

Pervaporation Separation of Water/Dimethylformamide Mixtures Using Poly(vinyl alcohol)-*g*-polyacrylamide Copolymeric Membranes

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ABSTRACT: Grafted copolymeric membranes of poly(vinyl alcohol) with acrylamide (PVA-*g*-AAM) were developed and used in the pervaporation separation of water–dimethylformamide mixtures by varying the amount of water in the feed from 0 to 100%. From these data, the permeation flux, pervaporation separation index, diffusion coefficient, swelling index, and separation selectivity were calculated at 25, 35, and 45°C. The Arrhenius activation parameters for permeation flux ranged between 22 and 63 kJ/mol, while the activation energy for diffusion ranged between 23 and 67 kJ/mol. Separation selectivity was between 15 and 22. The highest permeation flux of 0.459 kg m⁻² h⁻¹ was obtained for the 93% grafted membrane at 90% of water in the feed mixture. The results are discussed using the principles of the solution–diffusion model. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 273–282, 2002

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

INTRODUCTION

Pervaporation (PV) separation is an energy-intensive membrane-based technique used to separate selectively the desired components in organic–aqueous and organic–organic mixtures.¹ Membrane selectivity can be controlled by modification of the polymer backbone.^{2–4} Compared to poly(vinyl alcohol) (PVA), polyacrylamide (PAAm) absorbs more water and, hence, the membrane prepared from PVA will be water-selective. In a previous article,⁵ we prepared a PVA-grafted membrane of PAAm (i.e., PVA-*g*-AAM) and used it to separate water–acetic mixtures. These membranes are now used to separate water–dimeth-

ylformamide (DMF) mixtures. Even though several hydrophilic membranes have been used in the earlier literature^{6–8} for the PV separation of organic–aqueous mixtures, to the best of our knowledge, no PVA-*g*-AAM membranes have been used to separate water–DMF mixtures. The successful commercialization of PVA composite (GFT) membranes by Bruschke^{9,10} of the GFT Co. in Germany created a renewed interest in the PV separation of water–alcohol mixtures, but not for water–organic acid mixtures.

We are particularly interested in separating DMF because it is an important industrial chemical and is often present in wastes and/or recycling streams in chemical industries; its separation from water has been an industrial challenge. In the present work, membrane performance was studied by estimating the separation selectivity, permeation flux, and pervaporation separation index. In addition, other influencing parameters like sorption, membrane swelling, and diffusion

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were also studied. Sorption is coupled with membrane swelling and is dominated by the preferential solvation of one of the components of the feed mixtures onto the swollen upstream side of the membrane. Diffusion is controlled by the nature of the permeant as well as the barrier material. Temperature is also an influencing factor and, hence, experiments were conducted at 25, 35, and 45°C. From these data, activation parameters were calculated and the PV results are discussed in terms of solution–diffusion principles.

EXPERIMENTAL

Membranes were synthesized as per the procedures explained earlier.⁵ Totally, three membranes were prepared: (i) neat PVA; (ii) PVA with 48% grafting (PVA-1); and (iii) PVA with 93% grafting (PVA-2). The copolymers were synthesized by first polymerizing AAm in a 10% (w/w) PVA solution using ceric ammonium nitrate (0.1M) as an initiator at 25°C. The reaction was terminated by adding a saturated solution of hydroquinone. The polymer was precipitated by adding excess acetone, filtered, and dried in a vacuum oven at 60°C. The solid polymer was dissolved in DMSO and filtered to remove the undissolved PAAm homopolymer. The filtrate was concentrated and the dissolved graft copolymer was again precipitated using an excess amount of acetone. Two copolymers with 48 and 93% grafting (designated, respectively, 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%.

Swelling Experiments

Membranes of known masses were immersed in different known compositions of water + DMF mixtures, which were allowed to equilibrate for 72 h at the constant temperatures of 25, 30, and 45°C. The membranes were then removed from the solvent mixture, the adhered liquid drops were wiped off using soft-tissue papers, and the mass measurements were made within an accuracy of ± 0.01 mg using a single-pan microbalance (Mettler, Model AT-20, Switzerland). By knowing the amount of permeant sorbed by 1 g of the membrane, the degree of swelling (DS) of the membrane was calculated as

$$DS = W_f/W_i \quad (1)$$

where W_f is final mass (kg) of the swollen membrane, and W_i , the initial dry mass (kg) of the membrane.

PV Experiments

The PV apparatus used here was described earlier.⁵ A membrane with an effective surface area of 32.4 cm² and having a diameter of 5 cm was used. About 250 mL of the feed mixture was introduced into the upstream compartment and the temperature was maintained constant within $\pm 0.01^\circ\text{C}$. The downstream compartment was continuously evacuated using a vacuum pump (Toshniwal, High Vacuum Pump, Chennai, India) at a downstream pressure of 10 Torr. The test membrane was equilibrated for about 1 h with the feed mixture before the start of the experiment. After establishment of the equilibrium, the permeate was trapped in cold traps immersed in liquid nitrogen and its composition was determined by measuring the refractive index (± 0.0001 units) using an Attago refractometer (Model 3T, Japan). Triplicate measurements were done at 25, 35, and 45°C, and the average values were considered.

