

Resistance of Barrier Elastomers to Hazardous Organic Liquids

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SYNOPSIS

Sorption and transport of several hazardous, organic chemicals into elastomer membranes have been studied using a simple gravimetric method. The Fickian model was used to estimate the diffusion coefficients of the polymer-solvent systems. The Joshi-Astarita model was employed to investigate the concentration-dependence of diffusion coefficients. From a study of the temperature dependence of the transport coefficients, activation parameters for the process of sorption, diffusion, and permeation have been estimated. Furthermore, the sorption results have also been interpreted in terms of the semiquantitative estimates of the kinetic rate constants and other thermodynamic parameters (enthalpy and entropy) of interest.

INTRODUCTION

The molecular transport of organic liquids through polymer membranes has been the subject of intense investigation over the past several years.¹⁻⁷ This investigation is partly due to the production of innumerable polymer membranes of commercial interest.⁸ The solvent resistivity of these membranes is extremely important for applications including protective clothing, separation of liquid mixtures, and chemical waste pond lining. Thus, an understanding of the membrane transport properties, namely sorption, diffusion, and permeation with respect to organic liquids, is essential for commercial applications.

Recent advances⁹ in the production of commercial polymers, such as natural rubber (NR), neoprene (CR), nitrile butadiene rubber (NBR), styrene butadiene rubber (SBR), and ethylene pro-

pylene diene terpolymer (EPDM), prompted us to study the polymers' transport characteristics in the presence of hazardous chemicals. Thus, in this article, several halogenated, organic liquids, such as 1,2-dichlorobenzene, chloroform, bromoform, dichloromethane, 2-chloroethanol, and 1,4-dichlorobutane, in addition to other solvents, such as tetrahydrofuran, dioxane, dimethyl formamide, and methyl cyanide, have been used as probe molecules. Most of these liquids have been classified as hazardous liquids.^{10,11} Sorption (S), diffusion (D), and permeation (P) parameters of these polymer-solvent systems have been studied in the temperature interval of 25-60°C from a measurement of the rate of solvent uptake (weight gain) by a film of the polymer. Furthermore, attempts have been made to estimate the Arrhenius parameters of interest and the results were discussed in terms of the nature of polymer-solvent interactions.

EXPERIMENTAL

All the chemicals used were of reagent grade and were purified before use.¹² The physical properties

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Table I Some Properties of Hazardous Liquids and Their Toxicity Data

Liquids	Molar Volume (cm ³ /mol)	Boiling Point (°C)	Density at 25°C	TLV ^a ppm
Acetonitrile	52.87	81.60	0.7765	40
Dichloromethane	64.50	39.60	1.3168	500
2-Chloroethanol	67.29	128.60	1.1965	5
N,N-Dimethyl formamide	77.44	153.00	0.9439	10 ^b
Chloroform	80.68	61.18	1.4797	50
Tetrahydrofuran	82.12	65.97	0.8781	200
<i>p</i> -Dioxane	85.71	101.32	1.0280	100 ^b
Bromoform	87.82	149.21	2.8779	0.5 ^b
1,4-Dichlorobutane	111.40	156.00	1.1338	NA ^c
1,2-Dichlorobenzene	113.05	180.50	1.3003	50

^a Threshold limiting value toxicity.

^b For skin.

^c Not available.

and their toxicity data are given in Table I. The polymer membranes were obtained from UTEX Industries, Weimer, Texas (courtesy of Mr. A. Kutac) in sheets of different thicknesses ranging from 0.190 to 0.245 cm. The actual value was considered in each calculation.

Rubber compositions and some representative engineering properties were given earlier.¹³ The polymers used for SBR and EPDM are, respectively, SBR 1500 (Ameripol synpol) and EPDM 585 (Polysar). Neoprene W (DuPont) and NR (RSS-2) are the polymers used for neoprene and natural rub-

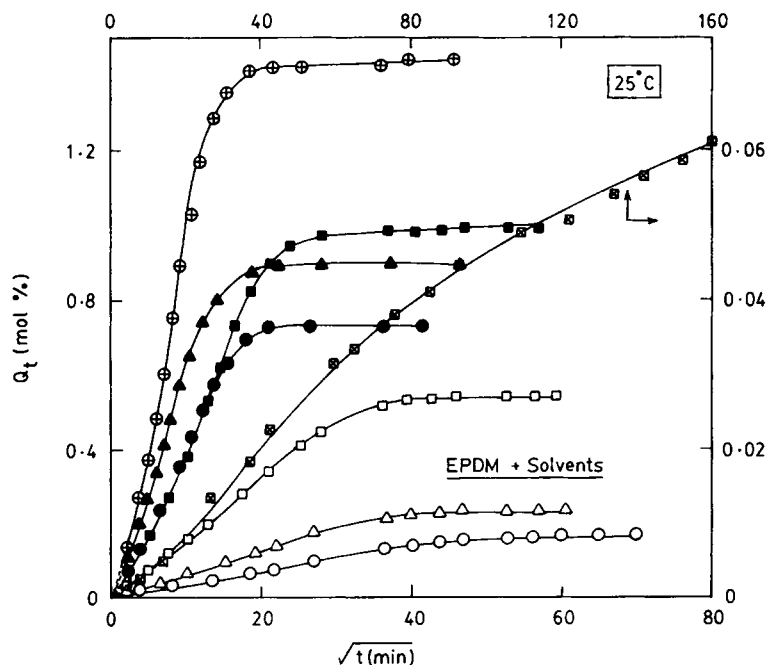


Figure 1 Mol % sorption Q_t vs. square root of time, $t^{1/2}$ at 25°C for EPDM with *p*-dioxane (O); 1,4-dichlorobutane (Δ); bromoform (□); THF (●); dichloromethane (▲); dichlorobenzene (■); chloroform (⊕); 2-chloroethanol (⊗).

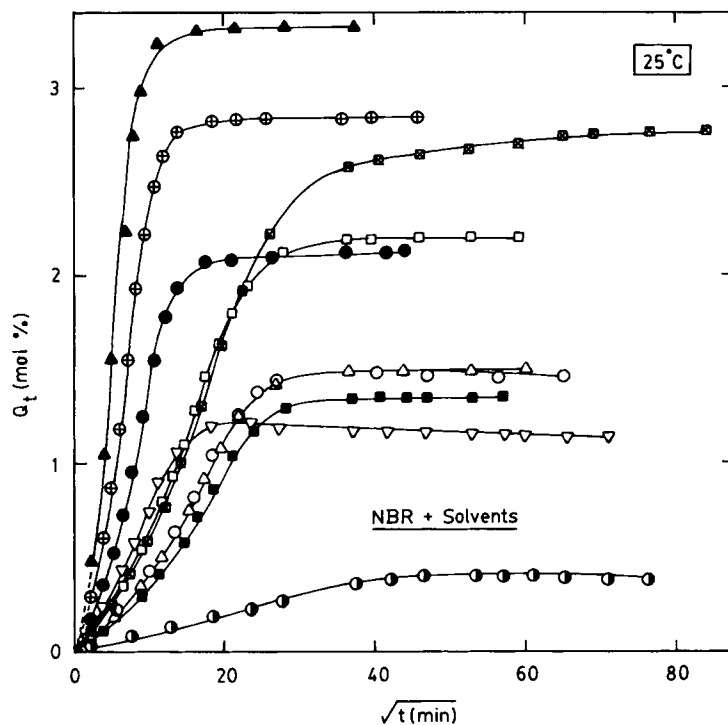


Figure 2 The same dependence as in Figure 1 for NBR with solvents at 25°C. All symbols have the same meaning as in Figure 1 and for acetonitrile (∇): DMF (\bullet).

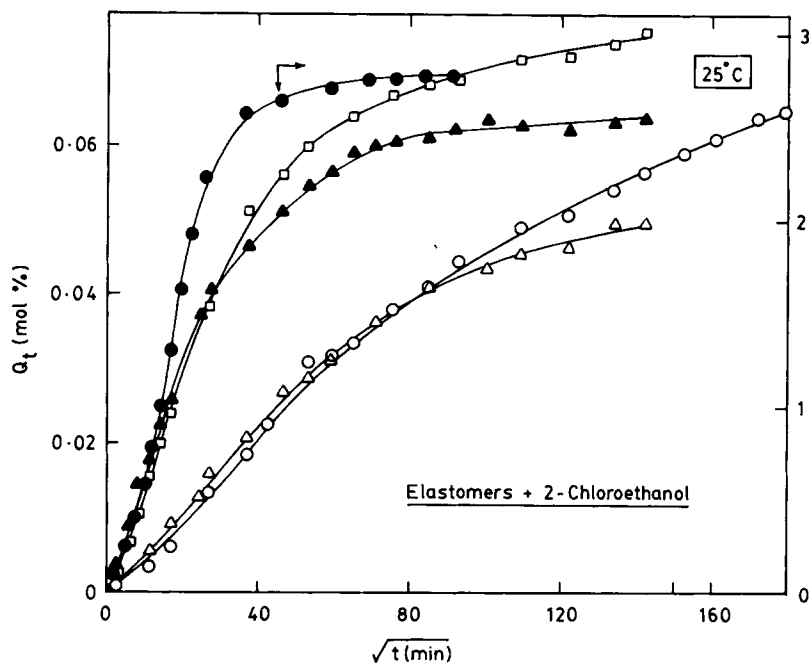


Figure 3 The same dependence as in Figure 1 for 2-chloroethanol with EPDM (\circ); CR (Δ); NR (\square); NBR (\bullet); SBR (\blacktriangle).

