting as a nonsolvent for the polymers prevented dissolution of the membrane, but water present in the solution was responsible for membrane swelling, which further facilitated crosslinking in the presence of glutaraldehyde. Except NaAlg membrane, both NaAlg-1 and NaAlg-2 membranes were brittle, probably because of the crystalline nature of acrylamide present in the grafted copolymers. To increase the flexibility of copolymer membranes, we added 10 mass % of PEG and 5 mass % of PVA. When 10 mass % of PVA was added, phase separation occurred in both NaAlg-1 and NaAlg-2 membranes.

Pervaporation performance

Results of equilibrium swelling versus mass % of water in the feed mixture are displayed in Figure 4. It is observed that at 10 mass % of water in the feed, equilibrium mass % swelling is quite identical for all the membranes. However, at higher amounts of water in the feed, a wide variation in membrane swelling was observed. Results of pervaporation flux and separation selectivity of all the membranes at 30°C are presented in Table II. Flux generally increases with an increase in the amount of water in the feed from NaAlg to NaAlg-1 and NaAlg-2 membranes. Results of flux presented in Figure 5(A) are in line with the trends shown by swelling data displayed in Figure 4. Flux increased with increasing swelling because of the hydrophilic nature of the membranes. Separation selectivity [see Fig. 5(B)] decreased with an increase in the amount of water in the feed. Pure NaAlg membrane has the highest selectivity of 3591 at 10 mass % of water in the feed, but NaAlg-1 and NaAlg-2 membranes exhibited a much lower value of α_{sep} at 20 mass % of water in the feed.

It was not possible to obtain J_p and α_{sep} values for NaAlg-1 and NaAlg-2 membranes for 10 mass % water containing feed mixture, because membranes became brittle at this composition. The present data suggest that pure NaAlg membrane is more promising than the grafted membranes in dehydrating 10 mass % of water-containing feed mixture along with 90 mass % of isopropanol. Because water and isopropanol form an azeotrope at 12.5 mass % of water, it is possible to dehydrate $>99\%$ of water by using pure NaAlg membrane.