RESULTS AND DISCUSSION

Liquid transport through a barrier membrane is governed by the sorption–diffusion mechanism. The transporting liquid first dissolves into the membrane and then diffuses due to the chemical potential gradient acting as a driving force. Preferential sorption of the component takes place at the feed side of the membrane and diffusion occurs until desorption takes place on the downstream side. Three parameters of interest to study the membrane performance are: (i) flux, J_P (kg m⁻² h⁻¹), (ii) selectivity, $\alpha_{W/D}$, and (iii) pervaporation separation index (PSI). These are calculated as

$$J_P = Q/At \quad (2)$$

$$\alpha_{W/D} = (P_W/P_D)/(F_W/F_D) \quad (3)$$

$$PSI = J_p(\alpha_{W/D} - 1) \quad (4)$$

In the above equations, Q is the mass of the permeate (kg); A , the effective membrane surface

Table I Mass % of Water in the Permeate (P_w), Separation Selectivity ($\alpha_{w/D}$), and Permeate Flux (J_p , $\text{kg m}^{-2} \text{h}^{-1}$) for PVA and Copolymer Membranes at Different Temperatures and Mass Percent of Water in the Feed

Membrane	Water in Feed (%)	P_w			$\alpha_{w/D}$			$J_p \times 10^2$		
		25°C	35°C	45°C	25°C	35°C	45°C	25°C	35°C	45°C
PVA	9.99	65.5	59.5	42.0	17.1	13.2	6.5	1.6	3.6	12.6
	20	85.0	79.0	77.0	22.7	15.1	9.3	5.0	5.9	14.0
	30	92.0	89.0	83.5	26.8	18.9	11.8	6.5	7.0	15.5
	40	95.0	94.0	90.0	28.5	23.5	13.5	7.4	10.7	19.2
	50	96.0	95.0	92.3	24.0	19.0	11.9	9.2	13.2	23.7
	60	97.5	96.5	96.0	26.0	18.4	16.0	11.1	18.7	27.4
	70	97.8	97.0	97.0	18.2	13.9	13.9	14.0	20.1	29.8
	80	98.5	97.8	97.8	16.4	10.9	10.9	15.5	25.5	33.9
	90	99.0	98.5	98.5	11.0	7.3	7.3	20.0	29.7	40.3
PVA-1	9.99	84.5	81.5	77.5	49.1	39.7	31.0	0.7	1.5	3.4
	20	91.3	89.0	87.8	41.7	32.4	28.8	1.0	3.5	6.8
	30	94.3	94.0	93.1	38.3	36.6	31.5	1.7	5.5	9.2
	40	97.0	95.8	94.4	48.5	33.8	25.3	4.1	9.1	11.9
	50	97.8	97.0	95.0	43.4	32.3	19.0	7.5	10.1	15.3
	60	98.5	97.8	97.0	43.8	29.0	21.6	9.4	12.9	17.3
	70	98.8	98.5	97.5	33.9	28.1	16.7	11.6	16.0	19.9
	80	99.0	98.8	98.5	24.8	19.8	16.4	12.9	18.1	20.8
	90	99.3	99.3	99.0	14.7	14.7	11.0	15.2	19.1	26.6
PVA-2	9.99	86.5	84.5	83.0	57.7	49.1	43.9	1.3	2.4	4.4
	20	94.0	93.0	91.8	62.7	53.1	44.5	2.0	5.4	8.0
	30	95.5	94.3	94.3	49.5	38.3	38.3	3.1	6.7	10.4
	40	97.8	97.5	96.0	65.2	58.5	28.5	4.8	12.1	17.9
	50	98.3	98.0	97.0	57.8	49.0	32.3	9.8	13.8	25.5
	60	98.5	98.5	98.0	43.8	43.8	32.7	11.9	17.5	28.3
	70	99.0	99.0	98.5	42.4	42.4	28.1	14.9	21.3	30.2
	80	99.3	99.3	99.0	35.5	33.1	24.8	16.6	28.0	41.2
	90	99.5	99.5	99.5	22.1	22.1	22.1	21.5	33.4	45.9

area (m^2); t , the operating time (h); F_w , F_D and P_w , P_D , respectively, the mass fractions of water and DMF, in the feed and in the permeate.

A good PV membrane should have high flux and separation selectivity with a long-term mechanical stability to maintain its permselectivity under the operating conditions. Since a trade-off between flux and separation selectivity exists, efforts have been made to achieve high fluxes and separation selectivities simultaneously. In PV separation studies, sorption (a thermodynamic phenomenon) depends on the solubility parameters of the polymer and the permeant molecule. But diffusion (a kinetic process) depends on the size, shape, and molecular mass of the permeants. When both sorption and diffusion are favorable to a given component, a high membrane permselectivity is observed. If either of the two processes is unfavorable to a given liquid for any membrane,

then poor permselectivity results. Thus, sorption and diffusion are extremely important in judging the PV performance of a membrane. Other factors like membrane swelling and membrane morphology also affect the PV separation since flux and selectivity depend on these parameters. In the present study, both the probe mixtures are polar in nature and separation is achieved by increasing the hydrophilicity of PVA by grafting with AAm and it is found that the grafted copolymeric membranes are more permeable to water than to DMF.

