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Sorption and Diffusion Kinetics of Binary Organic Mixtures of Bis(2-methoxyethyl) Ether with Organic Esters into Tetrafluoroethylene + Propylene Copolymer Membranes at 298.15 K

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Sorption kinetics and diffusion of liquids and binary liquid mixtures of bis(2-methoxyethyl) ether with methyl acetate, ethyl acetate, butyl acetate, diethyl succinate, methyl benzoate, ethyl benzoate, and methyl salicylate into tetrafluoroethylene + propylene copolymer membranes have been studied at 298.15 K using a sorption gravimetric method. Coefficients of diffusion have been calculated from Fick's equation. The dependence of sorption and diffusion coefficients on viscosity, molar volume, excess molar volume, and Flory−Huggins interaction parameter has been discussed.

Introduction

In recent years, elastomer membranes have received a renewed interest in view of their potential advantages as flexible engineering materials in extreme service conditions involving exposure to mixed solvent systems. Among the many commercially available elastomers, 3M's fluoroelastomers, viz., tetrafluoroethylene + propylene copolymers, are some of the versatile engineering materials used in a number of areas where solvent exposure is a problem (Aminabhavi and Phayde, 1994a, 1994b). These polymers are known to be the premium materials for applications requiring chemical resistance with high-temperature operating capacity.

In our earlier papers (Aithal et al., 1990; Aminabhavi and Phayde, 1995a, 1995b, 1995c; Aminabhavi and Munnolli, 1994, 1995; Aminabhavi et al., 1995), the sorption and diffusion kinetics of a variety of organic liquids into several engineering polymer membranes have been studied. It was realized that if the polymer membrane swells, then the sorbed liquid transport may deviate slightly from the Fickian mechanism because solvent diffusion in the swollen membrane is affected by the molecular size of the liquid, degree of cross-linking, and equilibrium swelling of the polymer (Aithal et al., 1990). With mixed solvents, the individual solvent components diffuse at different rates than their binary mixtures due to preferential sorption (Aminabhavi and Munk, 1979). The transport coefficients depend upon (i) the nature of interactions between the mixture components as studied in terms of excess mixing quantities (Aminabhavi et al., 1993a, 1993b, 1994b, 1994c; Aralaguppi et al., 1991, 1992a, 1992b) and (ii) overall interactions of the mixed solvents with the polymer chain segments.

In this paper, sorption data have been used to estimate the diffusion coefficients of pure liquids and binary mixtures. The dependence of sorption and diffusion on viscosity, η, molar volume, V_m, excess molar volume, V^E, and Flory−Huggins interaction parameter, χ_{1-p} have been studied. Such a study would be useful in selecting the suitable membrane in the pervaporation separation of organic−organic and organic−aqueous mixtures (Aminabhavi et al., 1994a). In the present paper, results of sorption and diffusion of eight liquids and seven binary mixtures comprising bis(2-methoxyethyl) ether, methyl acetate, ethyl acetate, butyl acetate, diethyl succinate, methyl benzoate, ethyl benzoate, and methyl salicylate at 298.15 K are published. These results are discussed in terms of the thermodynamic interactions between solvent mixtures and the individual components with the polymer chain segments.

Experimental Section

Materials and Methods. Bis(2-methoxyethyl) ether (B.D.H., England), methyl benzoate (Naarden, Holland), and diethyl succinate (Riedel, Germany) were used as supplied, whereas methyl acetate (Sisco, India), ethyl acetate (Fischer, India), butyl acetate (Sisco, India), ethyl benzoate (C.D.H., India), and methyl salicylate (Oversea Chinese Chemicals Factory, Shanghai, China) were purified by the recommended procedures (Riddick et al., 1986; Vogel, 1989). The purity of these solvents was ascertained by the constancy of their boiling temperatures during final distillation and also by comparing their density and refractive index values at 298.15 K with the published results. The gas chromatographic tests using a flame ionization detector (Nucon Series 5700/5765 with fused silica columns) having a sensitivity better than 10^{-8} g of fatty acid/μL of solvent showed a purity of >99 mol % in all cases (see Table 1).

Mixtures were prepared by mixing appropriate volumes of liquids in specially designed ground-glass airtight bottles and weighing in a single-pan Mettler balance (Model AE-240), to an accuracy of ±0.0001 g. The possible error in mole fractions, x_1, of bis(2-methoxyethyl) ether is ±0.0001. The stock solutions of the mixtures were kept in airtight glass stoppered bottles, and their physical properties like density, refractive index, and viscosity did not change during the period of measurements.