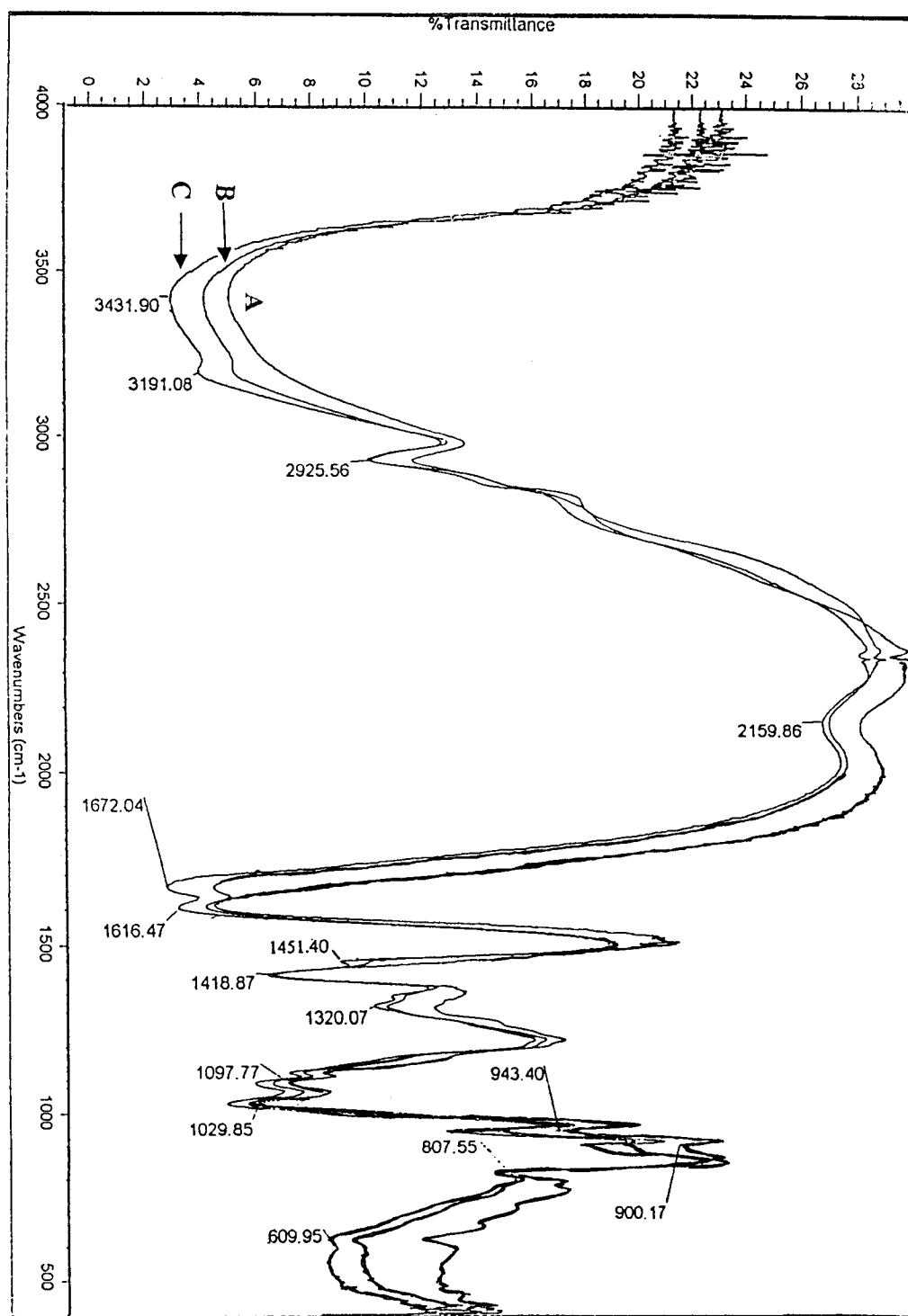


Figure 2 FTIR spectra of (A) NaAlg, (B) NaAlg-1, and (C) NaAlg-2.

The membranes of this study are more water-selective than isopropanol. Thus, D_i of water increased considerably with an increase in the amount of water in the feed. Such an increase in D_i is attributed to the availability of free volume within the membrane matrix. Diffusion coefficients of isopropanol are smaller than those observed for water by

an order of magnitude. These values showed a slight increase with an increase in the amount of water in the feed mixture except for NaAlg-2 membrane. Diffusion data of water have shown the trend: NaAlg > NaAlg-1 > NaAlg-2. In the case of isopropanol, diffusion coefficients increase from pure NaAlg to NaAlg-1, but no systematic trend

