

# Swelling Characteristics of Polymer Membranes in the Presence of Aromatic Hydrocarbon Liquids\*

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## SYNOPSIS

Swelling properties of some engineering polymer membranes in the presence of monocyclic aromatic hydrocarbons have been studied from the solvent immersion experiments. The liquids were chosen with varying methyl and methoxy substitutions to study the effect of substitutions on their transport properties. Diffusion coefficients have been extracted from the swelling results. The concentration dependence of diffusion coefficients has been investigated. Furthermore, the swelling and diffusion results have been used to assess the suitability of the polymer membranes in environments containing aromatic hydrocarbon liquids.

## INTRODUCTION

New specialty polymers are being commercialized in response to the demands of industry for materials development which are capable of operating under more severe conditions for longer periods of time. Nitrile butadiene rubber (NBR), neoprene (CR), styrene butadiene rubber (SBR), ethylene propylene diene terpolymer (EPDM), and natural rubber (NR) are the well-known polymers that have been widely used in a variety of industrial and engineering areas. This is partly due to their outstanding properties such as sunlight resistance and excellent compatibility to aqueous and nonaqueous media.<sup>1-3</sup> When in contact with organic liquids, these polymers may behave differently, depending on the nature of the solvent molecule. Thus, the dimensional stability of polymers in the presence of aggressive solvent media is extremely important for their successful applications. In many situations, the swollen polymers tend to lose the sorbed solvent molecules to attain their original shapes upon complete removal of the solvent from it. This is particularly true in

the case of crosslinked polymers, where the solvent molecules normally do not tend to destroy the molecules of the chain segments. However, the other possibilities are that the solvent molecules might interact somewhat strongly with the agglomerate fillers, thereby reducing the strength properties of the network materials. Several aspects of polymer swelling in the presence of organic liquids have been recently studied by Errede.<sup>4-7</sup>

Earlier publications<sup>8-16</sup> from this laboratory on the study of interactions of hydrocarbons with rubbery polymers reported that it is possible to correlate the solvent diffusion properties with the structure of polymer membranes. In continuation of this research, we present here some useful results on the swelling characteristics of NBR, CR, SBR, EPDM, and NR membranes versus some industrially important solvents like benzene, toluene, *p*-xylene, mesitylene, and anisole. The widespread use of these solvents in polymer-related industries prompted us to choose these solvents for the study. In several industrial applications, these solvents may come into contact with a variety of the polymer products wherein these products may be used as containers to store the solvents. Hence, accurate knowledge of swelling of these rubbers together with the diffusion parameters are helpful in assessing the stability of the polymeric products in the presence of aggressive environments containing organic liquids. Therefore, in this study, diffusion coefficients  $D$  have been cal-

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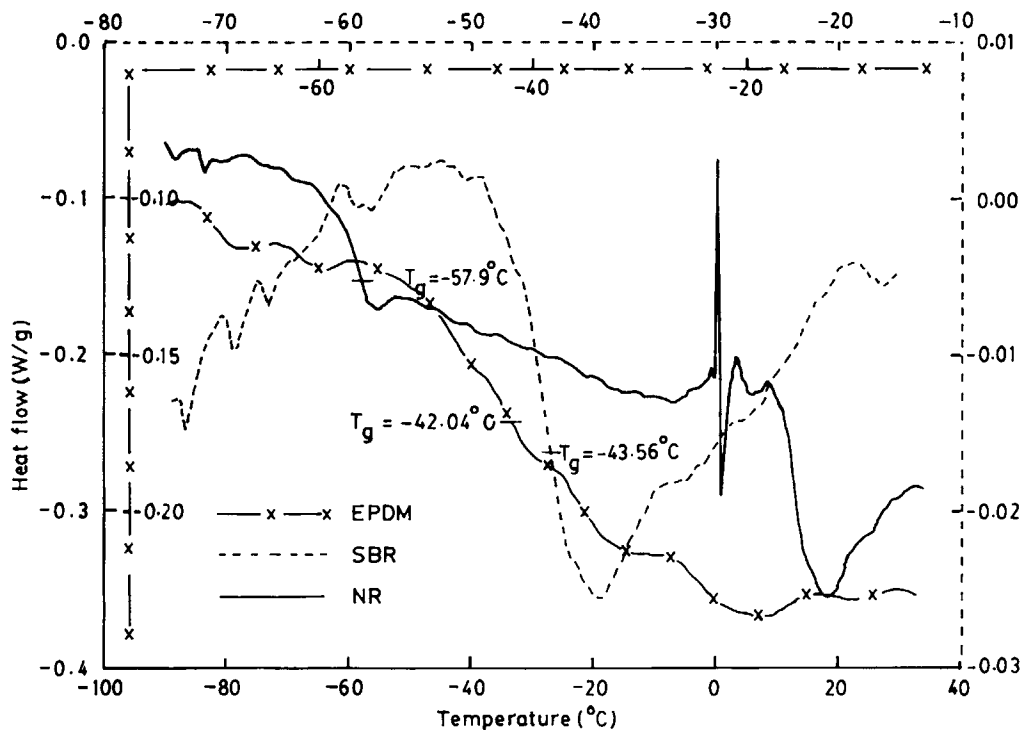


