

Sorption, Diffusion, and Swelling Characteristics of Sodium Alginate and Its Blend Membranes with Poly(Vinyl Alcohol) in Water–Acetic Acid Mixtures

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ABSTRACT: Sorption, diffusion, and swelling characteristics of sodium alginate and its blend membranes with poly(vinyl alcohol) were investigated for water–acetic acid mixtures by using a gravimetric method at 30, 40, and 50°C. The membranes were characterized by X-ray diffraction and Fourier transform infrared techniques. Concentration-independent diffusion coefficients were obtained by applying Fick's relationship before completion of equilibrium sorption. Permeation coefficients were calculated from sorption and diffusion coefficients. Concentration profiles of liquids

were computed considering the sheet geometry for the membrane by solving Fick's equation under suitable boundary conditions. Arrhenius activation parameters were computed for the transport processes. Experimental results and calculated quantities were discussed to understand membrane–solvent interactions. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1139–1150, 2004

Key words: sodium alginate; blends; swelling; transport; diffusion; sorption; acetic acid

INTRODUCTION

Study of molecular transport of aqueous/organic mixtures through polymeric membranes was studied extensively over the past decades because of its fundamental importance in membrane separation problems such as pervaporation (PV), microfiltration, ultrafiltration, and nanofiltration.^{1–4} In all these studies, an understanding of sorption, diffusion, and permeation of liquids/mixtures through barrier membranes is helpful in interpretation of experimental data.⁵ In continuation of our ongoing research, we now use sodium alginate (NaAlg) and blend membranes of NaAlg with poly(vinyl alcohol) (PVA) to study the molecular transport of water–acetic mixtures. These membranes are particularly chosen because of their importance in PV separation problems.^{6–8}

In the present study, we have made an attempt to evaluate sorption, diffusion, permeation, and swelling data on pure NaAlg as well as blend membranes of

NaAlg containing 10 and 20 mass % of PVA at 30, 40, and 50°C in water–acetic acid mixtures. By using these data, Arrhenius parameters for permeation and diffusion were estimated. Such data will be useful in understanding membrane–liquid/mixture interactions before seeking their successful applications in PV separation problems. Sorption results were analyzed by using Fick's equation to compute concentration-independent diffusion coefficients.⁹ By solving Fick's diffusion equation under appropriate boundary conditions,¹⁰ we generated concentration profiles of liquids/mixtures through the membranes. Results obtained are discussed in terms of diffusion characteristics of liquids or their mixtures through polymeric membranes.

EXPERIMENTAL

Materials

PVA (*M.W.* = 125,000) was purchased from S. D. Fine Chemicals (Mumbai, India). Sodium alginate was purchased from Loba Chemicals (Mumbai, India). Acetic acid (HAc), glutaraldehyde (GA), acetone, and hydrochloric acid (HCl) used were all of reagent grade samples purchased from S. D. Fine Chemicals (Mumbai, India). These were used without any further purification. Doubly distilled water was used throughout the research work.

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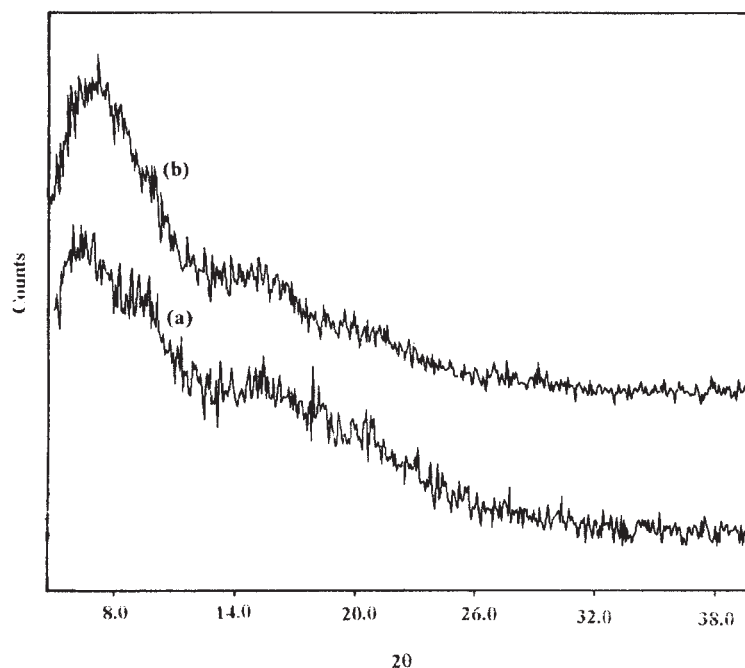


Figure 1 XRD spectra of (a) uncrosslinked and (b) crosslinked sodium alginate membrane.

Membrane fabrication

A 100-mL of stock solution containing 5 mass % of sodium alginate was prepared in a beaker. The solution was stirred for about 24 h and poured uniformly on a clean glass plate to form membranes and dried at room temperature for 2–3 days. Casted membrane was crosslinked by immersing it in a mixture of GA, HCl, acetone, and water to enhance the membrane properties. It was found that a mixture of 2.5 mL GA and 2.5 mL concentrated HCl was useful to impart flexible properties to the membranes, which could withstand resistivity of the solvents or their mixtures. Membranes were kept in crosslinking media for about 24 h and dried at ambient temperature. NaAlg membrane thus prepared is designated as M1. The blend membranes prepared by mixing 10 and 20 mass % of PVA with 90 and 80 mass % of NaAlg are designated as M2 and M3, respectively. Blend membranes were cast and crosslinked by the same procedure as used for the preparation of pure NaAlg membrane.

X-ray diffraction

From XRD tracings of the crosslinked and uncrosslinked NaAlg membranes as displayed in Figure 1, the observed small differences could be attributed to uncrosslinked (curve a) and crosslinked (curve b) polymeric membranes.

Fourier transform infrared (FTIR) spectra

FTIR spectra of the neat sodium alginate membrane were taken in the wavelength range of 400–4000 cm^{-1}

on a Nicolet, Model Impact 410 tester (Madison, WI, USA). Polymers were crushed in a mortar with KBr to make pellets under the hydraulic pressure of 300 kgf/cm^2 . Spectra of the crosslinked and uncrosslinked NaAlg membranes are displayed in Figure 2.

FTIR spectra of uncrosslinked [spectra (a)] and crosslinked [spectra (b)] NaAlg membranes displayed in Figure 2 show clear-cut evidence of NaAlg crosslinked by GA. The peaks appearing at 1098, 1030, and 1265 cm^{-1} show prominent shifts due to C=O stretching vibrations of ether linkages. However, in the case of crosslinked polymer membrane [spectra (b)], peak intensities have increased because of crosslinking of NaAlg membrane.