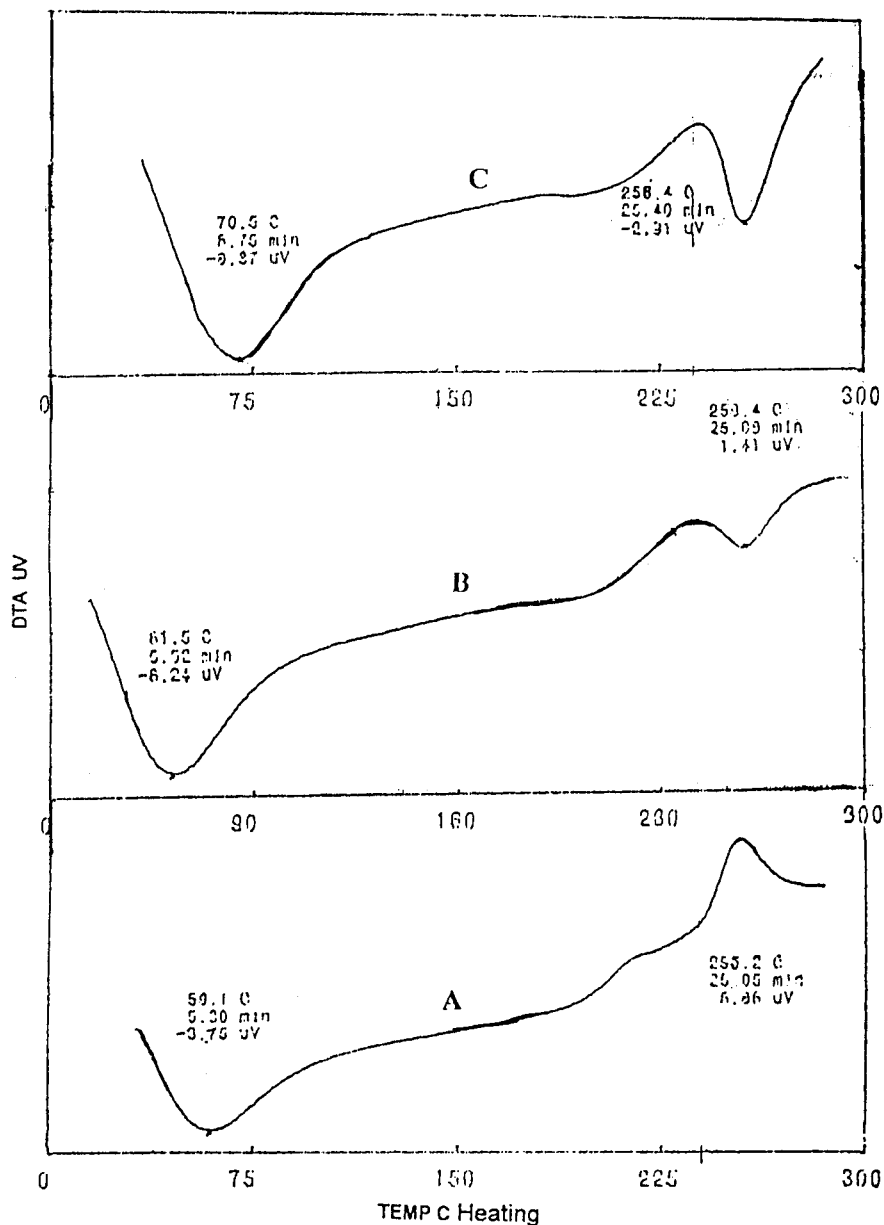


Figure 3 DTA tracings of (A) NaAlg, (B) NaAlg-1, and (C) NaAlg-2.

was observed between NaAlg-1 and NaAlg-2 membranes.

Effect of temperature

In an effort to study the temperature dependence of J_p (see Table III) and D_p , we have selected the data for feed mixture containing 20 mass % of water to estimate the activation parameters by using an Arrhenius-type relationship for J_p and D_i given in the forms:

$$J_p = J_{p0} \exp(-E_p/RT) \tag{5}$$

$$D_i = D_{i0} \exp(-E_D/RT) \tag{6}$$

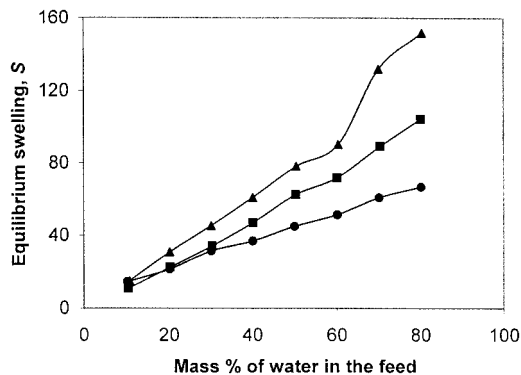


Figure 4 Plot of equilibrium mass % uptake versus mass % of water in the feed mixture for (●) NaAlg, (■) NaAlg-1, and (▲) NaAlg-2.

