Synthesis of Graft Copolymeric Membranes of Poly(vinyl alcohol) and Polyacrylamide for the Pervaporation Separation of Water/Acetic Acid Mixtures

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ABSTRACT: Graft copolymers of poly(vinyl alcohol) (PVA) with polyacrylamide were prepared and membranes were fabricated at 48 and 93% grafting of acrylamide onto PVA. These membranes were used in the pervaporation separation of water/acetic acid mixtures at 25, 35, and 45°C. The permeation flux, separation selectivity, diffusion coefficient, and permeate concentration were determined. The highest separation selectivity of 23 for neat PVA at 25°C and the lowest value of 2.2 for 93% acrylamide-grafted PVA membranes were observed. A permeation flux of 1.94 kg m^{-2} h^{-1} was found for the 93% grafted membrane at 90 mass % of water in the feed mixture. The diffusion coefficients in a water/acetic acid mixture had an effect on the membrane permselectivity. The Arrhenius equation was used to calculate the activation parameters for permeation as well as for the diffusion of water and of acetic acid. The activation energy values for the permeation flux varied from 97 to 28 kJ/mol. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 244–258, 2002

Key words: pervaporation; flux; separation selectivity; graft membranes; poly(vinyl alcohol)

INTRODUCTION

Acetic acid (HAc) is an important chemical commodity, which is often contaminated with aqueous wastes/recycling streams from chemical process industries. Its separation from an aqueous mixture has been an industrial challenge. Particularly, when we are dealing with water–HAc mixtures, it becomes more difficult to predict membrane permselectivity because both components of the mixtures are likely to interact equally with the membrane polymer through hydrogen-bond or dipole-type interactions. Many efforts have been made in the literature to separate water–HAc mixtures by the pervaporation (PV) method using a variety of poly(vinyl alcohol) (PVA)-based membranes.[1–10] However, to the best of our knowledge, grafted membranes of PVA with acrylamide (AAm), that is, PVA-*g*-AAm, giving acceptable flux and selectivity values for water have not been studied in the earlier literature for the PV separation of water–HAc mixtures.

This is our first effort to develop indigenous membranes for use in the PV separation of water–HAc mixtures with the idea of enhancing the total permeation flux and selectivity to water. Two PVA-*g*-AAm membranes were prepared at 48% (PVA-1) and 93% (PVA-2) by grafting AAm onto PVA. The PV separation characteristics of these membranes were compared with the neat PVA membrane at 25, 35, and 45 °C. The values of the

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Figure 1 Proposed reaction mechanism between PVA and AAm for the synthesis of the PVA-*g*-PAAm copolymer.

permeation flux, separation selectivity, and diffusion coefficient were calculated. From the temperature dependence of the permeation flux and diffusion coefficients, Arrhenius activation parameters were computed. These results are discussed in terms of the PV separation ability of the membranes.

EXPERIMENTAL

Materials

Pure AR-grade samples of PVA, AAm, glutaraldehyde (GA), dimethyl sulfoxide (DMSO), and HAc were procured from S.D. Fine Chemicals (Mumbai, India). Ceric ammonium nitrate (CAN) was obtained from Sisco-Chemicals (Mumbai, India). Iodine was purchased from Thomas Baker Chemicals (Mumbai, India) and potassium iodide (KI) was obtained from E. Merck (Mumbai, India). Double-distilled and deionized water was used throughout.

Synthesis of Copolymers

PVA-*g*-AAm copolymers were synthesized by first polymerizing AAm in a 10% (w/w) PVA solution using CAN.[11–13] In a three-necked round-bottom flask fitted with a condenser, a gas inlet, and a thermometer, about 10 g of PVA was dissolved in 100 mL of distilled water at 60°C under constant stirring and a nitrogen atmosphere. The solution was cooled and 0.12 mol of an AAm solution (previously dissolved in 75 mL of distilled water) was added to the PVA solution by stirring. To this, 2.5 mL of $0.1M$ of CAN in $1M$ HNO_3 was added and the reaction mixture was maintained between 20 and 25°C. Figure 1 shows the proposed grafting mechanism between PVA and AAm. The copolymerization was continued for 24 h and the reaction was terminated by adding a saturated solution of hydroquinone. The polymer was precipitated by adding excess acetone, filtered through a suction pump, and dried in a vacuum oven at 60°C. The polymer was dissolved in DMSO and filtered to remove the undissolved polyacrylamide homopolymer. The filtrate was concentrated and the dissolved graft copolymer was again precipitated using an excess amount of acetone. Two copolymers with grafting of 48 and 93% (respectively designated as PVA-1 and PVA-2) were prepared by taking 5 and 10 g of AAm. The percent conversion of AAm was 92 with a grafting efficiency of 100%.

Characterization of Copolymers

The copolymers were characterized for grafting by FTIR spectra scanned in the range 4000–500 cm^{-1} using KBr pellets on a Nicolet spectrometer (Model Impact 410, USA). The ^1H-NMR spectra were obtained at 60°C using 10 mg/dm^3 of the copolymer in DMSO on a Varian spectrophotometer (Gemini 200 NMR) available at RSIC, IIT, Mumbai, using tetramethylsilane as an internal standard.

For UV-visible experiments, 10 mL of an aqueous polymer solution, 2 mL of a 2.7 mass % iodine solution in KI (5 mass %), and 10 mL of a 4 mass % boric acid solution were added. The extinction coefficient was measured at the λ_{max} of 680 nm using a UV-visible spectrophotometer (Anthelie, Secomam, France).

The viscosities of PVA and the graft copolymer solutions in water were determined using an automatic Ubbelohde viscometer (Schott Gerate, Model AVS 350, Germany) thermostated at 30°C. A total of four concentrations ranging from 0.5 to 3.0 mass % were prepared. From these data, the intrinsic viscosity, $[\eta]$ was calculated and then the viscosity average molecular mass, $\bar{M}_\eta$, was calculated using the Mark–Houwink–Sakurada

(MHS) equation: $[\eta] = K\bar{M}_\eta^a$ with the parameter values of $a = 0.64$ and $K = 0.0453$ mL/g taken from the literature.[14] The calculated molecular mass for PVA was 35,400; for the graft copolymers (PVA-1 and PVA-2), these values were 69,700 and 1,15,000, respectively.

The density of the solid polymers was determined[15] by the solvent-displacement method using a capillary pycnometer (Lurex, NJ) having a volume capacity of 10 cm^3 and a capillary diameter of 1 mm. The inert solvent used was n-nonane. The densities of the polymer were 1.027, 1.2263, and 1.2567 cm^3/g, respectively, for PVA, PVA-1, and PVA-2.

Differential scanning calorimetry (DSC) experiments were performed in an argon atmosphere by taking 7.1 mg of the sample films on a DuPont 2000 instrument (RSIC, IIT, Mumbai). The maximum temperature employed was 250°C.

Thermogravimetric analyses (TGA) were performed on a Rheometric Scientific thermal analyzer at the maximum temperature of 100°C. A heating rate of 20°C/min was used in an argon atmosphere in both experiments.

