

Molecular transport of binary liquid mixtures into EPDM and NBR membranes at 25°C

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Diffusion and sorption of several organic solvents and their binary mixtures in the whole scale of mixture composition have been studied at 25°C with NBR and EPDM rubber membranes. Diffusion results of single solvents as well as binary mixtures have been analysed to study their dependence on concentration of the probe molecules in rubber membranes.

Permselective membranes have tremendous applications in separation techniques and related areas. The molecular design of a permselective membrane is based on both sorption and diffusion phenomena. While extensive experimental and theoretical studies have been carried out on separation of gaseous mixtures^{1,2}, relatively little has been published on separation of liquid mixtures using polymer membranes³⁻⁷. In this paper, transport data of binary solvent mixtures into NBR and EPDM membranes are presented. These membrane materials are chosen in view of their applications in several areas of science, engineering and technology wherein, they may come into contact with mixed organic liquid media. It is, therefore, useful to know how the polymer membranes would respond to the presence of such mixed solvent media. The conventional weight-gain experiments have been performed to measure sorption, diffusion and permeation of liquids through the selected membranes. However, no efforts are made to investigate the permselectivity; instead, details of molecular transport of mixed organic solvents have been considered.

Materials and Methods

All the solvents were of reagent grade and purified before use. Binary mixtures were prepared by weighing the samples in airtight glass stoppered bottles. Refractive indices of the pure samples and their binary mixtures were measured at 25°C both before and after the sorption experiments.

NBR and EPDM samples were obtained from UTEX Industries, Weimer, Texas. The method of preparation of the polymer films and the elastomer compositions are described in our earlier papers^{8,9}. The polymer sheets were cut into small circular pieces having a diameter of 1.94 cm with

thicknesses of 0.20-0.22 cm and weighing approximately 0.7 g. The sorption experiments were performed as per the procedures given earlier^{10,11}.

Results and Discussion

Sorption kinetics of EPDM

Typical sorption plots for EPDM with benzene + ethyl acetate and benzene + cyclohexane mixtures are given in Figs 1 and 2 while plots for NBR with benzene + carbon tetrachloride and benzene + methyl acetate mixtures are presented in Figs 3 and 4. As shown in Fig. 1, the sorption of benzene, ethyl acetate and their binary mixtures with EPDM increases linearly upto ~50% attainment of equilibrium. This is indicative of the Fickian sorption which should be expected because EPDM used is well above its glass transition temperature and thus, polymer chain segments respond almost instantaneously to the presence of penetrant molecules and their mixtures (i.e., benzene + ethyl acetate). The sorption of benzene is about eight times higher than that of ethyl acetate; however, their binary mixtures in the composition range from 0.2 to 0.8 mole fractions (x_1) show intermediate values.

Sorption results of EPDM with benzene, cyclohexane and their mixtures are presented in Fig. 2. Here, the equilibrium sorption of cyclohexane is higher than that of benzene and this is attributed to the fast movement of the more flexible cyclohexane molecule than the more rigid, flat and sluggish movement of the benzene molecule. Surprisingly, mixtures containing 80%, 60% and 40% of cyclohexane have shown systematically higher sorption values as compared to pure cyclohexane. However, 20% cyclohexane - containing mixture

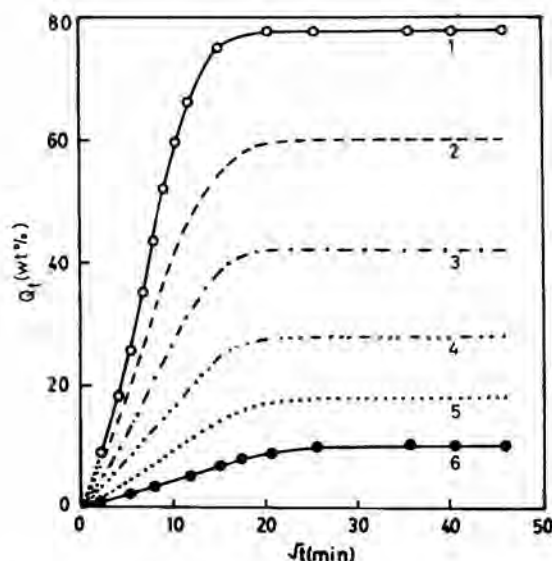


Fig. 1 - Sorption plots of EPDM with benzene + ethyl acetate mixtures at 25°C. 1, (○) Benzene; 2, (---) 80% benzene; 3, (- · - ·) 60% benzene; 4, (· · · ·) 40% benzene; 5, (- - - -) 20% benzene; 6, (●) ethyl acetate