Total flux and selectivity results as a function of the amount of water in the feed and permeate mixtures are presented in Table I. In the case of PVA at 25°C, when the amount of water varies between 10 and 90 mass % in the feed mixture, we obtain 66–99% water in the permeate side. However, with both PVA-1 and PVA-2 membranes,

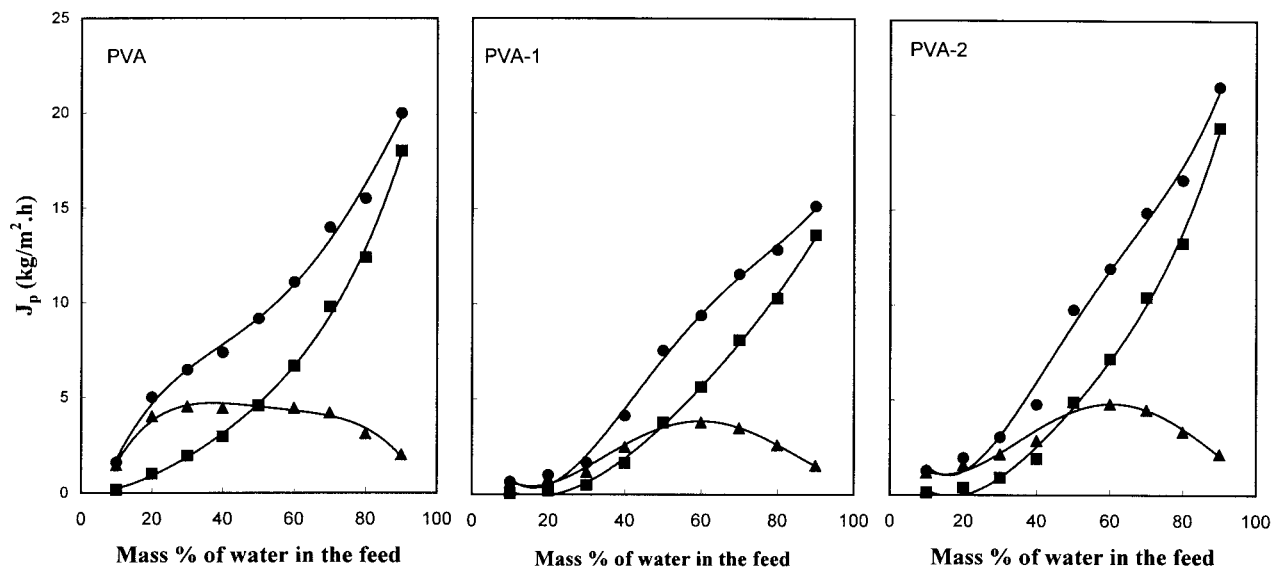


Figure 1 Permeation flux versus mass percent of water in the feed at 25°C: (●) total permeation flux; (■) water flux; (△) DMF flux.

water in the permeate is considerably higher (85%), even at lower amounts of water in the feed. With an increase in temperature, the amount of water in the permeate decreases because of the increased free volume due to increased intersegmental movement of the polymer chains. But the decrease is less in the case of PVA-1 and PVA-2 membranes when compared to PVA. This clearly indicates that the graft copolymer membranes are more selective for water than for DMF. This is also supported by an increase in selectivity of the copolymer membranes over that of the neat PVA membrane. Selectivity increases with an increase in the percentage grafting, but decreases with an increase in the amount of water in the feed mixture; this is because the increased swelling creates more free volume. A maximum selectivity is observed at 50 mass % of water in the feed mixture for the PVA membrane, whereas for the PVA-1 and PVA-2 membranes, it is at 90% and 50 mass % of water in the feed. Selectivity decreases with increasing temperature, but a reverse trend is observed for the flux values, which increase with increasing temperature.

Figure 1 displays the dependence of the total permeation flux as well as those of water and DMF on the mass percent of water in the feed. For all the membranes, total flux is higher than those of water and DMF; the total flux values increase substantially with an increasing amount of water in the feed mixture. This is attributed to the hydrogen-bond-type interactions between water

molecules and the membrane material. However, the flux of DMF reaches an optimum value up to 50% of water in the feed mixture and later it decreases. The total and water flux values for the PVA-2 membrane are higher than are those of PVA and PVA-1. This is probably because, at a higher amount of AAm (93%) in the grafted membrane (PVA-2), more of the hydrophilic free amide groups are available for interaction with the permeant molecules, thereby increasing the flux values. On the other hand, lower flux values exhibited by the PVA-1 membrane (49%) are due to the lesser number of available free amide groups. At a lower percentage of grafting, there is an increase in the amount of branching rather than an increase in the branching chain length.¹¹ Also, at lower grafting, AAm might act as a crosslinking agent, thus decreasing the permeation flux. The overall increase in the permeation flux with increasing water content in the feed is attributed to a selective interaction between water molecules and the hydrophilic membranes, leading to an increased total permeation flux due to an easier transport of water molecules. In all cases, the mass percent of water inside the membranes is slightly higher than in the feed mixture, further suggesting a higher water selectivity of the membranes. Unfortunately, we cannot compare our data with the literature values as no previous attempts have been made using these membranes for the PV separation of water-DMF mixtures.