Sorption experiments

Dynamic and equilibrium sorption experiments on blend membranes as well as pure NaAlg membrane were performed in water–acetic acid mixtures at 30, 40, and 50°C (temperature accuracy $\pm 0.5^\circ\text{C}$) by using an electronically controlled oven (WTB Binder, model BD-53, Tuttlingen, Germany). Circularly cut (diameter = 2.5 cm) disk-shaped membranes were stored in a desiccator over anhydrous calcium chloride maintained at 30°C for about 24 h before use. Initial mass of the membranes was taken on a single pan digital microbalance (Mettler, Model AE 240, Greifensee, Switzerland) sensitive to ± 0.01 mg.

Polymer samples were placed in airtight test bottles containing a 20-mL mixture of water–acetic acid in varying compositions from 10 to 90 mass % of water in acetic acid. Test bottles were placed inside the oven

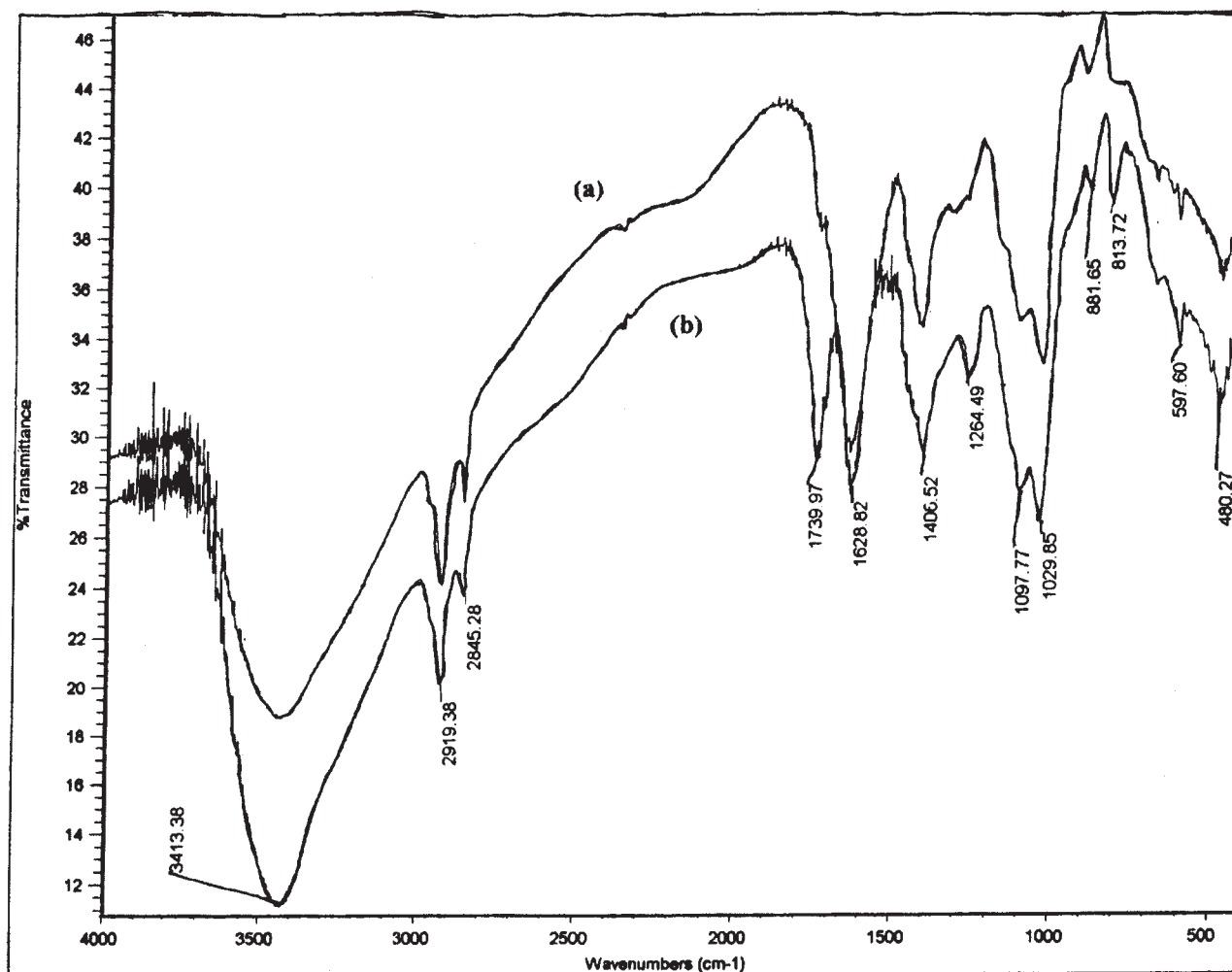


Figure 2 FTIR of spectra of (a) uncrosslinked and (b) crosslinked sodium alginate membrane.

maintained at constant temperature. Mass of the samples was determined at the selected time intervals by removing them from the test bottles and wiping the surface-adhered liquid droplets gently by pressing them in between soft tissue paper wraps, and samples were again placed back in the oven. To minimize solvent evaporation, this step was completed within 15–20 s. Sorption experiments were carried out for a period of 72 h until attainment of equilibrium.

RESULTS AND DISCUSSION

Sorption kinetics

A fundamental understanding of molecular transport of liquids through polymeric membranes is important before one chooses the membrane in PV separation. Membrane performance depends upon membrane structure, polymer morphology, etc.^{11,12} In the present study, sorption kinetics, permeation, and diffusion anomalies of water–acetic acid mixtures were investigated in view of their importance in PV separation. By

using the experimental gravimetric sorption data at different time intervals, mass % uptake, M_t , was calculated from the initial dry mass, W_0 , of the membrane as

$$M_t = \left(\frac{W_t - W_0}{W_0} \right) \times 100 \quad (1)$$

where W_t is mass of the membrane at different time intervals. Sorption depends upon physical–chemical factors such as temperature, nature of solvent, homopolymer, polymer blend ratio, polymer morphology, etc. From the sorption data presented in Table I at 30, 40, and 50°C, one can observe a systematic decrease with increasing temperature at all compositions of water–acetic acid mixture for all membranes. Such an anomaly could be due to leaching of the ingredients from the membranes at higher temperatures. Sorption increases systematically with increasing amount of water in the mixture for all the membranes, but not much difference is observed between the individual membranes.