Figure 1 DSC tracings of EPDM, SBR, and NR elastomers.

culated for solvent-polymer systems from the time-dependent swelling response of the polymers. The diffusion and swelling results have been used to assess the application conditions of polymers under the influence of the solvents chosen here. Solvents are selected with varying groups to see as to how the differences in their physical and chemical characteristics affect the overall diffusion properties of the selected polymer membranes.

## EXPERIMENTAL

Molded sheets of NBR, CR, SBR, EPDM, and NR in dimensions of  $\frac{1}{16} \times 6 \times 6$  in. were obtained from UTEX, Weimer, Texas (courtesy of Mr. Andy Kutac). A 12 in. laboratory mill was used to mix and prepare the rubber compounds for molding. The polymer sheets were cured at 160°C for 20 min. The cured polymer samples were then cut circularly (diameter = 1.94 cm) by using a sharp-edged steel die. Their thicknesses were measured at several points ( $\pm 0.001$  cm) by means of a micrometer screw gauge (Sargent Welch Co., USA). All the polymer samples except CR have thicknesses  $\approx 0.200$  cm whereas CR has a thickness of  $\approx 0.250$  cm.

The polymer membranes were characterized by the differential scanning calorimetry (DSC, DuPont

Model 951) to estimate their glass transition temperatures ( $T_g$ ). The DSC tracings are given in Figures 1 and 2. The  $T_g$  data obtained for different polymers are SBR ( $-44^\circ\text{C}$ ), EPDM ( $-42^\circ\text{C}$ ), NR ( $-57^\circ\text{C}$ ), CR ( $-38^\circ\text{C}$ ), and NBR ( $-12^\circ\text{C}$ ). The reagent grade solvents used were purified by the standard procedures.<sup>17</sup> The observed physical data, such as density and refractive index of the solvents, agreed well with the literature.

The dynamic swelling experiments were performed on cut polymer samples by immersing them in test bottles containing the solvent maintained at the constant ambient temperature ( $25 \pm 0.5^\circ\text{C}$ ) by using an electric oven (Memmert, Germany). The experimental details are the same as described previously.<sup>8-16</sup> At specified times, the samples were removed from the test bottles to measure the changes in thickness and diameter.

## RESULTS AND DISCUSSION

In all the polymer-solvent systems, swelling was observed in both the thickness and diameter directions. Some representative plots of percent increase in thickness,  $L_t$ , versus square root of time,  $t^{1/2}$ , are shown in Figures 3-5. These curves for all the systems are linear in the beginning up to about 50%