Densities of liquids and their binary mixtures were measured with a pycnometer having a bulb volume of about 20 cm^3 and a capillary of 1 mm internal diameter. The experimental details are the same as earlier (Aralaguppi et al., 1991, 1992a, 1992b). Density values at 298.15 K are considered significant to four figures. An average of triplicate measurements was taken into account, and these were reproducible within ±0002 g·cm^{-3}.

Viscosities were measured with a Cannon Fenske viscometer (size 75, ASTM D445) supplied by Industrial Research Glassware Ltd. An electronic stopwatch was used to measure the flow times, and the triplicate mea-

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Table 1. Comparison of Some Physical Properties of Liquids at 298.15 K

liquid (mol % purity)	V/cm^3·mol^{-1}	ρ/g·cm^{-3}	η/mPa·s	n	ref (for ρ and n_D)
bis(2-methoxyethyl) ether (>99.4)	142.8	0.9396 (0.9384)	0.973	1.4070 (1.4058)	Riddick et al., 1986
methyl acetate (>99.3)	80.4	0.9213 (0.9279)	0.385	1.3587 (1.3589)	Riddick et al., 1986
ethyl acetate (>99.2)	98.6	0.8939 (0.8946)	0.430	1.3714 (1.3698)	Riddick et al., 1986
butyl acetate (>99.5)	132.6	0.8759 (0.8764)	0.679	1.3929 (1.3918)	Riddick et al., 1986
diethyl succinate (>99.1)	125.6	1.0353	2.466	1.4196	Riddick et al., 1986
methyl benzoate (>99.3)	144.1	1.0837 (1.0790)[a]	1.810	1.5152 (1.5146)	Riddick et al., 1986
ethyl benzoate (>99.5)	129.2	1.0421 (1.0372)[a]	1.936	1.5046 (1.5035)	Riddick et al., 1986
methyl salicylate (99.3)	168.3	1.1782 (1.1782)	1.535	1.5350 (1.5365)[b]	Riddick et al., 1986

[a] At 303.15 K. [b] At 293.15 K.

surements were reproducible within ±0.01 s. Calibration of the viscometer and experimental details are the same as given earlier (Aralaguppi et al., 1991, 1992a, 1992b). In all cases, the viscosity values are accurate to ±0.001 mPa·s.

Refractive indices, n_D, for the sodium-D line were measured using a thermostated Abbe refractometer (Bellingham and Stanley Ltd., London) within a precision of ±0.0001 unit. Water was circulated into the instrument through a thermostatically controlled bath. The refractometer was calibrated using a glass test piece of known refractive index supplied with the instrument.

Sorption Experiments. The FA 100S grade Aflas tetrafluoroethylene + propylene copolymer membranes were procured from 3M Industrial Chemical Products Division, St. Paul, MN (courtesy of Ms. Nena McCallum). Details of their preparations and fabrication compositions have been described earlier (Aminabhavi and Phayde, 1994a, 1994b). The circular disk-shaped polymer samples (diameter 1.94−1.97 cm) were cut from large sheets using a sharp-edged carbon-tipped steel die.

Samples were dried in a vacuum incubator kept at 298.15 K overnight before use. These samples were then soaked in screwtight test glass bottles containing 15−20 of the mixed solvent system or the liquid. At specified intervals of time, the polymer samples were removed from the test bottles, and the surface-adhered liquid drops were removed by carefully pressing between smooth filter paper wraps and weighed immediately on a digital Mettler balance to the nearest accuracy of ±0.0001 g. Mass determinations were done until attainment of equilibrium saturation. The percent mass uptake, M_t, was calculated using

$$M_t = \left(\frac{w_t - w_0}{w_0}\right)100 \qquad (1)$$

where w_0 is the initial mass of the polymer sample and w_t refers to the mass at time t.

Results and Discussion

Sorption Kinetics. Sorption results of liquids and their mixtures calculated in mass percent units (g/g) are plotted as a function of square root of time in Figures 1−4. For mixtures of bis(2-methoxyethyl) ether + methyl acetate shown in Figure 1A, sorption of methyl acetate increases initially, exhibiting an overshoot effect, i.e., reaching a maximum and decreasing thereafter over a period of time to give the final equilibrium value. Such overshoot effects are also observed for mixtures of bis(2-methoxyethyl) ether + methyl acetate at x_1 = 0.20, 0.35, 0.50, and 0.65. However, at x_1 = 0.80 and for pure bis(2-methoxyethyl) ether, overshoot effects are not observed. The prevalence of overshoot effects may be attributed to changes in copolymer morphology or possibly due to a loss of additives from the polymer during immersion tests. The latter effect was ruled out because no additive loss occurred during sorption experiments.