TABLE I
Transport Data on M1, M2, and M3 Membranes at Different Temperatures in Different Water–Acetic Acid Mixtures

Mass % water	S (mass %)			$D \times 10^{10}$ (m ² /s)			$P \times 10^{10}$ (m ² /s)		
	30°C	40°C	50°C	30°C	40°C	50°C	30°C	40°C	50°C
M1 membrane									
10	26.84	27.67	29.23	0.006	0.013	0.06	0.002	0.003	0.017
20	43.66	33.79	42.21	0.066	0.068	0.13	0.02	0.023	0.054
30	46.47	41.37	38.84	0.21	0.274	0.38	0.098	0.11	0.14
40	58.36	61.49	46.03	0.92	1.11	1.21	0.053	0.68	0.55
50	72.91	82.4	65.28	0.922	1.59	1.58	0.67	1.31	1.03
60	94.25	98.2	81.58	1.29	1.66	2.09	1.21	1.63	1.7
70	97.98	113.3	103.2	1.67	1.75	2.21	1.63	1.98	2.29
80	114.82	125.5	120.9	1.81	2.63	2.9	1.7	3.3	3.5
90	122.04	136.1	127.1	1.84	2.67	3.12	2.24	3.63	3.96
M2 membrane									
10	34.04	31.57	24.61	0.03	0.036	0.057	0.01	0.011	0.014
20	41.66	40.61	29.19	0.096	0.108	0.248	0.04	0.043	0.070
30	55.79	46.84	45.32	0.311	0.417	0.447	0.17	0.195	0.202
40	72.75	61.08	61.15	0.523	0.77	0.774	0.37	0.47	0.473
50	82.79	73.05	70.14	0.82	0.92	0.91	0.67	0.672	0.637
60	91.23	95.58	87.93	1.41	1.46	0.89	1.28	1.32	1.33
70	103.4	107.67	98.17	1.56	1.54	1.65	1.61	1.65	1.62
80	105.7	113.15	115	1.64	1.6	2.81	1.73	1.81	3.22
90	114	118.96	121	1.66	2.21	2.83	1.89	2.82	3.42
M3 membrane									
10	51.94	40.11	36.48	0.01	0.07	0.051	0.005	0.021	0.025
20	49.25	45.47	42.1	0.064	0.131	0.32	0.031	0.059	0.126
30	58.8	52.1	48.6	0.316	0.53	0.844	0.185	0.276	0.41
40	66.35	63.75	60.2	0.416	0.819	1.41	0.276	0.522	0.84
50	80.17	78.47	72.86	0.802	0.899	1.69	0.641	0.705	1.23
60	89.03	88.58	88.77	0.807	0.898	1.76	0.718	0.795	1.56
70	96.2	94.19	93.41	1.53	1.53	1.77	1.47	1.44	1.65
80	94.68	103	101.2	1.72	1.7	2.2	1.62	1.7	2.2
90	100.2	105.2	116.5	1.74	2.51	2.53	1.74	2.62	2.78

Sorption data of pure NaAlg membrane (M1) at different temperatures vary widely, but not systematically; for instance, at 30 and 40°C, sorption values increase slightly for mixtures containing 50 to 90 mass % of water, whereas for mixtures containing 10 to 40 mass % of water at 30 and 40°C, there is a slight decrease in sorption from 30 to 40°C. This may be due to the plasticization effect. However, at 50°C, sorption values are systematically lower than those observed at 30 and 40°C. Even though this appears to be an unusual effect, such effects have already been observed in the literature.¹³ Typical sorption curves for M1 membrane at 10, 30, and 90 mass % of water in acetic acid media at 30, 40, and 50°C are displayed in Figure 3. One could observe different shapes of sorption curves with 10 mass % of water in the mixture at all temperatures, but at higher compositions of water (i.e., 70 or 90 mass %), sorption curves are identical at all temperatures. This suggests the effect of water composition in the mixture on transport. Sorption equilibrium occurs at a much shorter time at 90 mass % of water than at 10 mass %.

Sorption curves expressed as M_t/M_∞ versus $t^{1/2}$ for M2 membrane containing 10 mass % of PVA in different compositions of water–acetic acid mixtures displayed in Figure 4 at 30, 40, and 50°C show almost identical trends at all temperatures. Fickian trends are observed for mixtures containing 10 to 70 mass % of acetic acid, but non-Fickian trends are minimized at higher amounts of acetic acid (90 mass %) in the mixture. Trends in sorption curves at all three temperatures remain identical at a lower amount of acetic acid in the mixture. Similar trends are also observed for M3 membrane containing 20 mass % of PVA at all temperatures, as shown in Figure 5. This indicates that molecular transport of water–acetic acid mixture follows identical trends irrespective of the nature of the membrane. However, morphological changes in the polymers do not significantly affect the transport characteristics. Sorption is generally affected by the shape and or type of the penetrating molecule in addition to polymer morphology. The membranes used in this study are capable of withstanding the mixture. However, with aggressive organic liquids or mixtures, the

situation may be very different.¹⁴ Effect of concentration on diffusion becomes considerable particularly for elastomeric membranes,¹⁵ but it is much less in the present membranes.

Sorption mechanism

To understand the nature of sorption mechanism, we have fitted the experimental mass uptake data, M_t/M_∞ , to an empirical equation¹⁶

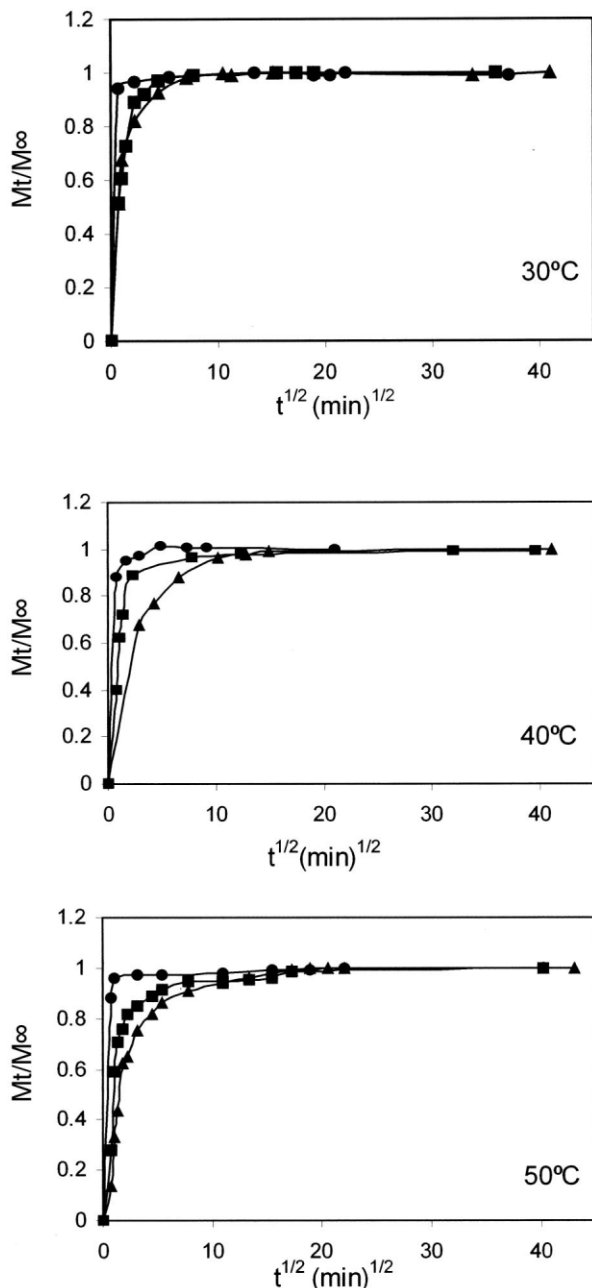


Figure 3 Sorption plots of NaAlg membrane (M1) in different compositions of HAc + water mixture at different temperatures. Symbols: ▲, 10% water; ■, 30% water; ●, 90% water.