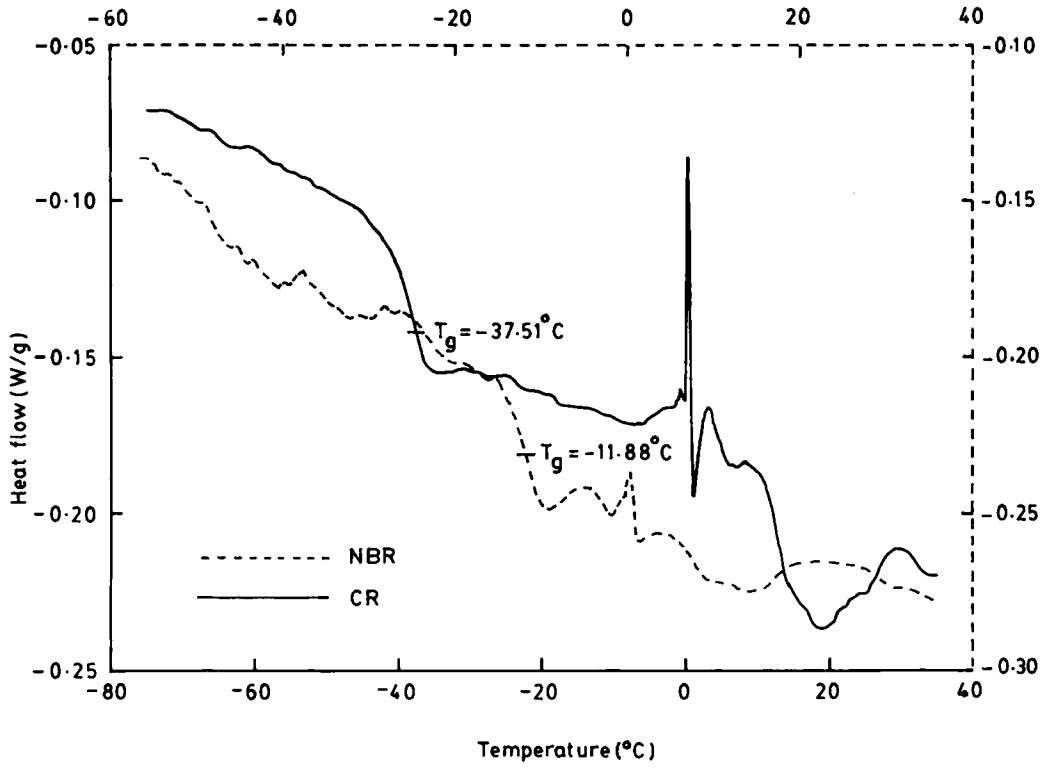


Figure 2 DSC tracings of NBR and CR elastomers.