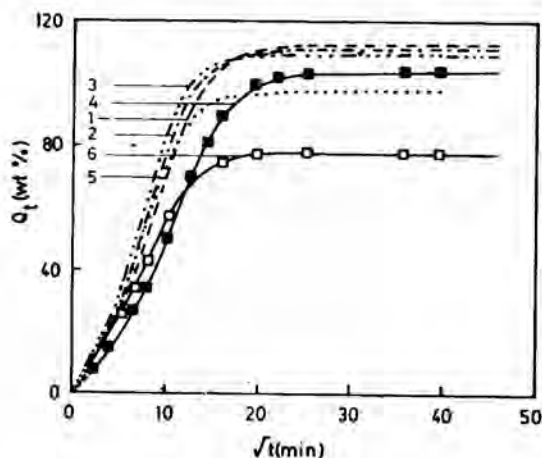


Fig. 2 - Sorption plots of EPDM with benzene + cyclohexane mixtures at 25°C. 6, (□) benzene; 4, (■) cyclohexane; 5, (· · ·) 20% cyclohexane; 3, (- · - ·) 40% cyclohexane; 2, (---) 60% cyclohexane; 1, (- - - -) 80% cyclohexane.

exhibits an intermediate value of equilibrium sorption. The enhanced sorption rates of mixtures of cyclohexane and benzene may be attributed to the change in solvent power of the mixtures at these compositions due to specific interactions. Additionally, benzene + cyclohexane mixture exhibits a non-Fickian diffusive transport mechanism as evidenced by the slight sigmoidal shapes of the Q_t versus $t^{1/2}$ curves.

Sorption results of EPDM with carbon tetrach-

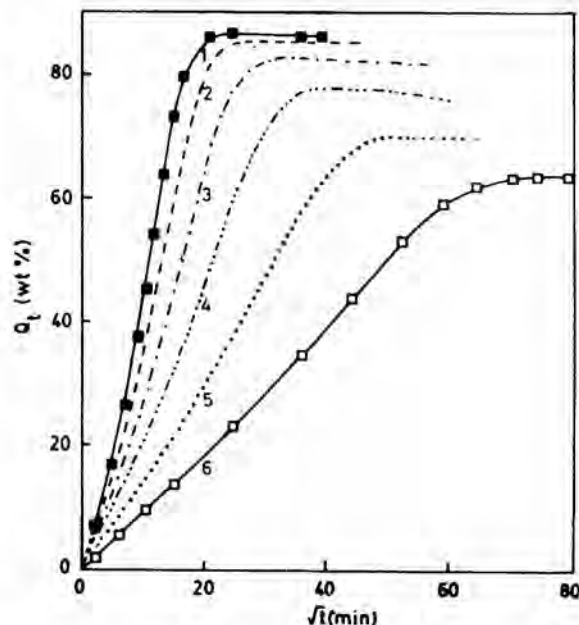


Fig. 3 - Sorption plots of NBR with benzene + carbon tetrachloride mixtures at 25°C. 1, (■) benzene; 6, (□) carbon tetrachloride; 5, (· · ·) 20% benzene; 4, (- · - ·) 40% benzene; 3, (---) 60% benzene; 2, (- - - -) 80% benzene.