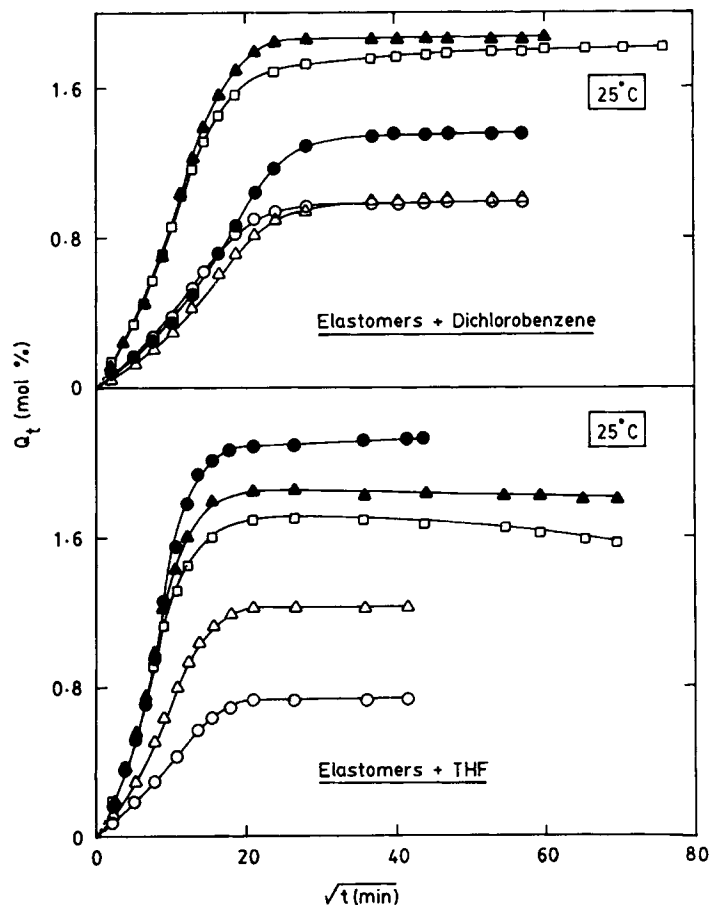


Figure 4 The same dependence as in Figure 1 at 25°C for THF and dichlorobenzene with elastomers. Symbols have the same meaning as in Figure 3.

ber sheets, respectively, while Hycar 1051 (B. F. Goodrich) is the base polymer for NBR. All these rubber samples contained 100 phr of polymer and 50 phr of carbon black (N 550), in addition to other ingredients.¹³

Sorption experiments¹⁴⁻¹⁶ were performed on circularly cut polymer samples of diameter 1.94 cm. The samples were dried in a vacuum desiccator over anhydrous CaCl_2 for 24 h before soaking in respective liquids taken in closed test bottles. These bottles were placed in a thermostatically controlled oven (Mettmert, Germany). At specified time intervals, the samples were taken out, the surfaces were dried between filter paper wraps, and the samples were weighed quickly to the nearest ± 0.05 mg. Samples were immediately placed back into the test bottles and were returned to the oven. This procedure was repeated for all liquids to determine the equilibrium sorption and the data were collected at 25, 44, and 60°C. Due to the toxicity of the chemicals used, we

performed these experiments in a hood with extreme precautions.

RESULTS AND DISCUSSION

Sorption Kinetics

Following our earlier suggestions,^{17,18} the sorption results have been interpreted in terms of mol % increase Q_t , with time t . These results, for some typical polymer-solvent systems at 25°C, are displayed in Figures 1-7. The maximum mol % sorption, as obtained from the plateau regions of sorption plots, represents sorption (or solubility) coefficient S , and the results at 25, 44, and 60°C are compiled in Table II. For solvents, such as acetonitrile and DMF with EPDM membrane, sorption was extremely small and could not be studied accurately by the gravi-

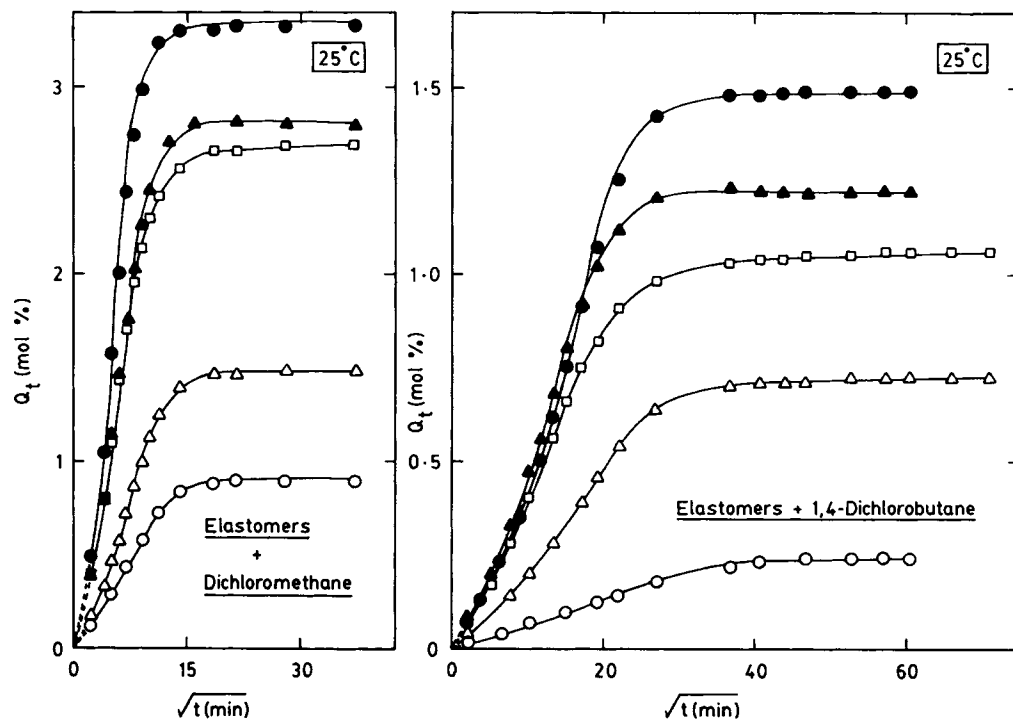


Figure 5 The same dependence as in Figure 1 at 25°C for dichloromethane and 1,4-dichlorobutane with elastomers. Symbols have the same meaning as in Figure 3.

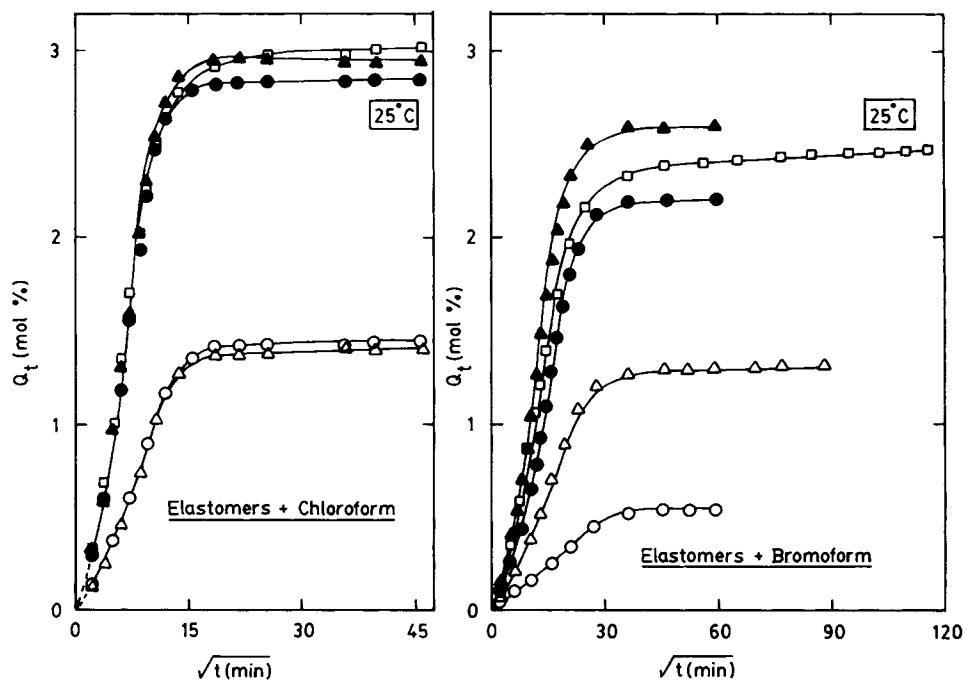


Figure 6 The same dependence as in Figure 1 at 25°C for chloroform and bromoform with elastomers. Symbols have the same meaning as in Figure 3.

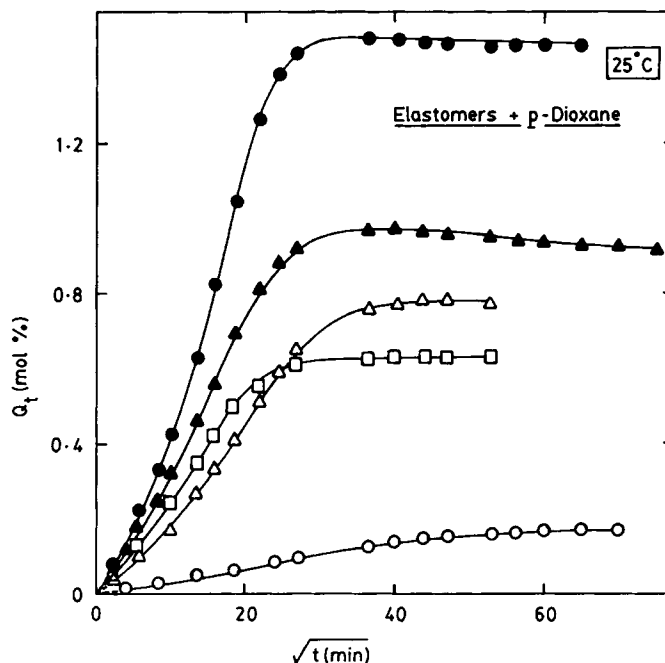


Figure 7 The same dependence as in Figure 1 at 25°C for p-dioxane with elastomers. Elastomers have the same meaning as in Figure 3.

metric method used here; hence, experiments for these systems were not performed. In the case of dioxane + NR system, the results were satisfactory only at room temperature but, at higher temperatures (44 and 60°C), dioxane severely attacked the NR membrane, as evidenced by the presence of small rubber particles in the test containers. For low boiling liquids, such as chloroform and dichloromethane, the sorption experiments were performed only at 25°C.

