

Sorption/Diffusion of Aqueous Mixtures of 1,4-Dioxane/Tetrahydrofuran through Blend Membranes of Poly(vinyl alcohol) and Sodium Alginate: Their Compatibility and Pervaporation Separation Studies

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ABSTRACT: Blend membranes of poly(vinyl alcohol) (PVA) and sodium alginate (NaAlg) were prepared by solution casting and crosslinked with glutaraldehyde (GA). Polymer blend compatibility was studied in water by measuring solution viscosity at 30°C. From the viscosity data, interaction parameters were determined to find the blend compatibility. Thickness of the membranes ranged between 35 and 40 μm . Circular disc-shaped samples were cut from the thin membranes to perform gravimetric sorption experiments in water + 1,4-dioxane and water + tetrahydrofuran mixtures at 30°C. Diffusion coefficients were calculated using Fick's equation. Concentration profiles of liquids were computed by solving Fick's equation under suitable boundary conditions. Diffusion coefficients show a dependence on the composition of the blends as well as composition of

binary mixtures. A correlation was attempted between concentration profiles and diffusion coefficients of the transporting liquids. Degree of swelling and sorption coefficients were calculated from the gravimetric sorption data. Sorption kinetics was studied using an empirical equation to understand the nature of sorption–diffusion anomalies. Membrane selectivity for water + 1,4-dioxane and water + tetrahydrofuran mixtures were calculated from the pervaporation experiments. A correlation between sorption and membrane selectivity was attempted. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 178–188, 2005

Key words: diffusion; sorption; blend membranes; sodium alginate; poly(vinyl alcohol); selectivity

INTRODUCTION

Study of molecular transport of aqueous/organic mixtures through polymeric membranes has been an area of intense investigation over the past decades due to its importance in membrane separation processes such as pervaporation (PV), microfiltration, ultrafiltration and nanofiltration.^{1–3} Particularly, pervaporation separation has emerged as one of the important membrane-based separation technologies to separate aqueous–organic mixtures,^{4–6} because it is environmentally friendly and cost effective compared to distillation. However, for a complete understanding of the PV process, it is important to know the sorption and diffusion of liquids through the sheet membranes.

In our earlier communications^{7–9} from this laboratory, we have used the blend membranes of sodium alginate (NaAlg) with poly(vinyl alcohol) (PVA) in different amounts to study the effect of blending on

PV separation capabilities for the aqueous/organic mixtures. Since PV is based on the sorption–diffusion principles,¹⁰ it becomes extremely important to understand sorption–diffusion anomalies of the permeating liquids through the chosen blend membranes.¹¹ Therefore, the objective of this paper is to investigate the sorption and diffusion characteristics of aqueous mixtures of 1,4-dioxane or tetrahydrofuran (THF) through the blend membranes of NaAlg and PVA and to establish a correlation with pervaporation and sorption data.

Over the past 15 years, Aminabhavi et al.^{12–20} published extensively on various aspects of sorption–diffusion anomalies for a variety of industrial membranes with reference to different types of organic liquids. In continuation of this program of research and as a part of our ongoing study on molecular transport of binary liquid mixtures through polymeric membranes,²¹ we report here experimental data of sorption, diffusion, and pervaporation separation on the aqueous mixtures of 1,4-dioxane or THF through the blend membranes of NaAlg with PVA prepared at different blending ratios (5 to 80 mass %). Blend compatibility was studied^{22–24} in water by measuring the solution viscosity at 30°C. Dynamic sorption results

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have been analyzed by using Fick's equation²⁵ to compute diffusion coefficients. Concentration profiles of liquids through the polymer membranes were calculated by solving Fick's diffusion equation under suitable boundary conditions.^{17,26,27} It is further demonstrated that such a database is useful in PV separation studies using membranes developed in our laboratory.⁷⁻⁹ Selectivity data of the membranes containing 5, 10, and 20 mass % of PVA with NaAlg as well as pure NaAlg were obtained from PV experiments at 30°C.

EXPERIMENTAL

Materials

Poly(vinyl alcohol), (approximate mol. wt. 125,000), sodium alginate, and glutaraldehyde (GA) were procured from s. d. fine Chemicals, Mumbai, India. Analytical reagent grade (high purity) 1,4-dioxane, tetrahydrofuran (HPLC grade), acetone, and hydrochloric acid (HCl) were also purchased from s.d. fine Chemicals, Mumbai, India. Double distilled water was used throughout and its purity was checked by conductivity measurements, which agreed with the literature value of $0.043 \times 10^{-6} \text{ S cm}^{-1}$.

Preparation of blend solutions

The 0.5 mass % of NaAlg and 0.5 mass % PVA were prepared in 200 mL distilled water separately in two different 250-mL stoppered conical flasks. Polymeric blend solutions were prepared by thoroughly mixing the above-prepared polymer solutions in separate conical flasks. Seven different mass ratios of the blend solutions of NaAlg and PVA were prepared by mixing NaAlg with PVA in different ratios of 5/95, 10/90, 20/80, 30/70, 40/60, 60/40, and 80/20. From these blend solutions, 0.1, 0.2, 0.3, 0.4, and 0.5 mass % solutions were prepared volumetrically. In a similar manner, mixtures containing 10 to 90 mass % of THF or 1,4-dioxane in water were prepared.

