Diffusion and Sorption of Organic Liquids through Polymer Membranes. VIII. Elastomers versus Monocyclic Aromatic Liquids

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SYNOPSIS

Sorption and diffusion of five monocyclic aromatic liquids—three halogenated benzenes, nitrobenzene, and aniline—with five engineering polymers—ethylene propylene diene terpolymer, nitrile butadiene rubber, styrene butadiene rubber, natural rubber, and neoprene—have been investigated in the temperature interval of 25–60°C. Solvent diffusivity into polymer membranes was determined from the immersion/weight gain experiments. Permeability coefficients were also calculated from the diffusion and sorption data. A temperature dependence of sorption and transport was also investigated to estimate the activation parameters. The experimental results and computed quantities were used to study the type of transport mechanism and the nature of polymer–solvent interactions.

INTRODUCTION

Over the past several years the molecular transport of organic solvents through commercial polymer membranes has been the subject of continuous interest in our laboratories.[1–7] In most of these studies an important finding is that above the glass transition temperatures most of the rubbery polymers exhibit diffusion anomalies that are characteristics of the Fickian mode of transport. However, in some cases, if the medium is highly aggressive and interacts strongly with the polymer segments as evidenced by high swelling, surface corrugation, crazing, etc., then the diffusion deviates slightly from the Fickian mode. Thus, depending on the nature of the polymeric material and the type of solvent media used, the diffusion phenomenon may vary. Many theoretical developments and experimental results for a variety of polymer–solvent systems have been reported in the literature and have been recently reviewed.[8–11]

Among the well-known engineering polymers, styrene butadiene rubber (SBR), nitrile butadiene

rubber (NBR), neoprene (CR), ethylene propylene diene terpolymer (EPDM), and natural rubber (NR) find extensive applications as hose materials, gasket rings, etc. In these application areas the rubbers may come in contact with unfavorable organic liquid media that might impair their characteristic properties leading to chemical degradations, etc. It would be therefore important to know about the transport characteristics of these materials in the presence of organic liquid media. In our previous study[6] from this series of investigation, the sorption and diffusion characteristics of these rubbers in the presence of methyl- and methoxy-substituted benzenes have been studied. In continuation of this work, we now extend our study to include other penetrants from the class of monocyclic aromatics such as chlorobenzene, bromobenzene, fluorobenzene, nitrobenzene, and aniline. The sorption experiments were carried out over the temperature interval of 25–60°C so as to calculate the thermodynamic quantities of interest. The experimental and computed results have been used to correlate the structure–property relationships. Such data may be useful in assessing the stability of the polymer membranes in situations involving their exposures to aromatic solvents.

EXPERIMENTAL

Polymer sheets of SBR, EPDM, CR, NR, and NBR in dimensions of $\frac{1}{16}$ × 6 × 6 in. were obtained from UTEX Industries, Weimer, Texas (courtesy of Mr. A. Kutac). Mixing and molding of polymer compounds was done in a 12-in. laboratory mill and the polymer sheets were cured at 160°C for 20 min. Details about the mixing formulations and the important engineering properties of the membrane materials were given in our earlier work.[5]

Reagent-grade solvents—chlorobenzene, bromobenzene, fluorobenzene, nitrobenzene, and aniline—were double distilled to ensure purity. A sharp-edged steel die was used to cut the circularly shaped polymer samples (diameter = 1.94 cm). The thicknesses were measured at several points by using a micrometer (±0.01 cm). Diffusion experiments were performed for each polymer–solvent pair at 25, 44, and 60°C. The experimental details have been given in our earlier studies.[1-7]

The output from a diffusion experiment at a given temperature is the percent weight gain versus square root of time, $t^{1/2}$. For data comparison purposes, we found[4,5] it convenient to express the concentration of the liquid sorbed as moles of liquid per 100 g of the polymer material, and thus, the concentrations in this study are expressed in mole percent units. For a Fickian diffusion the sorption curves are independent of the material thickness, and the mole percent sorption, $Q(t)$, varies linearly with the square root of time, $t^{1/2}$. If there is negligible concentration dependence of diffusivity over the concentration interval studied (which is generally the case with most of the elastomers) in a sorption experiment, a value of the mutual diffusion coefficient can be determined for each polymer–solvent system by using half-time of the sorption curve as[12]

$$D = \pi(h\theta/4M_\infty)^2 \qquad (1)$$

where θ is the slope of the linear portion of the sorption curve and M_∞ is the maximum percent uptake of the solvent by the polymer membrane.