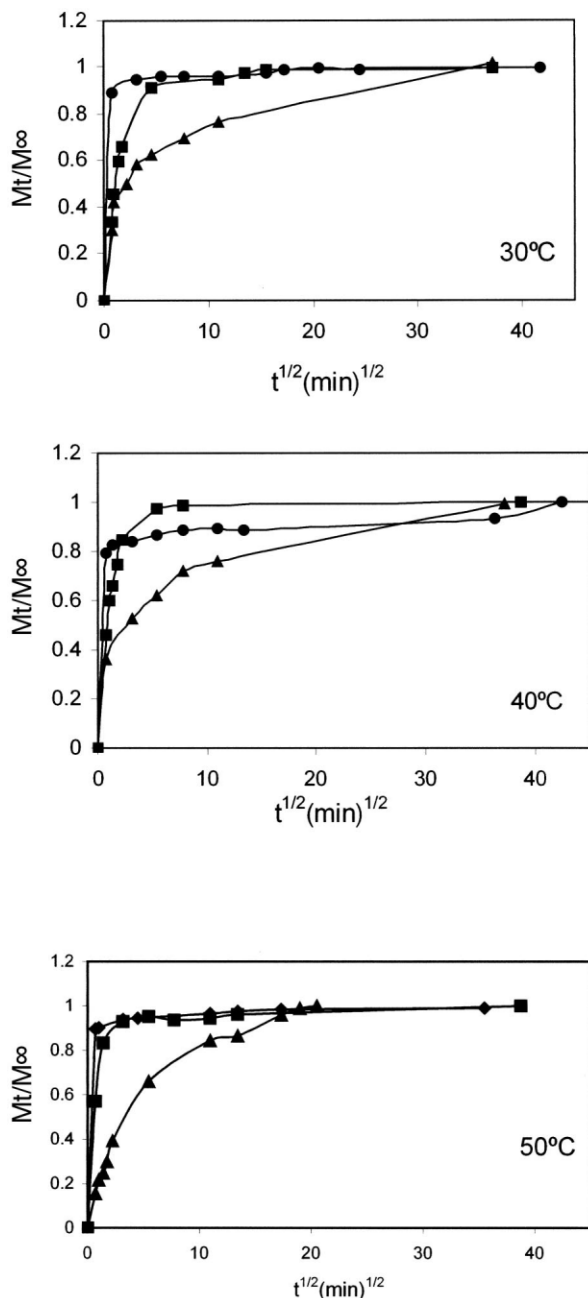


Figure 4 Sorption plots for 10 mass % PVA blend membrane (M2) in different compositions of HAc + water mixtures at different temperatures. Symbols have the same meanings as in Figure 3.

$$\frac{M_t}{M_\infty} = kt^n \tag{2}$$

where M_∞ represents the equilibrium mass uptake by the membrane and k is an empirical parameter indicating the nature of interactions between membrane and liquids. The exponent value, n , indicates the nature of transport mechanism.¹⁵ For Fickian transport, $n = 0.5$, whereas $n = 1.0$ for non-Fickian transport.

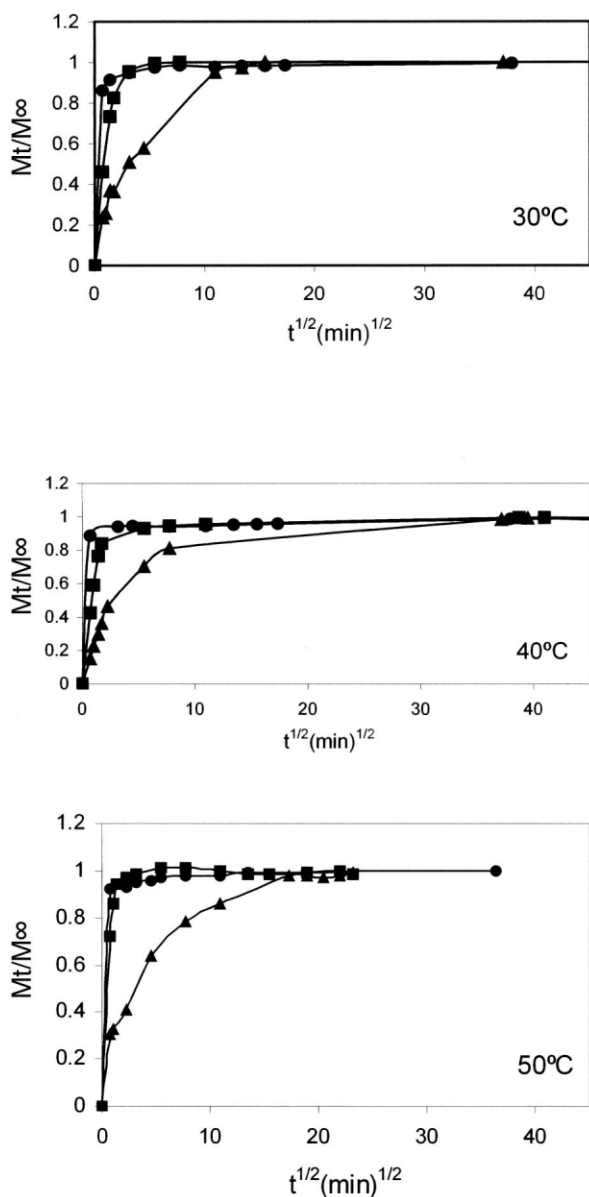


Figure 5 Sorption plots for 20% PVA (M3) in different compositions of water-acetic acid mixtures at different temperatures. Symbols have same meanings as in Figure 3.

Values of M_{∞} were calculated from the asymptotic (saturation) regions of the sorption curves; k and n are rather empirical parameters, calculated from the least-squares procedure by fitting sorption results to logarithmic form of eq. (2). These data are presented in Table II. It is observed that k values decrease with an increasing amount of acetic acid in the mixture, indicating hydrophobic interactions between acetic acid and the membranes. A decrease in k from 90 mass % water-containing mixture up to 10 mass % of water indicates lesser interactions of the mixture components with the membranes at lower water content. Values of n and k vary widely, but not systematically on temperature or even on water composition in the

mixture. Such anomalies have also been observed in the literature.^{12,17}

Diffusion and permeation

The concentration-independent diffusion coefficient, D , was calculated from Fick's equation¹⁸

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

where h is thickness of the membrane. Concentration-independent diffusion coefficient, D , was calculated from eq. (3) and these data are also included in Table I for all membranes at all compositions of water and for the temperature range investigated. Diffusion increases with increasing temperature and also, there is a rapid decrease in D for mixtures from 90 mass % of water up to 10 mass % for M1 membrane when compared to M2 and M3 membranes. Similar effects are seen for permeability coefficients (also presented in Table I) calculated as $P = DS$. Permeability values follow the same trends as those of diffusivity for all the membranes due to concentration-independent diffusivities calculated from eq. (3).