Membrane preparation

Blend membranes of NaAlg and PVA were prepared by solution casting method.⁷ The required amount of NaAlg was dissolved in 100 mL distilled water by stirring over a magnetic stirrer (Jenway, model 1103, Essex, UK) for 24 h. The mixtures were homogeneous as seen by visual observation. To this, different amounts of PVA (5, 10, and 20 mass %) were added and membranes thus prepared were designated as M-2, M-3, and M-4, respectively, while the pure NaAlg was designated as M-1. The solution was filtered to remove the suspended particles. The suspended particles were identified to be mostly the contaminants, not the undissolved polymers. The solution

was then poured onto a clean glass plate leveled perfectly on a tabletop kept in a dust-free atmosphere and dried at room temperature. Dried membranes were peeled off carefully and crosslinked by immersing them in water and acetone mixtures containing 2.5 mL HCl and 2.5 mL GA. Here, HCl acts as a catalyst for crosslinking. We measure the extent of crosslinking of the membrane, since the films were flexible and they could partially crosslink.

Viscosity measurements

Dilute solution viscosities of pure NaAlg, pure PVA, and their blends were measured at 30°C using a Scott-Gerate Viscometer (model AVS 350, Hofheim, Germany). The viscometer automatically measures the flow-through times in capillary tubes. Efflux times were determined on a digital display to an accuracy of $\pm 0.01 \text{ s}$. Temperature of the bath (Scott-Gerate, model CT 050/2, Hofheim, Germany) was maintained constant at 30°C within an accuracy of $\pm 0.01^\circ\text{C}$. The estimated error in viscosity was $\pm 0.001 \text{ mPa s}^{-1}$. Approximately, 5 cm^3 volume of the solution was taken in the viscometer tube and the liquid was allowed to equilibrate to the desired temperature for about 10 min and flow times were measured.

Sorption experiments

Dynamic and equilibrium sorption experiments on the blend membrane as well as pure NaAlg membranes were performed in water + 1,4-dioxane and water + THF mixtures at $30 \pm 0.5^\circ\text{C}$ using an electronically controlled incubator (WTB Binder, model BD-53, Tuttilgen, Germany) following previously published procedures.¹³⁻²¹ Circularly cut (surface area = 9.08 cm^2) disk-shaped membranes were stored in a desiccator over anhydrous calcium chloride maintained at 30°C for at least 48 h before their use. Initial mass of the membranes was taken on a single-pan digital Mettler microbalance (model AE 240, Greifensee, Switzerland) sensitive to $\pm 0.01 \text{ mg}$.

Polymer samples were placed inside the airtight test bottles containing mixtures of water + 1,4-dioxane and water + THF. Test bottles were placed inside the incubator maintained at a constant temperature of 30°C. Mass of the samples was determined at the selected time intervals by removing the samples from test bottles, wiping the surface-adhered liquid droplets and gently pressing them between filter paper wraps; these were again placed back into the oven. To minimize solvent evaporation, this step was completed within 15–20 s.

Pervaporation experiments

Pervaporation experiments were performed using the apparatus designed indigenously.^{28,29} The PV appara-

TABLE I
Degree of Swelling (*DS*), Diffusion Coefficient (*D*), and Sorption Coefficient (*S*) for Water + 1, 4-Dioxane Mixtures

Mass % water	M-1	M-2	M-3	M-4
	Degree of swelling, <i>DS</i> (kg/kg)			
10	1.38	1.43	1.50	1.56
20	1.56	1.69	1.72	1.88
30	1.55	1.77	1.98	1.99
40	1.73	1.94	2.00	2.14
50	1.74	2.13	2.04	2.19
	Sorption coefficient, <i>S</i> (kg/kg)			
10	37.83	43.20	49.82	56.05
20	54.90	68.74	72.19	97.65
30	56.11	76.51	88.33	99.60
40	72.74	94.17	104.1	114.3
50	73.58	99.31	113.2	119.2
	Diffusion coefficient, <i>D</i> × 10 ⁹ (m ² /s)			
10	0.95	1.08	1.36	1.75
20	0.95	3.84	5.11	5.20
30	1.02	4.52	5.22	5.39
40	2.98	5.35	5.97	5.98
50	3.10	5.85	5.73	6.24

tus consists of a stirred stainless-steel cell through which retentate is circulated to the feed tank. Effective surface area of the membrane in the cell is 32.43 cm² with a diameter of 6.4 cm and volume capacity of the cell is 250 cm³. Temperature of the feed mixture is kept constant using a thermostatic water jacket. The PV cell is provided with an efficient three-blade stirrer powered by a DC current motor in the feed compartment. Turbulent flows were obtained even at the low rotation of the stirrer, i.e., below 200 rpm. Mass transfer limitations due to concentration polarization were negligible. The downstream side of the PV apparatus was continuously evacuated by using a vacuum pump (Toshniwal, Mumbai, India) at a pressure of < 10 Torr.

The test membrane was equilibrated for about 3 h with the feed mixture before starting the PV experiment. After establishment of a steady state, permeate vapors were collected in traps immersed in liquid nitrogen. PV experiments were performed for 10 mass % water-containing feed mixtures. Water was added to the feed compartment to replace the depleted amount of water from the feed. To obtain 20 mass % of the mixture, water was again added to the feed compartment to the remaining feed solution. Likewise, higher water compositions of the mixtures were incorporated. The mass of permeate collected in the trap was taken and its composition was determined by measuring its refractive index by comparing it with the standard graph of refractive index versus mixture composition. Permeate composition was determined by measuring refractive index of the liquid solution using a refractometer (Atago, model 3T, Tokyo, Japan) and was also confirmed by running a GC experiment (HP, model 6890, Palo Alto, CA). Selectivity, α was calculated as

$$\alpha = \left(\frac{y_A}{1 - y_A} \right) \left(\frac{1 - x_A}{x_A} \right) \quad (1)$$

where x_A is mole fraction of water in the feed and y_A is mole fraction of water in the permeate.