The average diffusivity thus calculated by the initial gradient method of analyzing sorption experiments is approximately equal to the mutual diffusion coefficient at a concentration somewhere between the initial and final concentrations of the diffusion experiment. It is reasonable to expect that these results are approximately valid for average diffusivities determined by using the half-time sorption method.[12,13]

RESULTS AND DISCUSSION

Sorption Kinetics

The sorption curves expressed as mole percent penetrant uptake, $Q(t)$, versus square root of time, $t^{1/2}$, at 25°C are displayed in Figure 1 for NBR with all the solvents. It is observed that $Q(t)$ increases somewhat linearly in the early stages of sorption and later levels off near the saturation equilibrium. The sorption curves for chloro- and fluorobenzenes are quite identical, but for bromobenzene the time required to attain equilibrium saturation is longer and the shape of curve is also different. Moreover, the sorption in the initial stages, for all the solvents with NBR, tends to deviate from the normal Fickian behavior as evidenced by the slightly sigmoidal shape of the curves. In particular, deviations from the Fickian mode of transport are associated with the time taken by the polymer segments to respond to a swelling stress and rearrange themselves to accommodate more of the penetrant molecules.[13]

In the presence of aniline, NBR shows high sorption values, whereas for nitrobenzene the maximum sorption data are in between those of the halogenated benzenes and aniline. Even the times required for the attainment of equilibrium saturation are higher for nitrobenzene and aniline as compared to
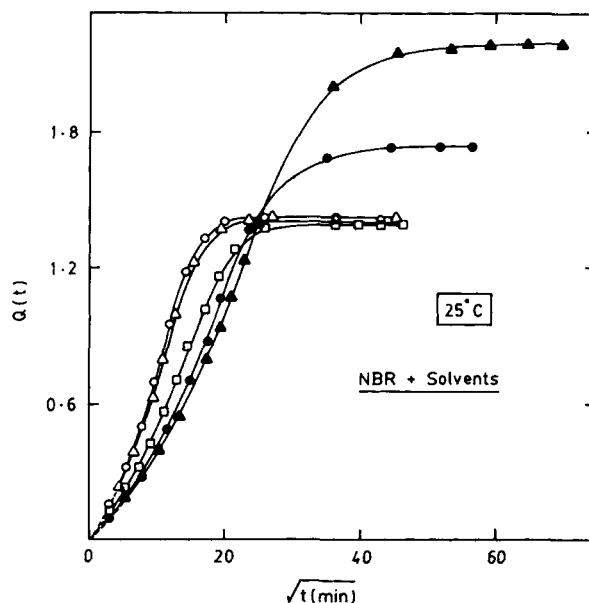

Figure 1   Mole percent sorption versus $t^{1/2}$ for NBR + solvents at 25°C. Symbols: (O) fluorobenzene, (△) chlorobenzene, (□) bromobenzene, (●) nitrobenzene, (▲) aniline.

the halogenated benzenes. This suggests that NBR chains respond almost instantaneously or elastically to the presence of halogenated benzenes than either nitrobenzene or aniline. Most elastomers are considered to have segmental relaxation times that are sufficiently rapid so that relaxation effects are absent and diffusion follows the Fickian kinetics.[14] However, there are some observations in the literature wherein elastomers have shown the evidence of non-Fickian behavior.[15,16]