Most of the crosslinked polymers tend to swell in the presence of polar liquids due to extensive interactions. A coupling effect between thermodynamic swelling and diffusion was studied earlier.¹² Therefore, PV performance of a membrane depends upon the thermodynamic swelling as well as the liquid diffusion through the polymeric membrane. Swelling results of all the three membranes are displayed in Figure 2. The degree of swelling is higher for PVA-2 and lower for PVA. Intermediate swelling is observed for PVA-1. This trend follows that swelling increases with an increasing degree of grafting and also due to an overall increase in the hydrophilicity of the PVA-g-AAm membranes. Using swelling data from the crosslinked matrices, one can estimate the membrane-solvent interaction parameter, χ_{ip} , from a knowledge of the solubility parameter, δ_p , of the polymer (or copolymer) along with that of the probe solvent, δ_s . The interaction between a polymer and a solvent will be higher when these values become closer. However, large differences in the values of the solubility parameter of the polymer, δ_p , and the solvent, δ_s , lead to lesser interactions between them.

The values of χ_{ip} were calculated using following equation¹³:

$$\chi_{ip} = 0.34 + \frac{V_i(\delta_s - \delta_p)^2}{RT} \quad (5)$$

where R is the gas constant, and T , the temperature in Kelvin. The δ_p was determined^{14,15} by

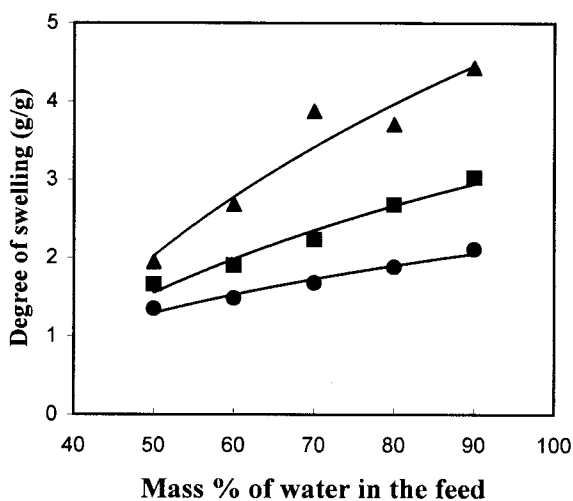


Figure 2 Degree of swelling versus mass percent of water in the feed: (●) PVA, (■) PVA-1, and (△) PVA-2 at 25°C.

Table II Solubility Parameter of Polymer [δ_p , (cal/cm³)^{1/2}], Interaction Parameter (χ_{ip}) of Water, and DMF with Membranes

Membrane	χ_{ip} for	
	Water	DMF
PVA	0.5318	3.5571
PVA-1	0.4491	2.7607
PVA-2	0.4418	2.6833

calculating the bulk modulus, B , as $B = 8.04 \times \delta_p^2$, where $B = u^2 d_p [(1 + \nu)/3(1 - \nu)]$ was determined by measuring the speed of sound, u , and density, d_p , of a 2 wt % polymer solution at 25°C using an interferometer (Mittal Enterprises, New Delhi, India, Model M-84) and a pycnometer, respectively. Poisson's ratio, ν , of the polymer solution used was 0.35. The χ_{ip} data presented in Table II indicate that the interaction between the water and the polymer is higher with graft copolymers than with PVA. In the case of graft copolymers, interaction of water is higher than that of DMF and, hence, water selectivity is higher. Thus, the interaction of water increases with increase in the grafting, but a reverse tendency is observed for DMF.

The dependence of separation selectivity on the mass percent feed water for the three membranes at the three temperatures is shown in Figure 3. The separation selectivity decreases with increasing temperature over the entire feed composition of water for all the membranes. This observation is quite opposite to that observed for the permeation flux, which increased with increasing temperature. From an observation of temperature dependence of $\alpha_{W/D}$, it is noticed that separation selectivity increases to 40–50 mass % of water in the feed and then decreases. This decrease in separation selectivity with an increase in temperature is due to an enlarged free volume within the membrane matrix due to an intersegmental movement, thereby facilitating the transport of feed mixture molecules.

The results of the PSI for different membranes and at different temperatures are displayed in Figure 4. It is observed that PSI values increase with increasing temperature to 60 mass % of water in the feed, and beyond which, a decline is observed in all cases. The PSI values increase with increase in the grafting of the membranes.