From the sorption results of EPDM at 25°C given in Figure 1, a wide variation in its solvent transport properties could be seen. For instance, polar solvents, such as chloroform, dichlorobenzene, dichloromethane, and THF, exhibit higher sorption values than the less polar solvents, such as dioxane, 1,4-dichlorobutane, and bromoform. It is also evident that solvents that exhibit high swelling attain equilibrium saturation more quickly than those solvents that exhibit low swelling. Moreover, the initial shapes of the sorption curves for high swelling liquids are slightly sigmoidal, thus exhibiting a concentration dependence of transport. The sorption of 2-chloroethanol is quite different, as indicated by a steady rise in the sorption with no indication of equilibrium saturation, even after 22 days of continuous solvent immersion. However, the results for

NBR membrane at 25°C, given in Figure 2, suggest an entirely different mode of transport for each of the solvents considered. For instance, with an NBR membrane, dichloromethane shows higher swelling, whereas other halogenated liquids show lower swelling; DMF shows the lowest swelling. For the majority of NBR + solvent systems, we observe sigmoidal shapes of the sorption curves indicating a considerable concentration dependence of transport phenomena. However, 2-chloroethanol attains equilibrium saturation only in the case of NBR within the laboratory period of investigation.

The sorption results of 2-chloroethanol with various membranes at 25°C are presented in Figure 3. A true equilibrium is reached only in the case of SBR and NBR membranes, but with others, we could not observe equilibrium sorption within the set experimental time. The sorption of 2-chloroethanol is higher for NBR than for an SBR membrane; however, with natural rubber, it is approximately 8–10 times smaller. The sorption plots of elastomers with dichlorobenzene and THF at 25°C are shown in Figure 4. It was found that during the early stages of sorption, dichlorobenzene transports identically with NR and SBR membranes. Similarly, EPDM, CR, and NBR membranes, in the presence of dichlorobenzene, exhibit identical sorption patterns

Table II Mol % Sorption, *S*, of Hazardous Liquids + Polymer Membrane Systems at Different Temperatures

Liquids	Temp. (°C)	<i>S</i> (mol %)				
		EPDM	CR	NR	NBR	SBR
Acetonitrile	25	—	0.077	0.025	1.205	0.053
	44	—	0.088	0.034	1.281	0.071
	60	—	0.105	0.046	1.374	0.087
Dichloromethane	25	0.886	1.479	2.686	3.317	2.784
2-Chloroethanol	25	0.065	0.047	0.075	2.772	0.064
	44	0.076	0.091	0.222	2.902	0.344
	60	0.084	0.158	0.758	3.025	0.437
N,N-Dimethyl formamide	25	—	0.102	0.041	0.402	0.037
	44	—	0.125	0.062	0.466	0.039
	60	—	0.133	0.078	0.536	0.046
Chloroform	25	1.440	1.397	3.015	2.842	2.940
Tetrahydrofuran	25	0.726	1.224	1.700	2.128	1.853
	44	0.813	1.256	1.807	2.024	1.851
	60	0.941	1.213	1.745	2.127	1.953
<i>p</i> -Dioxane	25	0.167	0.777	0.631	1.477	0.972
	44	0.217	0.826	—	1.473	1.193
	60	0.268	0.903	—	1.533	1.250
Bromoform	25	0.542	1.307	2.453	2.201	2.593
	44	0.686	1.314	2.562	2.110	2.542
	60	0.784	1.384	2.464	2.090	2.535
1,4-Dichlorobutane	25	0.237	0.722	1.064	1.490	1.227
	44	0.316	0.736	1.109	1.460	1.247
	60	0.382	0.742	1.188	1.470	1.242
1,2-Dichlorobenzene	25	0.987	1.004	1.808	1.348	1.864
	44	1.002	0.974	1.816	1.290	1.861
	60	1.027	1.001	1.977	1.274	1.842

initially, but at later stages, they exhibit different equilibrium values. This suggests that the polymer chains respond almost identically during the early stages of sorption and later, due to different inherent relaxation rates of polymer chain segments, different equilibria are observed. Similarly, in the presence of THF, membranes such as NBR, SBR, and NR behave almost identically before attaining 50% equilibrium, whereas CR and EPDM respond differently. For dichlorobenzene, the shapes of the sorption plots are slightly sigmoidal, suggesting a slow relaxation of the polymer chain segments in the presence of solvent molecules.²¹ The sorption plots for other liquids, namely dichloromethane, 1,4-dichlorobutane, chloroform, bromoform, and dioxane at 25°C, are given in Figures 5–7. From a com-

parison of the curves given in Figures 4 and 7, it is observed that, except for dioxane, similar effects can be seen with dichlorobenzene and THF. With dioxane, however, different polymers behave differently. With SBR and NBR membranes, sorption equilibria tend to decrease after the attainment of equilibrium saturation.

The equilibrium sorption data of various polymer-solvent systems are summarized in Table II. For the majority of liquids, both the NR and the NBR membranes showed high swelling, suggesting the response of polymeric chain segments to the presence of liquids. The acetonitrile + NR system showed a maximum sorption that varied from 0.025 to 0.046 mol %, whereas for the NBR + acetonitrile system, sorption varied from 1.205 to 1.374 mol %

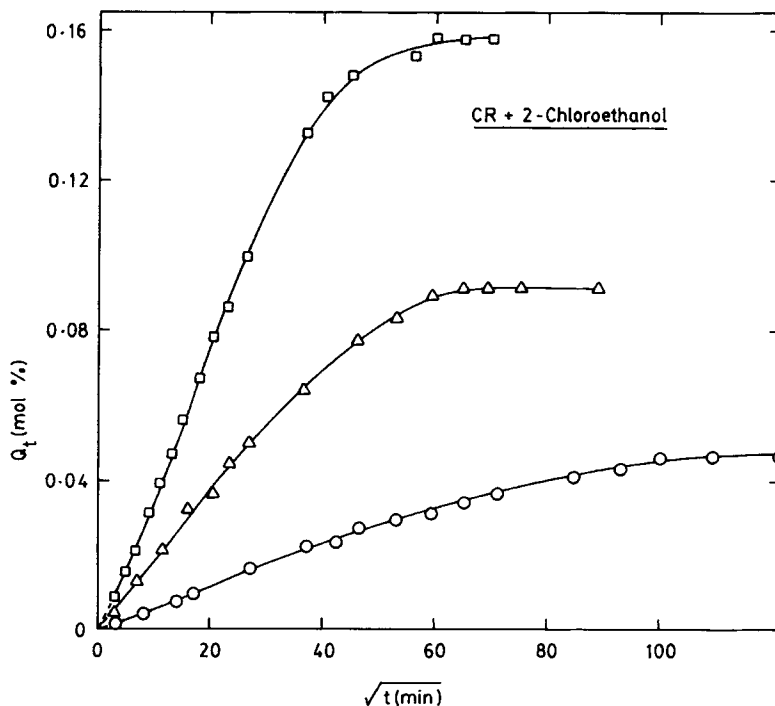


Figure 8 Temperature dependence of sorption for CR + 2-chloroethanol system: 25°C (○); 44°C (△); 60°C (□).

in the temperature interval of 25 to 60°C. High equilibrium sorption of acetonitrile into NBR was attributed to the polar-polar interactions between polymer chains and solvent molecules. Similarly, DMF, a polar molecule, showed smaller values of sorption for NR, whereas with NBR, sorption of DMF was about ten times higher. Similar arguments apply for 2-chloroethanol, THF, 1,4-dichlorobutane, dioxane, and dichloromethane, which exhibited lower sorption for NR than NBR. On the other hand, a reverse tendency is observed for bromoform, chloroform, and dichlorobenzene as these solvents showed lower swelling for NBR than NR membrane.

Swelling tendencies of CR and SBR membranes were intermediate to those of NR and NBR membranes for most of the liquids. For acetonitrile, sorption results of CR and SBR were similar. For the majority of the other solvents (except DMF), CR was a better barrier material than SBR because the latter showed higher sorption for these liquids than the former. One interesting observation is that for dichlorobenzene + SBR, we could observe a systematic decrease in sorption with a rise in temperature. Similar observations were also found with some other systems, presented in Table II, but the effects in these systems were not systematic enough

to warrant deeper analysis of the situation. In any case, the systematic decrease of sorption with an increase in temperature may be the result of induced crystallinity at higher temperatures in the presence of solvents. The induced crystallinity reduced the free energy of mixing, thereby decreasing the solvent uptake.^{19,20}

Results of the temperature dependence of sorption of 2-chloroethanol into CR is shown in Figure 8. The attainment of equilibrium sorption was slower at 25°C than at higher temperatures. An increase of 35°C (i.e., from 25 to 60°C) caused a considerable increase in the sorption capacity of the CR membrane for 2-chloroethanol. However, this effect was comparatively smaller in the case of the EPDM + bromoform system shown in Figure 9 and also with the NBR + 2-chloroethanol system shown in Figure 10. Similar observations can be found for the CR + bromoform (see Fig. 11) and the SBR + bromoform systems. The sorption curves for the dioxane + NR and DMF + NBR systems are given, respectively, in Figures 12 and 13. For the latter, at 60°C, sorption increases continuously while, at 44 or 25°C, sorption decreases after attainment of a maximum sorption (Fig. 13). On the other hand, with the NR + dioxane system, we find that sorption

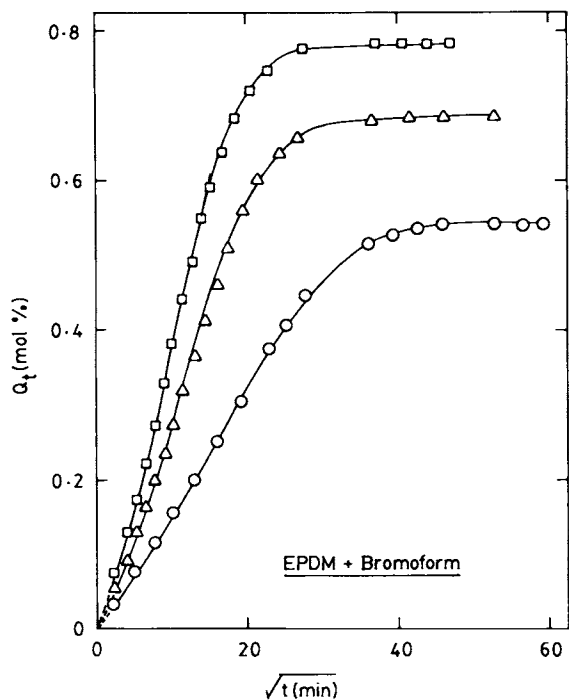


Figure 9 Temperature dependence of sorption for EPDM + bromoform system. Symbols for temperature are the same as in Figure 8.

