

Polyacrylonitrile-g-Poly(Vinyl Alcohol) Membranes for the Pervaporation Separation of Dimethyl Formamide and Water Mixtures

Mahaveer D. Kurkuri, Tejraj M. Aminabhavi

Center of Excellence in Polymer Science, Karnatak University, Dharwad 580 003, India

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ABSTRACT: Poly(vinyl alcohol) as well as its grafted copolymer membranes with polyacrylonitrile (PAN-g-PVA) were prepared and used to separate water and dimethyl formamide mixtures by the pervaporation technique. The three following membranes were prepared: (1) pure PVA; (2) 46% grafted PAN-g-PVA; and (3) 93% grafted PAN-g-PVA. Pervaporation separation experiments were carried out at 25°C for the feed mixture containing 10 to 90% water. By use of the transport data, permeation flux, separation selectivity, swelling index, and diffusion coefficients have been calculated. By increasing the grafting of the membrane,

flux decreased, whereas separation selectivity increased slightly over that of pure PVA membrane. Arrhenius activation parameters for transport processes were calculated for 10 mass % water containing feed mixture by using flux and diffusion data obtained at 25, 35, and 45°C. Transport parameters were discussed in terms of sorption-diffusion principles. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 4091–4097, 2004

Key words: pervaporation; diffusion; graft copolymer; selectivity; membranes; swelling

INTRODUCTION

Pervaporation (PV) separation has received much attention in recent years because it is considered to be an energy-efficient and environmentally clean process to separate azeotropes and aqueous-organic mixtures.^{1–5} Simultaneous enhancement of both selectivity and flux has been a challenging task in PV separation problems. To achieve this goal, many efforts have been made in the literature^{6–9} to fabricate or modify different types of membranes. In our earlier articles,^{10–15} several different types of membranes were prepared and used in the PV separation of aqueous-organic mixtures. These membranes were modified to achieve an optimum combination of flux and selectivity.

In an effort to address the separation of water-organic mixtures, we present here the procedure to synthesize grafted copolymer membranes of polyacrylonitrile (PAN) and poly(vinyl alcohol) (PVA) [i.e., (PAN-g-PVA)] and use them in the PV separation of water–dimethyl formamide (DMF) mixtures. DMF is

an important solvent used in many industrial sectors, and hence, it is useful to develop alternative methods of their separation. Membranes developed in this study are novel and are more highly selective to water than DMF. Membrane performance was studied at 25, 35, and 45°C for 10 mass % water-containing feed mixtures. From these data, Arrhenius activation parameters have been calculated and results are explained in terms of sorption-diffusion principles.

EXPERIMENTAL

Materials

PVA (mol. wt. 125,000), analytical reagent grade acrylonitrile (AN), laboratory reagent grade glutaraldehyde (25% in water), analytical reagent grade samples of DMF, ceric ammonium nitrate (CAN), dimethyl sulfoxide (DMSO), hydrochloric acid, and acetone were all purchased from S. D. Fine Chemicals Ltd. (Mumbai, India). All the chemicals were used without further purification. Double-distilled deionized water was used throughout the study.

Grafting procedure

In a three-necked round-bottom flask fitted with a condenser, gas inlet, and a thermometer, about 10 g PVA was dissolved in 100 mL DMSO at 60°C under constant stirring in a nitrogen atmosphere. After cooling the solution, AN was added while stirring. To this, 5 mL 0.1M CAN^{16,17} was added and the reaction mix-

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Correspondence to: T. M. Aminabhavi (aminabhavi@yahoo.com).

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ture was maintained between 50 and 60°C for 4 h. The polymer was precipitated by adding excess acetone, filtered under suction, and dried in a vacuum oven at 60°C. Two copolymers with % grafting of 46 and 93 (designated, respectively, as PVA-1 and PVA-2) were prepared by taking 5 and 10 g AN; 100% grafting efficiency was achieved with 92% conversion of AN.