RESULTS AND DISCUSSION

Using sorption data at different time intervals, mass % uptake, M_t , was calculated from the initial dry mass, W_o of the membrane using the equation

$$M_t = \left(\frac{W_t - W_o}{W_o} \right) \times 100 \quad (2)$$

where W_t is the mass of the membrane at different time intervals. The equilibrium degree of swelling, *DS*, of the membranes was calculated as

$$DS = \frac{W_\infty}{W_o} \quad (3)$$

where W_∞ is the equilibrium mass of the membrane. The concentration-independent diffusion coefficient, *D*, was calculated from Fick's equation:²⁵

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

where *h* is the thickness of the membrane and M_∞ is the equilibrium mass uptake. A detailed procedure to determine the values of *D* using eq. (4) was published earlier.³⁰

TABLE II
Degree of Swelling (*DS*), Diffusion Coefficient (*D*), and Sorption Coefficient (*S*) for Water + Tetrahydrofuran Mixtures

Mass % water	M-1	M-2	M-3	M-4
Degree of swelling, <i>DS</i> (kg/kg)				
10	1.39	1.53	1.54	1.59
20	1.68	1.70	1.80	1.89
30	1.80	1.83	1.86	2.00
40	1.92	2.00	2.07	2.26
50	2.02	2.11	2.53	2.54
Sorption coefficient, <i>S</i> (kg/kg)				
10	39.33	52.63	59.35	67.88
20	54.45	79.60	86.25	92.26
30	70.43	83.27	88.82	125.8
40	80.22	100.1	100.24	152.7
50	101.57	106.7	111.46	153.9
Diffusion coefficient, <i>D</i> × 10 ⁹ (m ² /s)				
10	1.01	2.32	3.79	5.30
20	3.04	3.57	5.12	5.84
30	4.52	5.26	5.47	5.91
40	5.24	5.81	5.83	6.02
50	5.87	5.96	6.24	6.42

Results of degree of swelling, sorption coefficients, and diffusion coefficients calculated from the above equations are summarized in Tables I and II, respectively, for water + 1,4-dioxane and water + THF mixtures. Results of degree of swelling versus mass % of water for all the membranes in water + 1,4-dioxane and water + THF mixtures are displayed in Figure 1. Compared to all the membranes, pure NaAlg membrane (M-1) showed the least swelling over the entire

range of water composition of the feed mixtures, while the blend membranes showed an increased swelling with increasing amount of PVA. Swelling also increased with increasing amounts of water in the binary mixture for all the membranes. Increase in swelling with increasing amounts of PVA in the blend is in accordance with the principle of "like sorbs like." PVA, being more hydrophilic than NaAlg, absorbs a larger amount of water than NaAlg. From the data displayed in Figure 1 and compared in Tables I and II, we observe that the degree of swelling is higher in water + THF mixtures than in water + 1,4-dioxane mixtures. This could be due to the fact that water + THF mixture has higher preferential interactions toward membrane than with water + 1,4-dioxane mixture for obvious thermodynamic reasons.

Results of dynamic sorption of liquids at 30°C through the membranes are displayed in Figures 2 and 3 for water compositions ranging from 10 to 50 mass % in both the feed mixtures of water + 1,4-dioxane and water + THF. Sorption can be controlled by the mutual diffusion of solvent molecules in relation to polymeric chain relaxation as described by Fickian transport.²⁵ Irregular trends in sorption curves are attributed to differences in the rate of molecular chain relaxation due to the locally induced stresses in the polymer matrix and the nature of molecular transport of liquids. In the majority of cases, a regularly increasing mass uptake was observed due to migration of higher amounts of solvent molecules through the void of the membranes. The time required to attain equilibrium sorption varies depending upon the morphology of the membrane. For instance, as shown in Figure 2, with pure NaAlg membrane, sorption attains equilibrium within 25 min for water + 1,4-dioxane

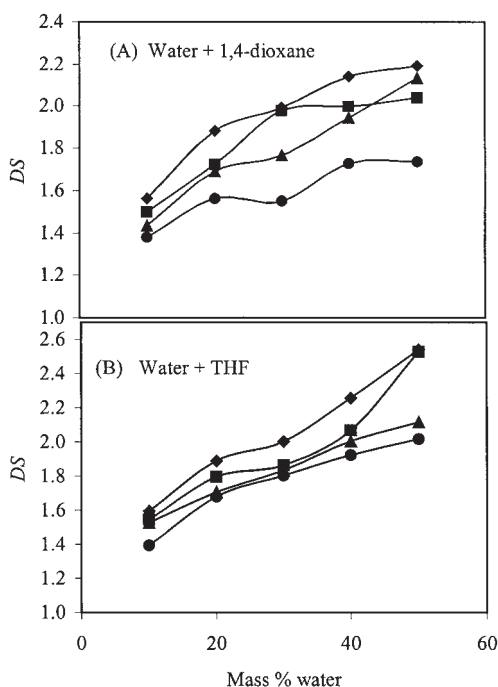


Figure 1 Plot of degree swelling versus mass % of water in 1,4-dioxane (a) and THF (b) for (●) M-1, (▲) M-2, (■) M-3, and (◆) M-4.