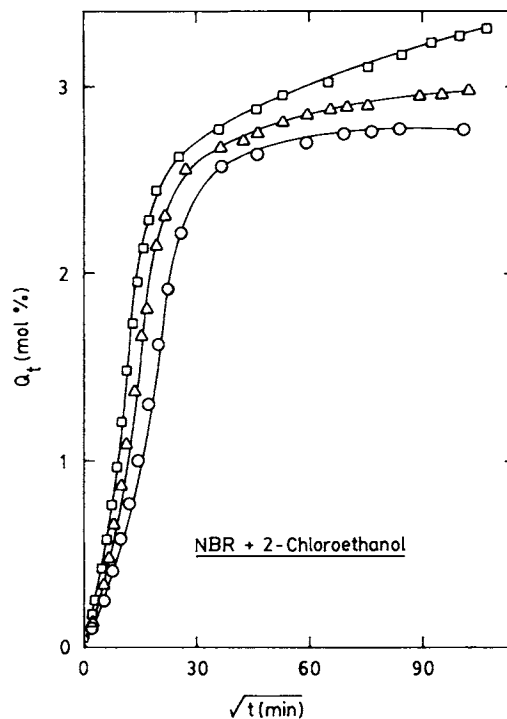


Figure 10 Temperature dependence of sorption for NBR + 2-chloroethanol system. Symbols for temperature are the same as in Figure 8.

increases continuously at higher temperatures (44 or 60°C), but a true equilibrium was observed at 25°C. This suggests that transport is clearly complicated. Swelling and diffusion occur simultaneously, resulting in the sigmoidal shapes of sorption curves. As swelling continued, the free volume of the polymer increased so that the exposed sites of free volume permitted diffusion at a higher rate. Numerous examples in the literature indicate that diffusion processes in polymeric systems sometimes do not follow the laws of classical molecular diffusion. Such non-Fickian diffusion behavior may be caused by swelling. Other influencing factors are the filler type, their compositions, and the extent of molecular crosslinks, which might influence the swelling results. Membranes, which exhibit low swelling, possess the highly rigid macromolecular network structures and are less prone to solvent attack.

In order to investigate the type of transport mechanism, the sorption results have been analyzed using the empirical relationship of the type used earlier.^{22,23}

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

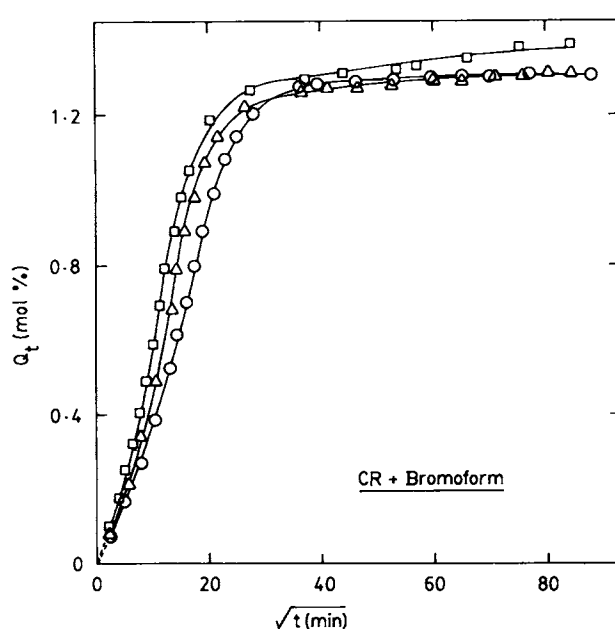


Figure 11 Temperature dependence of sorption for CR + bromoform system. Symbols for temperature are the same as in Figure 8.

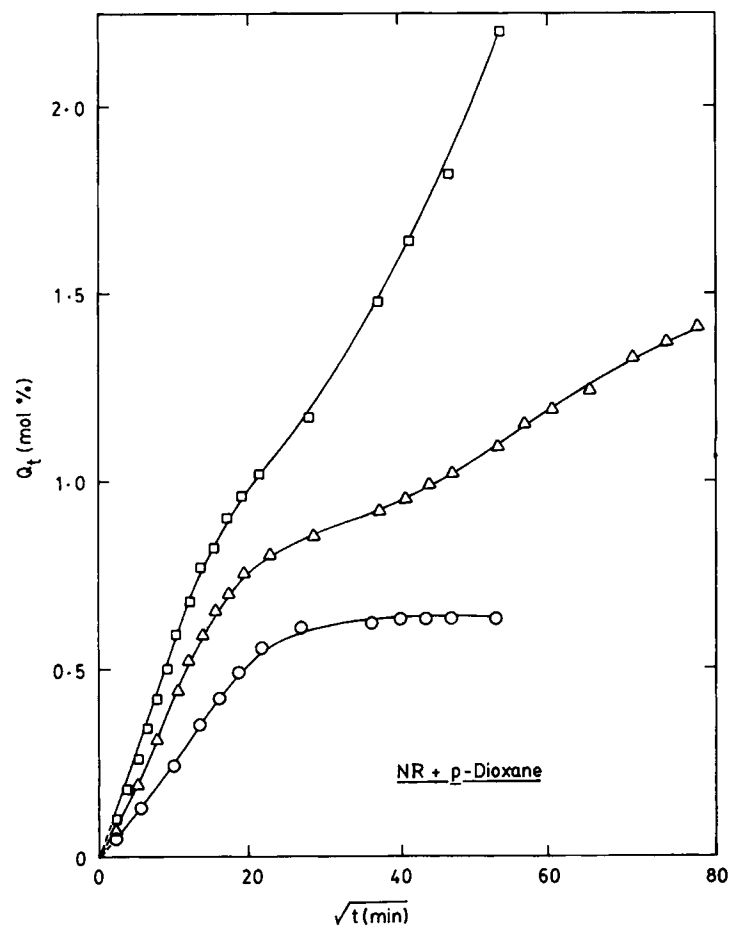


Figure 12 Temperature dependence of sorption for NR + dioxane system. Symbols for temperature are the same as in Figure 8.

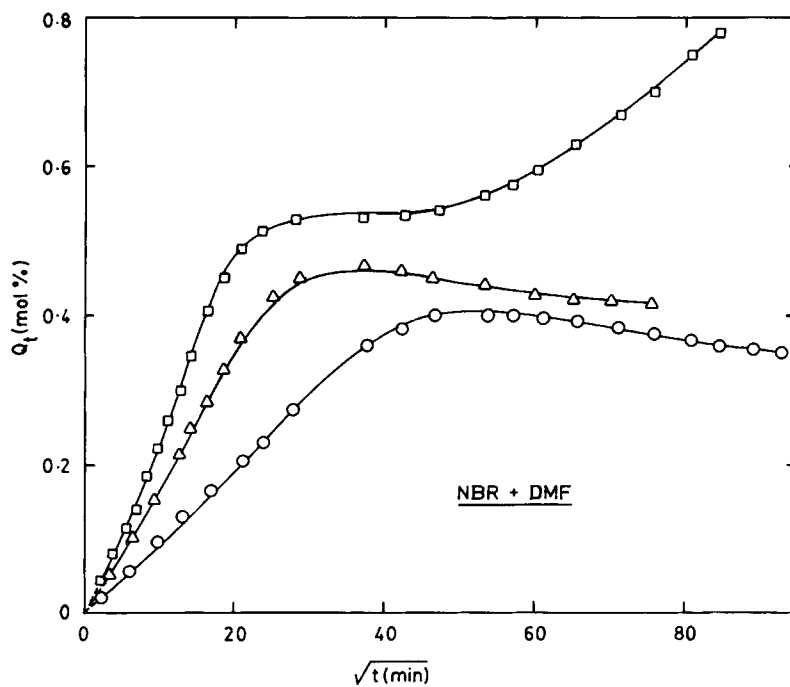


Figure 13 Temperature dependence of sorption for NBR + DMF system. Symbols for temperature are the same as in Figure 8.

where Q_t and Q_∞ represent the mol % sorption at time t and at equilibrium time, k is a constant that is characteristic of the polymer-solvent system. The value of exponent, n , suggests the type of transport mechanism.²⁴ The estimated values of k for each temperature and \bar{n} taken as the average over the temperature interval of 25 to 60°C are summarized in Table III. In all cases, the estimated error in n is approximately ± 0.01 . For the majority of polymer-solvent systems, \bar{n} varies between 0.5 and 0.6, suggesting the presence of a nearly Fickian transport mechanism. In some cases, however, we could observe higher values of \bar{n} , which vary from 0.6 to a maximum of 0.7. Such systems exhibit a slight departure from the Fickian mode of transport and are classified as anomalous transport.²⁵ This fact further supports the sigmoidal shapes of the sorption curves as observed with some polymer-solvent systems. The sigmoidal shapes of sorption curves are especially prevalent with those penetrants that showed

significant swelling of the membranes. The values of the constant k of eq. (1) increase with a rise in temperature except in the case of acetonitrile + NR and THF with EPDM and NBR membranes; the k values are to be regarded purely as empirical constants, which depend on the nature of the polymer-solvent interactions.