Membrane preparation

Pure PVA, PVA-1, and PVA-2 polymers (10 g each) were dissolved separately in 100 mL DMSO at 60°C with constant stirring under a slow stream of nitrogen gas and the solution was cooled to room temperature. To these polymer solutions, 0.0035 mol glutaraldehyde and 0.5 mL 1N HCl were added and stirred for 30 min to achieve an effective crosslinking of the copolymer. Films were cast on clean glass plates by uniformly pouring the polymer solutions under controlled humidity conditions. Membranes were dried at room temperature in a dust-free atmosphere and cured at 60°C in an oven. The dried membranes were peeled off from the glass plate and washed with water repeatedly to remove excess glutaraldehyde and HCl and then allowed to dry at room temperature for 24 h.

Characterization of copolymers

Copolymers were characterized for grafting by FTIR spectra scanned in the range of 4000–400 cm^{-1} by using KBr pellets on a Nicolet spectrometer (Model, Impact 410, USA). FTIR spectra of pure PVA and grafted copolymer are shown in Figure 1. A broad band appearing at $\sim 3382 \text{ cm}^{-1}$ corresponds to —OH stretching vibrations of hydroxyl groups of PVA; the peak at 2938 cm^{-1} is assigned to aliphatic —CH stretching vibrations. A strong band appearing at $\sim 2246 \text{ cm}^{-1}$ corresponds to —CN stretching vibrations of acrylonitrile,¹⁸ thus confirming grafting reaction between PAN and PVA.

Swelling experiments

Swelling experiments were performed in water and DMF mixtures of different compositions at $25 \pm 0.5^\circ\text{C}$ in an electronically controlled oven (WTB Binder, Model, BD-53, Germany) by following the procedures published earlier.¹⁹ Circularly cut (surface area = 9.08 cm^2) disk-shaped membranes were kept in a desiccator over anhydrous calcium chloride maintained at 25°C for 48 h before use. The initial mass of membranes was taken on a single-pan digital microbalance (Model AE 240, Switzerland), sensitive to $\pm 0.01 \text{ mg}$. Polymer samples were placed inside the air-tight test bottles containing different mixtures of water and DMF. Test bottles were placed in an oven maintained at 25°C . After 24 h (i.e., after complete attainment of

equilibrium), membranes were removed and surface-adhered solvent drops were removed by using soft filter papers and weighed immediately. Degree of swelling (DS) was calculated by taking the ratio of equilibrium mass, W_∞ , to that of dry mass, W_0 , of the membrane by using

$$\text{DS} = \frac{W_\infty}{W_0} \quad (1)$$

Pervaporation experiments

PV experiments were carried out for water–DMF mixtures by using the apparatus designed indigenously.^{13,14} The composition of DMF was varied from 10 to 90 mass % at 25°C . The temperature was controlled to the desired value by a calibrated thermometer immersed in the jacket and stirred continuously. The cut membrane (surface area = 32.4 cm^2) was placed on the porous stainless steel support and fixed tightly with nuts. Nearly 30 min was allowed for the feed mixture to attain equilibrium. Water was circulated around the PV cell to maintain a constant temperature and vacuum (10 Pa) was applied at the permeate side. Permeate was collected in glass tubes (trappers) immersed in liquid nitrogen. Cold traps containing permeate were allowed to attain room temperature and then were removed and weighed to determine the flux. Permeate composition was measured at 30°C by using an Abbe refractometer (Atago, Model 3T, Japan). From these data, separation selectivity, α_{sep} , was calculated using

$$\alpha_{\text{sep}} = \frac{P_W/P_{\text{DMF}}}{F_W/F_{\text{DMF}}} \quad (2)$$

where P_W and P_{DMF} are mass % of water and DMF, respectively, in the permeate; F_W and F_{DMF} are mass % of water and DMF in the feed, respectively. Permeation flux, was calculated by using

$$J_P = \frac{W_P}{At} \quad (3)$$

where W_P is mass of permeate, A is area of the membrane in contact with the feed mixture, and t is time. Results of pervaporation flux and separation selectivity for different mass % of water in the feed mixture at 25°C are presented in Table I.