Previous researchers¹⁹ studied the influence of microstructural morphology and membrane chemical composition on the transport of small molecules in the case of microphase-separated blends. Based on these observations, one can speculate that the mechanism of diffusion in microphase-separated blends may be similar to that existing in semicrystalline polymers. This analogy is particularly appropriate when one of the phases is a glassy polymer (viz., NaAlg with low diffusion characteristics), while the other phase (viz., PVA) is a continuous rubbery phase through which solvent molecules can diffuse relatively faster. Thus, any increase in transport rate due to tortuous path at the lower water composition may be adequate to explain the effect of morphology on solvent transport.

Membrane swelling

Degree of membrane swelling, DS , was calculated as

$$DS = \frac{W_{\infty}}{W_0} \quad (4)$$

where W_0 is the initial dry mass of the membrane and W_{∞} is the equilibrium mass of the membrane. Results of DS are presented in Table III. Degree of swelling for blend membranes at 10 mass % of water varies according to the blend composition sequence: 20 mass % PVA > 10 mass % PVA > pure NaAlg. As the amount of water in the mixture increases, the degree of swelling also increases for the entire composition of the

TABLE II
Analysis of Sorption Data Using Empirical eq. (2) at Different Temperatures for Different Membranes

Mass % water	30°C		40°C		50°C	
	<i>k</i> (g/g min)	<i>n</i>	<i>k</i> (g/g min)	<i>n</i>	<i>k</i> (g/g min)	<i>n</i>
M1 membrane						
10	0.671	0.41	0.580	0.11	0.326	0.33
20	0.611	0.34	0.534	0.12	0.453	0.36
30	0.570	0.25	0.553	0.34	0.582	0.67
40	0.690	0.38	0.758	0.25	0.727	0.17
50	0.612	0.32	0.696	0.16	0.792	0.22
60	0.831	0.08	0.860	0.03	0.870	0.14
70	0.910	0.06	0.908	0.02	0.916	0.09
80	0.930	0.03	0.882	0.02	0.945	0.01
90	0.941	0.01	0.945	0.04	0.959	0.12
M2 membrane						
10	0.242	0.31	0.430	0.23	0.223	0.34
20	0.351	0.23	0.342	0.37	0.414	0.11
30	0.448	0.41	0.571	0.25	0.769	0.43
40	0.626	0.40	0.758	0.30	0.789	0.15
50	0.747	0.54	0.806	0.33	0.847	0.21
60	0.814	0.18	0.886	0.09	0.895	0.06
70	0.869	0.06	0.895	0.06	0.915	0.02
80	0.898	0.06	0.869	0.06	0.908	0.02
90	0.904	0.02	0.890	0.03	0.911	0.02
M3 membrane						
10	0.283	0.33	0.265	0.48	0.330	0.21
20	0.332	0.40	0.375	0.30	0.466	0.34
30	0.578	0.43	0.577	0.42	0.896	0.20
40	0.684	0.27	0.737	0.39	0.828	0.26
50	0.787	0.28	0.826	0.05	0.886	0.05
60	0.895	0.10	0.886	0.05	0.941	0.03
70	0.828	0.17	0.918	0.03	0.932	0.03
80	0.910	0.05	0.891	0.01	0.923	0.02
90	0.885	0.03	0.899	0.02	0.924	0.01

mixture for pure NaAlg and blend membranes (M2 and M3). At a higher amount of PVA in the blend, *DS* also increases. Blend membranes have higher *DS* than pure NaAlg membrane due to the presence of more hydrophilic PVA present in the blend. The *DS* data

presented in Figure 6 indicate varying interactions between mixture components and membranes. This could be attributed to variations in the physical properties (dielectric constant or dipole moment) of liquid components in the mixture coupled with polymer

TABLE III
Degree of Swelling Data for Membranes at Different Temperatures Calculated from eq. (4)

Mass % of water	<i>DS</i> (kg/kg)								
	30°C			40°C			50°C		
	M1	M2	M3	M1	M2	M3	M1	M2	M3
10	1.268	1.340	1.519	1.277	1.316	1.401	1.100	1.246	1.364
20	1.437	1.417	1.520	1.338	1.406	1.455	1.237	1.291	1.421
30	1.465	1.558	1.588	1.414	1.468	1.522	1.388	1.453	1.486
40	1.584	1.728	1.664	1.615	1.611	1.638	1.460	1.611	1.601
50	1.729	1.828	1.802	1.825	1.730	1.785	1.652	1.701	1.728
60	1.943	1.912	1.890	1.983	1.952	1.886	1.815	1.879	1.887
70	1.980	2.034	1.911	2.133	2.077	1.942	2.026	1.980	2.034
80	2.148	2.057	1.947	2.255	2.230	2.038	2.208	2.159	2.102
90	2.220	2.139	2.003	2.360	2.190	2.052	2.271	2.211	2.065