In order to determine whether the anomalous transport behavior discussed above is due to the swelling-induced breakup of the agglomerate-filler structure, similar to the one observed during the first mechanical deformation of a molded filled elastomer (Mooney softening),²⁶ in some cases we have repeated the sorption experiments of the already desorbed samples to examine whether subsequent sorption showed the same anomalous character or not. Some representative plots of the first and second cycles of sorption data for THF with EPDM, CR, and NBR at 44°C are shown in Figure 14. With EPDM, we could not observe any changes between

Table III Analysis of Sorption Data of Hazardous Liquids and Polymer Membranes at Different Temperatures

Liquids	Temp. (°C)	EPDM		CR		NR		NBR		SBR		
		\bar{n}^a	$k \times 10^2$ (g/g min ⁿ)	\bar{n}^a	$k \times 10^2$ (g/g min ⁿ)	\bar{n}^a	$k \times 10^2$ (g/g min ⁿ)	\bar{n}^a	$k \times 10^2$ (g/g min ⁿ)	\bar{n}^a	$k \times 10^2$ (g/g min ⁿ)	
Acetonitrile	25	—	—	0.50	2.73	0.44	9.61	0.58	4.03	0.53	2.64	
	44	—	—	—	3.77	—	8.01	—	5.63	—	5.77	
	60	—	—	—	5.35	—	9.20	—	6.32	—	6.47	
Dichloromethane	25	0.58 ^b	5.16	0.64 ^b	4.01	0.67 ^b	4.73	0.73 ^b	4.44	0.70 ^b	4.24	
	2-Chloroethanol	25	0.61	0.31	0.59	0.70	0.59 ^b	1.15	0.64	1.22	0.54 ^b	2.04
		44	—	1.04	—	1.23	—	—	—	1.63	—	—
N,N-Dimethyl formamide	60	—	1.24	—	1.42	—	—	—	1.97	—	—	
	25	—	—	0.50	1.27	0.49	2.60	0.53	2.12	0.52	2.00	
	44	—	—	—	2.51	—	3.11	—	3.32	—	3.03	
Chloroform	60	—	—	—	2.21	—	2.65	—	3.36	—	3.54	
	25	0.64 ^b	3.32	0.66 ^b	3.16	0.70 ^b	3.57	0.71 ^b	3.15	0.69 ^b	3.62	
	Tetrahydrofuran	25	0.59	3.60	0.63	3.11	0.66	3.73	0.67	2.66	0.67	3.31
44		—	5.20	—	3.71	—	4.31	—	3.64	—	4.13	
60		—	4.87	—	4.47	—	4.69	—	3.57	—	4.75	
<i>p</i> -Dioxane	25	0.53	2.14	0.59	1.86	0.54 ^b	3.32	0.61	1.98	0.60	2.11	
	44	—	3.26	—	2.13	—	—	—	2.44	—	2.25	
	60	—	4.12	—	2.47	—	—	—	2.85	—	3.38	
Bromoform	25	0.53	2.65	0.59	1.87	0.61	2.02	0.64	1.55	0.63	2.06	
	44	—	3.20	—	2.32	—	2.56	—	2.01	—	2.67	
	60	—	3.88	—	2.58	—	3.32	—	2.53	—	3.09	
1,4-Dichlorobutane	25	0.52	2.69	0.58	1.94	0.60	2.42	0.64	1.59	0.61	2.34	
	44	—	3.57	—	2.61	—	3.21	—	2.15	—	3.05	
	60	—	4.13	—	3.12	—	3.66	—	2.72	—	3.39	
1,2-Dichlorobenzene	25	0.59	2.54	0.60	1.95	0.63	2.43	0.62	1.55	0.65	2.31	
	44	—	3.40	—	2.78	—	3.12	—	2.11	—	3.03	
	60	—	4.23	—	3.08	—	3.39	—	2.56	—	3.55	

^a Estimated errors in \bar{n} are around ± 0.01 .

^b Values taken at only one temperature, that is, at 25°C.

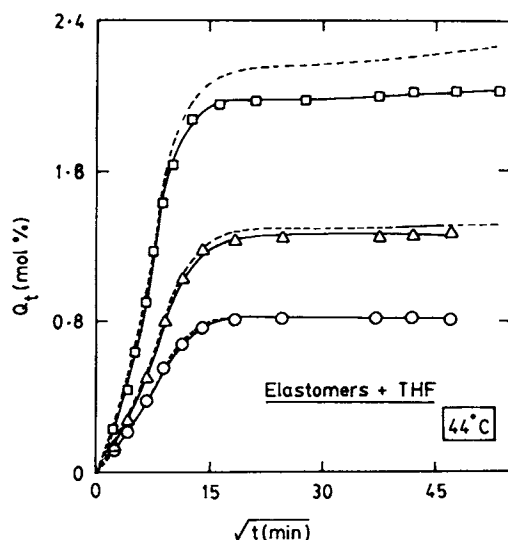


Figure 14 Mol % sorption vs. $t^{1/2}$ at 44°C for EPDM (○); CR (△); NBR (□). The dotted lines for NBR and CR represent the experiments for resorbed samples. For EPDM, both the lines merge together.

the first and second sorption cycles. However, in the case of CR and NBR, the equilibrium sorption data are higher, suggesting a loss in the weight of these samples during the first sorption cycles. Some indigenous additive/filler materials of the samples might have leached out of the rubber samples during the first sorption cycle.

Following our earlier suggestions,^{16,17} we have analyzed the sorption results in terms of the first order kinetic model. Thus, the first order kinetic rate constants, k' , have been evaluated using the integrated first order kinetic rate equation,

$$k't = 2.303 \log \left[\frac{Q_\infty}{Q_\infty - Q_t} \right] \quad (2)$$

where Q_t and Q_∞ have the same meanings as before. The calculated results for all the polymer-solvent systems are given in Table IV. In all the cases (except THF with EPDM), k' values tend to increase

Table IV Kinetic Rate Constants k' of Hazardous Liquids + Polymer Membranes at Different Temperatures

Liquids	Temp. (°C)	$k' \times 10^3$ (min ⁻¹)					
		EPDM	CR	NR	NBR	SBR	
Acetonitrile	25	—	1.32	6.07	8.62	3.19	
	44	—	4.13	9.52	13.49	7.55	
	60	—	7.31	11.62	17.37	11.07	
Dichloromethane	25	11.92	11.95	19.15	23.70	18.85	
	2-Chloroethanol	25	0.18	0.36	0.95	2.16	1.51
		44	0.93	1.15	—	3.30	—
N,N-Dimethyl formamide	60	1.20	1.39	—	4.67	—	
	25	—	0.36	1.23	1.48	0.91	
	44	—	0.98	1.71	3.22	2.54	
Chloroform	60	—	2.20	1.99	4.81	5.53	
	25	9.55	9.90	14.81	14.33	14.71	
	Tetrahydrofuran	25	7.05	7.93	11.83	9.07	11.57
44		12.44	11.19	16.42	12.82	15.41	
60		11.70	14.13	17.59	13.96	18.41	
<i>p</i> -Dioxane	25	1.08	1.94	3.98	2.77	3.21	
	44	4.39	3.47	—	5.08	4.99	
	60	5.73	4.93	—	7.13	7.37	
Bromoform	25	2.06	2.69	3.60	2.98	4.41	
	44	3.97	3.89	5.63	4.27	6.70	
	60	5.65	4.82	7.52	6.40	7.65	
1,4-dichlorobutane	25	1.78	2.37	3.79	2.76	4.05	
	44	4.34	4.04	6.64	5.34	6.93	
	60	6.03	5.52	8.03	6.98	8.19	
1,2-Dichlorobenzene	25	4.09	2.95	5.60	2.46	5.46	
	44	6.95	5.72	8.07	4.27	9.06	
	60	10.29	6.92	9.58	5.52	11.50	

with an increase in temperature. We find that the k' values are highest for the dichloromethane + NBR system. In general, we could not observe any relationship between the results of mol % sorption and k' values; however, the kinetics of sorption seem to follow a first order kinetic mechanism (a fact that was found earlier also^{16,17}), as evidenced by the straight line behavior of the plots of $\log(Q_\infty - Q_t)$ vs. t , shown in Figure 15.

Diffusion Coefficients

From the foregoing discussions, it is apparent that sorption follows what is known as the anomalous-type diffusion mechanism. However, concentration dependence of diffusion does exist with some of the polymer-solvent systems. As a rough approximation,

the diffusion coefficients D , have been estimated from the Fickian model by using the relationship,¹³⁻¹⁸

$$D = \pi(h\theta/4Q_\infty)^2/60 \quad (3)$$

where h is polymer sample thickness, θ is the slope of the linear portion of the graph of Q_t vs. $t^{1/2}$ before completion of 50% equilibrium, and Q_∞ is the maximum sorption, that is, S , in mol %. The results of concentration-independent diffusion coefficients are compiled in Table V. The values of D are accurate to ± 0.01 units. The diffusion coefficients, derived from these experiments and calculated from eq. (3), may be regarded as the apparent diffusion coefficients being affected by the swelling process.