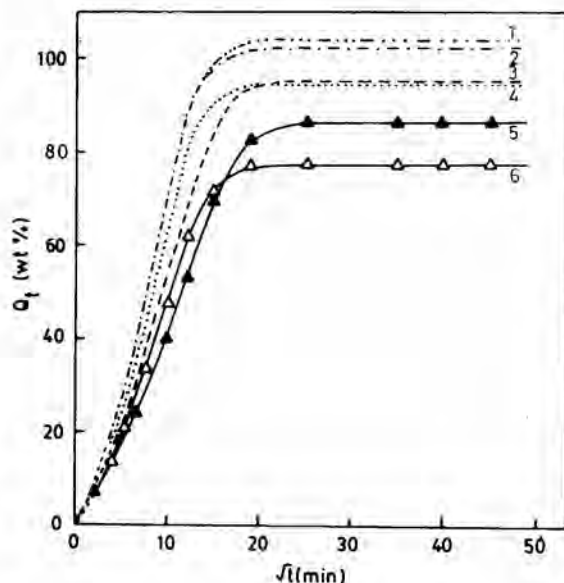


Fig. 4 - Sorption plots of NBR with benzene + methyl acetate mixtures at 25°C. 6, (△) Methyl acetate; 5, (▲) benzene; 4, (· · ·) 20% benzene; 3, (---) 80% benzene; 2, (- · - ·) 60% benzene; 1, (- - - -) 40% benzene

loride, benzene and their mixtures are not presented graphically. However, it may be observed from the data given in Table 1 that sorption of carbon tetrachloride is about two times higher than that of benzene, but their binary mixtures

show sorption data which are in between pure components of the mixture as expected. The sorption results of the mixtures of carbon tetrachloride and cyclohexane are intermediate to those of their pure components; these systems show similar trends as observed in case of benzene and carbon tetrachloride mixtures. The behaviour of EPDM in the presence of mixtures of benzene + methyl acetate is identical to that of benzene + ethyl acetate mixture, but the magnitudes of the sorption data are somewhat different.

Sorption kinetics of NBR

The sorption data shown in Fig. 3 for NBR with benzene, carbon tetrachloride and their binary mixtures exhibit sorption kinetic behaviour typical of sorption of insignificant swelling penetrants in a rubbery polymer. A linear uptake of the penetrants as a function of $t^{1/2}$ was observed in all cases and the sorption curves for the binary mixtures of different compositions lie in between those of pure components comprising the mixed-solvent system. The sorption process is controlled by the relaxation rate which is very slow in comparison to the rate of concurrent diffusion process. Attainment of equilibrium sorption was quicker with benzene than with carbon tetrachloride. This is ascribed to a concentration increase of benzene in the central core of the polymer membrane which might have resulted in accelerated relaxation of the chain and thereby increasing the sorption rate at longer times.

Figure 4 shows the dependence of Q_t on $t^{1/2}$ for NBR with benzene, methyl acetate and their

mixtures. The sorptions of benzene and methyl acetate are not widely different; however, sorption of mixtures of benzene + methyl acetate is higher than either of the pure components. A similar situation exists for NBR with benzene, ethyl acetate and their binary mixtures; however, this dependence is not shown graphically. The sorption results of other binary mixtures may be explained in terms of the established solubility parameter concepts¹². According to this theory, the smaller the difference between the solubility parameters of the two components, the larger is the solubility in the binary mixture.

A similar approach has also been attempted earlier¹³. Benzene, carbon tetrachloride and ethyl acetate are well known swelling agents for EPDM and NBR, while methyl acetate and cyclohexane act as non-solvents. In case of ethyl acetate + carbon tetrachloride mixture, a different behaviour may be expected as these solvents show mutual dipole-induced-dipole interactions on account of their respective electron donating and accepting characters¹⁴. However, in case of benzene + cyclohexane and benzene + carbon tetrachloride mixtures no specific interactions are present and hence, these might not cause deviations. The sorption coefficients S , expressed in weight percent are summarised in Table 1 for all the polymer-mixed solvent systems.