Some typical examples of sorption curves for NR and EPDM membranes with all the solvents at 60°C are presented, respectively, in Figures 2 and 3. For natural rubber the sorption tendencies with all the solvents are quite different than NBR (see Figure 2). For instance, nitrobenzene and aniline, which showed high sorption values for NBR, exhibit lower values of sorption for NR. However, for the halogenated benzenes the sorption values are higher than aniline and nitrobenzene. Similar behavior is also exhibited by EPDM membrane for all the solvents at 60°C as shown in Figure 3. With SBR and CR membranes the general trend in the shapes of $Q(t)$ versus $t^{1/2}$ curves remain the same as those of NR and EPDM membranes. However, the data for these systems are not displayed graphically.
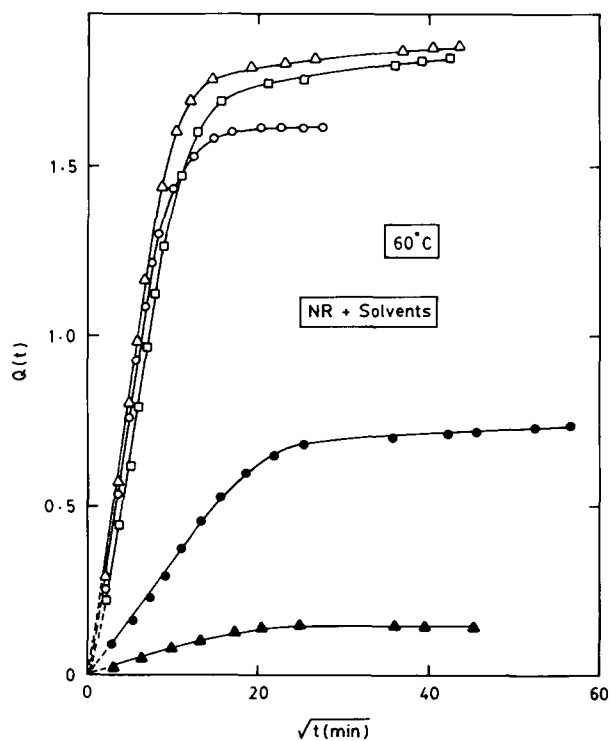

Figure 3 Sorption plots for EPDM + solvents at 60°C. Symbols have the same meaning as in Figure 1.
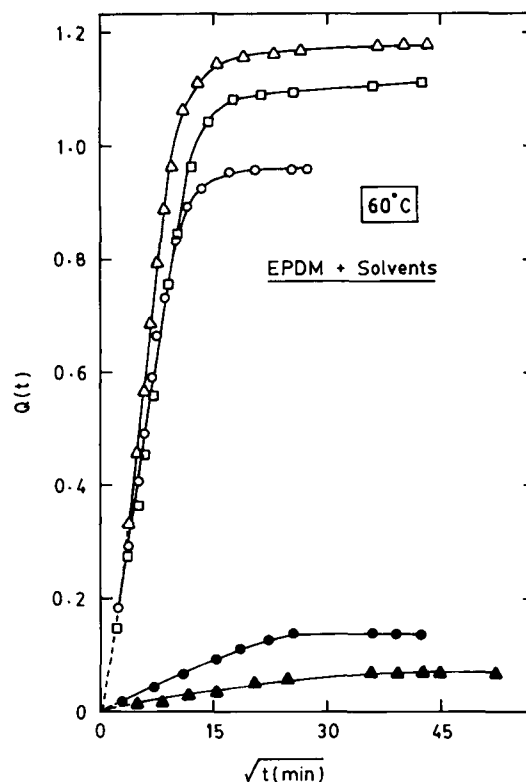

Figure 2 Sorption plots for NR + solvents at 60°C. Symbols have the same meaning as in Figure 1.