It can be seen that in all polymer-solvent systems,

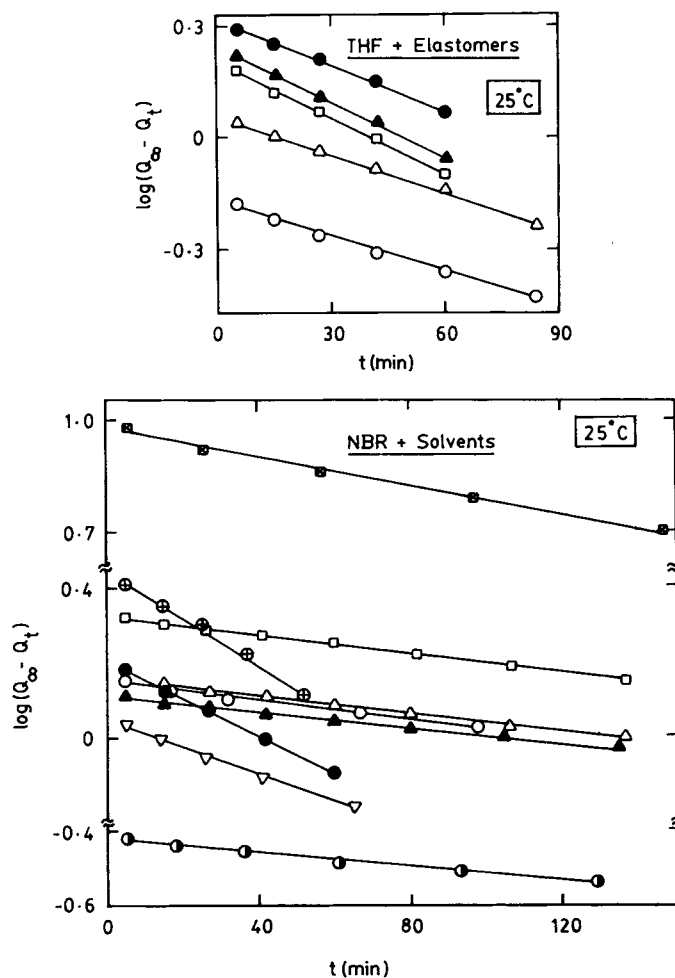


Figure 15 Kinetic plots of $\log(Q_\infty - Q_t)$ vs. time t , for elastomers + THF at 25°C and for NBR + solvents at 25°C. Symbols for solvents are the same as given in Figures 1 and 2, and for elastomers, symbols are the same as in Figure 3.

Table V Diffusion Coefficients of Hazardous Liquids into Polymer Membranes at Different Temperatures

Liquids	Temp. (°C)	$D \times 10^7$ (cm ² /s)				
		EPDM	CR	NR	NBR	SBR
Acetonitrile	25	—	1.06	2.50	5.85	1.97
	44	—	3.78	6.45	9.07	4.75
	60	—	6.00	10.27	13.14	7.06
Dichloromethane	25	9.57	11.94	13.38	19.61	16.05
2-Chloroethanol	25	0.13	0.29	0.72	1.21	0.82
	44	0.62	0.93	—	2.16	—
	60	0.84	1.15	—	3.14	—
N,N-Dimethyl formamide	25	—	0.29	0.55	0.88	0.52
	44	—	0.76	0.96	2.14	1.71
	60	—	1.78	1.08	3.47	3.82
Chloroform	25	8.59	8.83	10.61	11.45	11.23
Tetrahydrofuran	25	5.73	7.83	9.19	5.57	9.42
	44	8.54	10.67	12.06	8.90	12.61
	60	10.32	13.68	13.98	11.43	14.70
<i>p</i> -Dioxane	25	0.76	1.60	2.45	1.53	2.16
	44	2.74	3.11	—	3.22	2.76
	60	4.72	4.62	—	4.58	4.95
Bromoform	25	1.60	2.24	2.42	1.68	2.71
	44	3.22	3.58	3.54	3.34	4.50
	60	3.94	4.35	4.63	4.21	5.53
1,4-Dichlorobutane	25	1.36	1.85	2.26	1.96	2.30
	44	3.24	3.60	4.24	3.85	4.50
	60	4.94	4.86	5.38	4.70	6.08
1,2-Dichlorobenzene	25	2.92	2.62	3.24	1.60	3.56
	44	5.03	4.62	5.97	3.07	6.90
	60	7.36	6.23	6.81	3.99	8.34

diffusion coefficients increase systematically with a rise in temperature, as expected. We could not, however, observe any systematic relationship between the size of the liquid molecules and diffusion coefficients. This may be attributed to several factors: (1) the solvents used here possess varying complexity and different side groups; (2) the rubbers used as barrier materials also possess different chemical groups and void volumes. In some cases, the conditions for sorption become so favorable that regardless of whether the liquid molecule is big or small, it will penetrate through the barrier material giving higher values of diffusion coefficients. In some cases, where the solvent plays an inert role, or its barrier resistivity is high, diffusion coefficients for such systems will be lower. In our earlier articles^{18,20,27} on *n*-alkane transport through these rubbers and on a polyurethane (phase-segregated) membrane, we found an inverse dependence of diffusivity on the size of the liquid molecules. Other published data also support this conjecture.²⁸⁻³⁰

The results of diffusion, given in Table V, and sorption (g/g), given in Table II, were used to calculate the permeability coefficient P , by using $P = D.S$. In this calculation, the units of P are cm²/s. The permeability data, summarized in Table VI, show the same trend as those of the diffusion results and need not be discussed in detail. Realizing the temperature dependence of D and P and by using the Arrhenius relation, the activation parameters were calculated as:

$$X = X_o \exp(-E_x/RT) \quad (4)$$

where X ($= D, P, \text{ or } k'$), X_o ($= D_o, P_o, \text{ or } k'_o$), and E_x ($= E_D, E_P, \text{ or } E_A$) have their usual meanings, as found in the Arrhenius theory. Some representative Arrhenius plots of $\log D$, $\log P$, and $\log k'$ vs. $1/T$ are given in Figures 16, 17, and 18, respectively. It is to be noted that the present range of temperature from 25 to 60°C is a useful range for the membranes

Table VI Permeation Coefficients of Hazardous Liquids into Polymer Membranes at Different Temperatures

Liquids	Temp. (°C)	$P \times 10^7$ (cm ² /s)				
		EPDM	CR	NR	NBR	SBR
Acetonitrile	25	—	0.03	0.03	2.90	0.04
	44	—	0.14	0.09	4.78	0.14
	60	—	0.26	0.19	7.41	0.25
Dichloromethane	25	7.21	15.01	30.54	55.25	38.50
2-Chloroethanol	25	0.01	0.01	0.04	2.70	0.04
	44	0.04	0.07	—	5.05	—
	60	0.06	0.15	—	7.65	—
N,N-Dimethyl formamide	25	—	0.02	0.02	0.26	0.01
	44	—	0.07	0.04	0.73	0.05
	60	—	0.17	0.06	1.36	0.13
Chloroform	25	14.27	14.73	38.19	38.84	39.43
Tetrahydrofuran	25	3.00	6.91	11.27	8.55	12.59
	44	5.01	9.67	15.72	12.99	16.84
	60	7.00	11.96	17.59	17.52	20.70
<i>p</i> -Dioxane	25	0.11	1.10	1.36	1.99	1.85
	44	0.52	2.27	—	4.17	3.35
	60	1.11	3.68	—	6.19	5.45
Bromoform	25	2.19	7.39	14.98	9.34	17.77
	44	5.58	11.89	22.91	17.82	28.88
	60	7.81	15.22	28.84	22.24	35.40
1,4-Dichlorobutane	25	0.41	1.70	3.06	3.71	3.59
	44	1.30	3.37	5.96	7.15	7.13
	60	2.40	4.58	8.12	8.78	9.59
1,2-Dichlorobenzene	25	4.24	3.87	8.61	3.17	9.76
	44	7.41	6.61	15.95	5.81	18.87
	60	11.12	9.17	19.78	7.48	22.58

used. From the slopes of the Arrhenius lines, the activation parameters for the process of diffusion E_D , permeation E_P , and kinetic activation energy E_A , have been calculated and these are summarized in Table VII. The errors involved in the estimation of these quantities were less than 0.001%.

Attempts were also made to estimate the activation energy, E_A , from the temperature-dependent kinetic rate constants, k' , given in Table IV. When the results of E_A (Table VII) are compared with E_D , we observe some differences; this suggests that the kinetics of the sorption mechanism are different than the sorption due to diffusion. However, permeation being a concentration-dependent quantity, the energy of activation for the process of permeation, E_P , should be different than E_D , and this is indeed the case with the present polymer-solvent systems.

In our earlier articles,^{23,25} a procedure was suggested to compute the equilibrium sorption constant K_s , for polymer-solvent systems under complete

equilibrium saturation conditions. In other words, K_s is equivalent to maximum sorption, Q_∞ , or sorption coefficient S . The values of K_s have been fitted to temperature by means of the van't Hoff equation to estimate enthalpy, ΔH_s , and entropy, ΔS , of sorption as:

$$\log K_s = \frac{\Delta S}{2.303 R} - \frac{\Delta H_s}{2.303 R} (1/T) \quad (5)$$

The estimated quantities are also included in Table VII. A typical van't Hoff plot is shown in Figure 19. The ΔS values are negative for all the systems except CR + 2-chloroethanol, suggesting the retention of liquid state structure of penetrant molecules, even in the sorbed state. However, widely varying values of ΔH_s are obtained, depending on the nature of the sorption mechanism. In the case of THF with CR and NBR, ΔH_s values are negative (i.e., -0.140 and -0.127 kJ/mol, respectively). Similarly, for bro-

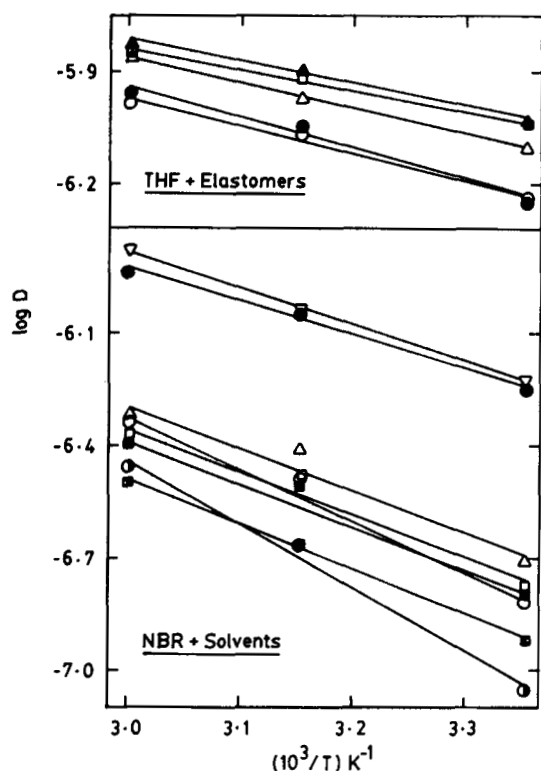


Figure 16 Arrhenius plots of $\log D$ vs. $1/T$ for THF + elastomers and NBR + solvents. The symbols for solvents are the same as in Figures 1 and 2, and for elastomers, symbols are the same as in Figure 3.