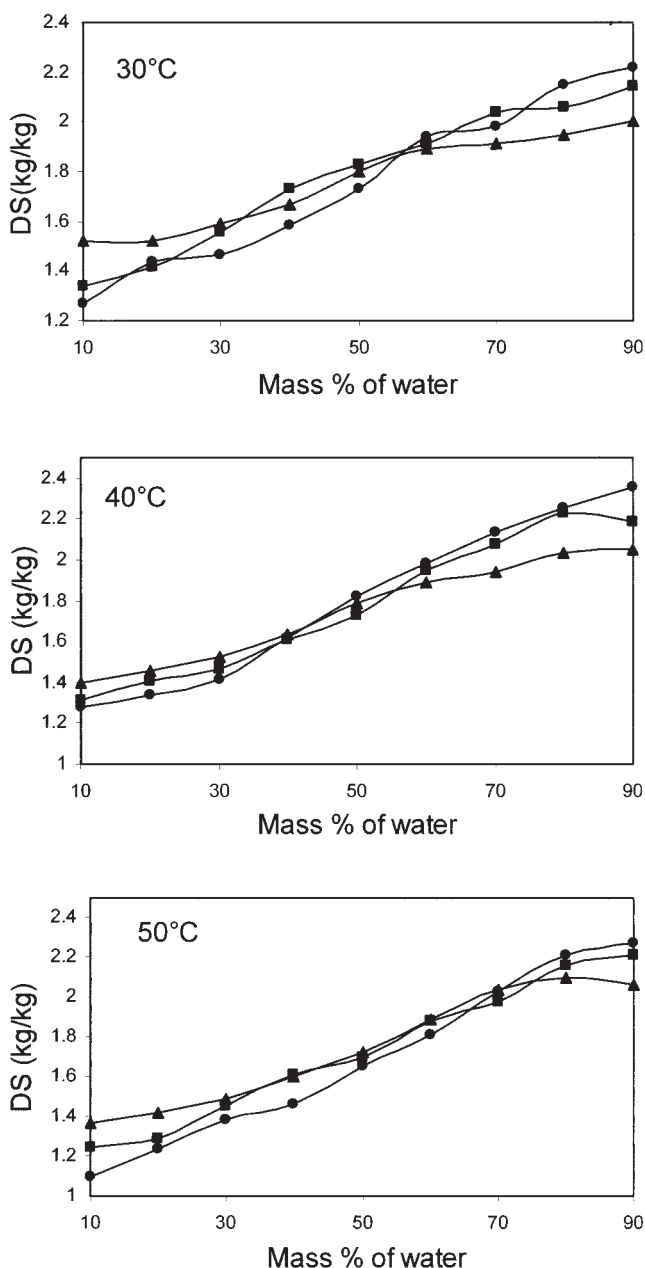


Figure 6 Degree of swelling versus mass % water for different membranes at different temperatures. Symbols for membranes: ●, M1; ■, M2; ▲, M3.

chain relaxation.^{15,20} As regards the dependence of DS on temperature (see Table III), both the pure NaAlG membrane and the blend membranes do not show systematic effects over the entire range of mass % of water in the mixture.

Concentration profiles

For successful applications of polymeric membranes in PV separation studies, it is essential to compute liquid concentration profiles of the transporting media across the barrier membrane. This was done by solv-

ing Fick's second-order differential equation by using appropriate boundary conditions to derive an equation to calculate solvent uptake $c_{(x,t)}$ inside the blend membrane of thickness, h , as a function of time, t , and depth of penetration (distance), x ,

$$\left(\frac{\partial C}{\partial t}\right) = D\left(\frac{\partial^2 C}{\partial x^2}\right) \quad (5)$$

$$\left(\frac{C(x,t)}{C_\infty}\right) = 1 - \frac{4}{\pi} \sum_{m=0}^{\infty} \frac{1}{(2m-1)} \exp\left[-\frac{D(2m-1)^2\pi^2 t}{h^2}\right] \sin\left[\frac{(2m-1)\pi x}{h}\right] \quad (6)$$

In the above equation, m is an integer and D is diffusion coefficient (assumed to be constant) computed from eq. (3). To solve eq. (5) to obtain eq. (6), several assumptions were made¹⁰: (1) when the membrane is soaked into liquid media, its concentration on the membrane surface reaches equilibrium immediately; (2) time required to attain thermal equilibrium for the membrane is negligible when compared to sorption (immersion) time; and (3) changes in membrane dimensions are negligible during the entire period of liquid immersion. Then, by using the following boundary conditions,

$$\begin{aligned} t = 0 & \quad 0 < x < h & \quad C = 0 \\ t > 0 & \quad x = 0 \quad x = h & \quad C = C_x \end{aligned} \quad (7)$$

we have generated the concentration profiles for water + acetic acid mixtures at 30, 40, and 50°C at different exposure times for imaginary varying depths of liquid penetration into the membranes. These data are displayed in Figures 7-9. Concentration profiles follow the same sequences as those of sorption and diffusion data discussed before, thus validating the Fickian model used in data analysis. If diffusivity is considered constant, the concentration profiles could change smoothly, but if diffusivity increases with concentration (see Table I), then concentration sharpening of the profile occurs (see Figs. 7-9), producing a sharp front. This is because for the same concentration gradient, flux increases if water composition is high. This results in a parabolic nature of the profiles with minima at the middle of the membrane thickness as observed in Figures 7-9. During desorption, fraction desorbed is equal to fractional mass uptake when D is considered constant. If D increases with concentration, then desorption becomes slower than sorption and this is not observed in Figures 7-9.

Computer simulation

Profiles of concentration calculated from eq. (6) and displayed in Figures 7, 8, and 9, respectively, for M1,

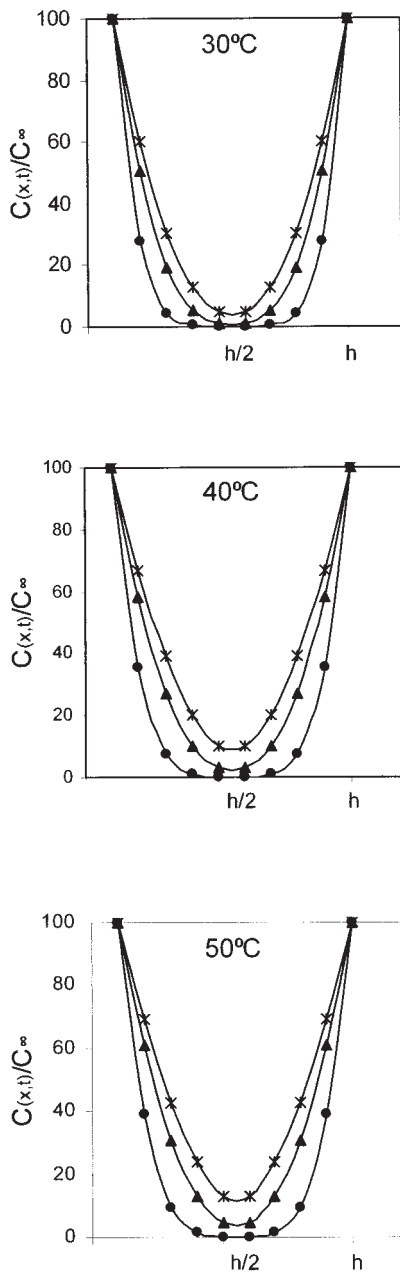


Figure 7 Concentration profiles calculated from eq. (6) for 90 mass % of acetic acid in water for M1 membrane. Symbols: ×, 150 min; ▲, 90 min; ●, 30 min.

M2, and M3 membranes at different temperatures were simulated by writing programs in C language.¹⁰ Concentration profiles have been generated for liquid transport through different thicknesses (penetration depths) of the membranes at different time intervals. It is observed that the profile values show minima at the middle of the membranes, but decreasing and increasing tendencies are observed at the face and the bottom sides of the membrane, indicating the validity of the model used. The curves show a systematic variation with temperature (i.e., with an increase in temperature, the concentration profiles also increase with time,

suggesting a close relationship between concentration profiles and diffusion coefficients).