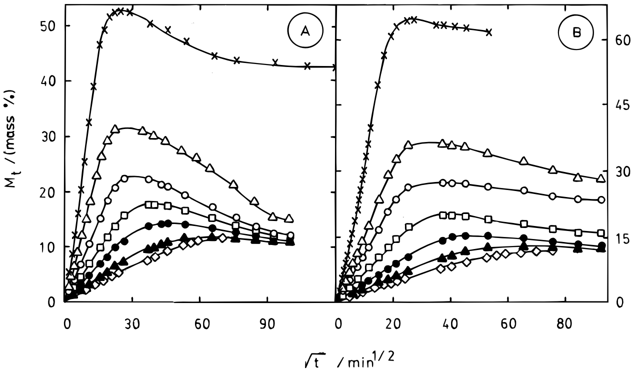

Figure 1. Sorption curves for mixtures of bis(2-methoxyethyl) ether (A) with methyl acetate and (B) with ethyl acetate into tetrafluoroethylene/propylene copolymer membranes. Symbols: (×) x_1 = 0.0; (△) x_1 = 0.2; (○) x_1 = 0.35; (□) x_1 = 0.5; (●) x_1 = 0.65; (▲) x_1 = 0.8; (◇) x_1 = 1.0.

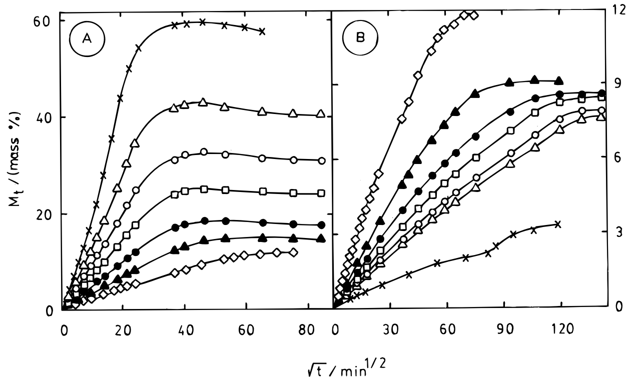

Figure 2. Sorption curves for mixtures of bis(2-methoxyethyl) ether (A) with n-butyl acetate and (B) with diethyl succinate into tetrafluoroethylene/propylene copolymer membranes. Symbols have the same meanings as in Figure 1.

Sorption of bis(2-methoxyethyl) ether is nearly 5 times smaller than that observed for methyl acetate. For mixtures of bis(2-methoxyethyl) ether with ethyl acetate (Figure 1B), sorption values are slightly higher but the overshoot effects and the time to attain equilibrium sorption are somewhat smaller than the methyl acetate containing mixtures. For both these mixtures, the mixture sorption properties are influenced by bis(2-methoxyethyl) ether and this effect is more for methyl acetate than ethyl acetate containing mixtures. This may be attributed to higher specific interactions in these mixtures, as evidenced by their negative values of V^E.

The sorption results for mixtures of bis(2-methoxyethyl) ether + butyl acetate and +diethyl succinate are presented in Figure 2. The sorption curves for bis(2-methoxyethyl) ether + butyl acetate mixtures are quite widely spaced compared to those presented in Figure 1. This indicates

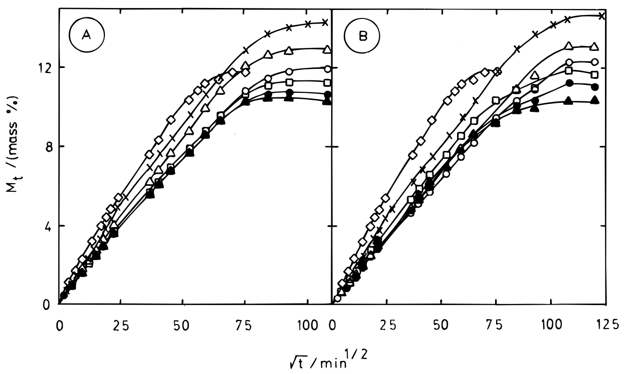

Figure 3. Sorption curves for mixtures of bis(2-methoxyethyl) ether (A) with methyl benzoate and (B) with ethyl benzoate into tetrafluoroethylene/propylene copolymer membranes. Symbols have the same meanings as in Figure 1.

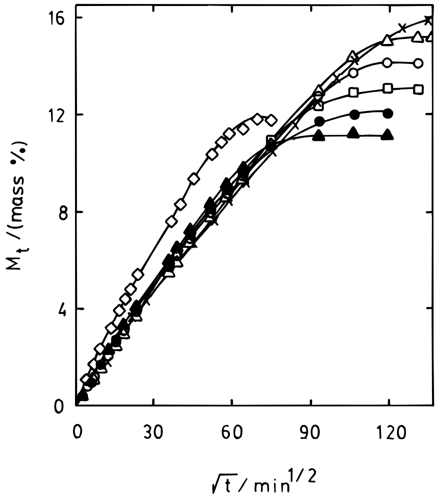

Figure 4. Sorption curves for mixtures of bis(2-methoxyethyl) ether + methyl salicylate into tetrafluoroethylene/propylene copolymer membranes. Symbols have the same meanings as in Figure 1.