RESULTS AND DISCUSSION

Transport in PV experiments can be understood in terms of sorption and diffusion of liquids through the barrier membranes.²⁰ When liquids permeate through the swollen polymeric membrane, there will be a cou-

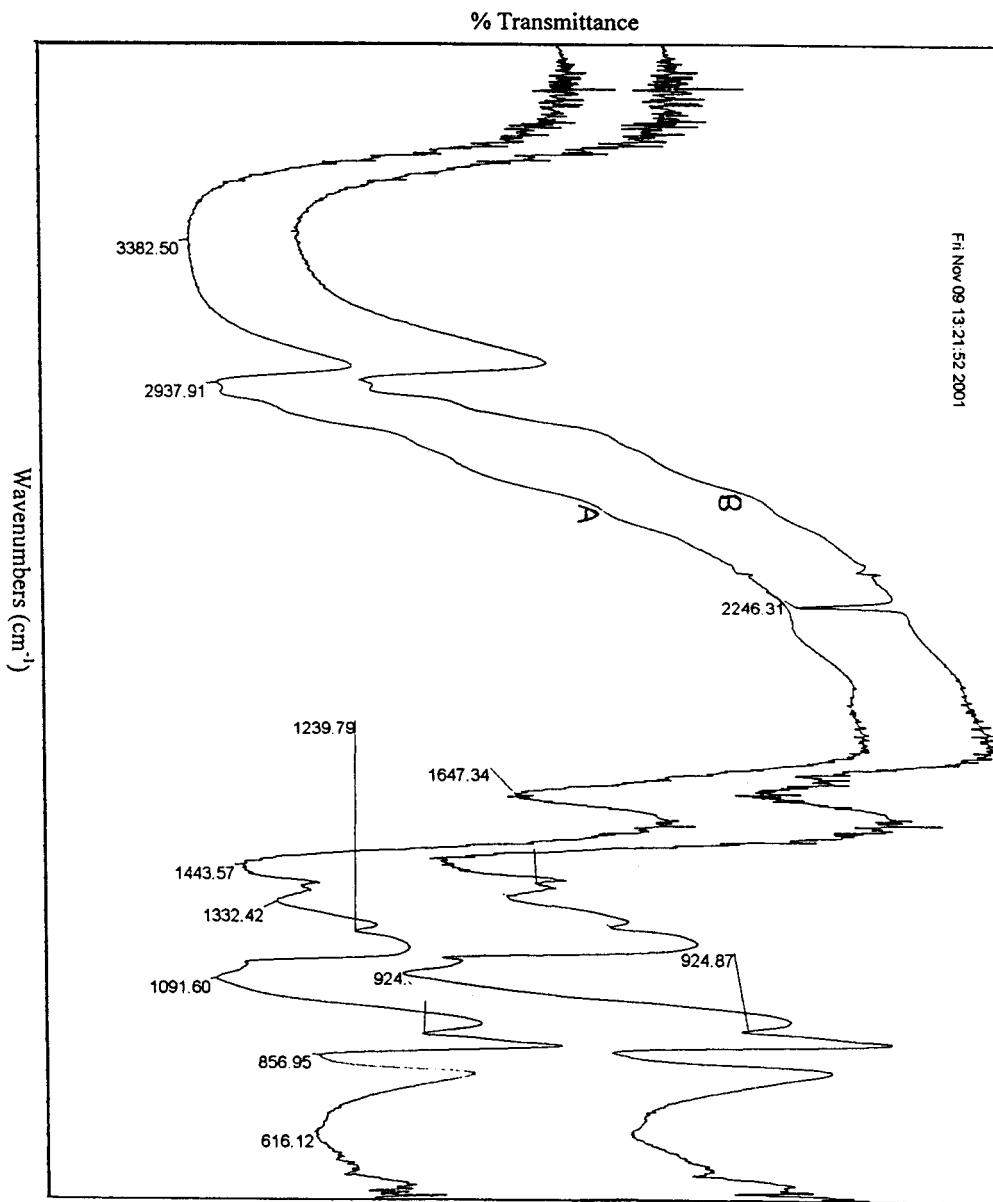


Figure 1 FTIR spectra of pure PVA (A) and PAN-g-PVA (B).