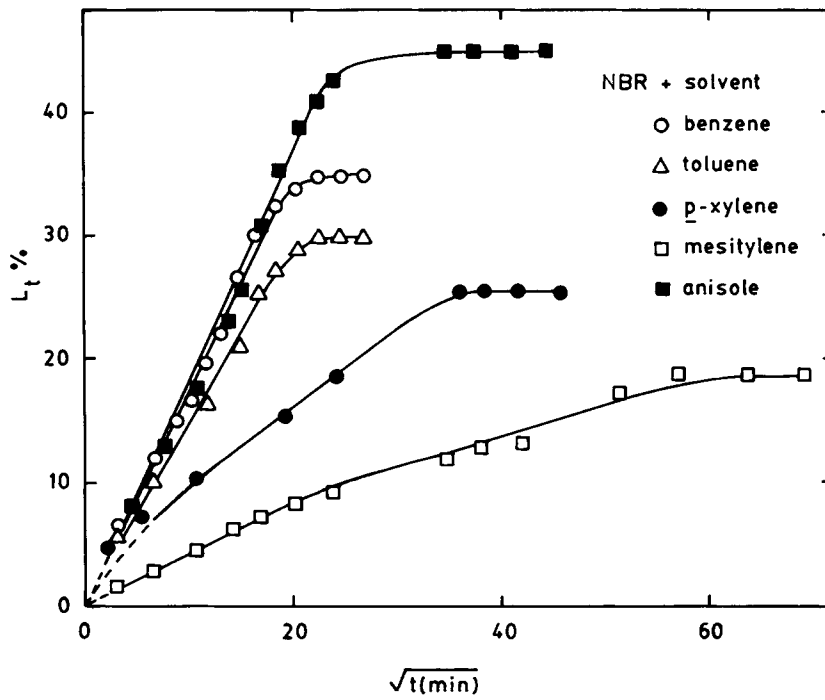
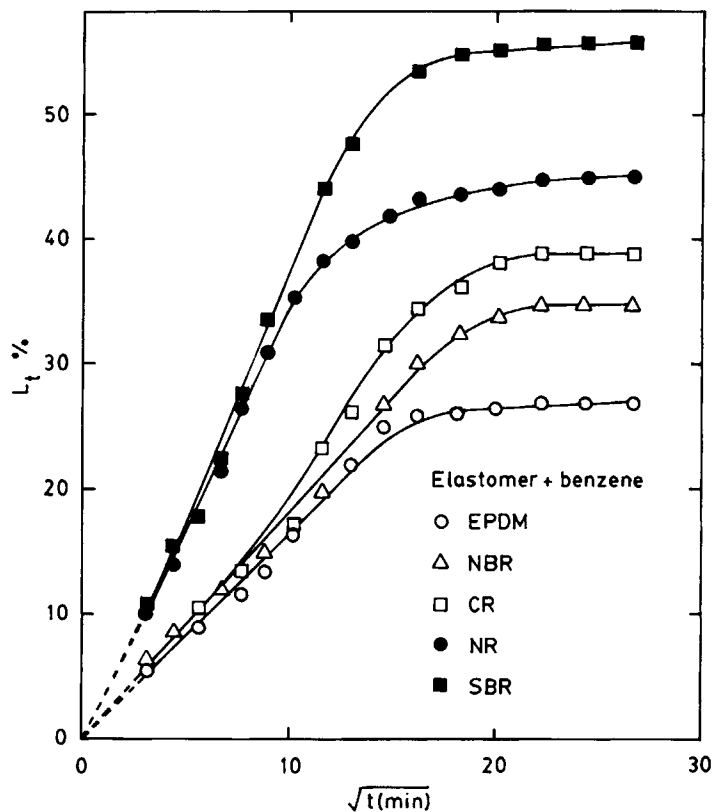
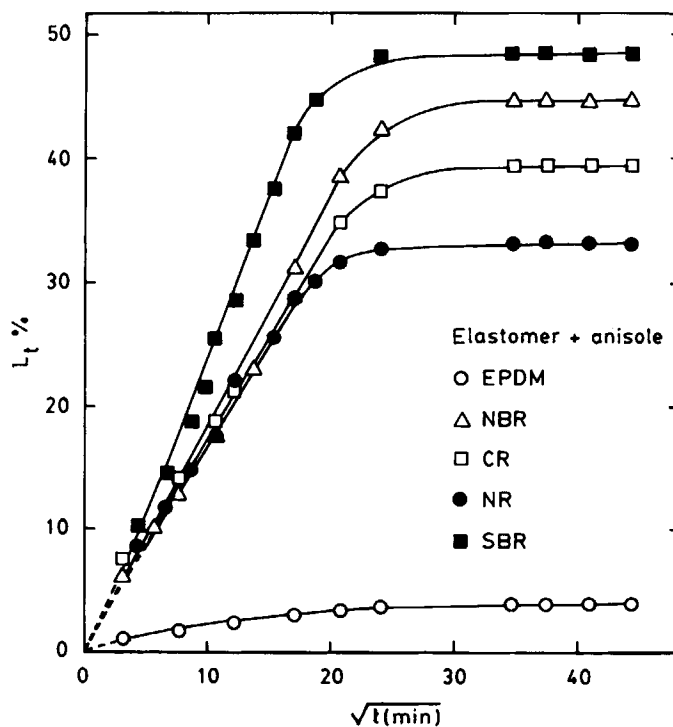


Figure 3 Percent increase in thickness versus square root of time for NBR + solvent systems at 25°C.



**Figure 4** Percent increase in thickness versus square root of time for benzene + elastomer systems at 25°C.



**Figure 5** Percent increase in thickness versus square root of time for anisole + elastomer systems at 25°C.

attainment of equilibrium and, later, level off showing the equilibrium swelling. The procedure of Marom et al.<sup>18-20</sup> was used to estimate the diffusion coefficients  $D$  of the solvents into membrane materials. However, the procedure of Marom et al. was originally applied to the heterogeneous composite materials. The polymers used in this research contain additives/fillers and may thus be regarded as heterogeneous materials to justify the use of the Marom et al theory. Diffusion coefficients were thus calculated as

$$D = \pi(h\theta/4L_m)^2 \quad (1)$$

where  $\theta$  is the slope as obtained from the least-squares estimation of the linear part of the plots of  $L_t$  vs.  $t^{1/2}$  (Figs. 3-5),  $h$  is the initial thickness of the polymer, and  $L_m$  is the maximum percent swelling observed at the end of the immersion experiments. The estimated errors in the calculation of  $D$  was around  $\pm 0.04$ . The results of  $L_m$ ,  $D$ , and  $d_m$  (i.e., percent maximum increase in diameter) for all the polymer-solvent systems are listed in Table I. Due to significant lateral swelling of the membranes, it was also decided to compute the effective diffusion coefficients  $\bar{D}$  by making use of the empirical relationship suggested earlier by Aithal et al.<sup>10</sup> Thus,