Numerical solutions of eq. (5) or (6) to understand the diffusion phenomenon may be somewhat approximate. The partial differential equations are converted into algebraic equations (more accurately, difference equations). Instead of the continuous variable, x , we have selected a discrete set of points $\{x_j\}$ and instead of time, t , we have selected the set $\{t_i\}$. Likewise, the concentrations become $C_{i,j}$ and the derivative equations will be written as

$$\frac{\partial C}{\partial t} \approx \frac{C_{i+1,j} - C_{i,j}}{\Delta t} \tag{8}$$

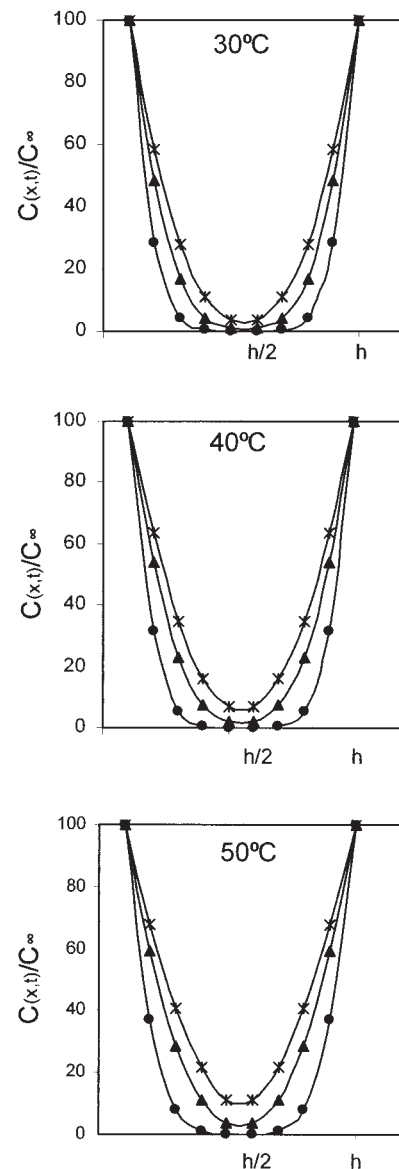


Figure 8 Concentration profiles calculated from eq. (6) for 90 mass % of acetic acid in water for M2 membrane. Symbols have same meanings as in Figure 7.

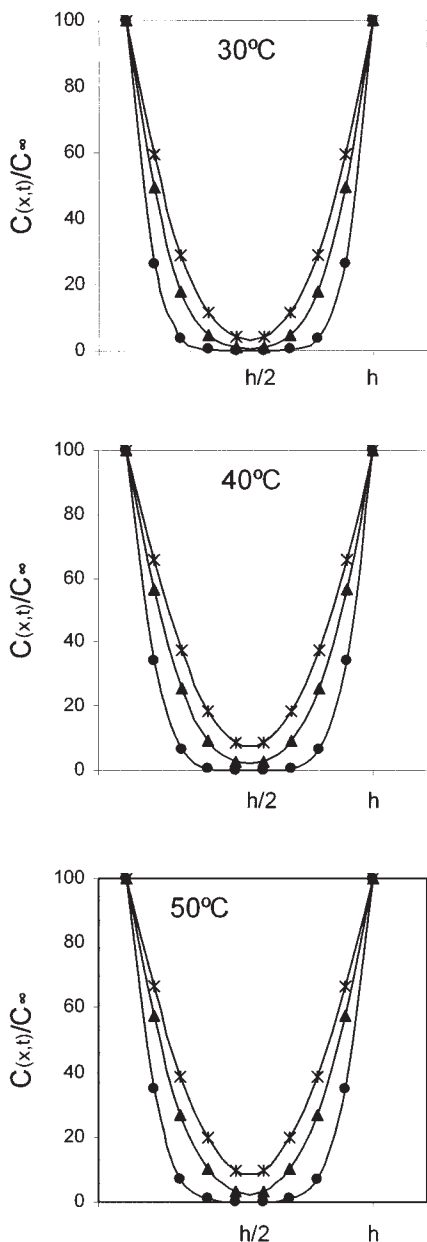


Figure 9 Concentration profiles calculated from eq. (6) for 90 mass % of acetic acid in water for M3. Symbols have same meanings as Figure 7.

and

$$\frac{\partial^2 C}{\partial x^2} \approx \frac{C_{i,j+1} - 2C_{i,j} + C_{i,j-1}}{(\Delta x)^2} \tag{9}$$

In eqs. (8) and (9), higher order terms are negligible, and hence, are eliminated. Inserting eqs. (8) and (9) into eq. (5) and by rearranging, we get the final relationship

$$C_{i+1,j} = C_{i,j} + \frac{D(\Delta t)}{(\Delta x)^2} + (C_{i,j+1} - 2C_{i,j} + C_{i,j-1}) \tag{10}$$

Here, the increments, $\Delta t = t_{i+1} - t_i$ and $\Delta x = x_{j+1} - x_j$ are constants. If the initial concentration profiles $C_{i,j}$ are known, then eq. (10) provides a means for moving up in time to $C_{i\pm 1,j}$. Such iterations are repeated until the numerical approximation to equilibrium or steady state is achieved. It may be noted that the values of Δt are considered in the computational procedure by dividing the solid polymer membrane into several finite slices of equal thickness, Δx , by the concentration difference planes. The computer program in C language was developed to solve these equations.

Effect of temperature and Arrhenius parameters

Sorption (*S*), diffusion (*D*), and permeability (*P*) coefficients showed a dependence on temperature, and hence, typical Arrhenius plots of $\ln D$ or $\ln P$ versus $1/T$ exhibit linear trends. This type of linear relationship suggests that activation energy for diffusion, permeation, and sorption are consistent over the temperature range investigated so that we can calculate the activation parameters from the Arrhenius equation by using the general equation of the type,

$$X = X_0 \exp(-E_x/RT) \tag{11}$$

where $X = D$ or P , $X_0 = D_0$ or P_0 , and $E_x = E_D$ or E_P (activation parameters). Heat of sorption data, ΔH_s , is calculated as

$$\Delta H_s = E_P - E_D \tag{12}$$

where ΔH_s involves contributions from (1) Henry’s law needed for the formation of a site and the dissolution of species into that site. The formation of a site involves an endothermic contribution, and (2) Langmuir’s (hole filling) type sorption mechanism; in which case, the site already exists in the polymer membrane and sorption by hole-filling mechanism gives exothermic heats of sorption.

Effect of temperature on molecular transport has been analyzed by using the Arrhenius relationship given by eq. (11). Typical plots of $\ln D$ versus $1/T$ and $\ln P$ versus $1/T$ for the three membranes at 10, 60, and 90 mass % of water are displayed in Figures 10 and 11. Linear trends observed are indicative of the fact that temperature-dependent transport follows the Arrhenius rule in all the cases. From the slopes of these straight lines, we have calculated the activation energy for diffusion (E_D) and permeation (E_P). These data along with ΔH_s values calculated from the difference ($E_P - E_D$) are presented in Table IV. It is observed that both E_D and E_P values decrease with increasing amount of water in the mixture, but ΔH_s values vary depending upon the amount of water in the mixture. For instance, with M1 membrane, negative ΔH_s ($= -7.710$ J/mol) at 60 mass % of water and for M2

membrane at 10 mass % of water, a still higher negative value of $\Delta H_s = -12.55 \text{ J/mol}$ is observed. However, for M3 membrane, the negative ΔH_s values were observed for 10 and 60 mass % of water in the mixture. Thus, no conclusive remarks on ΔH_s values can be made at this juncture.