pling of fluxes facilitating permeation, thereby affecting the membrane performance. Figure 2 displays the dependence of degree of swelling on mass % of water in the feed mixtures. Degree of swelling increases with increasing mass % of water in the feed for all the membranes. Degree of swelling is higher for pure PVA when compared to PVA-1 and PVA-2 membranes; the lowest DS is observed for PVA-2 membrane, indicating that degree of swelling decreases with increasing % grafting of the copolymer. This is due to an increase in hydrophobic character of the membrane with increasing grafting.

Total permeation flux, J_p , for PVA is higher than those observed for the grafted membranes (PVA-1 and PVA-2). A decreasing trend in J_p with increasing co-

TABLE I
Pervaporation Flux and Separation Selectivity for Different Mass % of Water in the Feed Mixture at 25°C

Mass % water	$J_p \cdot 10^2$ (kg/m ² h)			α_{sep}		
	PVA	PVA-1	PVA-2	PVA	PVA-1	PVA-2
10	1.6	0.9	0.18	17.1	18.1	21.2
20	5.0	4.2	1.0	22.7	20.3	24.0
30	6.5	3.3	2.2	26.8	27.1	29.4
40	7.4	5.5	1.8	28.5	30.0	31.1
50	9.2	9.7	5.3	24.0	28.8	34.1
60	11.1	9.1	7.5	26.0	32.1	33.4
70	14.0	12.3	7.3	18.2	30.1	36.7
80	15.5	12.3	10.8	16.4	24.5	31.2
90	20.0	16.4	9.3	11.0	15.0	23.9

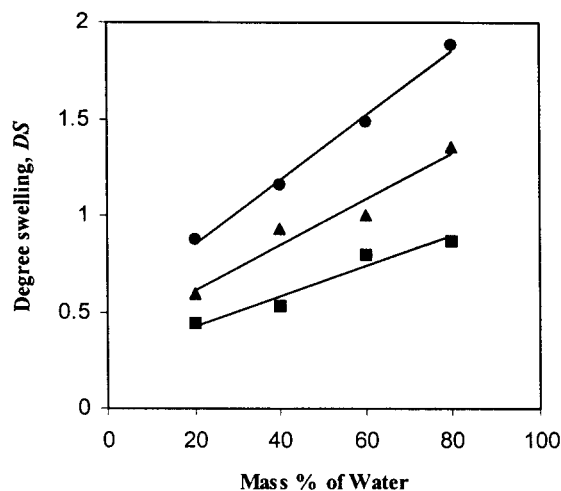


Figure 2 Degree of swelling versus mass % of water in the feed mixture at 25°C. (\bullet) PVA, (\blacktriangle) PVA-1, (\blacksquare) PVA-2.

polymer grafting could be due to increased hydrophobicity of the copolymer resulting in lower water flux. As the mass % of water in the feed mixture increases, hydrophilic interactions between water molecules and membrane will also increase and hence, total flux increases systematically (see Table I). Results of water flux versus mass % of water in the feed for all the membranes are displayed in Figure 3.