Diffusion coefficients, D_i , of the migrating species through the barrier materials, assumed to be

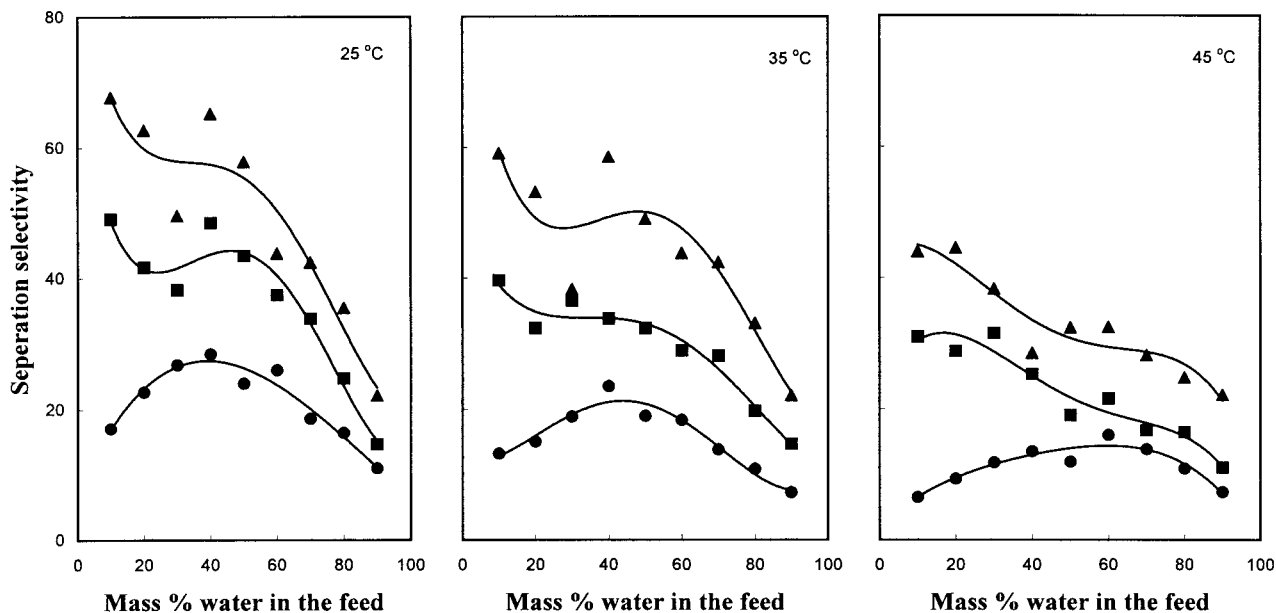


Figure 3 Separation selectivity versus mass percent of water in the feed for different membranes at (●) 25°C, (■) 35°C, and (△) 45°C.

constant across the effective membrane thickness, h , were calculated using¹⁶

$$J_i = P_i [p_{i(\text{feed})} - p_{i(\text{permeate})}] = \frac{D_i}{h} [C_{i(\text{feed})} - C_{i(\text{permeate})}] \quad (6)$$

Here, $C_{i(\text{feed})}$ and $C_{i(\text{permeate})}$ are, respectively, the concentration of DMF or water in the feed and in

the permeate. The computed values of D_i (where subscript i stands for water or DMF) are presented in Table III. Water diffusion increases continuously with an increasing amount of water in the feed for all the membranes at all the temperatures, but diffusion of DMF follows an opposite trend. Water diffusion follows the same trend as those of flux values discussed before, that is, the D 's of water for PVA and PVA-2 membranes are