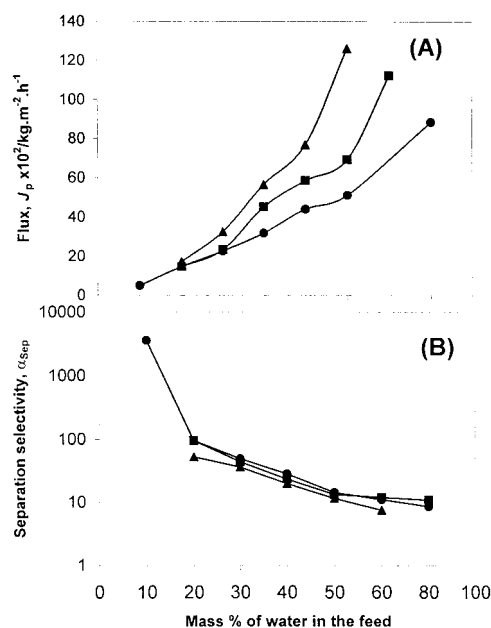


Figure 5 Plot of permeation flux and separation selectivity versus mass % of water in the feed mixture for (●) NaAlg, (■) NaAlg-1, and (▲) NaAlg-2.

Here, E_P and E_D are activation energies for permeation and diffusion, J_{p0} and D_{i0} are permeation and diffusion rate constants, R is gas constant, and T is the temperature in Kelvin. If activation energy is positive, then permeation flux increases with increasing temperature, which is generally observed in PV experiments.^{29,30}

The Arrhenius plots of $\log J_P$ versus $1000/T$ and $\log D_i$ versus $1000/T$ for flux of water and isopropanol are linear (not displayed to minimize the number of plots), signifying that temperature dependence of permeation and diffusion followed the Arrhenius trend. Apparent activation energy data for permeation, E_P , and diffusion, E_D , calculated from the slopes of straight lines of the Arrhenius plots by using the least-squares method are presented in Table IV. The E_P values varied as per the sequence: NaAlg > NaAlg-1 > NaAlg-2, suggesting their dependencies on polymer morphology. Heat of sorption values were calculated as $\Delta H_S (\cong E_P - E_D)$ and these results are also included

TABLE III
Pervaporation Flux and Separation Selectivity at Different Temperatures for 20 Mass % of Water in the Feed Mixture

Temp. (°C)	$J_p \times 10^2$ (kg/m ² h) [eq. (2)]			α_{sep} [eq. (3)]		
	NaAlg	NaAlg-1	NaAlg-2	NaAlg	NaAlg-1	NaAlg-2
30	13.8	15.1	17.2	96.0	96.0	53.1
40	19.1	18.1	19.7	68.7	60.0	43.1
50	25.9	20.5	21.9	55.3	53.1	30.8

TABLE IV
Permeation and Diffusion Activation Energies, Heat of Sorption of Water, and Energy Difference Values of the Membranes

Parameters	NaAlg	NaAlg-1	NaAlg-2
E_P (kJ/mol) [eq. (5)]	25.60	11.59	9.84
E_D (kJ/mol) [eq. (6)]	27.07	14.05	12.38
ΔH_S (kJ/mol)	-1.49	-2.47	-2.54
$E_{\text{Iso-OH}} - E_w$ (kJ/mol)	26.63	24.24	22.16

in Table IV. The ΔH_S values are negative in all cases, suggesting an endothermic sorption process. The E_D values of the membranes exhibited the sequence: NaAlg > NaAlg-1 > NaAlg-2.

Temperature dependence of α_{sep} was also investigated (see Table III) by employing the relationship proposed by Ping et al.,³¹

$$Y_w = \frac{1}{1 + (J_{\text{Iso-OH}}/J_w) \exp[-(E_{\text{Iso-OH}} + E_w)/RT]} \quad (7)$$

where Y_w is the water composition in the permeate, J_w and $J_{\text{Iso-OH}}$ are permeation fluxes; E_W and $E_{\text{Iso-OH}}$ are the Arrhenius activation energies for water and isopropanol, respectively, at the average energy level. A positive value of $[E_{\text{Iso-OH}} - E_W]$ indicates that α_{sep} decreases with increasing temperature, while the negative value indicates that α_{sep} increases with increasing temperature.³² For all the membranes of this study, the difference ($E_{\text{Iso-OH}} - E_W$) is positive (see Table IV), suggesting that α_{sep} decreases with increasing temperature.

In conclusion, pure sodium alginate membrane, which gave higher separation selectivity than both the grafted membranes, is quite suitable for the dehydration of water–isopropanol mixtures.

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