CONCLUSION

The present study is an effort towards the understanding of transport of water + acetic acid mixture on sodium alginate and its blend membranes with PVA. Sorption data were obtained at 30, 40, and 50°C by

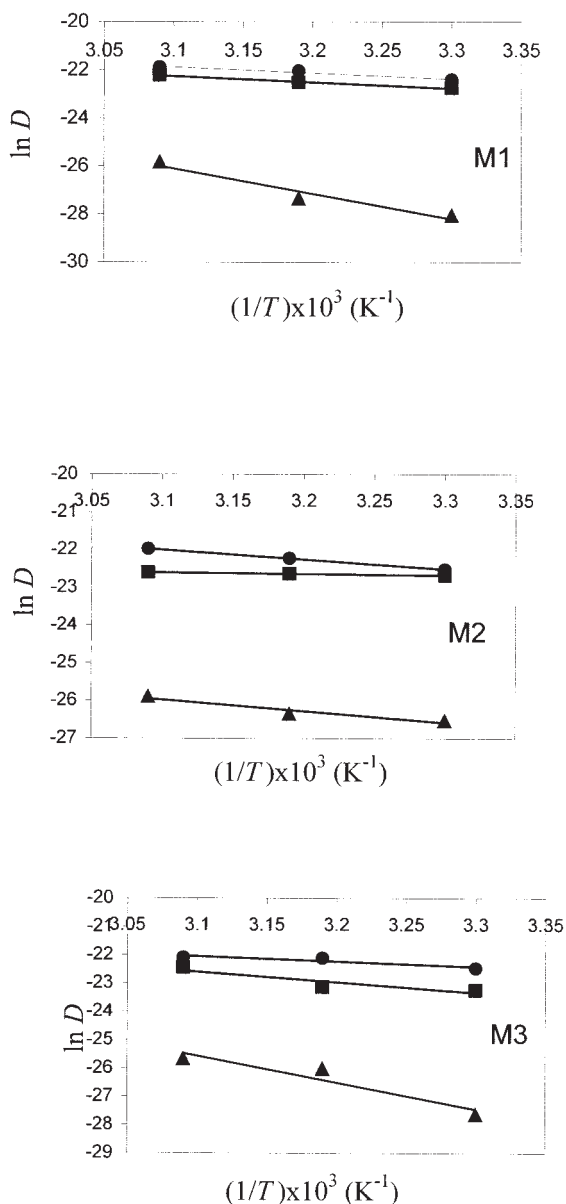


Figure 10 Arrhenius plots of $\ln D$ versus $1/T$ for M1, M2, and M3 membranes. Symbols: \blacktriangle , 10% water; \blacksquare , 60% water; \bullet , 90% water.

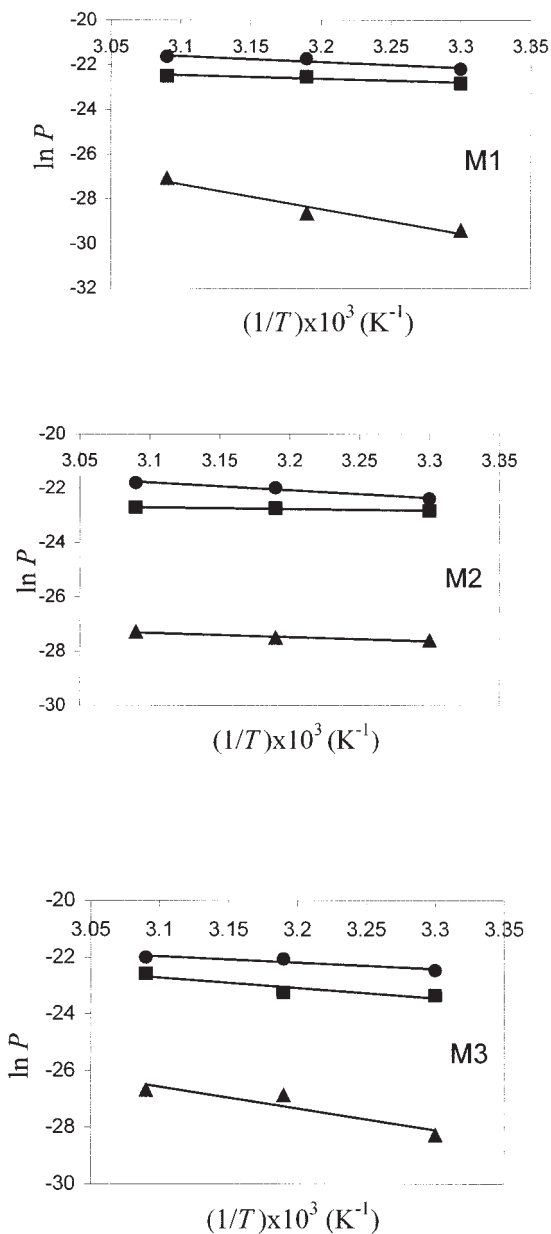


Figure 11 Arrhenius plots of $\ln P$ versus $1/T$ for M1, M2, and M3 membranes. Symbols have the same meanings as in Figure 10.

using a gravimetric technique. Results can be interpreted in terms of the nature of liquid molecules and morphology of the membranes. Transport parameters were studied in terms of the nature of solvent molecules and temperature. Activation energy for diffusion, permeation, and heat of sorption was estimated to gain more information about the transport phenomenon. The transport followed anomalous trends. Model equations used in simulation studies are presented. Irregular trends or the anomalies observed are attributed to leaching of the ingredients from the membranes under different experimental conditions. Results of this study are useful in pervaporation sep-

TABLE IV
Activation Energy for Diffusion (E_D), Permeation (E_P),
and Enthalpy of Sorption (ΔH_s) for all the Membranes at
Different Mass % of Water in the Mixture

Mass % water	E_D (J/mol)	E_P (J/mol)	ΔH_s (J/mol)
M1 membrane			
10	87.696	91.653	3.957
60	21.320	13.618	-7.710
90	21.099	22.392	1.293
M2 membrane			
10	25.141	12.586	-12.550
60	22.892	14.780	1.892
90	21.387	23.472	2.087
M3 membrane			
10	77.92	63.660	-14.270
60	30.501	30.103	-0.398
90	15.247	18.812	3.565

ation studies of water-organic mixtures to be published in a future communication.

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