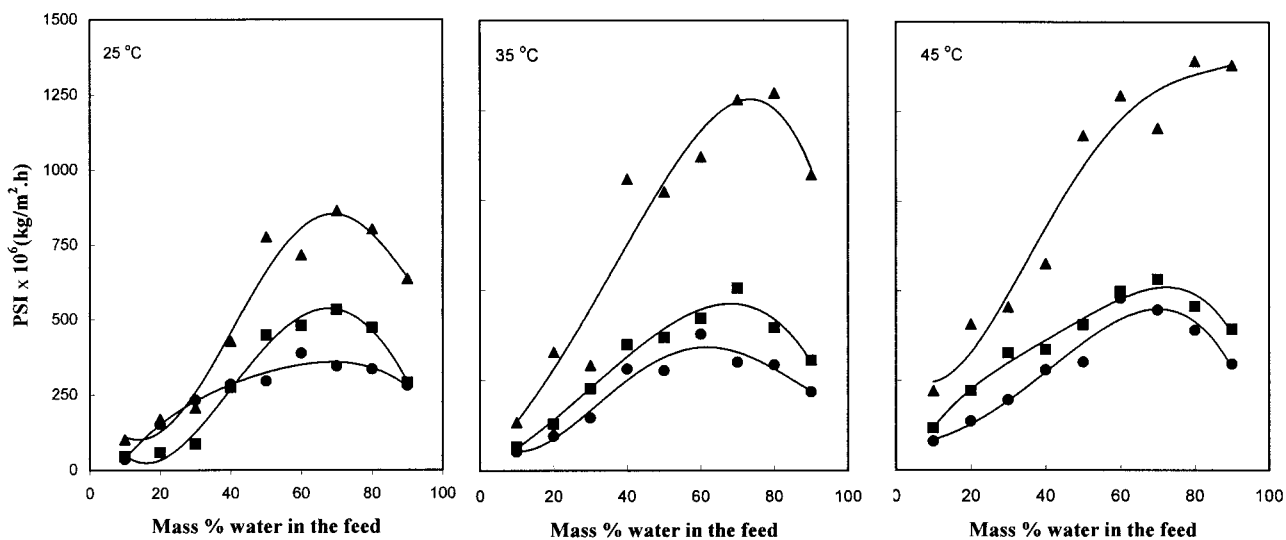


Figure 4 PSI versus mass percent of water in the feed for (●) PVA, (■) PVA-1, and (△) PVA-2 at (A) 25°C, (B) 35°C, and (C) 45°C.

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

Membrane	Water in Feed (%)	$D_{\text{water}} \times 10^5$ (cm ² /s)			$D_{\text{DMF}} \times 10^5$ (cm ² /s)		
		25°C	35°C	45°C	25°C	35°C	45°C
PVA	10	0.40	1.03	5.50	3.63	9.27	49.53
	20	2.16	2.78	6.89	8.63	11.13	34.31
	30	4.37	4.99	12.20	10.20	11.65	24.84
	40	7.48	11.11	21.46	11.27	16.66	32.20
	50	14.00	20.56	39.27	13.95	20.56	51.44
	60	24.86	42.91	63.86	16.57	28.61	42.58
	70	49.42	72.87	108.1	21.18	31.23	46.33
	80	93.95	160.9	214.1	23.49	40.23	53.52
	90	280.1	440.2	597.6	31.12	48.91	66.39
PVA-1	10	0.13	0.29	0.70	15.47	21.78	33.76
	20	0.41	1.43	2.82	10.28	43.71	98.07
	30	1.09	3.59	6.11	6.75	22.35	38.95
	40	4.06	9.16	12.20	9.37	21.42	28.94
	50	11.05	15.01	23.86	11.05	15.01	23.86
	60	20.51	28.78	39.25	9.00	12.54	16.98
	70	39.47	54.95	70.91	7.07	9.80	12.38
	80	75.88	108.4	125.7	4.56	6.45	7.41
	90	206.4	260.3	372.2	2.38	3.00	4.18
PVA-2	10	0.24	0.45	0.84	46.30	54.43	79.25
	20	0.74	2.07	3.13	15.66	46.53	76.42
	30	1.95	4.38	6.83	11.71	27.08	42.20
	40	4.62	11.75	18.27	10.59	27.02	43.06
	50	14.14	20.14	38.03	14.14	20.14	38.04
	60	26.05	38.08	62.53	11.42	16.71	27.31
	70	50.31	72.01	103.7	9.06	12.85	18.49
	80	96.40	162.9	242.7	5.87	9.89	14.59
	90	285.4	442.3	608.5	3.37	5.22	7.18

higher than for PVA-1. Wide variations in the diffusion values for both water and DMF are observed at different mass percent of water in the feed. For instance, with PVA, D_i values of water (at >50 mass % water in the feed) are higher than are those observed for both PVA-1 and PVA-2 membranes. However, at >50 mass % feed water, D_i values for PVA-2 are higher than for the PVA-1 membrane. The D_i values of the PVA membrane at higher water content in the feed are somewhat comparable or slightly lower than are those observed for PVA-2. This dependence is similar to the permeation flux values discussed before. However, the observed lower D_i values for the grafted membranes are due to the hindered diffusion in a more dense or tightly crosslinked matrix of PVA-1 or PVA-2 than in the neat PVA membrane.

From the temperature dependence of J_p , α_{sep} , and D_i , we calculated the Arrhenius parameters by the least-squares method:

$$A = A_0 \exp(-E_A/RT) \quad (7)$$

where $A = J_p$ or D_i and $A_0 = J_{p0}$ or D_{i0} . The values of E_A refer to the activation energy for permeation, E_p or diffusion, E_D ; RT is the conventional energy term. The driving force in molecular transport is the concentration gradient resulting from a difference in 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 vapor pressure at the permeate side is not affected. This results in an increase of driving force with increasing temperature. For these reasons, the amount of DMF in the permeate decreases; nevertheless, the total permeation flux as well as that of water flux will increase.