Table 2. Sorption Coefficients, S (mass %), and Diffusion Coefficient, D (10^{-7} cm^2·s^{-1}), for Bis(2-methoxyethyl) Ether (1) + Ester (2) Mixtures at Different Mole Fractions (x_1) of Bis(2-methoxyethyl) Ether at 298.15 K

Bis(2-methoxyethyl) ether with	x_1						
	0.0	0.20	0.35	0.50	0.65	0.80	1.0
				S/mass %			
methyl acetate	52.51	31.24	22.26	17.71	14.33	11.76	11.80
ethyl acetate	64.31	36.20	27.35	19.93	15.32	12.83	11.80
butyl acetate	59.59	42.87	32.66	25.07	18.42	14.77	11.80
diethyl succinate	2.89	7.60	7.90	8.42	8.57	9.14	11.80
methyl benzoate	14.36	12.89	11.94	11.23	10.74	10.46	11.80
ethyl benzoate	14.72	13.08	12.33	11.92	11.27	10.39	11.80
methyl salicylate	15.97	15.17	14.12	13.07	12.02	11.21	11.80
				$D/10^{-7}$ cm^2·s^{-1}			
methyl acetate	6.06	4.41	2.94	2.15	1.38	0.97	0.61
ethyl acetate	4.23	3.32	2.25	1.69	1.34	0.83	0.61
butyl acetate	2.08	1.77	1.51	1.25	1.03	0.75	0.61
diethyl succinate	0.12	0.12	0.15	0.18	0.25	0.33	0.61
methyl benzoate	0.25	0.23	0.25	0.27	0.31	0.36	0.61
ethyl benzoate	0.19	0.17	0.20	0.20	0.26	0.33	0.61
methyl salicylate	0.14	0.17	0.20	0.25	0.30	0.38	0.61

that the mixture sorption properties are not influenced by the individual components (Figure 2A). For bis(2-methoxyethyl) ether + diethyl succinate mixtures (Figure 2B), the sorption curves for mixtures are closely spaced and are not greatly influenced by the pure components. This is attributed to lower specific interactions; i.e., V^E values are larger for mixtures containing butyl acetate than for those with diethyl succinate. Another contrasting observation in Figure 2B is that the sorption values of diethyl succinate are about 4 times smaller than those observed for bis(2-methoxyethyl) ether. Also, the attainment of equilibrium sorption for bis(2-methoxyethyl) ether is quicker when compared to diethyl succinate.

Sorption curves for bis(2-methoxyethyl) ether + aromatic esters (i.e., methyl benzoate and ethyl benzoate) presented in Figure 3 exhibit quite contrasting behavior when compared to those for the mixtures containing aliphatic esters presented in Figures 1 and 2. Bis(2-methoxyethyl) ether exhibits a higher sorption initially, and later its equilibrium values are lower than those of methyl or ethyl benzoates. Also, sorption curves for these mixtures at $x_1 = 0.2$ and $x_1 = 0.35$ lie between those of their liquid components. For the remaining mixtures containing higher compositions of bis(2-methoxyethyl) ether, sorption values are lower than observed for the individual components of the mixtures. This may be due to higher specific interactions in these mixtures, as evidenced by higher negative values of V^E. Moreover, the initial slopes (<55% completion of sorption) of the linear part of the sorption curves are almost identical for these mixtures, suggesting identical transport mechanisms. Similar patterns are also observed for mixtures bis(2-methoxyethyl) ether + methyl salicylate shown in Figure 4. In this case, at $x_1 = 0.8$, the equilibrium sorption is lower than that observed for bis(2-methoxyethyl) ether. For the remaining mixture compositions, sorption curves are between those of their pure components. Also, the initial slopes of the sorption curves for all the compositions are quite identical. In all systems presented in Figures 1−4, initially the mass % uptake shows an increase with $t^{1/2}$. This is indicative of the fact that the crystalline polypropylene and the glassy poly(tetrafluoroethylene) chains move differently relative to the solvent diffusion, resulting in Fickian transport.