Values of α_{sep} , also included in Table I, increase systematically from pure PVA to grafted membranes. The membrane selectivities are found to be optimum between 40 and 70 mass % of water containing feed mixture, and beyond 70 mass % of water in the feed, values of α_{sep} show decreasing trends. It is observed that α_{sep} is maximum at 40 mass % of water for PVA, whereas for PVA-1, maximum α_{sep} is observed at 60 mass % of water in the feed. The PVA-2 membrane exhibits maximum α_{sep} of 36.7 at 70 mass % of water

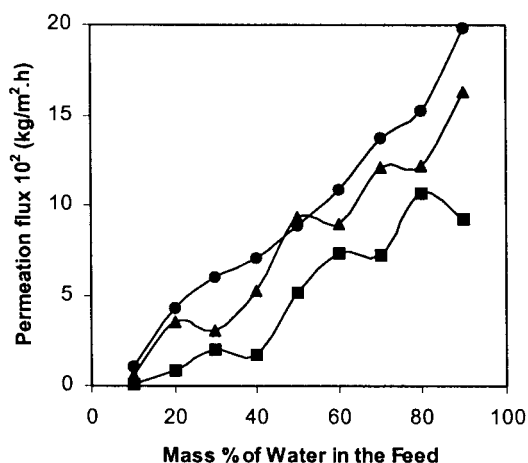


Figure 3 Permeation flux versus mass % of water in the feed mixture at 25°C. Symbols are the same as in Figure 2.

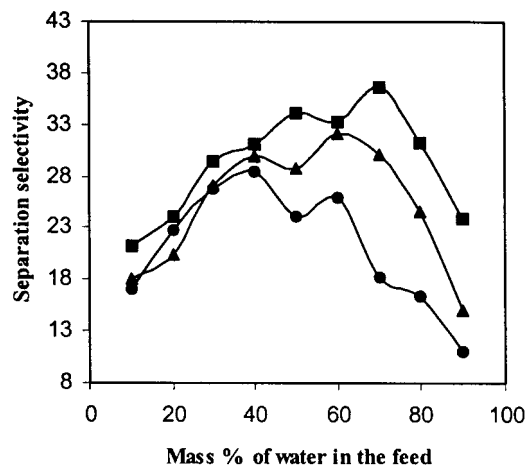


Figure 4 Separation selectivity versus mass % of water in the feed mixture at 25°C. Symbols are the same as in Figure 2.

in the feed mixture, indicating effect of polymer morphology on separation selectivity data. Results of separation selectivity displayed in Figure 4 exhibit convex type of trends for all the membranes. A comparison of the present α_{sep} values with the earlier data¹⁴ on water-DMF mixtures for PVA-grafted-acrylamide copolymer membranes indicates that the present α_{sep} and J_p values are somewhat lower.

Results of pervaporation flux of water and DMF as a function of mass % of water in the feed are presented at 25°C in Table II. For pure PVA membrane, water flux (J_w) increases systematically with increasing amount of water in the feed mixture, but for PVA-1 and PVA-2 membranes, flux values do not vary systematically with increasing amount of water in the feed. In general, there is an increase in water flux with increasing amount of water in the feed mixture. Similarly, flux values of DMF for all the membranes decrease with increasing amount of water in the feed, but such dependence is not very systematic. A comparison between flux data of water and DMF (Table II)

TABLE II
Pervaporation Flux for Water and DMF for Different Mass % of Water in Feed Mixture at 25°C

Mass % water	J_w 10^2 (kg/m ² ·h)			J_{DMF} 10^2 (kg/m ² ·h)		
	PVA	PVA-1	PVA-2	PVA	PVA-1	PVA-2
10	1.1	0.6	0.13	0.55	0.30	0.05
20	4.3	3.5	0.86	0.75	0.69	0.14
30	6.0	3.1	2.0	0.52	0.26	0.16
40	7.0	5.2	1.7	0.37	0.26	0.08
50	8.8	9.4	5.2	0.37	0.33	0.15
60	10.8	8.9	7.4	0.28	0.19	0.15
70	13.7	12.1	7.2	0.32	0.17	0.08
80	15.3	12.2	10.7	0.23	0.12	0.09
90	19.8	16.3	9.3	0.20	0.12	0.04

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

Temp. (°C)	J_P (10^2 (kg/m ² h))			α_{sep}		
	PVA	PVA-1	PVA-2	PVA	PVA-1	PVA-2
25	1.6	0.9	0.18	17.1	18.12	21.2
35	3.6	1.5	1.2	13.2	15.41	19.13
45	12.6	5.3	4.01	6.5	13.52	16.41

indicates that water has shown considerably higher flux than DMF, particularly at higher amounts of water in the feed. This indicates the water-selective nature of the membranes prepared.