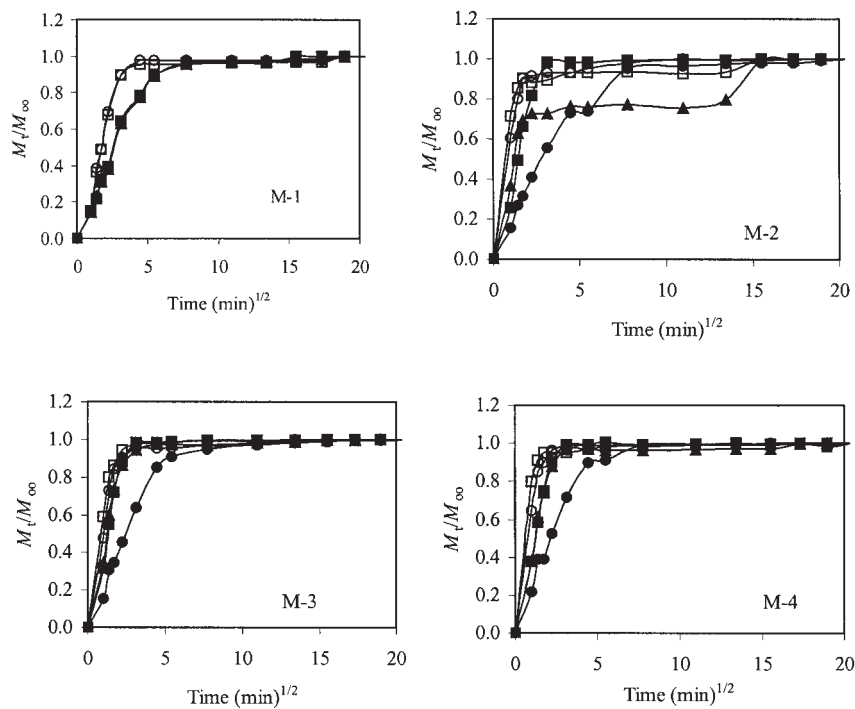


Figure 2 Plot of M_t/M_{∞} versus square root of time (in min) for 1,4-dioxane–water mixture at (●) 10, (▲) 20, (■) 30, (□) 40, and (○) 50 mass % of water in 1, 4-dioxane.

mixture, whereas, for water + THF mixture, sorption saturation is attained much faster (i.e., before 25 min). On the other hand, with M-2 membrane, sorption curves presented in Figures 2 and 3 for 10 and 20 mass

% of water in the respective organic phases show some variations, but these anomalies are not observed for M-3 and M-4 membranes. For water + THF mixtures with M-3 and M-4 membranes, the attainment of

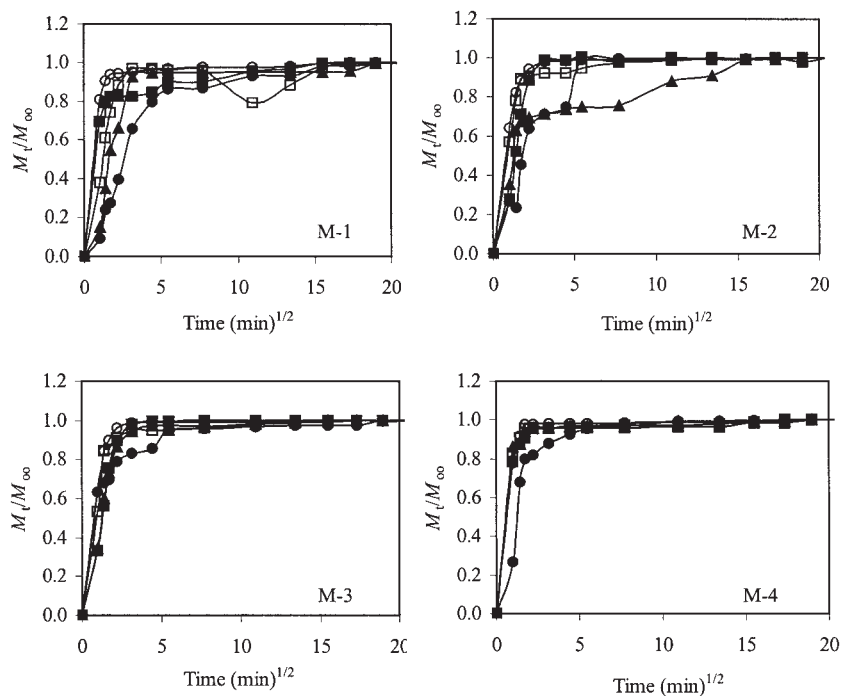


Figure 3 Plot of M_t/M_{∞} versus square root of time (in min) for THF–water mixture at (●) 10, (▲) 20, (■) 30, (□) 40, and (○) 50 mass % of water in THF.

TABLE III
Degree of Swelling (*DS*), Diffusion Coefficient (*D*), and Sorption Coefficient (*S*) for Different Membranes in Pure Water at 30°C

Membrane	<i>DS</i> (kg/kg)	<i>S</i> (kg/kg)	<i>D</i> × 10 ⁹ (m ² /s)
M-1	2.05	105.0	3.79
M-2	2.19	119.3	8.85
M-3	2.63	113.2	9.08
M-4	2.81	126.0	9.60

equilibrium is very fast (i.e., < 10 min), indicating that sorption is much faster with water + THF mixtures than with water + 1,4-dioxane mixtures. In both systems, equilibrium sorption occurs within 30 min, but experiments were continued for a longer time to ensure equilibrium saturation.