Preparation of Membranes

PVA, PVA-1, and PVA-2 polymers were dissolved in 100 mL of distilled water at 70°C by constant stirring under a slow stream of nitrogen gas and the solution was cooled to room temperature. To this, 0.0035 mol of GA (0.2 mL of 25 mass % in water) and 5×10^{-4} mol of HCl (0.5 mL of 1N HCl) were added and the mixture was stirred for 30 min to produce the crosslinked PVA-g-AAm copolymer. This mixture was then poured onto a glass plate and left overnight to evaporate the water. The cast membranes were cured at 60°C in an oven to ensure complete crosslinking of the PVA-g-AAm copolymer. The membranes were washed with distilled water to remove any excess of GA and HCl present and then allowed to dry at room temperature for 24 h. The membranes were peeled off from the glass plate and used in the PV measurements.

PV Apparatus

The PV apparatus designed in this work consists of a stirred cell through which the retentate is circulated to the feed tank. The effective surface area of the membrane is 32.4 cm^2 with a diameter of 5 cm. The total solvent capacity of the cell is about 250 mL. The feed mixture was first placed on the upstream side of the membrane and water at a constant temperature was circulated through the PV apparatus. The feed mixture was stirred with an efficient three-blade stirrer powered by a dc motor in the feed compartment to maintain uniform mixing and to keep the temperature constant as monitored by a thermometer. Turbulent flows were maintained at a low rotation ($\sim$200 rpm) of the stirrer so that mass-transfer limitations due to the concentration polarization are negligible. The downstream compartment was continuously evacuated using a vacuum pump (Toshniwal, Chennai, India) at a downstream pressure of 10 Torr as measured by an accurate pressure gauge.

The test membrane was equilibrated for about 1 h with the feed mixture before the start of the PV experiment. After establishment of a steady state, the permeate was trapped into cold traps immersed in liquid nitrogen. The permeate composition was determined by measuring the refractive index within an accuracy of $\pm$0.0001 units using an Attago refractometer (Model 3T, Japan). The PV experiments were performed at 25, 35, and 45°C.

In a PV experiment, preferential sorption of the more permeable component of the feed mixture onto the membrane takes place at the upstream side. Then, diffusion of the sorbed liquid occurs and, finally, liquid desorption takes place at the downstream side. The separation performance of the membrane can be assessed in terms of the permeation flux, J_P, and the separation selectivity, $\alpha_{W/HAc}$, calculated using

$$J_P = \frac{Q}{At} \tag{1}$$

$$\alpha_{W/HAc} = \frac{P_W/P_{HAc}}{F_W/F_{HAc}} \tag{2}$$

where Q is mass of the permeate (kg); A, the effective membrane surface area (m^2), and t, the operating time; F_W and F_{HAc} are the mass fractions of water and HAc, respectively, in the feed, and P_W and P_{HAc}, the respective mass fractions in the permeate mixture.

RESULTS AND DISCUSSION

Spectral and Thermal Characterization

PVA, when treated with iodine in the presence of boric acid, develops a deep blue coloration, char-

acteristic of the hydroxyl group of PVA. The intensity of the blue color (absorbance) decreased with an increase in grafting. This indicates that the —OH group of PVA responsible for the deep blue color is involved in the grafting and, thereby, reducing the number of hydroxyl groups.

The FTIR spectra of PVA and PVA-1 presented in Figure 2 shows a characteristic broad band at ~ 3440 cm^{-1} corresponding to an associated O—H stretching vibration of the hydroxyl group of PVA. These O—H stretchings are also observed in the spectra of PVA-1, indicating that all the hydroxyl groups in PVA are not involved in grafting. A sharp band at 1258 cm^{-1} corresponds to an acetyl $>$C$=$O group of PVA because the polymer was prepared by 80% hydrolysis of poly(vinyl acetate); however, some acetate groups may not have been fully converted into hydroxyl groups. The peak due to an asymmetric N—H stretching vibration of the primary amide overlaps with the O—H stretching vibrations. The aliphatic C—H stretching vibrations appear at ~ 2925 cm^{-1}. A characteristic peak at 1731 cm^{-1} is due to the carbonyl ($>$C$=$O) stretch of the AAm polymeric chain in PVA-1. Grafting was also confirmed by the presence of strong bands at 1665 and 1433 cm^{-1}, corresponding to asymmetric N—H bending and C—N stretching, respectively.

The ^{1}H-NMR spectra of PVA and PVA-1 presented in Figure 3 represent the characteristics of the proton environments in the polymers. A broad peak at ~ 1.4 ppm is assigned to DMSO, which was used as a solvent. The pentalet appearing at ~ 2.5 ppm is due to the coupling of C—H proton, with the neighboring four protons of the —CH$_2$ group satisfying the $n + 1$ rule. Two protons of the CH$_2$ group are coupled with the neighboring two protons of the C—H group and these appear as a triplet at ~ 3.2 ppm. The triplet near the downfield observed at ~ 4.4 ppm, which disappears on D$_2$O exchange, is attributed to the hydroxyl proton. A small peak appearing near the far downfield shift at ~ 9.5 ppm is due to the N—H proton. This confirms the grafting of AAm onto the PVA backbone.

DSC analyses were performed to understand the thermal behavior of the graft copolymers. The DSC tracings presented in Figure 4 for PVA-1 are different from those of PVA. The T_g of PVA is observed as a small dip near 100°C, but for PVA-1, a sharp endothermic peak is observed at ~ 101°C, with an enthalpy value of 142.6 J/g. This indicates an increase in the crystallinity of PVA-1, thereby confirming grafting. The TGA

data presented in Figure 5 show that decomposition does not involve oxygen, but there is a steady dehydration char residue of about 17%. Both the spectral and thermal analysis data confirm the possible mechanism proposed in Figure 1 for the grafting reaction.

PV Performance of the Membranes

A good PV membrane should have a high permeation flux and acceptable separation selectivity with a long-term mechanical stability to maintain the optimum permselectivity under the operating conditions of temperature and pressure. Efforts in this direction were made to achieve, simultaneously, high flux and separation selectivity. Permselectivity is controlled by the sorption and diffusion of the permeants across the membrane; when these are favorable to a given component, then high permselectivity results. If any of these two processes is unfavorable to a given liquid component for a particular membrane, then poor permselectivity results. In addition, membrane swelling and operating temperature also influence the membrane performance.

Table I contains data on the mass percent of water in the permeate, separation selectivity, and flux as a function of the feed water composition at 25, 35, and 45°C. It is observed that the permeate water content is higher than is the feed water content for all the membranes, indicating their high water selectivities. The permeate water content decreases with increasing temperature. The permeate water contents of PVA-1 and PVA-2 membranes are quite lower than are those of the PVA membrane, indicating not much improvement in water selectivity of the grafted membranes over the neat PVA membrane. The decrease in the permeate water content with increased grafting indicates higher interactions of HAc with the active amide groups of the graft copolymer. These interactions may be between the active —COOH group of HAc and the electron-deficient $>$C$=$O carbon atom of the amide moiety, thus hydrolyzing the amide group to an acidic group. Such an interaction might lead to a decrease in the water composition, giving an increasing amount of HAc in the permeate mixture.