From a close observation of the sorption data given in Table I and from a comparison of sorption curves given in Figures 1–3, it can be inferred that solvent transport within the polymer matrices seems to depend greatly on the type of polymer backbone structure in addition to their chain flexibilities. There is also a possibility that the solvent properties seem to exert a considerable influence on the transport phenomenon. Nitrobenzene is a more polar solvent and has higher dielectric constant ($\epsilon = 34.78$ at 25°C) than the remaining solvents. Hence, it interacts more strongly with NBR, which has a polar nitrile group on its backbone. An opposite effect is seen for nitrobenzene transport with other membranes that do not contain polar sites. However, with the halogenated solvents, the polarity increases from fluoro-, bromo- to chlorobenzene, and thus we could see a systematic variation of sorption values for these solvents. For instance, the sorption of chlorobenzene is higher than that of bromo- and fluorobenzene with all the membranes. In general, comparatively, NBR appears to be more resistant to the halogenated aromatic solvents than nitrobenzene and aniline. On the other hand, for SBR the extent of solvent sorp-

Table I   Maximum Sorption Data (S. 10^2 mol/g) for Polymer–Solvent Systems

Polymer	Temp. (°C)	Chlorobenzene	Bromobenzene	Fluorobenzene	Nitrobenzene	Aniline
EPDM	25	1.147	1.029	0.878	0.087	0.029
	44	1.168	1.070	0.939	0.118	0.056
	60	1.180	1.113	0.960	0.138	0.070
NBR	25	1.417	1.393	1.422	1.734	2.193
	44	1.378	1.358	1.346	1.740	2.188
	60	1.347	1.330	1.273	1.752	2.204
CR	25	1.138	1.138	0.966	0.777	0.390
	44	1.127	1.129	0.942	0.801	0.507
	60	1.100	1.108	0.915	0.825	0.591
NR	25	1.873	1.784	1.650	0.519	0.078
	44	1.846	1.796	1.612	0.638	0.114
	60	1.843	1.819	1.614	0.737	0.150
SBR	25	2.219	2.137	1.988	0.986	0.219
	44	2.155	2.123	1.948	1.069	0.284
	60	2.107	2.093	1.861	1.103	0.367

tion is higher with the halogenated solvents than with other solvents used in this research.

Figures 4 and 5 present two typical sorption plots, one at 25°C for nitrobenzene (a higher polar solvent)
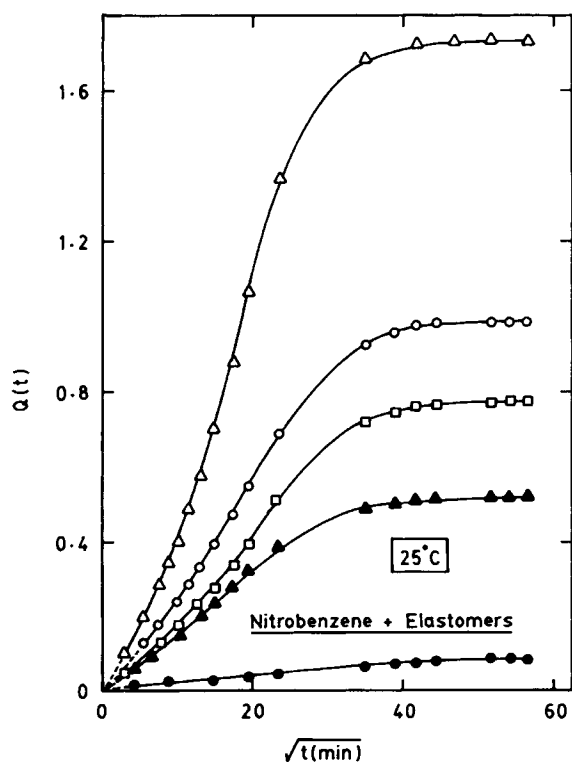
and the other for fluorobenzene (a less polar solvent) to display their interactions with all the membranes. It is observed that for these solvents, the sorption curves are quite different and the maximum sorption depends not only on the solvent properties but also on the structural characteristics of the membrane materials.