Values of sorption and diffusion coefficients presented, respectively, in Tables I and II for water + 1,4-dioxane and water + THF mixtures are calculated from the equilibrium sorption data. Results of diffusion coefficients presented in Tables I and II show increasing trends with an increasing amount of PVA in the blend membranes. The *D* values increase with increasing amounts of water in the mixtures. It may be noted that values of *S* and *D* for water + THF are slightly higher than those observed for water + 1,4-dioxane mixtures. For pure water, the degree of swelling, sorption, and diffusion coefficients are presented in Table III. Results of *DS* increase with increasing amounts of PVA in the blend membrane. The lowest value of *DS* of about 2 is observed for M-1, whereas the highest value of 2.81 is observed for M-4. The highest sorption coefficient of 126 is observed for M-4, while the lowest value of 105 is found for M-1. Diffusion coefficients show an increase from $3.79 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for M-1 to $9.60 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for M-4. This is due to increased hydrophilicity of the blend membranes from M-1 to M-4 as a result of increasing amounts of PVA in the blends. Sorption curves of all of the membranes in water at 30°C are displayed in Figure 4. It is noted that few variations are observed in the shapes of sorption curves for all the blend membranes except for M-1. However, sorption experiments for pure THF and pure 1,4-dioxane were not performed because the membranes became brittle in these solvents and no mass gain was observed.

Sorption kinetics

Sorption depends upon the physicochemical factors such as nature of solvent, nature of polymer, blend ratio, blend compatibility, etc.^{31,32} To understand the nature of sorption kinetics, experimental mass uptake data, M_t/M_{∞} , have been fitted to the empirical relationship.^{13–21}

$$\frac{M_t}{M_{\infty}} = kt^n \quad (5)$$

Here, M_{∞} is the equilibrium mass uptake of the membrane calculated from the asymptotic (saturation) region of the sorption curves; *k* and *n* are the empirical parameters, of which *k* represents the nature of polymer–solvent interactions. Values of *n* indicate the nature of transport kinetics.²⁵ For Fickian transport, *n* = 0.5 while *n* = 1.0 for non-Fickian transport. Values of *n* ranging between 0.5 and 1.0 suggest anomalous transport kinetics.^{13,16} The values of *n* and *k* have been calculated from the least squares method by fitting the sorption data to eq. (5).

The calculated parameters of eq. (5) are compiled in Table IV for water + 1, 4-dioxane and water + THF mixtures. Computed values of *n* vary from the lowest value of 0.16 for M-4 with 40 mass % water containing 1,4-dioxane mixture (see Table IV) to the highest value of 0.93 for M-1 with 40% as well as 50 mass % water containing 1,4-dioxane mixtures. Values of *k* vary between –0.22 and –1.85, suggesting strong membrane–solvent interactions. For the water + THF mixture, the values of *n* vary from a minimum value of 0.07 for M-4 with 20 mass % of water to a maximum value of 0.77 for M-1 with 20 mass % water containing THF mixtures; the values of *k* range between –0.16 and –2.05.

Blend compatibility

Miscibility of polymeric blends is important in membrane applications using the PV method. In this study, we have investigated the blend compatibility at lower polymer concentration by calculating the reduced viscosity (η_{sp}/c) and then by judging the nature of the plot of (η_{sp}/c) versus concentration³³ (see Figure 5). Miscibility of polymer blends in solution was investigated by calculating the polymer–polymer interaction

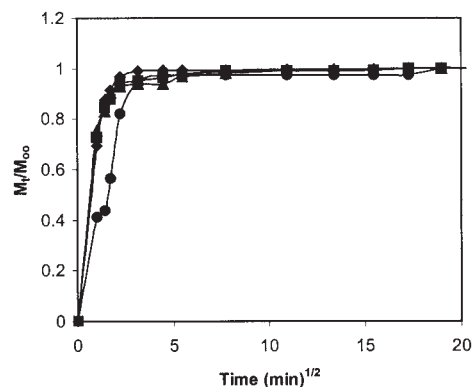


Figure 4 Plot of M_t/M_{∞} versus square root of time (in min) for pure water. Symbols have the same meaning as given in Figure 1.

TABLE IV
Parameters n and k Calculated from Eq. (5) for Different Membranes with Water + 1,4-Dioxane
and Water + THF System at 30°C

Mass % water	M-1		M-2		M-3		M-4	
	n	k	n	k	n	k	n	k
	Water + 1,4-dioxane							
10	0.54	-1.85	0.49	-1.74	0.50	-1.67	0.41	-1.37
20	0.54	-1.85	0.43	-0.90	0.58	-1.00	0.52	-0.92
30	0.55	-1.85	0.57	-1.19	0.65	-1.10	0.55	-0.95
40	0.93	-1.80	0.21	-0.33	0.29	-0.49	0.16	-0.22
50	0.93	-1.77	0.37	-0.50	0.40	-0.68	0.31	-0.43
	Water + THF							
	n	k	n	k	n	k	n	k
10	0.62	-2.05	0.59	-1.50	0.11	-0.45	0.71	-1.13
20	0.77	-1.68	0.42	-0.93	0.58	-0.99	0.07	-0.16
30	0.16	-0.36	0.73	-1.21	0.63	-1.05	0.12	-0.23
40	0.53	-0.92	0.42	-0.56	0.32	-0.54	0.13	-0.19
50	0.14	-0.21	0.24	-0.41	0.26	-0.41	0.21	-0.25

parameter, Δb of blends using the following equation:³⁴

$$b_m = x_1^2 b_{11} + 2x_1 x_2 b_{12} + x_2^2 b_{22} \quad (6)$$

where x_1 and x_2 are mass fractions of polymers 1 and 2, b_{11} and b_{22} are the respective interaction parameters, b_{12} is the interaction parameter of the blend, and b_m defines the global interaction between the polymeric species. Interaction parameters, b_{11} , b_{22} , and b_m were calculated from the slopes of the plot of reduced viscosity of polymer solutions and their blend solutions versus concentration (Figure 5).