Figure 6 displays the dependence of total flux, J_P, on the mass percent of water in the feed mixture at 25°C for the three membranes. The total permeation flux and that of water increases with an increasing water content of the feed mixture; this flux is dominated by the water transport
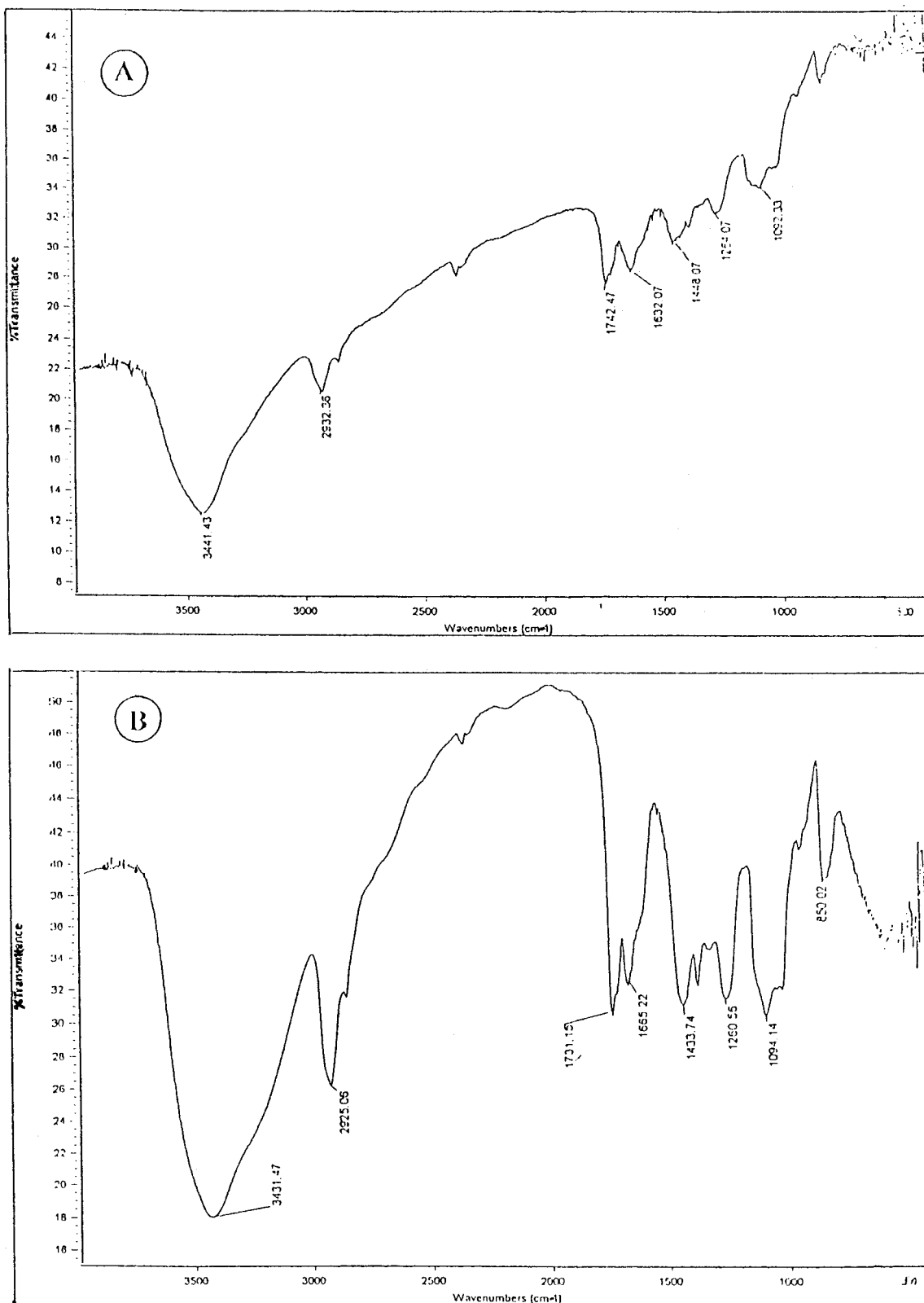
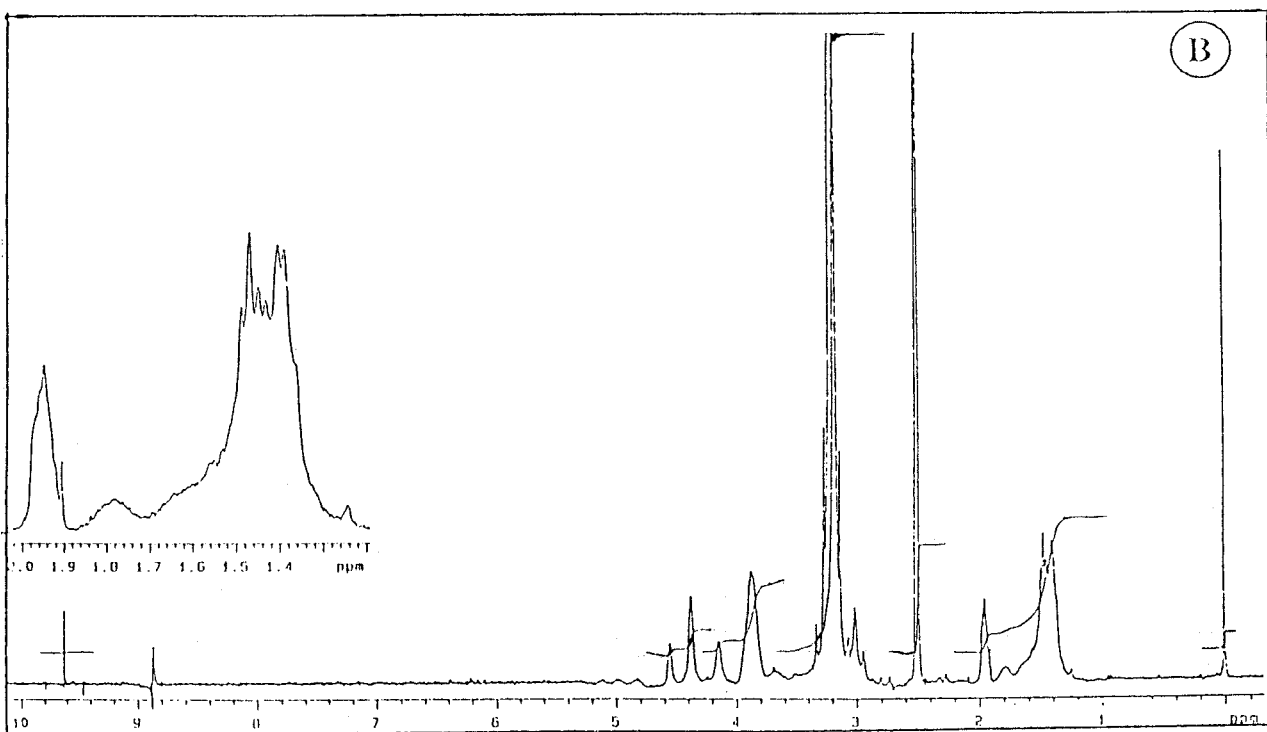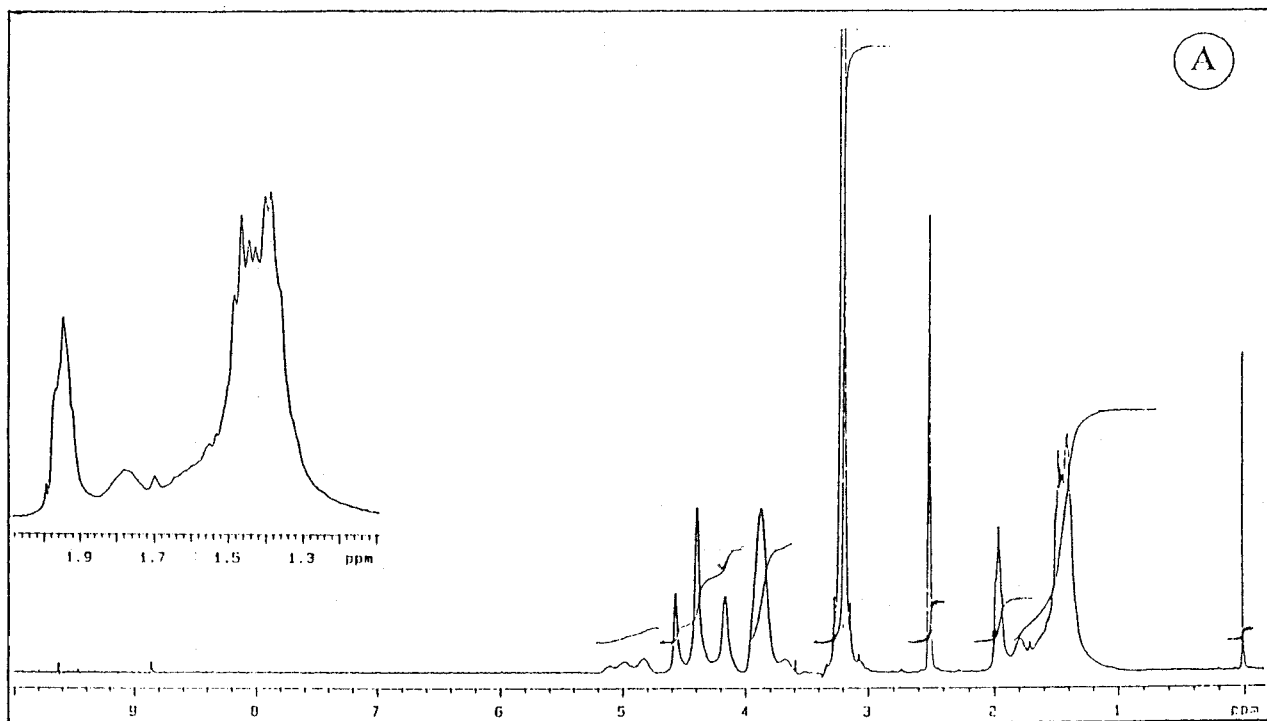**Figure 2**   FTIR spectra of (A) PVA and (B) PVA-1.