The sorption results have been further analysed^{10,11} by Eq. (1),

$$Q_t/Q_\infty = Kt^n \quad \dots (1)$$

Table 1 - Sorption (S) data for elastomers + binary mixture systems at 25°C

Binary mixtures	S (Wt%) for different mole fractions (x_1) of the first named component					
	$x_1 = 0$	0.2	0.4	0.6	0.8	1.00
EPDM						
$C_6H_6 + C_6H_{12}$	104.13	113.14	111.22	110.30	98.14	77.54
$C_6H_6 + CCl_4$	215.11	192.44	161.57	137.93	105.68	77.75
$C_6H_6 + MeAc$	7.08	14.94	26.36	44.81	66.26	87.26 ^(a)
$C_6H_6 + EtAc$	10.26	18.08	28.14	42.29	59.98	77.77
$CCl_4 + C_6H_{12}$	108.34	130.33	154.55	175.97	200.42	219.77
NBR						
$C_6H_6 + CCl_4$	63.71	69.89	76.56	81.80	85.12	86.13
$C_6H_6 + MeAc$	76.82	95.02	104.30	102.58	95.83	86.60
$C_6H_6 + EtAc$	73.22	82.64	90.14	92.99	92.39	85.32

^(a) refers to EPDM used in refs 8 & 9.

Table 2—Sorption data for elastomers + binary mixtures at 25°C

Binary mixtures	Parameters	Mole fraction (x_1) of first named component of the mixture					
		$x_1 = 0$	0.2	0.4	0.6	0.8	1.00
EPDM							
$C_6H_6 + C_6H_{12}$	$K \times 10^2$	2.09	2.74	3.36	3.55	3.43	3.14
	n	0.66	0.65	0.63	0.65	0.66	0.61
$C_6H_6 + CCl_4$	$K \times 10^2$	2.24	2.64	3.00	3.25	3.85	3.90
	n	0.66	0.65	0.64	0.64	0.61	0.63
$C_6H_6 + MeAc$	$K \times 10^2$	3.54	4.26	4.52	4.46	3.93	4.38
	n	0.51	0.52	0.55	0.54	0.59	0.59
$C_6H_6 + EtAc$	$K \times 10^2$	3.90	3.85	5.12	4.81	5.45	4.16
	n	0.52	0.56	0.52	0.55	0.53	0.61
$CCl_4 + C_6H_{12}$	$K \times 10^2$	2.21	2.27	2.25	2.35	2.28	2.34
	n	0.66	0.65	0.66	0.66	0.66	0.65
NBR							
$C_6H_6 + CCl_4$	$K \times 10^2$	1.08	1.35	2.12	2.20	2.37	2.93
	n	0.55	0.57	0.55	0.58	0.61	0.60
$C_6H_6 + MeAc$	$K \times 10^2$	3.25	3.30	3.20	3.21	2.97	2.74
	n	0.63	0.63	0.64	0.63	0.62	0.61
$C_6H_6 + EtAc$	$K \times 10^2$	2.81	2.45	2.72	2.69	2.75	2.65
	n	0.61	0.64	0.63	0.63	0.62	0.63

^(a) K is expressed in $g/g \cdot min^n$.

where Q_∞ is equilibrium sorption coefficient. The least-squares estimations of K and n are given in Table 2. For majority of polymer-mixed solvent systems, the values of n vary in the range 0.60–0.66 suggesting the presence of anomalous diffusive transport. This enigma is also supported by the slight sigmoidal shapes of the sorption curves for these systems. In case of EPDM with benzene + ethyl acetate mixtures (Fig. 1) and for NBR with benzene + carbon tetrachloride mixture, (Fig. 3), the values of n vary from 0.50 to 0.60 suggesting that the diffusive transport in these systems closely resemble the Fickian mode. This is particularly obvious from the sorption data presented in Fig. 1 for EPDM with benzene + ethyl acetate mixtures. It is seen that the K values of Eq. (1) do not show any systematic effect on the polymer-penetrant interactions.

Diffusion behaviour

Diffusion coefficients were calculated from the initial linear portions of the sorption curves¹⁵ as shown by Eq. (2),

$$D = \pi \left[\frac{h\theta}{4Q_\infty} \right]^2 \quad \dots (2)$$

where h is polymer sample thickness and θ is the slope of the linear part of Q_t versus $t^{1/2}$ plots. These data are summarised in Table 3. The results of D and S for all the binary mixtures as a function of mole fraction are plotted in Fig. 5 (a, b, c and d) and Fig. 6(d) for EPDM and in Fig. 6 (a, b, and c) for NBR.