Intrinsic viscosity values have been calculated for both the individual polymers and their blends from

the intercepts calculated by extrapolating the straight lines are shown in Figure 5. Values of $[\eta]_m$ were then obtained from such plots for noninteracting blends using the following equation:³⁵

$$[\eta]_m = x_1 [\eta]_1 + x_2 [\eta]_2 \quad (7)$$

Interaction parameter, b_{12}^* , can be calculated theoretically using the equation

$$b_{12}^* = (b_{11} b_{22})^{1/2} \quad (8)$$

Here, the values of b_{11} and b_{22} are the slopes of the plots of reduced viscosity versus concentration of individual polymers calculated using the classical Huggins equation.³⁴⁻³⁶

$$[\eta]_{sp}/c = [\eta]_0 + bc \quad (9)$$

Thus, the difference, Δb , between the theoretically calculated b_{12}^* , from eq. (8) and that of experimental b_{12} calculated from eq. (6) is expressed as

$$\Delta b = (b_{12} - b_{12}^*) \quad (10)$$

It has been stated³⁷ that if $\Delta b > 0$, then the polymer blends are miscible; if $\Delta b < 0$, phase separation occurs. The calculated Δb values along with experimental, theoretical intrinsic viscosities, and b_{12} values are presented in Table V. Positive values of Δb suggest that 5, 10, and 20 mass % PVA containing NaAlg blend membranes are more compatible compared to high PVA-containing blends. However, the negative values of Δb are observed for 30, 40, 60, and 80% PVA-containing blend membranes with NaAlg, indicating the phase separation at these compositions. Despite this difficulty, we were able to fabricate membranes by varying

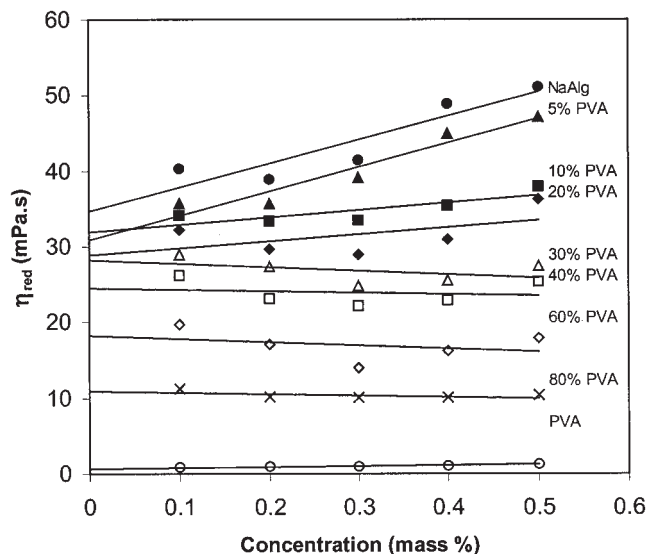


Figure 5 Plot of (η_{sp}/c) versus c for (●) pure NaAlg, (▲) 5% PVA, (■) 10% PVA, (◆) 20% PVA, (△) 30% PVA, (□) 40% PVA, (◇) 60% PVA, (×) 80% PVA, and (○) pure PVA.

TABLE V
Experimental/Theoretical Intrinsic Viscosity and Interaction Parameters for the Blends at 30°C

% PVA in the blend	Intrinsic viscosity (dl/g)		Parameter calculated		Δb Eq. (10)
	Experimental (intercept)	Theoretical Eq. (7)	Experimental, b_{12} values (slope)	Theoretical b_{12}^* values Eq. (8)	
0	34.61	22.03	—	—	—
5	30.85	20.99	32.19	5.93	26.26
10	31.91	19.95	9.831	5.93	3.90
20	28.81	17.86	9.410	5.93	3.48
30	28.21	15.78	-4.604	5.93	-10.53
40	24.50	13.69	-1.899	5.93	-7.82
60	18.25	09.53	-4.306	5.93	-10.23
80	10.92	05.36	-1.863	5.93	-7.79
100	0.685	01.20	—	—	—

the amount of crosslinking agent during membrane fabrication and all of the membranes were quite useful in PV^{7,37,38} experiments.

Concentration profiles

For a successful application of the membranes in PV experiments, we have computed the liquid concentration profiles of the transporting liquids as a function of time and membrane thickness by solving Fick's second-order differential equation²⁵ under appropriate initial and boundary conditions. This gives us an equation for

solvent uptake $c(x, t)$ inside the blend membranes of thickness h , as a function of time, t and distance, x .

$$\left(\frac{c(x,t)}{c_\infty}\right) = 1 - \frac{4}{\pi} \sum_{m=0}^{\infty} \frac{1}{(2m-1)} \times \exp\left[-\frac{D(2m-1)^2\pi^2 t}{h^2}\right] \sin\left[\frac{(2m-1)\pi x}{h}\right] \quad (11)$$

Here, m is an integer and the values of D used were from eq. (4). Equation (11) was solved to obtain concentration profiles of the migrating liquids.