In order to see the effect of temperature on solvent transport, the sorption experiments were also carried

Figure 4   Sorption plots for nitrobenzene + polymer membranes at 25°C. Symbols: (O) SBR, (△) NBR, (□) CR, (▲) NR, (●) EPDM.
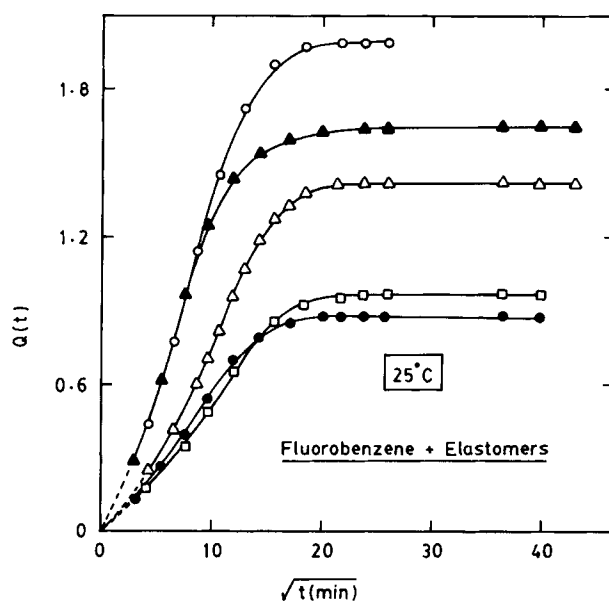

Figure 5   Sorption plots for fluorobenzene + polymer membranes at 25°C. Symbols have the same meaning as in Figure 4.

out at 44 and 60°C. These results are included in Table I. While all the membranes did not show any systematic effect of temperature on solvent sorption, some general observations could be made. EPDM membrane in the presence of all the solvents shows a continuous increase in sorption with temperature. The increase in sorption in case of EPDM suggests that within the membrane matrix, more of the free volume is created to accommodate larger numbers of solvent molecules. Similarly, other membranes in the presence of nitrobenzene and aniline show increase in sorption with temperature. However, NBR, CR, and SBR exhibit a decrease in sorption with a rise in temperature. This effect is attributed to the stress-induced crystallinity at higher temperatures in the presence of solvents. The induced crystallinity reduces the free energy of mixing, thereby decreasing the solvent uptake. Such effects have also been observed earlier in the literature.[17,18] The sorption data of all the polymer–solvent systems in the temperature interval of 25–60°C follow the sequence for NBR as: aniline > nitrobenzene > fluorobenzene > chlorobenzene > bromobenzene. However, with NR, EPDM, SBR, and CR, the sorption varies as chlorobenzene > bromobenzene > fluorobenzene > nitrobenzene > aniline. Thus, NBR responds quite differently to the presence of solvents as compared to other membranes.

In order to investigate the type of transport mechanism, the dynamic swelling results (up to 50% equilibrium) were fitted to the empirical relation[19,20]

$$\log(M_t/M_\infty) = \log k + n \log t \qquad (2)$$

Here, the constant k depends on the structural characteristics of the polymer in addition to its interaction with the solvent; M_t and M_∞ represent the mass uptake at time t and at equilibrium, t_∞, respectively. The magnitude of n decides the type of transport. If $n = 0.5$, it is indicative of the Fickian mode; and for $n = 1$, a non-Fickian diffusion is predicted. However, the intermediate values of n ranging from 0.5 to 1.0 suggest the existence of the anomalous transport behavior.[2-7]

From a least-squares analysis, values of n and k were estimated, and these are presented in Table II. While there is no systematic variation of n with temperature for any of the systems, the values of k tend to increase with temperature. In case of aniline and nitrobenzene with all the polymers except NBR, values of n are closer to 0.5, suggesting that the Fickian mechanism may be operative in these systems. However, with the majority of other polymer–solvent systems, values of n are around 0.65, suggesting the departure from the Fickian transport. This observation is also supported by the slight sigmoidal shapes of the $Q(t)$ versus $t^{1/2}$ plots in these systems.