Arrhenius plots of $\log J_p$ or $\log D_i$ versus $1/T$ are presented in Figure 5. In all cases, straight lines are obtained, signifying the validity of the

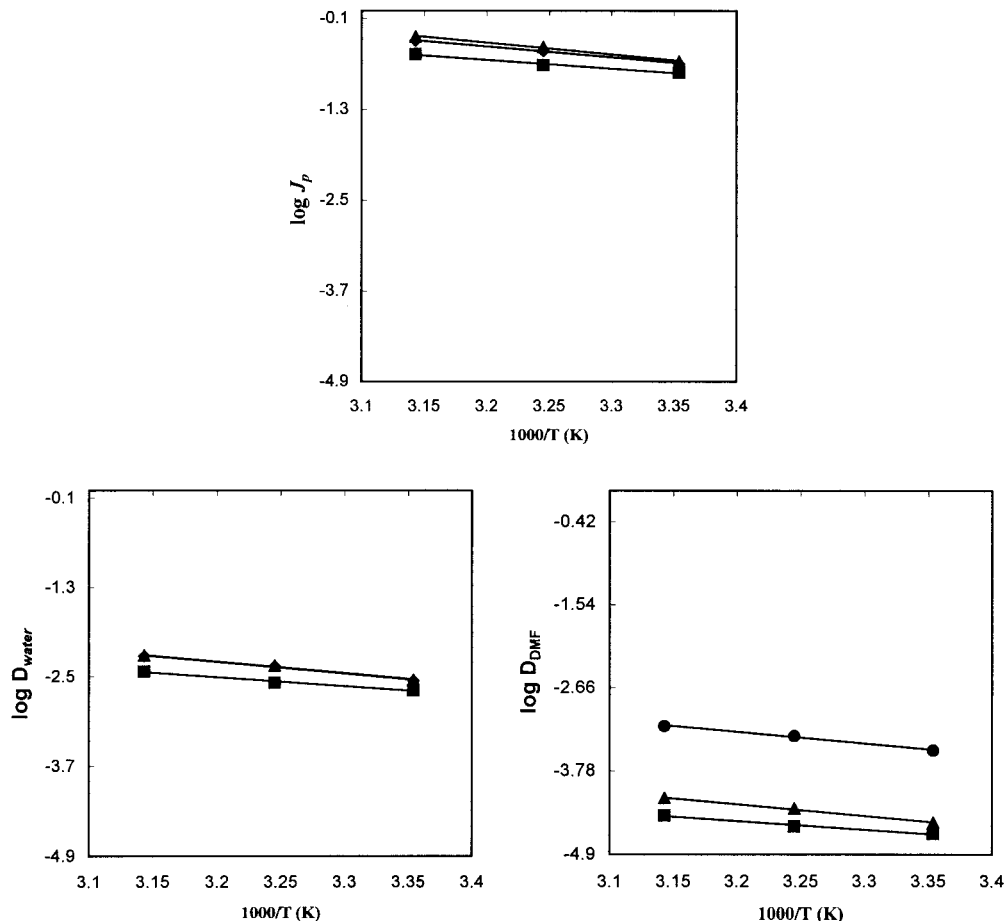


Figure 5 Arrhenius plots of (A) $\log J_p$ versus $1/T$, (B) $\log D_{\text{water}}$ versus $1/T$, and (C) $\log D_{\text{DMF}}$ versus $1/T$ for (●) PVA, (■) PVA-1, and (△) PVA-2 membranes.

Arrhenius equation. The results of E_P or E_D were calculated from the slopes of the lines by the least-squares method. These data are presented in Table IV. The E_P values for PVA range between 28 and 81 kJ/mol. For PVA-1, the E_P values range between 19 and 63 kJ/mol, whereas for PVA-2 these values are between 28 and 56 kJ/mol, but the E_P values do not show any systematic variation with the amount of water in the feed. Since both PVA and graft copolymers are semicrystalline in nature, the calculated E_P values are less than are those observed for the rubbery polymeric membranes.¹⁷

By taking the values of E_P and E_D for water, we computed the heat of sorption, ΔH_S , or water permeation as $\Delta H_S = E_P - E_D$. Table IV lists the values of E_D , E_P , and ΔH_S for water transport. The E_P and ΔH_S values of the PVA, PVA-1, and PVA-2 membranes increase with a decreasing amount of water in the feed. However, no systematic dependence of these parameters is observed

with the type of membrane used. The results of ΔH_S in all cases are negative, indicating an exothermic sorption process. The ΔH_S values depend upon the nature of the membrane used, that is, these values increase with increasing grafting.

The temperature dependency of the separation selectivity was also investigated using the relationship proposed by Ping et al.¹⁸:

$$Y_w = \frac{1}{1 + (J_{0,D}/J_{0,W}) \exp(-(E_D + E_W)/RT)} \quad (8)$$

where Y_w is the mass percent of water in the permeate; J_W and J_D , the permeation fluxes of water and DMF, respectively; and E_W and E_D , the Arrhenius activation energies of water and DMF, respectively, at the average energy level. A positive value of $E_D - E_W$ indicates that separation selectivity decreases with an increase in the temperature¹⁸ and a negative value indicates an in-

Table IV Results of Activation Energy (E_P , in kJ/mol) for Total Permeation, Activation Energy (E_D , kJ/mol) for Diffusion, and Heat of Sorption (ΔH_S , kJ/mol)