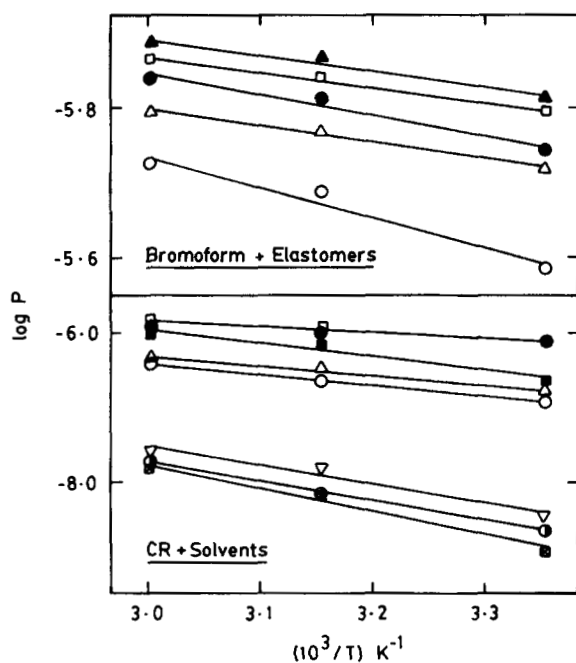


Figure 17 Arrhenius plots of $\log P$ vs. $1/T$ for bromoform + elastomers and CR + solvents. Symbols for solvents are the same as in Figures 1 and 2, and for elastomers, symbols are the same as in Figure 3.

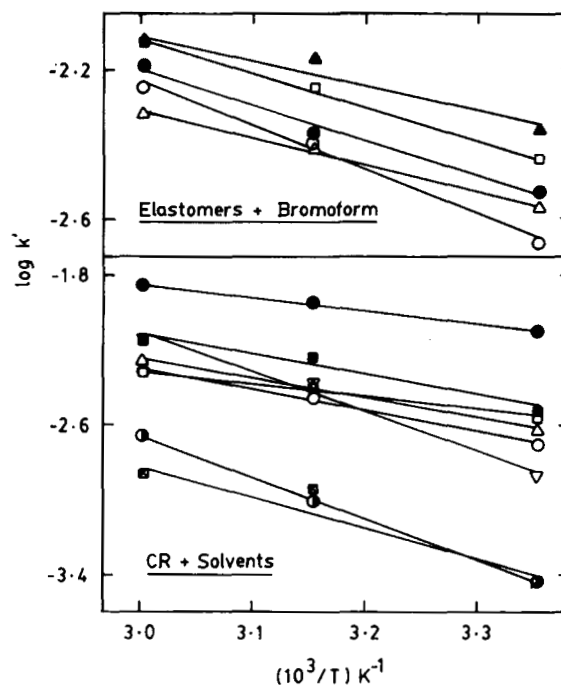


Figure 18 Arrhenius plots of $\log k'$ vs. $1/T$ for elastomers + bromoform and CR + solvents. The symbols for elastomers are the same as given in Figure 3 and for solvents are the same as in Figures 1 and 2.

moform with NBR and SBR membranes, ΔH_s values are more negative (i.e., -1.244 and -0.553 kJ/mol, respectively); also, 1,4-dichlorobutane with NBR and 1,2-dichlorobenzene with CR, NBR, and SBR exhibit negative values of ΔH_s . However, with the remaining polymer-solvent systems, we find positive values of ΔH_s . This ΔH_s is a composite parameter involving both Henry's law and Langmuir (hole filling) type sorption mechanisms. Thus, sorption depends upon both polymer-penetrant interactions and the volume available for hole filling. The Henry's mode requires both the formation of a site and the dissolution of species into that site. The formation of a site involves an endothermic contribution to this process. For the Langmuir mode, the site already exists in the polymer matrix and, consequently, sorption by hole filling yields more exothermic heats of sorption. This appears to be the case with some of the present systems, which exhibit negative values of ΔH_s .

Concentration Dependence of Diffusion Coefficients

The slight, sigmoidal, sorption-rate curves, as observed for some polymer-solvent systems, have been

Table VII Activation Parameters (E_A , E_D , E_P , and ΔH_s in kJ/mol; ΔS in J/mol/degree) for Polymer + Hazardous Liquids

Liquids	Parameters	EPDM	CR	NR	NBR	SBR
Acetonitrile	E_A	—	40.89	15.52	16.67	29.72
	E_D	—	41.57	33.69	19.05	30.43
	E_P	—	49.02	48.44	22.12	42.24
	ΔH_s	—	7.290	13.850	3.063	11.940
	$-\Delta S$	—	35.46	22.55	26.50	22.55
2-Chloroethanol	E_A	45.83	32.70	—	18.22	—
	E_D	44.44	33.32	—	22.62	—
	E_P	55.75	61.82	—	24.67	—
	ΔH_s	6.039	28.479	—	2.057	—
	$-\Delta S$	40.75	-31.73	—	22.92	—
N,N-Dimethyl formamide	E_A	—	42.51	11.62	28.11	42.64
	E_D	—	43.15	16.24	32.74	47.34
	E_P	—	49.60	31.31	39.41	52.50
	ΔH_s	—	6.514	15.113	6.789	5.170
	$-\Delta S$	—	35.34	13.97	23.143	48.58
Tetrahydrofuran	E_A	12.60	13.66	9.61	10.41	11.02
	E_D	14.03	13.17	9.97	17.10	10.59
	E_P	20.06	13.03	10.68	16.98	11.76
	ΔH_s	6.032	-0.140	0.709	-0.127	1.174
	$-\Delta S$	20.80	37.00	31.39	32.55	29.30
<i>p</i> -Dioxane	E_A	40.37	22.16	—	22.46	19.50
	E_D	43.60	25.17	—	26.17	19.11
	E_P	54.71	28.68	—	27.00	25.51
	ΔH_s	11.04	3.509	—	0.838	6.080
	$-\Delta S$	15.93	28.96	—	32.29	17.99
Bromoform	E_A	24.00	13.87	17.50	17.89	13.25
	E_D	21.71	15.92	15.38	22.06	17.04
	E_P	30.49	17.21	15.58	20.82	16.48
	ΔH_s	8.78	1.286	0.196	-1.244	-0.553
	$-\Delta S$	13.87	31.81	30.07	35.93	32.24
1,4-Dichlorobutane	E_A	29.33	20.12	18.03	22.23	16.93
	E_D	30.75	23.03	20.75	21.04	23.18
	E_P	42.04	23.69	23.31	20.69	23.50
	ΔH_s	11.292	0.654	2.558	-0.351	0.314
	$-\Delta S$	12.35	38.79	29.25	36.18	35.51
1,2-Dichlorobenzene	E_A	21.80	20.55	12.81	19.25	17.77
	E_D	21.87	20.61	17.97	21.89	20.47
	E_P	22.79	20.47	19.97	20.52	20.20
	ΔH_s	0.927	-0.132	2.004	-1.366	-0.268
	$-\Delta S$	35.31	38.77	26.75	40.41	34.00

analyzed using the Joshi and Astarita procedure³¹ in which the model parameters were varied incrementally over a prescribed range and the fit to the experimental data was subjected to a least-squares test to select the best set of values. The diffusion coefficients, thus obtained over a range of concentration values, are displayed graphically in Figures 20 and 21 for some typical systems. For liquids that

exhibit high swelling, the dependence of D on C goes through maxima; however, the maxima decrease considerably for low swelling liquids, suggesting a mild concentration dependence on diffusion. Particularly, for the acetonitrile + CR system, no pronounced dependence of D on C can be observed (see Fig. 20). Similar findings have also been observed earlier by us²⁰ and in the work of Waksman et al.³²

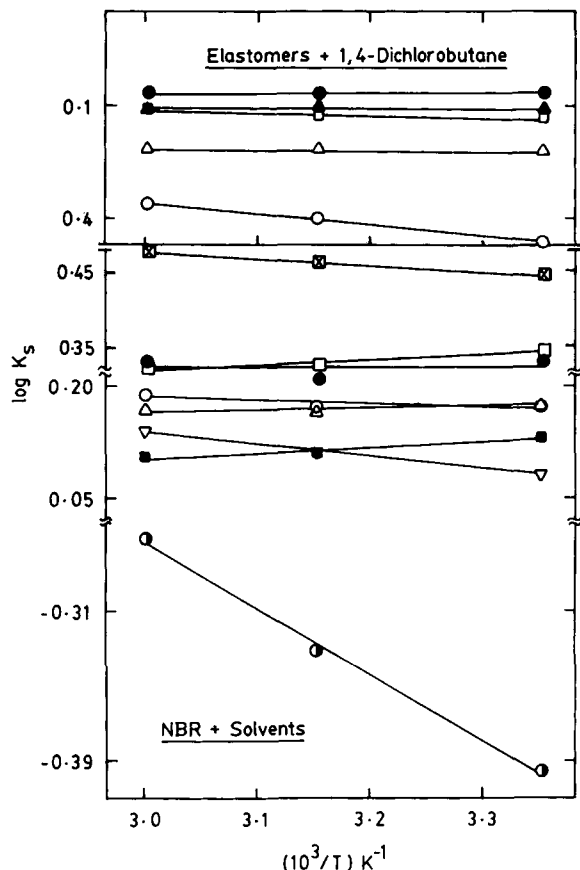


Figure 19 van't Hoff plots of $\log K_s$ vs. $1/T$ for 1,4-dichlorobutane + elastomers and NBR + solvents. Symbols for solvents are the same as given in Figures 1 and 2. Symbols for elastomers are the same as in Figure 3.

for toluene diffusion into natural rubber. At this point, we are not in a position to compare our data with the literature, for several reasons. First, no extensive database is available on the type of systems investigated in this study and, second, even if some scanty data were available, we could not directly compare these with the present results because of changes in the morphology of polymer membranes.