Attempts were also made to calculate the permeability coefficients, P, from a knowledge of sorption and diffusion coefficients as $P = DS$ (S has the same meaning as M_∞); the results of D and P for all the polymer–solvent systems are given in Table

Table II Estimated Values of n and k (g/g · min^n), from Eq. (2) for Polymer–Solvent Systems

Polymer	Temp. (°C)	Chlorobenzene		Bromobenzene		Fluorobenzene		Nitrobenzene		Aniline	
		n	k ($\times 10^2$)	n	k ($\times 10^2$)	n	k ($\times 10^2$)	n	k ($\times 10^2$)	n	k ($\times 10^2$)
EPDM	25	0.63	3.43	0.61	3.16	0.60	3.81	0.50	2.56	0.50	2.55
	44	0.61	4.56	0.59	4.19	0.61	4.75	0.50	3.20	0.54	2.72
	60	0.60	5.62	0.59	5.00	0.62	5.73	0.50	4.80	0.50	3.55
NBR	25	0.66	2.30	0.62	1.97	0.64	2.57	0.63	1.28	0.62	1.01
	44	0.62	3.18	0.63	2.68	0.65	3.51	0.64	1.74	0.65	1.59
	60	0.61	3.91	0.61	3.60	0.64	4.39	0.64	2.65	0.65	1.99
CR	25	0.63	2.71	0.62	2.34	0.63	2.73	0.57	1.57	0.53	1.34
	44	0.63	3.50	0.62	3.10	0.62	3.50	0.60	2.01	0.54	1.80
	60	0.63	4.24	0.60	3.79	0.63	4.27	0.57	2.70	0.57	2.16
NR	25	0.66	3.69	0.66	3.03	0.68	3.67	0.55	2.25	0.51	2.68
	44	0.64	4.75	0.64	3.87	0.66	4.84	0.55	2.94	0.51	4.06
	60	0.63	5.74	0.64	4.41	0.67	5.41	0.54	3.61	0.50	5.64
SBR	25	0.68	3.12	0.67	2.50	0.67	3.03	0.57	1.80	0.50	2.37
	44	0.65	4.09	0.65	3.35	0.67	4.01	0.57	2.53	0.50	3.72
	60	0.64	4.86	0.64	4.01	0.65	4.86	0.56	3.29	0.51	4.21

Table III Diffusion ($D \times 10^7$, cm^2/s) and Permeation Coefficients ($P \times 10^7$, cm^2/s) for Polymer–Solvent Systems

Polymer	Temp (°C)	Chlorobenzene		Bromobenzene		Fluorobenzene		Nitrobenzene		Aniline	
		D	P	D	P	D	P	D	P	D	P
EPDM	25	7.49	9.67	4.91	7.93	6.94	5.85	0.71	0.08	0.58	0.02
	44	10.01	13.16	6.49	10.90	10.34	9.32	1.40	0.20	0.91	0.05
	60	12.41	16.48	9.13	15.95	14.02	12.93	2.54	0.43	1.77	0.11
NBR	25	4.43	7.06	2.76	6.04	5.30	7.25	1.48	3.16	0.84	1.72
	44	6.24	9.68	3.91	8.34	7.78	10.05	2.64	5.65	1.87	3.81
	60	7.72	11.71	5.58	11.66	9.47	11.57	4.04	8.51	3.51	7.20
CR	25	6.55	8.39	4.47	7.99	6.47	6.00	1.29	1.23	0.53	0.19
	44	8.56	10.85	6.67	11.82	8.46	7.65	2.25	2.22	1.09	0.51
	60	10.88	13.48	8.31	14.44	11.32	9.94	3.50	3.55	2.10	1.16
NR	25	9.93	20.92	5.98	16.94	10.67	16.90	1.37	0.88	1.04	0.08
	44	12.30	25.27	7.66	21.46	13.39	21.48	2.22	1.74	2.52	0.27
	60	14.44	29.94	9.51	27.17	17.19	26.64	2.86	2.59	3.87	0.54
SBR	25	8.90	22.19	5.09	17.07	8.32	15.88	1.36	1.65	0.62	0.13
	44	10.69	25.93	6.90	22.99	11.48	21.46	2.30	3.03	1.43	0.38
	60	13.26	31.46	8.86	29.10	14.70	26.26	3.18	4.32	2.86	0.98