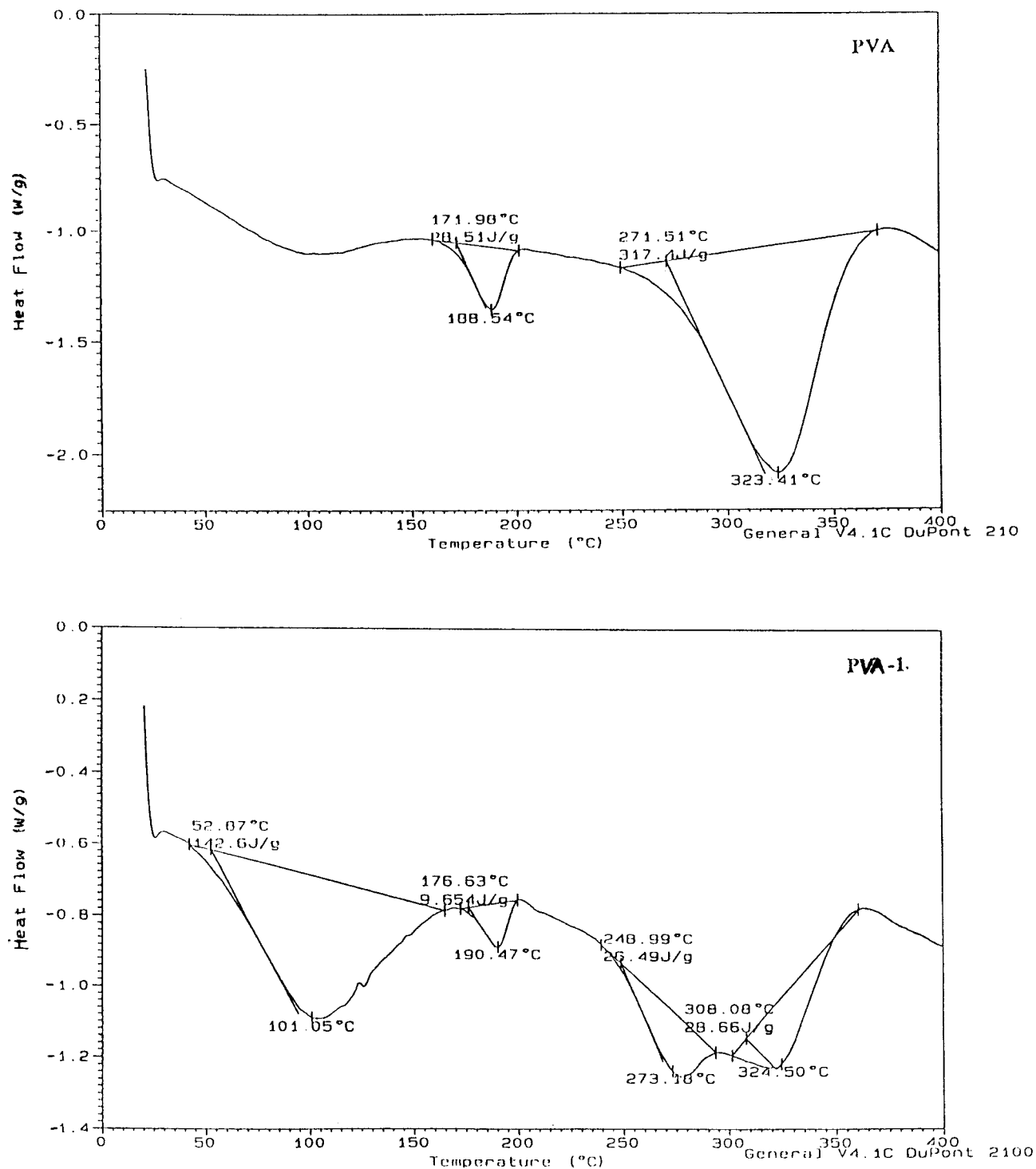**Figure 3** ^{1}H-NMR spectra of (A) PVA and (B) PVA-1.