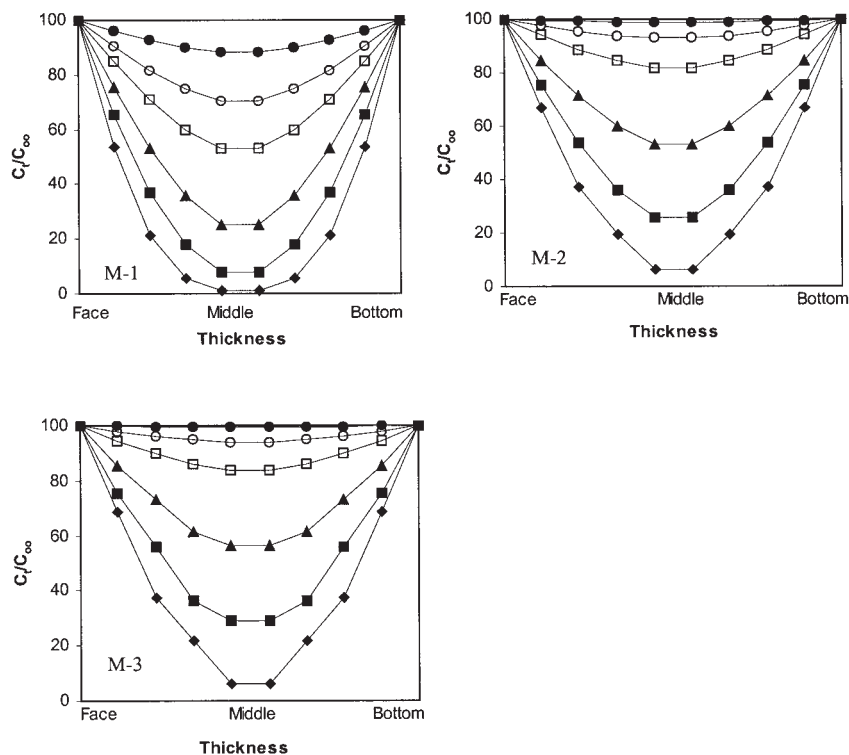


Figure 6 Concentration profiles calculated from eq. (11) for blend membranes mixtures containing 10 mass % of water in dioxane at (●) 25 min, (○) 50 min, (□) 100 min, (▲) 200 min, (■) 300 min, and (◆) 500 min at 30°C.

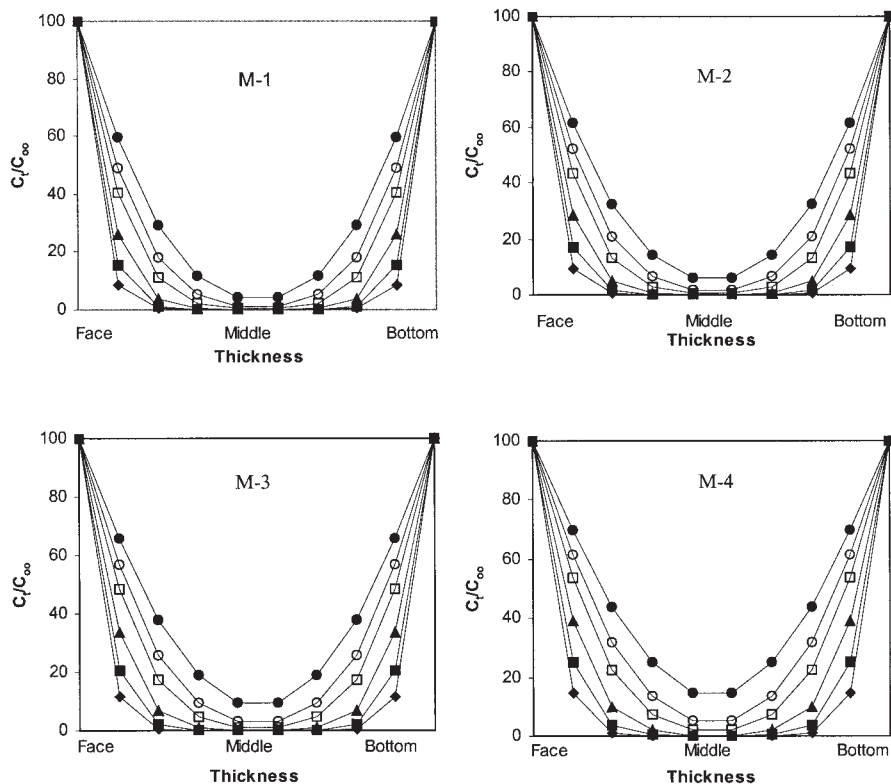


Figure 7 Concentration profiles calculated from eq. (11) for mixtures containing 10 mass % of water in THF at (●) 25 min, (○) 50 min, (□) 100 min, (▲) 200 min, (■) 300 min, and (◆) 500 min at 30°C.

$$\left(\frac{\partial c}{\partial t}\right) = D \left(\frac{\partial^2 c}{\partial x^2}\right) \quad (12)$$

$$\frac{\partial C}{\partial t} \approx \frac{C_{i+1,j} - C_{i,j}}{\Delta t} \quad (14)$$

To solve eq. (11), it was tacitly assumed that (1) when the membrane is soaked into the liquid media, its concentration on the surface reaches equilibrium immediately, (2) the time required to attain thermal equilibrium for the membrane is negligible compared to sorption time, and (3) changes in membrane dimensions are negligible during the entire period of liquid immersion. Then, by using the following boundary conditions,

$$\begin{aligned} t = 0 \quad 0 < x < h \quad c = 0 \\ t > 0 \quad x = 0 \quad x = h \quad c = c_x \end{aligned} \quad (13)$$

we have solved eq. (12) to obtain liquid concentration profiles.