Experimental PV data at 25, 35, and 45°C are presented in Table III. With increasing temperature, flux increases, whereas selectivity decreases for all the membranes. Flux decreases from pure PVA to PVA-1 and PVA-2 membranes for all temperatures, thus showing the effect of extent of grafting. On the other hand, α_{sep} values increase from pure PVA to PVA-1 and PVA-2 membranes for all temperatures. These results are in conformity with the findings of Neel et al.,²¹ who considered that selective diffusion in the dry region of the membrane at the downstream side is important to determine the overall membrane selectivity. Similarly, Mulder et al.²² interpreted the selectivity data as due to preferential sorption of one of the components in a binary mixture with the swollen polymer membrane at the upstream side. Indeed, the membranes of this study are preferentially more selective to water than DMF.

Results of enrichment factor, β , calculated from the relation C_W^P/C_W^F , where C_W^P and C_W^F are, respectively, the concentration of permeate and feed water, are presented in Figure 5. For all membranes, β values

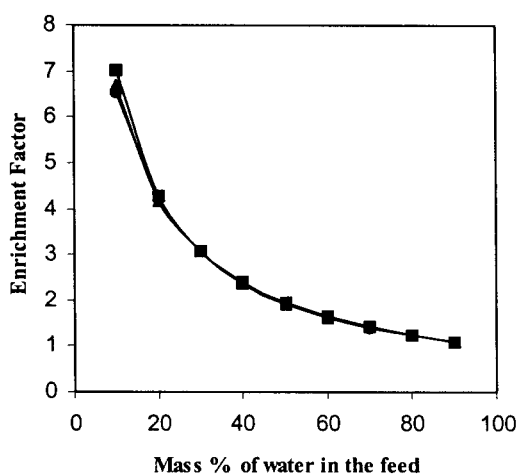


Figure 5 Enrichment factor (β) versus mass % of water in the feed mixture at 25°C. Symbols are the same as in Figure 2.

TABLE IV
Diffusion Coefficients of Water and DMF Calculated from Eq. 4 at 25°C

Mass % water	$D_W \times 10^9$ (m ² /s)			$D_{DMF} \times 10^9$ (m ² /s)		
	PVA	PVA-1	PVA-2	PVA	PVA-1	PVA-2
10	2.64	1.48	0.29	1.39	0.74	0.12
20	9.15	7.73	1.83	1.61	1.52	0.30
30	13.50	6.93	4.56	1.18	0.60	0.36
40	17.90	13.23	4.34	0.94	0.66	0.21
50	26.88	28.22	15.29	1.12	0.68	0.45
60	40.40	32.93	27.06	1.04	0.68	0.54
70	69.13	59.37	34.88	1.63	0.85	0.41
80	115.6	89.76	78.10	1.76	0.92	0.63
90	308.0	246.0	135.9	3.11	1.82	0.63

decrease steadily with increasing amount of water in the feed mixture. The β values are quite high at 10 mass % water containing DMF mixture. Molecular transport phenomenon in PV experiments depends upon sorption and diffusion of liquid molecules through barrier membranes and hence, attempts were made to compute diffusion coefficients, D_i , of the permeants across the effective membrane thickness, h , by using the Fick's relation given in the form²³