Figure 4   DSC tracings of PVA and PVA-1.

through the membranes. On the other hand, the permeation flux of HAc is much lower than that of those observed for water and total fluxes. For HAc, the flux increases slightly up to 50% of water in the feed, but later it decreases slowly, prob-ably due to the rejection of HAc molecules at the higher amount of water. With an increasing amount of water in the feed mixture, the interaction of water with the membrane also increases and this leads to a higher permeation flux. The
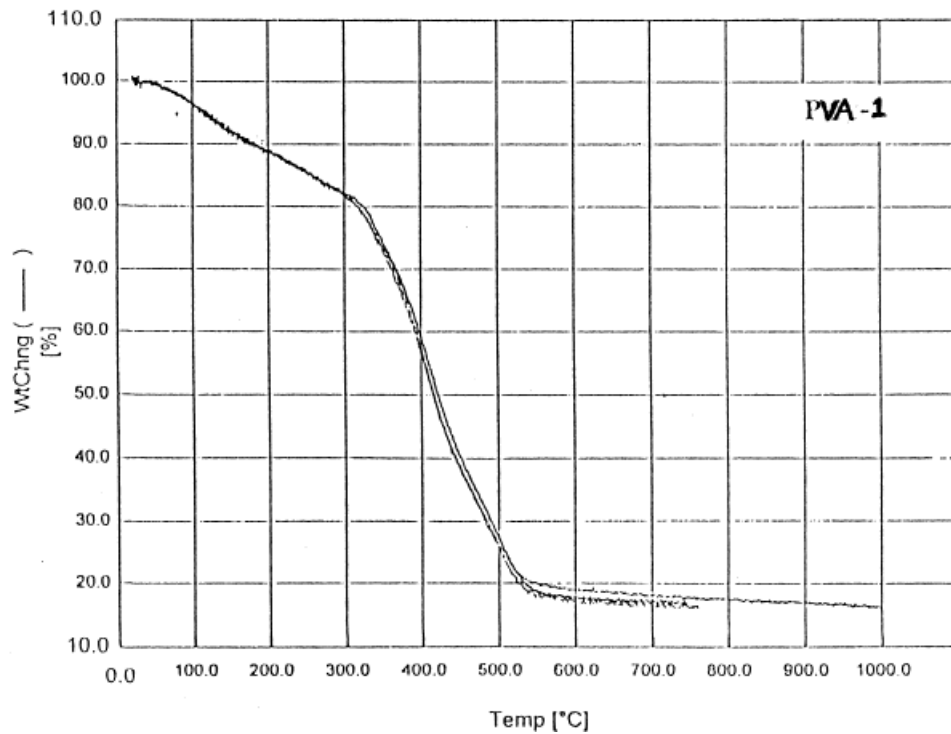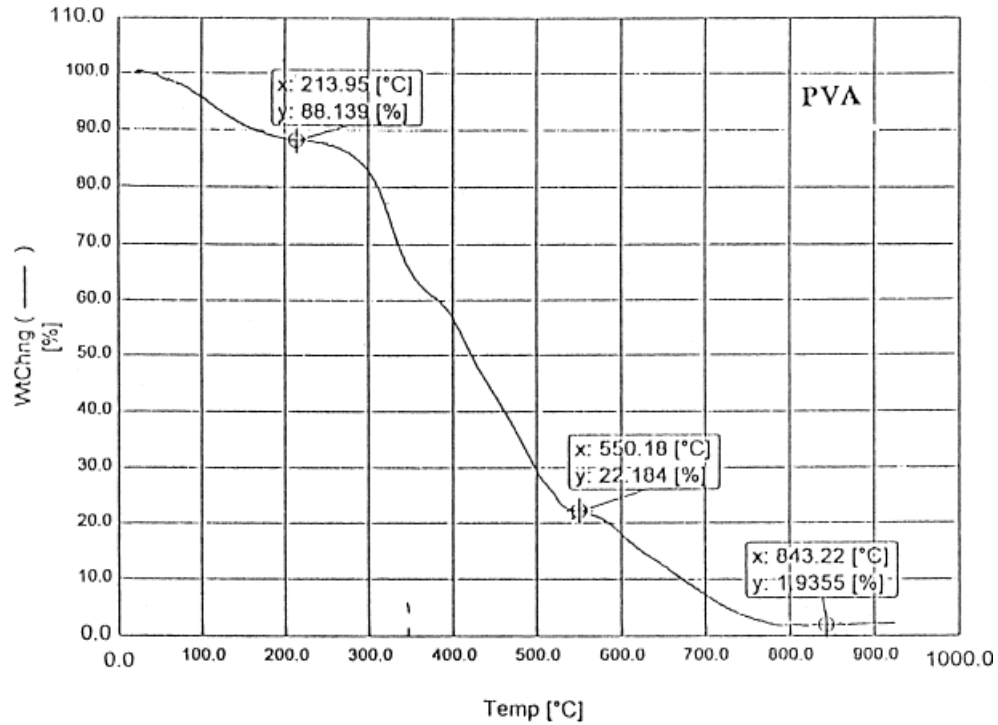
Figure 5   TGA tracings of PVA and PVA-1.

total permeation flux as well as that of water tend to increase with an increase in grafting, which suggests higher interactions of the membrane with the water–HAc mixtures. Even the permeation flux of HAc increases slightly with an increase in grafting, suggesting increased interac-

Table I   Mass % of Water in the Permeate (P_W), Separation Selectivity ($\alpha_{W/HAc}$) and Permeate Flux (J_P, kg/m².h) for PVA and Copolymer Membranes at Different Temperatures and Feed Content of Water