Values of sorption coefficients, S, have been calculated in mass % units (g/g) from the equilibrium sorption curves, and these results are presented in Table 2. It is observed that sorption values for mixtures containing all esters except diethyl succinate decrease with the increasing amount of bis(2-methoxyethyl) ether in the mixture. On the other hand, for mixtures of bis(2-methoxyethyl) ether + diethyl succinate, extremely smaller values of S are observed and these increase with increasing values of x_1. Among the aliphatic esters studied, ethyl acetate exhibits the highest value of S, while diethyl succinate has the lowest S. Though butyl acetate has a lower S than ethyl acetate, its binary mixtures exhibit higher S values than either ethyl acetate or methyl acetate containing mixtures. This suggests that mixtures of bis(2-methoxyethyl) ether + butyl acetate exhibit stronger thermodynamic interactions with the polymer chain segments than methyl or ethyl acetate containing mixtures.

Sorption results have been further analyzed using the generalized relation for the transport kinetics (Lustig and Peppas, 1988):

$$M_t/M_\infty = Kt^n \qquad (2)$$

where M_t and M_∞ are the mass uptakes at time t and equilibrium time, K is a constant incorporating the characteristics of the macromolecule and penetrant systems, and n is the diffusional exponent, which is indicative of the transport mechanism. If $n = 0.5$ or close to it, then the transport is considered as Fickian. For $n = 1.0$, the transport becomes non-Fickian. If n varies between 0.5 and 1.0, then the transport is described as anomalous.

Table 3. Analysis of Sorption Results of Mixtures by Eq 2 for Different Mole Fractions (x_1) of Bis(2-methoxyethyl) Ether at 298.15 K

bis(2-methoxyethyl) ether with	x_1						
	0.0	0.20	0.35	0.50	0.65	0.80	1.0
	10^2 K/(g/g (min)^n)						
methyl acetate	3.85	4.33	3.90	3.32	3.05	2.42	2.01
ethyl acetate	3.50	3.46	3.53	3.39	2.91	2.41	2.01
butyl acetate	2.42	2.61	2.70	2.73	2.71	2.51	2.01
diethyl succinate	1.19	1.24	1.24	1.45	1.65	1.77	2.01
methyl benzoate	1.29	1.51	1.59	1.73	1.78	1.97	2.01
ethyl benzoate	1.06	1.23	1.33	1.63	1.69	1.73	2.01
methyl salicylate	1.04	1.16	1.29	1.45	1.60	1.69	2.01
	n						
methyl acetate	0.58	0.53	0.52	0.51	0.50	0.50	0.50
ethyl acetate	0.56	0.54	0.53	0.51	0.50	0.50	0.50
butyl acetate	0.56	0.53	0.52	0.51	0.50	0.50	0.50
diethyl succinate	0.50	0.50	0.50	0.50	0.50	0.50	0.50
methyl benzoate	0.51	0.50	0.50	0.50	0.50	0.50	0.50
ethyl benzoate	0.51	0.50	0.50	0.50	0.50	0.50	0.50
methyl salicylate	0.50	0.50	0.50	0.50	0.50	0.50	0.50

From the least-squares estimations of K and n presented in Table 3, the values of n vary between 0.50 and 0.58, suggesting Fickian diffusion. This fact is also supported from the nonsigmoidal nature of the sorption curves shown in Figures 1−4. K increases with an increasing amount of bis(2-methoxyethyl) ether in the mixtures containing methyl benzoate, ethyl benzoate, methyl salicylate, or diethyl succinate. However, for mixtures containing lower esters, the trend is not very systematic.

Diffusion Coefficients. When an organic liquid migrates into the membrane material which does not dissolve in it, then the diffusion process follows Fick's law (Crank, 1975):

$$J = -D \operatorname{grad} C \tag{3}$$

where J, D, and C are respectively flux, diffusion coefficient, and concentration of the solvent in the polymer. In the case of binary mixtures, a coupling effect exists between the flow of the respective components and the mixture diffusion can be regarded as effective diffusion. It may be assumed that the diffusing molecules enter or leave the barrier material through the parallel faces with a negligible amount through edges.

Thus, the one-dimensional diffusion inside the membrane with two parallel planes at $x = 0$ and $x = h$ is considered along the x-axis so that the effective diffusion coefficient, D, is calculated by solving Fick's second-order equation (Crank, 1975) before 55% of equilibrium sorption (Aithal et al., 1990):

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

To calculate diffusion coefficients from eq 4, the initial linear sorption results are used. These results are compared in Table 2. The calculated diffusivity values are accurate within ±0.005 units of diffusivity but are approximated to two decimal places.