For EPDM with benzene + ethyl acetate mixture (Fig. 5(a)), D varies linearly with mixture compositions whereas, S varies in a slight concave manner. However, with benzene + methyl acetate mixture, D varies in a convex manner while S varies with a concave shape (Fig. 5(b)). On the other hand, mixtures of cyclohexane + carbon tetrachloride with EPDM show quite different tendencies i.e., S varies linearly while D varies in a sinusoidal manner (Fig. 5(c)). The diffusion behaviour of benzene + cyclohexane mixture is quite different

Table 3 – Diffusivity (D) for elastomers + binary mixture systems at 25°C
 $D \times 10^7$ (cm²/s) for different mole fractions (x_1) of the first named component

Binary mixtures	$x_1 = 0$	0.2	0.4	0.6	0.8	1.00
EPDM						
$C_6H_6 + C_6H_{12}$	3.547	4.520	5.267	6.483	6.807	6.664
$C_6H_6 + CCl_4$	4.207	4.745	5.285	5.958	6.355	7.420
$C_6H_6 + MeAc$	2.142	3.694	5.115	5.535	6.411	6.724
$C_6H_6 + EtAc$	2.570	3.892	4.231	5.270	5.681	6.781
$CCl_4 + C_6H_{12}$	3.489	3.609	3.912	3.640	3.548	3.782
NBR						
$C_6H_6 + CCl_4$	0.315	0.661	1.207	1.866	2.692	3.521
$C_6H_6 + MeAc$	5.222	5.935	6.002	5.158	4.380	3.527
$C_6H_6 + EtAc$	3.745	4.271	4.198	4.250	4.207	4.135

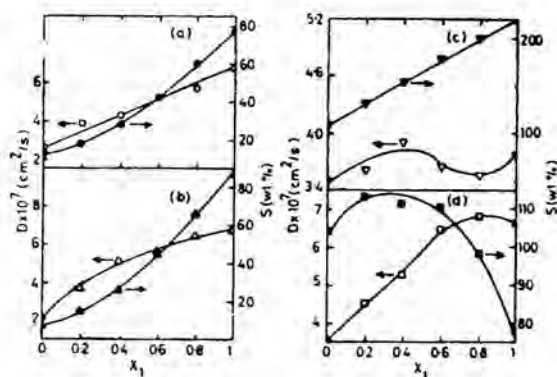


Fig. 5 – Dependence of diffusion coefficients, D, and sorption coefficients S, on mole fraction of the first component in the mixture at 25°C. (a) (○) and (●) EPDM with benzene + ethyl acetate mixtures. (b) (△) and (▲) EPDM with benzene + methyl acetate (c) (▽) and (▼) EPDM with cyclohexane + carbon tetrachloride mixtures. (d) (□) and (■) EPDM with benzene + cyclohexane mixtures.

from other systems in that both the curves (D or S versus x_1) exhibit a maxima (Fig. 5(d)).

For EPDM with benzene + carbon tetrachloride mixture, the dependence of both D and S on x_1 is almost linear (Fig. 6(d)). Similarly, for NBR with benzene + methyl acetate mixture, we could observe pronounced maxima for both D and S around the middle of the mixture composition (Fig. 6(b)). However, this is not true in case of NBR with benzene + ethyl acetate mixtures (see Fig. 6(a)); here, S exhibits a slight maximum whereas, D is almost independent of the mixture composition. On the other hand, for NBR with benzene and carbon tetrachloride mixture, the de-

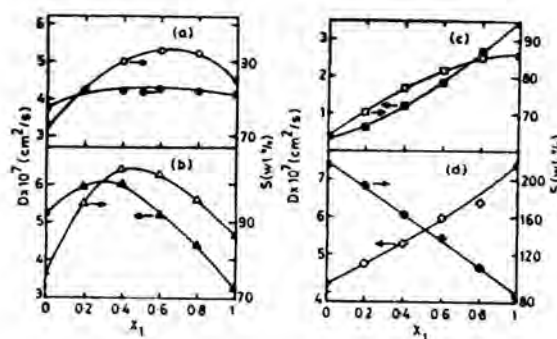


Fig. 6 – Dependence of diffusion coefficients D, and sorption coefficients S, on mole fraction of the first component in the mixture at 25°C. (a) (○) and (●) NBR with benzene + ethyl acetate mixtures. (b) (△) and (▲) NBR with benzene + methyl acetate mixtures. (c) (□) and (■) NBR with benzene + carbon tetrachloride mixtures. (d) (◇) and (◆) EPDM with benzene + carbon tetrachloride mixtures.