Membrane	Water in Feed (%)	P_W 25°C	P_W 35°C	P_W 45°C	$\alpha_{W/HAc}$ 25°C	$\alpha_{W/HAc}$ 35°C	$\alpha_{W/HAc}$ 45°C	$J_P \times 10^2$ 25°C	$J_P \times 10^2$ 35°C	$J_P \times 10^2$ 45°C
PVA	9.99	72.0	60.0	56.3	23.14	16.71	11.61	0.60	2.85	3.71
	20	79.3	62.7	61.5	15.35	6.71	6.39	0.84	5.57	12.40
	30	83.7	74.7	67.7	11.98	6.88	4.88	4.45	11.52	21.12
	40	84.1	80.0	77.3	7.90	6.00	5.12	8.72	17.37	36.53
	50	87.2	86.0	83.3	6.81	6.14	5.00	9.62	19.18	45.30
	60	91.7	89.5	87.3	7.33	5.68	4.60	11.83	22.65	59.45
	70	94.3	92.7	91.5	7.13	5.42	4.61	12.23	39.94	64.55
	80	96.5	95.7	95.7	6.89	5.52	5.52	19.19	39.86	60.38
	90	98.3	98.0	97.7	6.56	5.44	4.65	15.53	38.48	45.88
PVA-1	9.99	48.7	48.7	40.7	8.53	8.53	6.17	0.82	3.03	6.68
	20	52.7	57.3	45.0	8.53	5.38	3.27	3.80	8.62	13.74
	30	61.3	68.2	57.0	3.70	5.00	3.09	6.58	14.10	23.81
	40	72.0	75.7	72.0	3.86	4.66	3.86	10.27	20.23	46.60
	50	76.7	81.3	80.0	3.29	4.36	4.00	17.68	26.79	52.73
	60	82.7	86.7	86.2	3.18	4.33	4.15	16.05	45.55	59.58
	70	89.3	92.0	90.7	3.59	4.93	4.16	27.73	50.71	66.79
	80	93.3	95.5	93.0	3.50	5.31	3.32	35.52	56.06	82.66
	90	98.0	98.5	98.0	5.44	7.30	4.65	36.59	58.37	92.85
PVA-2	9.99	37.3	38.5	33.5	5.36	5.63	4.53	4.22	6.21	9.80
	20	49.3	48.8	42.7	3.89	3.81	2.98	5.63	9.37	22.78
	30	56.3	54.5	51.7	3.01	2.80	2.49	8.66	25.58	43.73
	40	66.7	65.0	61.3	3.00	2.79	2.40	17.57	33.18	53.31
	50	75.7	72.0	71.0	3.11	2.57	2.45	21.60	42.74	69.75
	60	82.3	80.0	77.3	3.11	2.67	2.27	34.11	61.66	94.68
	70	89.8	91.0	82.2	3.79	4.33	1.97	47.36	74.46	106.17
	80	93.3	94.7	92.0	3.50	4.44	2.88	60.44	80.27	138.22
	90	97.7	97.2	97.3	4.65	3.81	4.06	65.24	87.59	193.86

tions of HAc molecules with the acrylamide portion of the grafted copolymer

The effect of temperature on the permeation flux also shows a dependency on the type of polymer used. As shown in Table I, for the PVA-2 membrane (93% grafted), the permeation flux is higher than that of the PVA-1 membrane (48% grafted). For both the PVA-1 and PVA-2 membranes, permeation flux values are higher than are those observed for the neat PVA membrane at all the temperatures. The permeation flux results of the present study (0.6 kg m^{-2} h^{-1}) agree with those of the PVA membranes reported by Nguyen et al.[16] (0.5 kg m^{-2} h^{-1}). The temperature dependency of permeation flux was investigated by the Arrhenius relationship given in the form

$$J_P = J_{P0} \exp(-E_P/RT) \qquad (3)$$

where E_P is the activation energy for permeation; J_P, the permeation rate constant; R, the gas constant; and T, the temperature in Kelvin. If E_P is positive, then the permeation flux increases with increasing temperature and this was observed commonly in the PV experiments.[17,18] 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 the difference in the partial vapor pressure of the permeants between the feed and the permeate. As the feed temperature increases, 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 the driving force with increasing temperature.

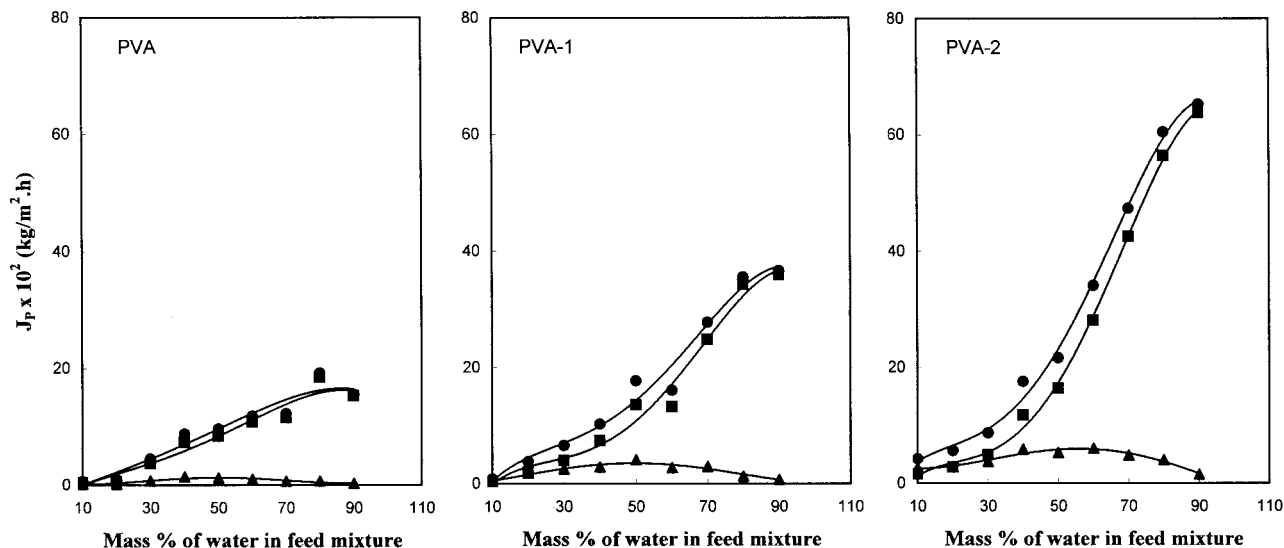Arrhenius plots of log J_P versus $1/T$ are shown in Figure 7. In all cases, straight lines are ob-

Figure 6 Permeation flux versus composition of water in the feed at 25°C: (●) total permeation flux; (■) water flux; (▲) HAc flux.

served, signifying that the temperature dependence of the permeation flux follows an Arrhenius relationship. The apparent values of E_P calculated from the slopes of the straight lines by the least-squares procedure are compiled in Table II. The E_P values for PVA range between 42.7 and 96.8 kJ/mol, but for both grafted copolymer membranes, the E_P values decrease with an increase in grafting except at 20 and 30% of water in the feed mixture. In the case of PVA-1, the E_P values range between 31.9 and 75.8 kJ/mol, whereas, for PVA-2, these values vary from 28.4 to 60.7 kJ/mol. The E_P values do not show any systematic variation with the mass percent of water in the feed mixture. Since both PVA and the grafted copolymers are semicrystalline in nature, the calculated E_P values are lower than are those observed for the rubbery polymer membranes.[19]

Diffusion Coefficients

Since flux is directly related to the nature of the permeant transport through the dense polymer matrix, an attempt was made to measure the diffusion coefficient, D_i, using[20]

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

(4)

Here, D_i is assumed to be constant across the effective membrane thickness, h; $C_{i(feed)}$ and C_{i-}

(permeate) are, respectively, the solution concentration in the feed and in the permeate. The computed values of D_i (where the subscript i stands for water or HAc) at all the temperatures are presented in Table III. As expected, the diffusion coefficients of water increase with an increase in the temperature and this increase is quite dramatic at higher compositions of water in the feed mixture. Even though similar trends are observed for HAc, the D_i values of HAc do not vary systematically with the mass percent of water in the feed. Also, the diffusion coefficients increase with an increase in grafting. This dependence is similar to the permeation flux data discussed before. In an earlier study by Harogoppad and Aminabhavi,[21] it was observed that the D of water in the phase-segregated polyurethane membrane was higher than that of HAc. Thus, a considerable increase in D with an increasing amount of water in the feed mixture is due to the creation of extra free volume within the membrane.