III. Both D and P values are found to be increasing with a rise in temperature. For the halogenated benzenes with NBR, both diffusivity and permeability data vary in the order fluorobenzene > chlorobenzene > bromobenzene. With EPDM, CR, and SBR membranes, the trend is chlorobenzene > fluorobenzene > bromobenzene. The highest P and D values are observed for fluorobenzene with NR and SBR membranes. With CR, NBR, and EPDM membranes the D values for the halogenated benzenes vary within a narrow range. Extremely small D and P values are observed for aniline and nitro-

benzene with EPDM membrane while for NBR these values are comparatively higher. On the whole, it appears that solvent transport does not only depend on the size of the solvent molecules, but polymer–solvent interactions and the structural characteristics of polymer membranes also play important roles.

Arrhenius Parameters

The Arrhenius activation parameters for the processes of diffusion, E_D, permeation, E_P, and solu-

Table IV Activation Parameters (E_D, E_P, ΔH_s all in kJ/mol) for Polymer–Solvent Systems

Polymer	Parameter	Chlorobenzene	Bromobenzene	Fluorobenzene	Nitrobenzene	Aniline
EPDM	E_D	11.93	14.49	16.60	29.82	25.94
	E_P	12.61	16.31	18.77	41.05	46.84
	ΔH_s	0.68	1.82	2.17	11.23	20.90
NBR	E_D	13.18	16.51	13.82	23.73	33.74
	E_P	12.00	15.43	11.23	23.46	33.85
	ΔH_s	−1.18	−1.08	−2.59	−0.27	0.11
CR	E_D	11.94	14.75	13.10	23.55	32.38
	E_P	11.18	14.12	11.82	24.97	42.23
	ΔH_s	−0.76	−0.63	−1.28	1.42	9.85
NR	E_D	8.85	10.92	11.17	17.53	31.34
	E_P	8.43	11.37	10.71	25.81	46.81
	ΔH_s	−0.42	0.45	−0.46	8.28	15.47
SBR	E_D	9.32	13.07	13.44	20.16	36.04
	E_P	8.12	12.59	11.92	22.86	48.18
	ΔH_s	−1.20	−0.48	−1.52	2.70	12.14

bility, ΔH_S, were computed from the temperature dependence of D, P, and S, respectively, using the relation

$$\log X = \log X_0 - (E_x/2.303RT) \qquad (3)$$

where X refers to P, D, or S and X_0 is a constant representing P_0, D_0, and S_0; E_x denotes the activation energy for the processes under consideration, and RT has the conventional meaning. The estimated parameters E_D, E_P, and the values of heat of sorption, ΔH_s, as obtained from the difference ($E_p - E_D$) are given in Table IV. Typical Arrhenius plots describing the temperature dependence of diffusivity and permeability for nitrobenzene and fluorobenzene for all the polymer membranes are given respectively, in Figures 6 and 7. We could observe a linear variation of these quantities within the investigated range of temperatures.