pendence of D and S are non-linear over the entire mole fraction range (Fig. 6(c)). While we cannot advance quantitative arguments for the shapes of curves of D or S versus x_1 , their shapes appear to be mainly dominated by the type of specific interactions between the components of the mixtures. In each case, D initially increases with concentration, reaches a maximum, and then drops off.

To investigate details about the concentration dependence of diffusivity, we have estimated D values at different intervals from the original sorption curves by using the procedure of Joshi and Astarita¹⁶. These results are typically present-

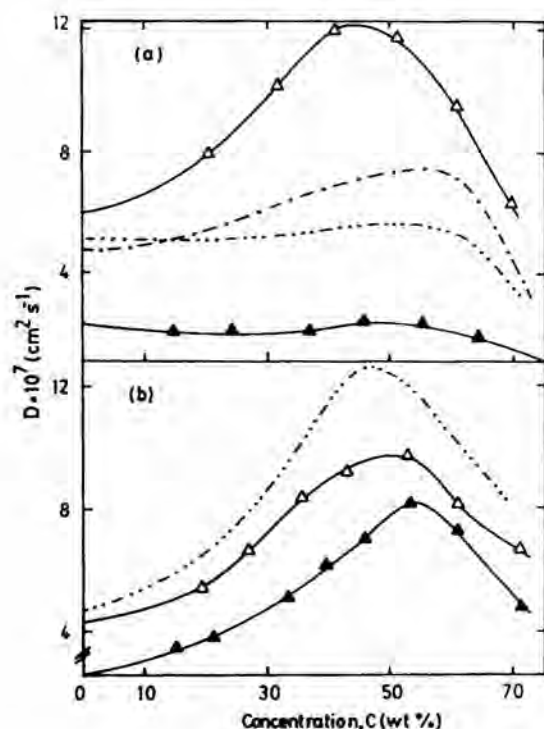


Fig. 7—Dependence of diffusion coefficient D , on concentration at 25°C. (a) EPDM with benzene+methyl acetate mixtures. Symbols: (Δ) benzene; ($---$) 60% benzene; ($- \cdots -$) 40% benzene; ($\blacktriangle$) methyl acetate. (b) NBR with benzene+methyl acetate mixtures. Symbols: ($\blacktriangle$) benzene; (Δ) methyl acetate; ($- \cdots -$) 40% benzene.

ed for EPDM and NBR membranes with benzene+methyl acetate mixtures (Fig. 7). For EPDM+methyl acetate, D does not vary considerably because methyl acetate did not show significant swelling for EPDM. However, with benzene, we observe a sharp maximum in D versus concentration plot which tends to decrease with an increase in concentration of methyl acetate in the binary mixture. On the other hand, when NBR is considered in the presence of benzene+methyl acetate mixture (each of these liquids have considerable swelling tendencies towards NBR), a sharp maximum is observed suggesting significant concentration dependence of diffusivity for these systems. Their binary mixtures, however, show considerable dependence of D on concentration as the maximum peak for

40% benzene-containing mixture is somewhat sharper than either of the pure components, namely, benzene or methyl acetate.

In this study, it was observed that: (i) the sorption kinetics change progressively from Fickian to non-Fickian as a function of mixture composition and depends on the size of the penetrant molecule; (ii) the sorption behaviour can be explained by a consideration of the rates of diffusion and molecular relaxation processes; (iii) molecular transport of mixed solvent media follow the same pattern as those of pure components suggesting that in mixtures, the molecules move as a single unit and preferential sorption may be operative, though its effect is not really significant; (iv) perhaps other spectroscopic methods such as laser interferometry, NMR-imaging, etc., can be used in conjunction with the present gravimetric technique to study solvent diffusion rates into these polymeric systems.

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