The results of $\alpha_{W/HAc}$ as a function of the mass percent of water in the feed at different temperatures displayed in Figure 8 show a decrease with an increase in the percent grafting. By increasing the temperature, the $\alpha_{W/HAc}$ values decrease for all the membranes over the entire feed composition of water in the mixture, indicating higher interactions between the amide group of the grafted copolymer and the acidic group of HAc. This observation is quite opposite to those of the permeation flux results. Separation selectivity in-
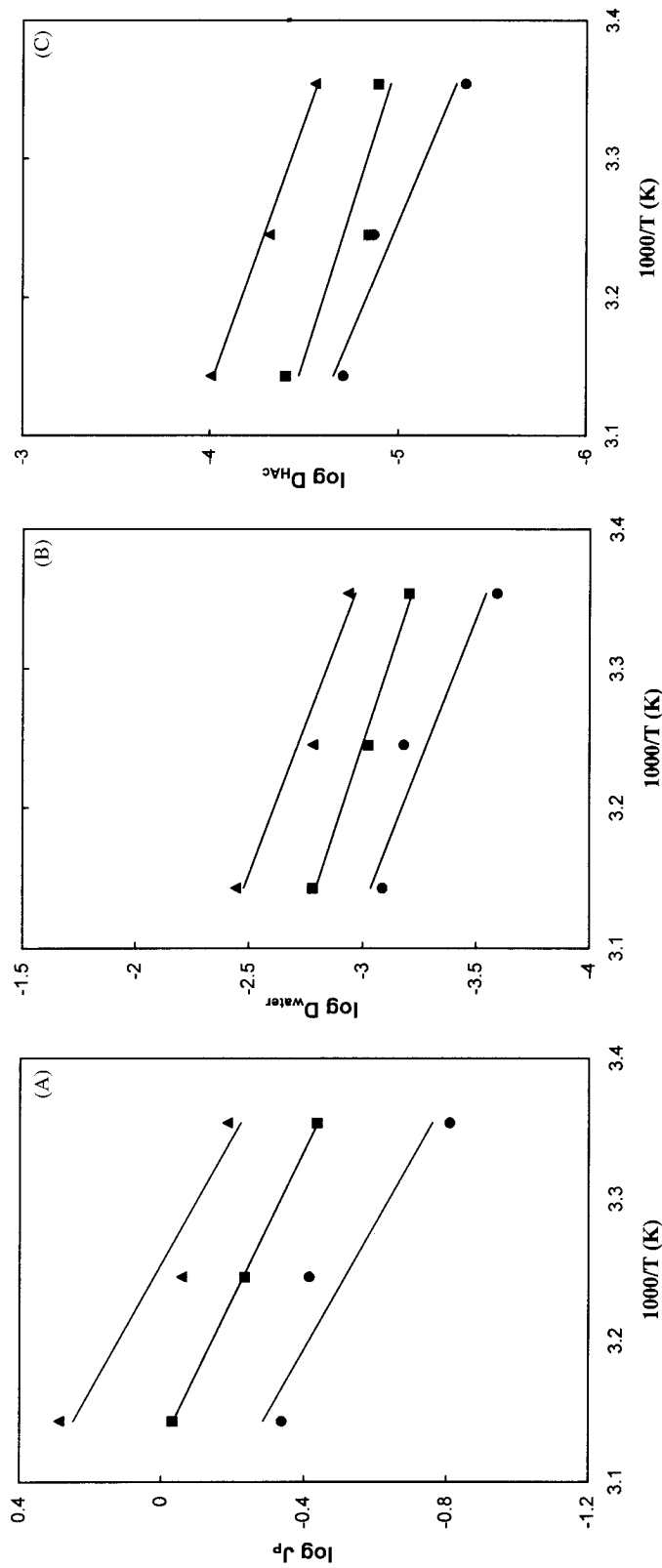
Figure 7 Arrhenius plots of (A) log J_D versus $1/T$, (B) log D_{Water} versus $1/T$, and (C) log D_{HAc} versus $1/T$ for (●) PVA, (■) PVA-1, and (▲) PVA-2 membranes.

Table II   Permeation and Diffusion Activation Energies (E_P and E_D, kJ/mol) and Heat of Solution (ΔH_S, kJ/mol) for Water

F_W (%)	E_P			E_D			ΔH_S		
	PVA	PVA-1	PVA-2	PVA	PVA-1	PVA-2	PVA	PVA-1	PVA-2
9.99	62.8	75.8	28.8	73.1	83.4	34.8	−10.3	−7.6	−6.0
20	96.8	44.8	49.2	109.9	58.3	59.2	−13.1	−13.5	−10.0
30	53.1	48.0	60.7	67.2	53.7	68.4	−14.1	−5.7	−7.7
40	53.1	59.6	40.6	59.7	59.3	54.3	−6.6	−0.1	−13.7
50	59.2	44.6	43.8	63.5	39.9	52.7	−4.3	4.7	−8.9
60	61.6	53.7	37.8	67.3	48.0	47.8	−5.7	5.7	−10.0
70	64.7	35.4	28.4	69.5	32.7	47.4	−4.8	2.7	−19.0
80	45.0	31.9	31.9	47.0	34.1	36.0	−2.0	−2.2	−4.1
90	42.7	36.7	42.6	46.0	38.2	44.4	−3.3	−1.5	−1.8

creases to 40–50 mass % of water in the feed mixture and then decreases. This decrease in the separation selectivity with an increase in temperature is due to an increased free volume within the polymer matrix, thus facilitating the transport of the feed mixture.[22]

Table III   Diffusion Coefficients (D_i) of Water and HAc Through Membranes at Different Temperatures