F_W (%)	$E_{P(\text{total})}$			$E_{D(\text{water})}$			$\Delta H_{S(\text{water})}$		
	PVA	PVA-1	PVA-2	PVA	PVA-1	PVA-2	PVA	PVA-1	PVA-2
9.99	81.2	63.1	48.5	102.8	67.0	50.4	-21.67	-3.909	-1.873
20	40.2	74.7	55.8	40.2	76.7	57.1	-5.205	-1.975	-1.223
30	34.3	67.4	48.7	34.3	68.1	49.5	-5.795	-0.720	-0.773
40	37.5	41.8	52.5	37.5	43.6	54.4	-3.916	-1.837	-1.935
50	37.4	27.9	37.8	37.4	30.3	38.9	-3.334	-2.330	-1.070
60	35.6	24.0	34.0	35.6	25.6	34.5	-1.617	-1.564	-0.512
70	29.8	21.4	27.8	29.8	23.1	28.5	-1.090	-1.741	-0.681
80	30.9	19.0	35.8	30.9	20.0	36.4	-1.653	-1.051	-0.614
90	27.6	22.1	29.9	27.7	23.3	29.9	-2.276	-1.208	-0.001

crease in separation selectivity with an increase in temperature. The calculated values of $E_D - E_W$ are presented in Table V. In general, these values are positive, further supporting that separation selectivity decreases with increasing temperature. However, for 10 mass % of water in the feed, the values of $E_D - E_W$ are negative at 25°C; also, at 35 and 45°C, the magnitude of $E_D - E_W$ is negative for the PVA membrane. Similarly, with PVA-1 and PVA-2 membranes at 10 mass % of water in the feed mixture, negative values are observed for $E_D - E_W$, indicating a higher activation energy for water than for DMF. This is likely at the lower content of water due to the preferential solvation of water molecules onto the grafted copolymer membranes than with PVA. The $E_D - E_W$ values decrease with increasing temperature up to 50 mass % of water in the feed in all cases. However, at a higher amount of water, a reverse trend is observed.

Table V Activation Energy Difference ($E_D - E_W$) Calculated from Eq. (8) for Different Membranes

Water in Feed (Mass Percent)	PVA	PVA-1	PVA-2
10	17.41	3.40	1.63
20	3.92	1.50	0.95
30	3.81	0.48	0.52
40	2.12	1.07	1.12
50	1.56	1.12	0.52
60	0.61	0.61	0.20
70	0.31	0.50	0.20
80	0.30	0.20	0.12
90	0.20	0.10	0.00

CONCLUSIONS

PVA and its grafted membranes with AAm are found to be efficient in the PV separation of water-DMF mixtures. These membranes are more selective to water than to DMF. However, selectivity depends upon the degree of swelling as well as the membrane grafting. Separation selectivity values increase considerably with an increase in percent grafting. However, flux values did not show any considerable change with the extent of grafting. The temperature dependency of the permeation flux, diffusion coefficient, and separation selectivity followed the Arrhenius trend.

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REFERENCES

1. Aminabhavi, T. M.; Khinnavar, R. S.; Harogopad, S. B.; Aithal, U. S.; Nguyen, Q. T.; Hansen, K. C. *J Macromol Sci-Rev Macromol Chem Phys C* 1994, 43, 139.
2. Shieh, J. J.; Huang, R. Y. M. *J Membr Sci* 1998, 148, 243.
3. Djebbar, M. K.; Nguyen, Q. T.; Clement, R.; Germain, Y. *J Membr Sci* 1998, 146, 125.
4. Ren, J.; Jiang, C. *Sep Sci Technol* 1998, 33, 517.
5. Naik, H. G.; Aminabhavi, T. M. *J Appl Polym Sci*, in press.
6. Huang, R. Y. M.; Rhim, J. W. *Polym Int* 1993, 30, 123.
7. Chiang, W.-Y.; Hu, C.-M. *J Appl Polym Sci* 1991, 43, 2005.

8. Liang, L.; Ruckenstein, E. *J Membr Sci* 1995, 106, 167.
9. Bruschke, H. E. A.; Tusel, G. F.; Rautenbach, R. *Pervaporation Membranes: Application in the Chemical Process Industry*; ACS Symposium Series 281; American Chemical Society: Washington, DC, 1985; p 467.
10. Bruschke, H. E. A. *Ger Patent DE 3 220 570 A1*, 1983.
11. Mino, G.; Kaizerman, S. *Ger Patent 1 082 408*, May 25, 1960.
12. Aminabhavi, T. M.; Naik, H. G. *J Haz Mater* 1998, 60, 175.
13. Hildebrand, J. H.; Scott, R. L. *The Solubility of Nonelectrolytes*, 3rd ed.; Reinhold: New York, 1950.
14. Deslandes, N.; Bellenger, V.; Jaffiol, F.; Verdu, J. *J Appl Polym Sci* 1998, 69, 2663.
15. Bellenger, V. J.; Kaltenecker-Commereon, J.; Verdu, J. *Polymer* 1997, 38, 4175.
16. Kusumocahyo, S. P.; Sudoh, M. *J Membr Sci* 1999, 161, 77.
17. Harogoppad, S. B.; Aminabhavi, T. M. *Macromolecules* 1991, 24, 2598.
18. Ping, Z. H.; Nguyen, Q. T.; Clement, R.; Neel, J. *J Membr Sci* 1990, 48, 296.