Effective diffusion coefficients for pure components and their mixtures are presented in Table 2. These values decrease with increasing amounts of bis(2-methoxyethyl) ether in mixtures of methyl acetate, ethyl acetate, or butyl acetate. This may be due to the fact that the molar volume of bis(2-methoxyethyl) ether is higher than the above mentioned esters (Table 2), and with the increasing amount of bis(2-methoxyethyl) ether in the mixture, the average molar volume of the mixture also increases, thereby a decrease in diffusivity. On the other hand, no such trends are observed with the remaining binary mixtures. The results of D for pure components and their mixtures vary with respect to the second component of the mixture according to the sequence methyl acetate > ethyl acetate > butyl acetate > methyl benzoate > ethyl benzoate > methyl salicylate > diethyl succinate.

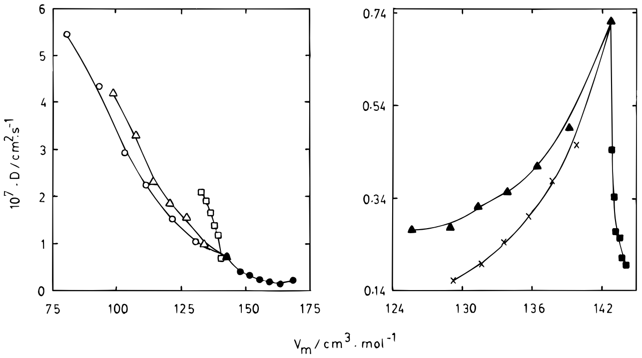

Figure 5. Diffusivity versus molar volume of mixtures of bis(2-methoxyethyl) ether + aliphatic esters. Symbols: (○) methyl acetate; (△) ethyl acetate; (□) n-butyl acetate; (●) diethyl succinate; (▲) methyl benzoate; (■) ethyl benzoate; (×) methyl salicylate.

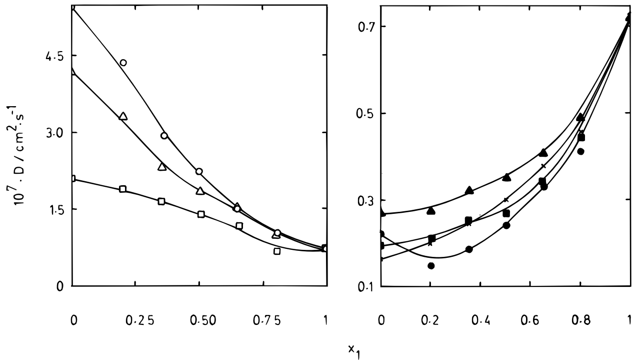

Figure 6. Diffusivity D versus mole fraction (x_1) for mixtures of bis(2-methoxyethyl) ether + esters. Symbols have the same meanings as in Figure 5.

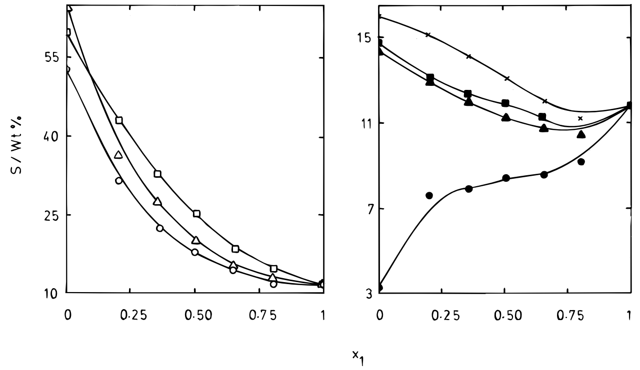

Figure 7. Sorption coefficient S versus molar fraction (x_1) for mixtures of bis(2-methoxyethyl) ether + esters. Symbols have the same meanings as in Figure 5.

The dependence of diffusivity on the molar volume of the mixtures, shown in Figure 5, is different for mixtures of aliphatic esters than aromatic esters. The variation of D on the mole fraction of the mixtures is presented in Figure 6, while that of solubility is displayed in Figure 7. Both the plots exhibit nonlinear curves for all the mixtures, and this is indicative of the specific interactions between the mixture components and the polymer chain segments. To investigate this effect quantitatively, the Flory−Huggins (Flory, 1953) interaction parameter, χ_{1-p} was calculated for

Table 4. Density, ρ_m, viscosity, η_m, Excess Molar Volume, V^E, Molar Volume, V_m, and Interaction Parameter, χ_{1-p}, of Binary Mixtures at 298.15 K