The estimated E_D and E_P values have shown variations from one polymer–solvent system to the other. For instance, with EPDM + nitrobenzene system, E_D values increased from 12 kJ/mol for chlorobenzene to 29.8 kJ/mol; but E_P values ranged from 12.6 kJ/mol for chlorobenzene to 46.8 kJ/mol for aniline. With NBR and CR membranes, E_D and
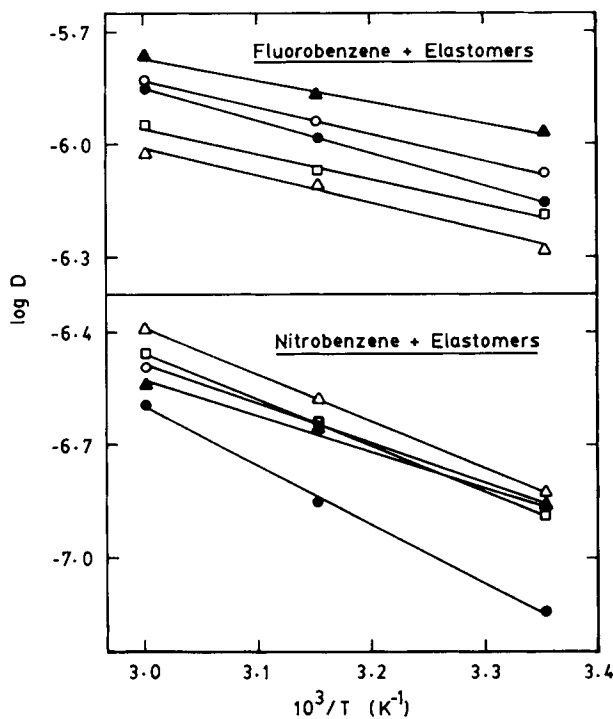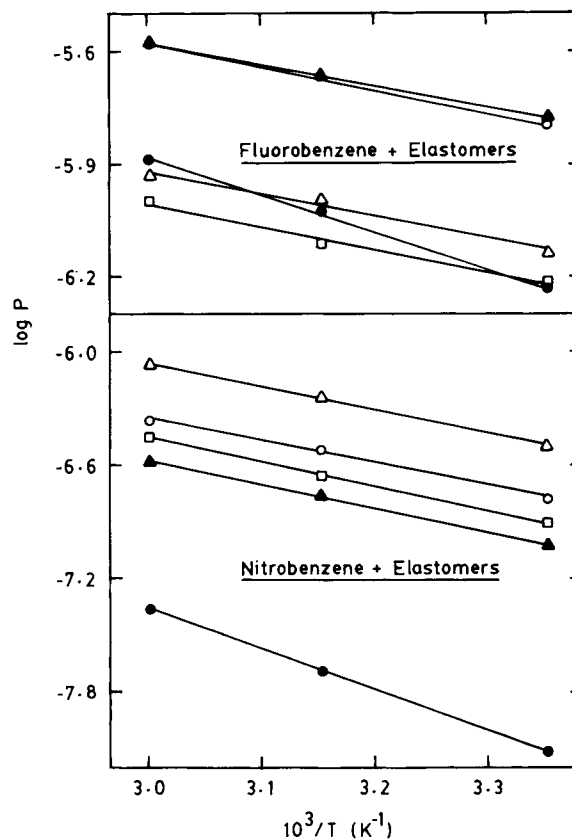

Figure 7 Arrhenius plots ($\log P$ vs. $1/T$) for nitrobenzene and fluorobenzene with polymer membranes. Symbols have the same meaning as in Figure 4.

E_P values increase according to the sequence aniline > nitrobenzene > bromobenzene > fluorobenzene > chlorobenzene. With NR and SBR membranes, E_D and E_P values tend to increase from chlorobenzene to aniline via bromobenzene, fluorobenzene, and nitrobenzene. However, we could not observe any linear relationship between the penetrant size and the activation parameters. The negative ΔH_s values as observed with some polymer–penetrant systems are attributed to the mild exothermic reactions, which might have occurred during sorption. The positive values of ΔH_s are indicative of the endothermicity of sorption process.

CONCLUSION

Solvent diffusion in polymers is important to the study of physical properties of materials from processing to end use and shelf-life. The results of this study indicate that some aspects of non-Fickian behavior may be attributed to slow segmental relaxation or structural response, which can be observed

Figure 6 Arrhenius plots ($\log D$ vs. $1/T$) for nitrobenzene and fluorobenzene with polymer membranes. Symbols have the same meaning as in Figure 4.

during solvent transport within membrane matrices. Further structural and molecular data in conjunction with solvent swelling are needed to sort out the origin of the individual effects. It should be noted that the phenomenological theories used to analyze the data were formulated for homogeneous polymers and might require some modification for systems of this study.

From a technological viewpoint, the present results suggest that it is possible to assess the suitability of polymer membranes before their successful field applications, especially in situations where these membranes come into contact with organic solvents. None of the membranes studied here were destroyed by any of the solvents in the temperature interval studied. Such transport data on a variety of polymer–solvent systems may be useful to field engineers and technologists.

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