Conclusions

Resistance of barrier materials to the presence of aggressive solvents depends mainly on the polymer structure and its morphology in addition to interacting groups of solvent molecules. In the absence of highly sophisticated instrumentation, the conventional weight gain method appears to be reliable for studying solvent transport through polymer membranes. In the present investigation, solvents have been selected from various groups and their

interactions have been studied with structurally different elastomer membranes. From this study, it would be possible to forecast conditions and penetrant types which would cause the polymer degradation and it would be possible to predict their consequences on transport behavior. An increase in polymer-solvent interactions leads to increased sorption and transport of the liquids, such that the diffusion process often becomes concentration-dependent. Thus, depending upon the relative rates of polymer relaxation concurrent with the sorption-diffusion processes, the overall transport phenomenon may exhibit the Fickian mode with simple concentration-dependent diffusion, or it may deviate from the Fickian transport due to complicating relaxation effects. Furthermore, the diffusion data have been analyzed in terms of the Joshi-Astarita theory to study the concentration dependence of diffusion. The study has indicated that, except for dioxane, none of the remaining solvents attacked the rubber membranes. Activation parameters and diffusion data did not show any systematic relationship with the size or shape of the liquid molecules used in this study.

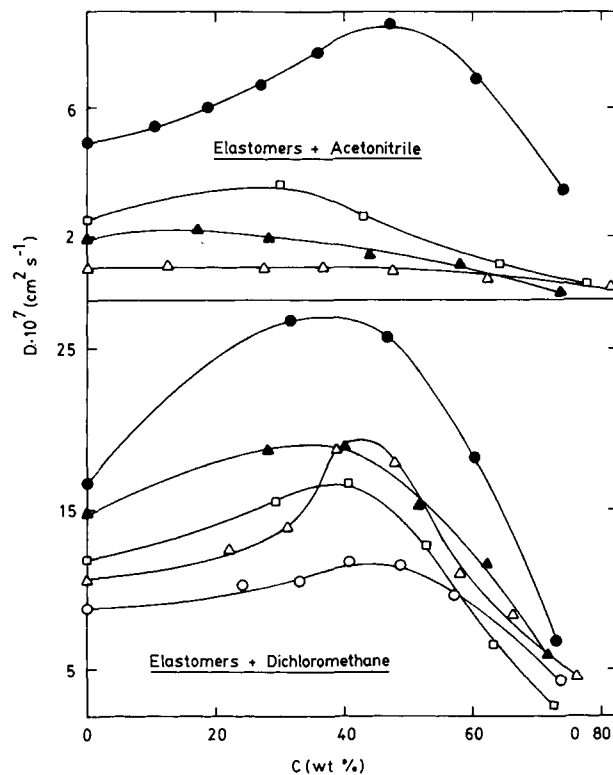


Figure 20 Concentration dependence of diffusion coefficient for elastomers with acetonitrile and dichloromethane. Symbols for elastomers are the same as in Figure 3.

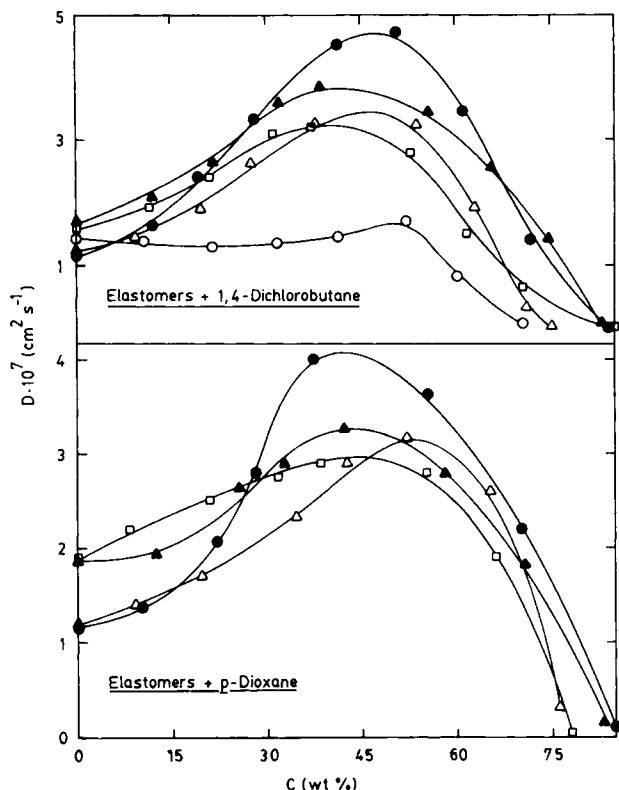


Figure 21 Concentration dependence of diffusion coefficient for elastomers with 1,4-dichlorobutane and dioxane; symbols for elastomers are the same as in Figure 3.

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REFERENCES

1. T. M. Aminabhavi, U. S. Aithal, and S. S. Shukla, *J. Macromol. Sci. Revs. Macromol. Chem. Phys.*, **C28**(3, 4), 421 (1988).
2. T. M. Aminabhavi, U. S. Aithal, and S. S. Shukla, *J. Macromol. Sci. Rev. Macromol. Chem. Phys.*, **C29**(2, 3), 319 (1989).
3. U. S. Aithal, T. M. Aminabhavi, R. H. Balundgi, and S. S. Shukla, *J. Macromol. Sci. Revs. Macromol. Chem. Phys.*, **C30**(1), 43 (1990).
4. R. McGregor, *Diffusion and Sorption in Fibers and Films*, Vol. 1, Academic, New York, 1974.
5. J. Comyn, *Polymer Permeability*, Elsevier, London, 1986.
6. H. B. Hopfenberg, *Permeability of Plastic Films and*

Coatings to Gases, Vapors, and Liquids, Plenum, New York, 1974.

7. S. A. Stern and H. L. Frisch, *Ann. Rev. Mater. Sci.*, **11**, 223 (1981).
8. L. H. Sperling, *Interpenetrating Polymer Networks and Related Materials*, Plenum, New York, 1981.
9. B. F. Greek, *Chem. Eng. News.*, March 26, 1988, p. 26.
10. *Guide for Safety in the Chemical Laboratory*, Van Nostrand, Princeton, New Jersey, 1954.
11. *The Condensed Chemical Dictionary*, 5th Ed. Reinhold, New York, 1956.
12. J. A. Riddick, W. B. Bunger, and T. K. Sakano, *Techniques of Chemistry*, Vol. 2, in *Organic Solvents*, IV ed., 1986.
13. S. B. Harogopad and T. M. Aminabhavi, *J. Appl. Polym. Sci.*, **42**, 2329 (1991).
14. U. S. Aithal, T. M. Aminabhavi, and P. E. Cassidy, *Polym. Prepr.*, **30**(1), 17 (1989).
15. U. S. Aithal, T. M. Aminabhavi, and P. E. Cassidy, *J. Membr. Sci.*, **50**, 225 (1990).
16. L. N. Britton, R. B. Ashman, T. M. Aminabhavi, and P. E. Cassidy, *J. Appl. Polym. Sci.*, **38**, 227 (1989).
17. S. B. Harogopad and T. M. Aminabhavi, *Polymer*, **32**, 870 (1991).
18. S. B. Harogopad and T. M. Aminabhavi, *J. Chemical Educ.*, **68**, 343 (1991).
19. B. D. Barr-Howell, N. A. Peppas, and T. G. Squires, *J. Appl. Polym. Sci.*, **31**, 39 (1986).
20. S. B. Harogopad and T. M. Aminabhavi, *Macromolecules*, **24**, 2598 (1991).
21. D. J. Enscoe, H. B. Hopfenberg, and V. T. Stannett, *Polym. Eng. Sci.*, **20**, 102 (1980).
22. L. M. Lucht and N. A. Peppas, *J. Appl. Polym. Sci.*, **33**, 1557 (1987).
23. U. S. Aithal, T. M. Aminabhavi, and S. S. Shukla, *J. Chem. Eng. Data*, **35**, 298 (1990).
24. J. Crank and G. S. Park, *Diffusion in Polymers*, Academic, New York, 1968.
25. U. S. Aithal, T. M. Aminabhavi, and P. E. Cassidy, in *Barrier Polymers and Barrier Structures*, W. J. Koros, Ed., American Chemical Society, Washington DC, 1990, Chap. 19.
26. C. I. MacKenzie and J. Scarlan, *Polymer*, **25**, 559 (1984).
27. R. S. Khinnavar and T. M. Aminabhavi, *J. Appl. Polym. Sci.*, **42**, 2321 (1991).
28. J. M. Ottino and N. Shah, *Polym. Eng. Sci.*, **24**, 153 (1984).
29. V. T. Stannett, H. B. Hopfenberg, and J. H. Petropoulos, *Int. Rev. Sci. Phys. Chem. Ser. 1*, **8**, 329 (1970).
30. A. F. A. Asfour, M. Saleem, D. Dekee, and B. H. Harrison, *J. Appl. Polym. Sci.*, **38**, 1503 (1989).
31. S. Joshi and G. Astarita, *Polymer*, **20**, 455 (1979).
32. L. S. Waksman, N. S. Schneider, and N. H. Sung, in *Barrier Polymers and Barrier Structures*, W. J. Koros, Ed., American Chemical Society, Washington DC, 1990, Chap. 20.

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