x_1	ρ_m/ $cm^3 \cdot mol^{-1}$	η_m/ mPa·s	$10^2 V^E$/ $cm^3 \cdot mol^{-1}$	V_m/ $cm^3 \cdot mol^{-1}$	χ_{1-p}
Bis(2-methoxyethyl) Ether (1) + Methyl Acetate (2)					
0.20	0.9277	0.498	−7.858	93.0	1.004
0.35	0.9309	0.590	−11.722	103.0	1.138
0.50	0.9342	0.683	−14.350	111.2	1.150
0.65	0.9361	0.772	−14.323	121.5	1.180
0.80	0.9380	0.861	−9.225	130.4	1.224
Bis(2-methoxyethyl) Ether (1) + Ethyl Acetate (2)					
0.20	0.9069	0.527	−9.256	107.4	0.667
0.35	0.9140	0.608	−13.611	114.3	0.757
0.50	0.9220	0.690	−16.299	120.8	0.975
0.65	0.9280	0.779	−16.195	127.1	1.093
0.80	0.9337	0.867	−11.875	133.9	1.141
Bis(2-methoxyethyl) Ether (1) + Butyl Acetate (2)					
0.20	0.8894	0.734	0.936	134.7	0.506
0.35	0.8990	0.778	1.448	136.3	0.622
0.50	0.9090	0.822	0.412	137.8	0.743
0.65	0.9194	0.873	−1.080	139.2	0.920
0.80	0.9294	0.924	−1.594	140.6	1.033
Bis(2-methoxyethyl) Ether (1) + Diethyl Succinate (2)					
0.20	1.0190	2.009	−8.515	163.1	1.529
0.35	1.0054	1.773	−13.073	159.2	1.491
0.50	0.9920	1.535	−15.759	155.3	1.435
0.65	0.9771	1.361	−15.466	151.5	1.412
0.80	0.9621	1.187	−11.348	147.8	1.355
Bis(2-methoxyethyl) Ether (1) + Methyl Benzoate (2)					
0.20	1.0530	1.622	−15.482	128.9	1.184
0.35	1.0311	1.494	−26.690	131.4	1.221
0.50	1.0096	1.367	−31.884	133.9	1.247
0.65	0.9885	1.248	−30.440	136.4	1.268
0.80	0.9670	1.129	−22.464	139.2	1.276
Bis(2-methoxyethyl) Ether (1) + Ethyl Benzoate (2)					
0.20	1.0222	1.694	−14.119	143.7	1.156
0.35	1.0070	1.541	−20.793	143.6	1.184
0.50	0.9926	1.389	−24.528	143.2	1.210
0.65	0.9774	1.262	−26.039	143.1	1.223
0.80	0.9618	1.134	−23.659	142.8	1.267
Bis(2-methoxyethyl) Ether (1) + Methyl Salicylate (2)					
0.20	1.1275	2.134	−12.218	131.8	1.123
0.35	1.0910	1.850	−18.792	133.6	1.149
0.50	1.0544	1.567	−23.004	135.7	1.180
0.65	1.0199	1.380	−23.396	138.0	1.209
0.80	0.9855	1.194	−18.221	139.8	1.237

the polymer−solvent systems using

$$\chi_{1-p} = -\frac{\ln(1-\phi_P)+\phi_P}{\phi_P} \tag{5}$$

where ϕ_P is volume fraction of the polymer calculated by using (Aithal et al., 1990):

$$\phi_P = \left[1 + \frac{\rho_P M_a}{\rho_S M_b} - \frac{\rho_P}{\rho_S}\right]^{-1} \tag{6}$$

where ρ_P, ρ_S, M_a, and M_b are the density of the polymer, density of the solvent, mass of the polymer after swelling, and mass of the polymer before swelling, respectively. Computed values of χ_{1-p} are included in Table 4. Generally, the large value of χ_{1-p} indicates a weaker interaction between the liquids and the polymer segments.

The values of χ_{1-p} for all the mixtures except the one containing diethyl succinate increase with the increasing amount of bis(2-methoxyethyl) ether, suggesting weak thermodynamic interactions with the polymer chain segments. This observation is consistent with the decreasing sorption values (Table 2). Furthermore, a systematic decrease in the values of χ_{1-p} is observed for mixtures containing methyl acetate, ethyl acetate, or butyl acetate. Similar trends are observed for mixtures containing methyl benzoate, ethyl benzoate, or methyl salicylate. The values of χ_{1-p} for bis(2-methoxyethyl) ether + diethyl succinate mixtures are higher than the remaining mixtures, indicating lower interactions with the membrane.

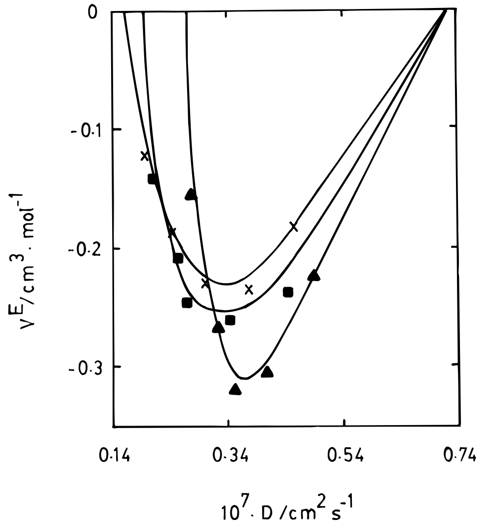

Figure 8. Diffusivity versus excess molar volume for mixtures of bis(2-methoxyethyl) ether + aromatic esters. Symbols are the same as in Figure 5.