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

In the above equation, $C_i(\text{feed})$ and $C_i(\text{permeate})$ are, respectively, the concentration of liquid molecules at the membrane surfaces (i.e., feed and permeate sides). The concentration difference term used in eq. (4) was calculated by taking liquid concentration in a dimension of g/cm³. Computed values of D_i (where the subscript i stands for water or DMF) at 25°C are presented in Table IV. Values of D_W for water are quite higher than those observed for DMF for all the membranes at all the feed compositions, suggesting that membranes of this study are more water-selective than DMF. Because pure PVA is more hydrophilic than PVA-1 and PVA-2, diffusion coefficients of water and DMF are higher for pure PVA when compared to the grafted copolymer membranes; PVA-1 has higher diffusivity than PVA-2. Diffusion coefficients for 10 mass % of water in the feed mixture at different temperatures are presented in Table V. It may be noted that experimental determination of any composition lower than 10 mass % of water on the feed side was difficult to estimate by refractive index measurements, and hence, these experiments were not conducted. However, at present we are developing a gas chromatographic method to assess lower water containing permeate composition and this will be communicated in our forthcoming publications.

By increasing the amount of water, the membrane swells because of plasticization of the polymer matrix,

TABLE V
Diffusion Coefficients of Water and DMF Calculated from Eq. 4 at Different Temperatures for 10 Mass % of Water in the Feed Mixture

Temp. (°C)	$D_W \times 10^9$ (m ² /s)			$D_{DMF} \times 10^9$ (m ² /s)		
	PVA	PVA-1	PVA-2	PVA	PVA-1	PVA-2
25	2.64	1.48	0.29	1.39	0.74	0.12
35	6.06	2.50	1.97	4.12	1.46	9.27
45	23.15	8.90	6.64	3.20	5.93	3.64

thereby resulting in a coupling interaction between DMF and water molecules. At lower composition of water in the feed, there is a minimum coupling interaction and thus, diffusion coefficients increase with increasing water of the feed. In the present study, polymer being hydrophilic, it preferentially interacts with water molecules more than DMF. This leads to lower values of diffusion coefficients of DMF than water. As per the established facts, D_i for both water and DMF increase with increasing temperature.

Temperature-dependent permeation flux data (Table III) have been fitted to Arrhenius equation of the type,

$$J_P = J_{PO} \exp(-E_P/RT) \quad (5)$$

where E_P is activation energy for permeation, J_{PO} is permeation rate constant, R is the gas constant, and T is the temperature in Kelvin. If activation energy is positive, then permeation flux increases with increasing temperature. Arrhenius plots of $\log J_P$ versus $1000/T$ presented in Figure 6 are linear, from which E_P values were estimated. Similarly, apparent activation energy, E_D , for diffusion was calculated by fitting the temperature-dependent diffusivity data (Table V) to Arrhenius equation of the type

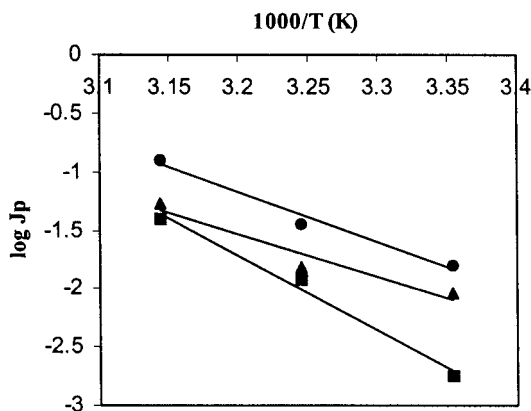


Figure 6 Arrhenius plot of $\log J_P$ versus $1000/T$ for 10 mass % of water in the feed mixture. Symbols are the same as in Figure 2.