$$\bar{D} = D[1 + \bar{h}/\bar{r} + \bar{h}/2\pi\bar{r}]^2 \quad (2)$$

The correction factor for  $D$  given in eq. (2) considers diffusion of the solvent molecules along the radial and the angular directions of the disc-shaped polymer samples. The quantities  $\bar{h}$  and  $\bar{r}$  represent, respectively, the average thickness and average radius of the samples taken before and after swelling. The correction for  $D$  as given in eq. (2) appears legitimate because it is based on the approach suggested earlier by Shen and Springer<sup>21</sup> for rectangular geometry. The computed  $\bar{D}$  values are also included in Table I. In all cases, the  $\bar{D}$  values are higher than those of  $D$  values suggesting the concentration dependencies of  $D$  for the polymer-solvent systems studied here.

A knowledge of the structure of liquids, the amount of swelling and diffusion data would be useful to discuss tentatively the mechanism of transport of liquids with structurally different polymer membranes. For NBR with a polar —CN group, the percent increase in thickness and diameter seem to decrease systematically from benzene to mesitylene. However, with anisole the swelling is highest possibly due to the H-bond type interactions between the —CN group of NBR and the —OCH<sub>3</sub> group of anisole. Diffusion coefficients of toluene are higher than benzene for all the membranes except SBR. However, for *p*-xylene and mesitylene, the diffusivities are subsequently lower than benzene and toluene. We could not observe any systematic relationship between swelling and diffusivity for the

**Table I Swelling and Diffusion Data for Polymer + Solvent Systems at 25°C**

Solvent	Parameter <sup>a</sup>	NBR	CR	EPDM	SBR	NR
Benzene	$L_m$	34.9	38.8	26.9	55.7	45.1
	$d_m$	28.9	32.0	24.7	45.6	39.2
	$D \times 10^7$ (cm <sup>2</sup> /s)	2.65	3.62	3.91	6.08	6.33
	$\bar{D} \times 10^7$ (cm <sup>2</sup> /s)	4.21	6.14	6.27	9.71	9.89
Toluene	$L_m$	29.9	41.5	31.4	57.5	45.5
	$d_m$	25.5	33.5	29.9	46.4	41.0
	$D \times 10^7$ (cm <sup>2</sup> /s)	3.19	4.28	4.18	4.91	6.62
	$\bar{D} \times 10^7$ (cm <sup>2</sup> /s)	5.02	7.31	6.69	7.89	10.22
<i>p</i> -Xylene	$L_m$	25.5	43.0	34.7	55.7	47.5
	$d_m$	23.2	33.8	32.0	48.0	41.2
	$D \times 10^7$ (cm <sup>2</sup> /s)	1.08	2.10	4.42	1.50	3.24
	$\bar{D} \times 10^7$ (cm <sup>2</sup> /s)	1.69	3.60	7.10	2.42	5.04
Mesitylene	$L_m$	18.8	39.9	34.7	56.6	44.2
	$d_m$	16.0	30.7	32.0	46.4	40.0
	$D \times 10^7$ (cm <sup>2</sup> /s)	0.68	1.60	2.38	2.15	2.21
	$\bar{D} \times 10^7$ (cm <sup>2</sup> /s)	1.04	2.74	3.79	3.43	3.47
Anisole	$L_m$	44.8	39.4	12.6	48.6	33.2
	$d_m$	38.1	30.4	12.9	41.0	29.6
	$D \times 10^7$ (cm <sup>2</sup> /s)	1.91	2.61	3.10	3.36	2.05
	$\bar{D} \times 10^7$ (cm <sup>2</sup> /s)	3.15	4.41	4.89	5.39	3.20

<sup>a</sup>  $L_m$  = % maximum swelling in thickness;  $d_m$  = % maximum swelling in diameter.

polymer-solvent systems. Mesitylene and anisole exhibit identical swelling for CR, but swelling increases systematically from benzene to *p*-xylene. However, no systematic dependence of diffusivity on either size or nature of the hydrocarbon molecules is observed. Diffusivity is higher for toluene than benzene, but *p*-xylene showed the highest swelling.