Realizing the fact that the binary mixture properties affect the transport results, the excess molar volume, V^E, which represents the interaction in binary mixtures has been calculated (Aralaguppi et al., 1991) as

$$V^E/cm^3 \cdot mol^{-1} = V_m - V_1 x_1 - V_2 x_2 \tag{7}$$

where molar volumes V_m, V_1, and V_2 of the mixtures of pure components 1 and 2 are calculated as

$$V_m/cm^3 \cdot mol^{-1} = \frac{M_1 x_1 + M_2 x_2}{\rho_m};$$

$$V_1/cm^3 \cdot mol^{-1} = \frac{M_1}{\rho_1}; \qquad V_2/cm^3 \cdot mol^{-1} = \frac{M_2}{\rho_2} \tag{8}$$

In the above equations, M_1 and M_2 are the molecular weights of components 1 and 2; ρ_i represents density of the ith component of the mixture. The experimental density ρ_m, viscosity η_m, and the calculated values of V^E and V_m are compiled in Table 4.

The V^E results of all mixtures except bis(2-methoxyethyl) ether + butyl acetate are negative, suggesting the specific dipole−dipole interactions between the components. The extent of these interactions varies depending upon the nature of the ester. Mixtures of bis(2-methoxyethyl) ether + aromatic esters (Aminabhavi et al., 1993a, 1993b, 1994b, 1994c) exhibit larger negative V^E than the mixtures containing aliphatic esters. A typical graph showing the dependence of V^E on D for the binary mixtures containing aromatic esters is displayed in Figure 8. The interactions in bis(2-methoxyethyl) ether + aromatic esters may originate from the dipole-induced dipole forces resulting from the polarization of esters by the dipoles of the bis(2-methoxyethyl) ether molecule. This effect, when superimposed on the dipole−dipole interactions, leads to an increase in the attraction, giving large V^E. This may be the reason for the increased diffusivity of these mixtures with the increasing value of the mole fraction.

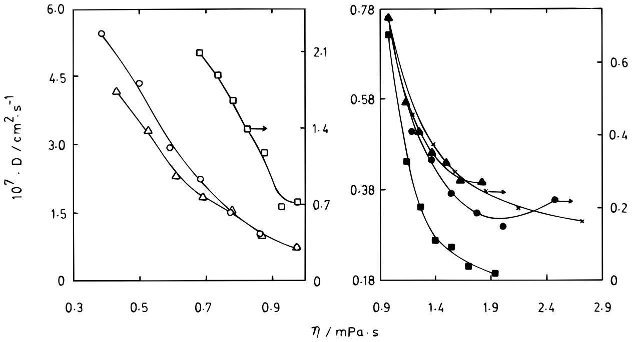

Figure 9. Diffusivity versus viscosity for mixtures of bis(2-methoxyethyl) ether + esters. Symbols have the same meanings as in Figure 5.

The diffusion results of the mixtures vary systematically with mixture viscosities, as shown in Figure 9. This type of variation was also observed by Vahdat (1991) for the elastomer−solvent systems and is in accordance with the Stokes−Einstein equation (Atkins, 1986):

$$D = \frac{kT}{6\pi\eta r} \tag{9}$$

Here, k is the Boltzmann constant, T is the absolute temperature, η is the mixture viscosity, and r is the hydrodynamic radius of the transporting molecules or mixture as a whole. Here, D is inversely proportional to η and this explains the results presented in Figure 9.

Conclusions

Aspects of sorption and diffusion kinetics of seven binary mixtures of bis(2-methoxyethyl) ether with methyl acetate, ethyl acetate, butyl acetate, diethyl succinate, methyl benzoate, ethyl benzoate, and methyl salicylate are studied at 298.15 K using a sorption gravimetric method. Sorption and diffusion coefficients of the mixtures depend upon the type of mixture components and nature of solvent−solvent interactions. For the mixtures containing aliphatic esters, sorption lies between the pure components, and this trend is not seen for mixtures of aromatic esters. Diffusion and sorption coefficients exhibit a systematic dependence on molar volume and viscosity of the mixtures. Correlations have been attempted between diffusivity and excess molar volume of the binary mixtures. The present study may be useful to field engineers and technologists for a proper selection of the membranes in areas that involve the mixed-solvent media.

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