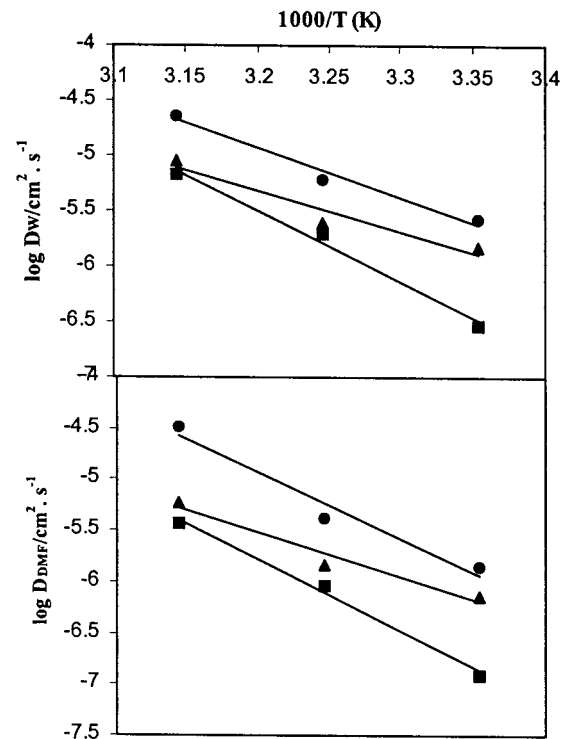


Figure 7 Arrhenius plot of $\log D_W$ and $\log D_{DMF}$ versus $1000/T$ for 10 mass % of water in the feed mixture. Symbols are the same as in Figure 2.

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

where i stands for water or DMF. Arrhenius plots of $\log D_i$ versus $1000/T$ for water and DMF are shown in Figure 7. The E_P and E_D values estimated by the method of least squares are given in Table VI. By using E_P and E_D values for water, heats of sorption, ΔH_S , were calculated as $\Delta H_S = E_P - E_D$; these data are also included in Table VI. The ΔH_S values are negative in all cases, suggesting endothermic sorption.

The temperature dependence of separation selectivity (Table III) was also analyzed by the equation proposed by Ping et al.²⁴ to estimate the activation parameters

$$Y_W = \frac{1}{1 + \left(\frac{J_{DMF}}{J_W}\right) \exp\left(\frac{-(E_{DMF} + E_W)}{RT}\right)} \quad (7)$$

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

Parameter	PVA	PVA-1	PVA-2
E_P (kJ/mol), eq. (5)	63.73	65.34	119.3
E_D (kJ/mol), eq. (6)	85.30	160.1	123.2
ΔH_S (kJ/mol)	-21.57	-94.78	-3.48
$E_{DMF} - E_W$ (kJ/mol)	37.83	11.55	10.10

Here, Y_W is water compositions in permeate, J_W and J_{DMF} are permeation fluxes; E_W and E_{DMF} are Arrhenius activation parameters for water and DMF, respectively, at the average energy level. A positive value of $(E_{DMF} - E_W)$ indicates that α_{sep} decreases with increasing temperature; negative values indicate that α_{sep} increases with increasing temperature.²⁵ In the present study, the values of $(E_{DMF} - E_W)$ are positive, indicating that α_{sep} decreases with increasing temperature, as can be seen in Table VI.

CONCLUSION

In this article, pervaporation separation studies have been made with the objective of separating water-DMF mixtures by employing polyacrylonitrile-grafted-poly(vinyl alcohol) membranes prepared by $Ce^{(IV)}$ -initiated free-radical polymerization. Performance of pure PVA membrane was compared with those of the grafted membranes. Membrane selectivity was dependent upon the degree of swelling as well as extent of grafting. Separation selectivity was better with increasing percentage of grafting. Diffusion, selectivity, flux, and swelling of the membranes all suggest the water-selective nature of the membranes prepared. Separation by distillation near 50 mass % mixture compositions is generally an easy task, but the range in which membrane is good (at 10 mass % of water or less) may need only one equilibrium plate for separation. Even though the main challenge of pervaporation lies in separating dilute regions of the mixtures, the membranes of this study should also perform well for breaking the azeotropes at lower water compositions of the mixture. Our efforts to study these effects have been successful, but are proprietary data due to patent rights.

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