| Polymer	Water in Feed (%)	$D_{water} \times 10^6$ (cm²/s)			$D_{HAc} \times 10^6$ (cm²/s)		
		25°C	35°C	45°C	25°C	35°C	45°C
PVA	10	1.0	4.8	6.3	0.4	3.2	4.9
	20	1.6	11.5	25.7	0.4	6.8	16.1
	30	9.7	27.0	53.1	1.9	6.2	25.4
	40	23.3	48.7	105.9	4.4	12.2	31.1
	50	31.6	64.2	158.6	4.6	10.4	31.7
	60	48.0	96.2	265.9	4.4	11.3	38.6
	70	66.4	228.6	384.4	4.0	18.1	35.7
	80	157.1	340.8	516.2	5.7	15.4	23.4
	90	256.6	659.9	818.3	4.4	13.5	19.6
PVA-1	10	1.5	5.3	12.4	1.5	5.6	18.1
	20	7.9	18.5	34.6	8.4	13.8	42.3
	30	18.0	35.3	70.4	11.4	16.5	53.1
	40	32.3	60.1	145.8	12.6	19.3	57.1
	50	71.2	97.4	196.9	21.7	22.3	49.2
	60	81.9	207.2	274.7	17.2	31.9	44.1
	70	179.4	296.9	410.2	21.4	25.8	42.2
	80	348.1	483.6	827.9	24.9	22.8	62.1
	90	627.5	947.0	1655.9	12.8	14.4	39.6
PVA-2	10	8.1	11.8	19.6	13.6	18.8	38.8
	20	13.3	22.2	60.0	13.6	23.3	80.7
	30	25.9	79.7	146.0	20.1	66.5	136.6
	40	61.5	120.8	243.7	30.7	65.0	106.1
	50	89.2	195.8	338.7	28.7	76.2	126.3
	60	176.0	345.3	591.4	37.8	86.3	173.3
	70	300.3	451.7	1003.8	34.0	44.7	217.9
	80	592.3	725.4	1483.5	42.3	40.9	129.0
	90	1163.6	1662.5	3602.3	27.8	48.5	98.7
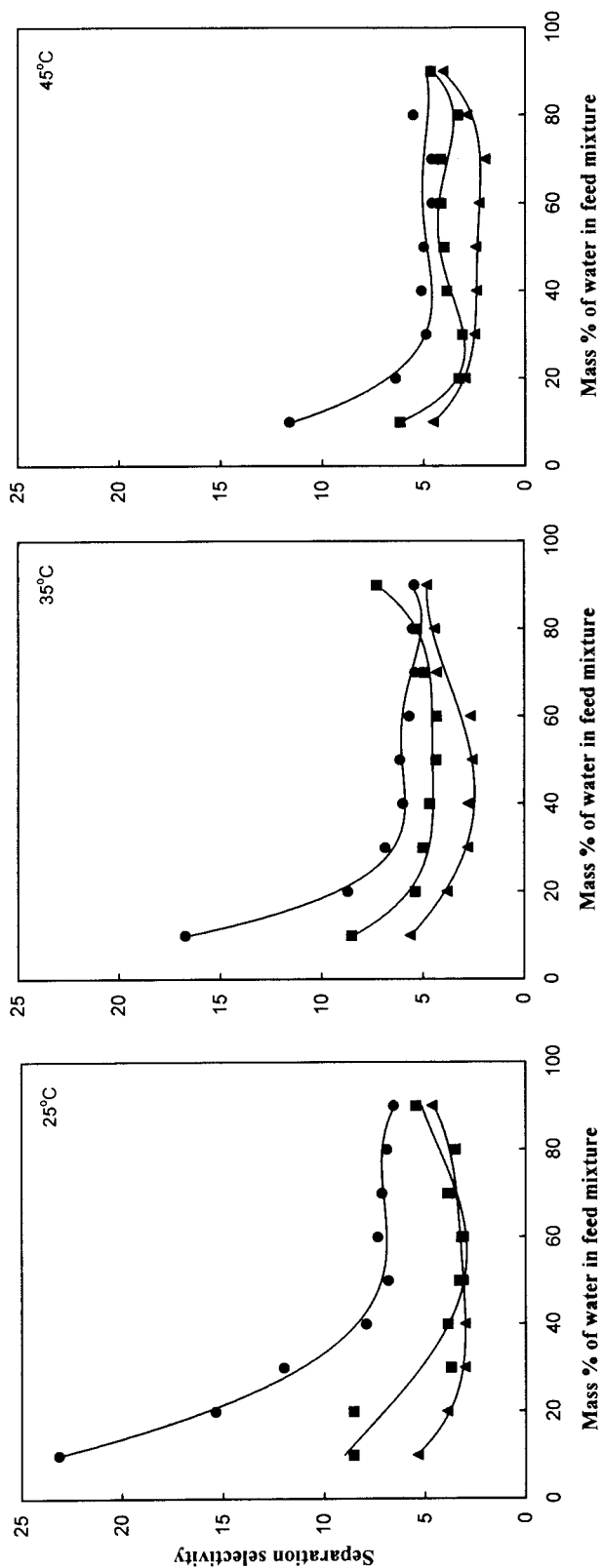
Figure 8   Separation selectivity versus composition of water in the feed at different temperatures for (●) PVA, (■) PVA-1, and (▲) PVA-2 membranes.

Since the values of D_i increase with increasing temperature, these data were analyzed using the Arrhenius relationship given below:

$$D_i = D_{i0} \exp(-E_D/RT) \qquad (5)$$

Here, E_D is the energy of activation for diffusion and i stands for water or acetic acid. The E_D values estimated by the least-squares method, included in Table II, are higher for PVA than for the PVA-1 and PVA-2 membranes. Generally, a decrease in E_D is observed with an increase in the water content of the feed mixture. Using the E_P and E_D values, we calculated the heat of sorption, ΔH_S, as $\Delta H_S = E_P - E_D$. These data are presented in Table II. The ΔH_S values are negative in all the cases except for the PVA-1 membrane for 50–70 mass % of water in the feed mixture, suggesting an endothermic mode of sorption.

The temperature dependence of the separation selectivity was studied using the relationship proposed by Ping et al.[23]:

$$Y_w = \cfrac{1}{1 + \left(\cfrac{J_{0,\mathrm{HAc}}}{J_{0,\mathrm{W}}}\right)\exp\left(\cfrac{-(E_{E_D(\mathrm{HAc})} + E_{E_D(\mathrm{Water})})}{RT}\right)}$$

$$(6)$$

where Y_w is the water composition in the permeate; J_W and J_{HAc}, the permeation fluxes; and E_W and E_{HAc}, Arrhenius activation energies for water and HAc, respectively, at the average energy level. A positive value of $E_{D(\mathrm{HAc})} - E_{D(\mathrm{Water})}$ indicates that separation selectivity decreases with an increase in the temperature[23] and a negative value indicates that the separation selectivity increases with an increasing temperature (see Table IV). In the majority of cases, these values are positive, further supporting that $\alpha_{\mathrm{W/HAc}}$ decreases with increasing temperature except for PVA-1, for which $E_{D(\mathrm{HAc})} - E_{D(\mathrm{Water})}$ is negative for mixtures containing 40–70% of water in the feed, indicating an increase in the separation selectivity with temperature.

CONCLUSIONS

Separation selectivity and permeation flux are the key parameters in PV separation of water–HAc mixtures. Diffusion coefficients are also equally important in understanding the PV sep-

Table IV   Energy Difference ($E_{\mathbf{HAc}}$-$E_{\mathbf{Water}}$ in kJ/mol) Calculated from Eq. (6) for Different Membranes

Water in Feed (%)	PVA	PVA-1	PVA-2
10	9.72	7.00	4.19
20	10.13	6.06	5.66
30	8.39	2.77	3.40
40	3.29	−0.04	3.28
50	2.35	−1.70	2.53
60	1.91	−1.66	2.47
70	1.20	−0.61	3.46
80	0.34	0.12	0.55
90	0.27	−0.01	0.14

aration phenomenon. These parameters are sensitive to the amount of water present in the feed mixture. A hydrophilic membrane such as PVA exhibits a low separation efficiency in spite of its high total permeation flux. The temperature dependency of the permeation flux as well as diffusion followed an Arrhenius relationship. The PVA-g-AAm copolymer membranes prepared here are effective in the selective separation of HAc from its aqueous mixture.

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