Equation (11) was solved by the finite-difference method. The partial differential equations were converted into algebraic equations (more accurately, difference equations). Then, instead of using 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, concentrations become $C_{i,j}$ and derivatives will be given as follows:

and

$$\frac{\partial^2 C}{\partial x^2} \approx \frac{C_{i,j+1} - 2C_{i,j} + C_{i,j-1}}{(\Delta x)^2} \quad (15)$$

In eqs. (14) and (15), higher order terms are negligible and are thus eliminated. Upon inserting eqs. (14) and (15) into eq. (11) and rearranging, we get

$$C_{i+1,j} = C_{i,j} + \frac{D(\Delta t)}{(\Delta x)^2} (C_{i,j+1} - 2C_{i,j} + C_{i,j-1}) \quad (16)$$

TABLE VI
Pervaporation Selectivity Data on Membranes at 10 Mass % of Water in Water + 1,4-Dioxane and Water + THF Mixtures

Membrane	Selectivity	
	Water + 1,4-dioxane	Water + THF
NaAlg (M-1)	111.0	291.0
5% PVA + 95% NaAlg (M-2)	63.0	216.0
10% PVA + 90% NaAlg (M-3)	57.7	135.0
20% PVA + 80% NaAlg (M-4)	42.4	119.6

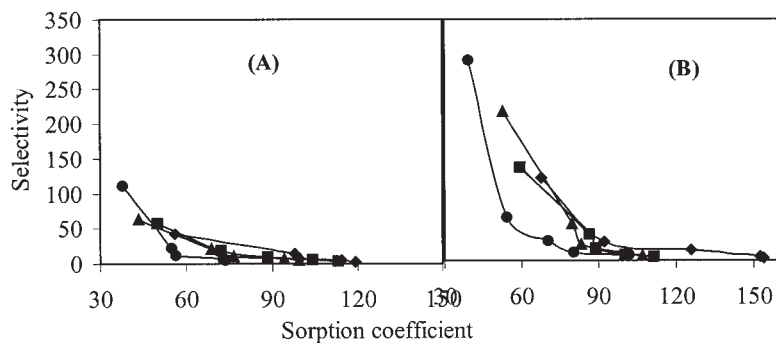


Figure 8 Plot of PV selectivity versus sorption coefficients of permeating molecules membranes. Symbols have the same meaning as given in Figure 1.

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. (16) computes increasing concentrations moving upward with time, i.e., $C_{i+1,j}$ (representing upward curves). Such iterations are continued until the numerical approximation to equilibrium or steady state is achieved (minima). Values of Δt are considered in the numerical analysis and the barrier membrane is divided into the number of equal finite slices of thickness, Δx , by the concentration difference planes.

Concentration profiles for water + 1,4-dioxane mixtures calculated at 30°C from eq. (11) at different exposure times and imaginarily divided depths of liquid penetration through the membranes are displayed in Figure 6 for M-1, M-2, and M-3 membranes. Concentration profiles follow the same sequence as those of sorption and diffusion data discussed before for a particular membrane-liquid mixture. However, it was not possible to compute the concentration profiles for M-4 since these curves skipped out of the graphic scale that was initially fixed in the program. However, we would expect similar dependencies for M-4 as observed for M-1, M-2, and M-3 membranes. Similar plots are displayed in Figure 7 for M-1, M-2, M-3, and M-4

membranes for water + THF mixtures. Here, the concentration profiles are much smaller than those observed for water + 1,4-dioxane mixtures. These data fall in line with sorption and diffusion results. It was observed from Figures 6 and 7 that concentration profiles exhibit the minima values at the middle of the barrier membrane for both the mixtures, but decreasing and increasing trends are observed at the face as well as bottom sides, indicating the validity of the model used.

Pervaporation selectivity versus equilibrium sorption/diffusion coefficients

The optimum PV selectivity data of all the membranes calculated from eq. (1) are presented in Table VI for mixtures containing 10 mass % of water. An attempt was made to correlate between PV selectivity data with sorption and diffusion coefficients of the permeating molecules through the membranes. PV selectivity versus sorption coefficients for both of the mixtures are displayed in Figure 8. It can be noticed that sorption values are higher for water + THF mixtures than water + 1,4-dioxane mixtures. Membrane selectivity to water decreased with increasing sorption. This could be due to higher swelling of the membrane at

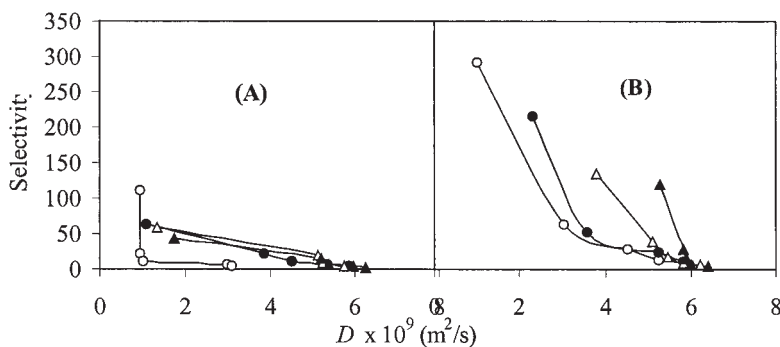


Figure 9 Plot of PV selectivity versus diffusion coefficients of permeating molecules through membranes. Symbols have the same meaning as given in Figure 1.

the higher composition of water. Results of PV selectivity versus diffusion coefficients of the permeating molecules are displayed in Figure 9. It is observed that, as the diffusion coefficients increase, membrane selectivity decreases. Thus, there exists a correlation between membrane swelling, sorption, and diffusion coefficients of the permeating molecules with the membrane selectivity.

CONCLUSIONS

The present study is a unified approach to understand the preferential transport in mixed media viz., water + 1,4-dioxane and water + THF through the pure as well as blend membranes of sodium alginate and poly(vinyl alcohol). Blend compatibility was studied by solution viscosity. Sorption and diffusion coefficients were obtained by the gravimetric technique. Diffusion anomalies and concentration profiles have been computed to understand their relationships with the pervaporation separation characteristics of the membranes. Membranes of this study are water selective.

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