For EPDM, however, we could observe a systematic increase in swelling from benzene to mesitylene; the extent of swelling for mesitylene and *p*-xylene is identical in both thickness and radial directions. However, diffusion coefficients for EPDM seem to increase from benzene to *p*-xylene whereas, for mesitylene,  $D$  is smaller than the other methyl-substituted benzenes. EPDM, being a hydrophobic polymer, shows extremely low swelling (i.e.,  $L_m$  or  $d_m$  of about 12%) for anisole, yet diffusive trends of anisole are higher than that of mesitylene.

SBR shows very high swelling tendencies in the presence of aromatic hydrocarbons. This may be due to the presence of aromatic benzene ring on SBR backbone, thereby rendering it more susceptible to attack by molecules of similar structures. All the solvents exhibit high swelling rates for SBR, but the extent of swelling is almost identical for all the methyl-substituted benzenes (i.e.,  $L_t \approx 55\%$ ). However, with anisole the swelling is smaller than other liquids. Diffusion coefficients decrease systematically from benzene, toluene, and *p*-xylene while for mesitylene and anisole the diffusion coefficients are somewhat higher. This suggests that diffusion coefficients are independent of molecular size of the methyl- or methoxy-substituted benzenes for SBR as a barrier. For natural rubber in the presence of benzene or toluene, swelling and diffusion data are almost identical. However, mesitylene, whose swelling is identical to that of benzene, shows lower values of diffusion coefficients than the other methyl-substituted aromatics. On the other hand, swelling and diffusivity of anisole is very small as compared to NR-solvent systems.

It would be instructive to make some generalized comments on the shapes of the  $L_t$  versus  $t^{1/2}$  curves. Figure 3 depicts such a dependence for NBR + solvent systems, where more rapid swelling occurs for anisole, benzene, and toluene than for mesitylene. With other membrane-solvent systems, we find quite different swelling tendencies; these plots are not shown. In Figure 4, the dependence of  $L_t$  on  $t^{1/2}$  is presented for benzene with all the elastomers. The swelling curves for benzene are almost identical initially, but at longer times higher swelling is observed for SBR than NR. However, in the presence of benzene, the swelling behaviors of EPDM, NBR,

and CR are quite different and the maximum swelling values are smaller than those of NR and SBR membranes. With anisole-polymer systems (Fig. 5), however, the swelling tendencies of NR and SBR are different as compared to EPDM, NBR, and CR membranes. For instance, anisole shows high swelling for SBR and low swelling for NR while the intermediate swelling values are observed in the case of CR and NR. EPDM, on the other hand, shows almost negligible swelling characteristics for anisole as compared to other membranes (Fig. 5).

Due to the significant swelling of the polymer membranes and in view of the fact that the swelling curves presented in Figures 3-5 show slightly sigmoidal shapes,  $\bar{D}$  values calculated from eq. (2) are more believable than concentration-independent  $D$  values calculated from eq. (1). This prompted us to carry out the analysis of diffusion data further to study their concentration dependencies. In this respect, the slight sigmoidal shapes of the swelling curves were analyzed by using the model of Joshi and Astarita,<sup>22</sup> in which the model parameters have been varied incrementally over a prescribed range and the fit to the experimental data was subjected to least-squares test to select the best set of values. The diffusion coefficients thus obtained for some typical systems, viz., mesitylene + elastomers and EPDM + solvents are, respectively, given in Figures 6 and 7. The solvent concentrations in the membrane systems are expressed in weight percent units

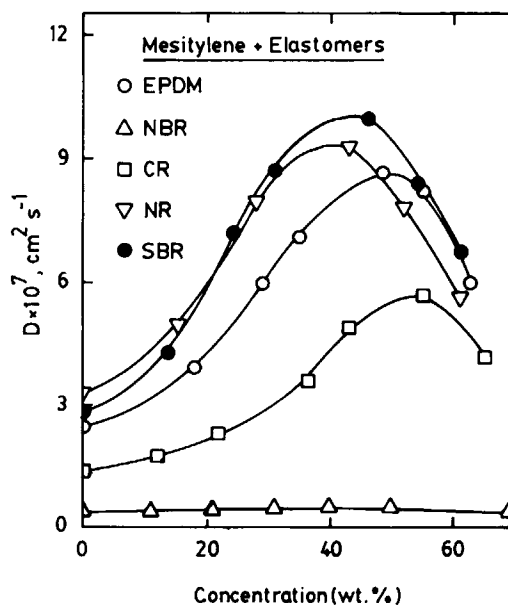
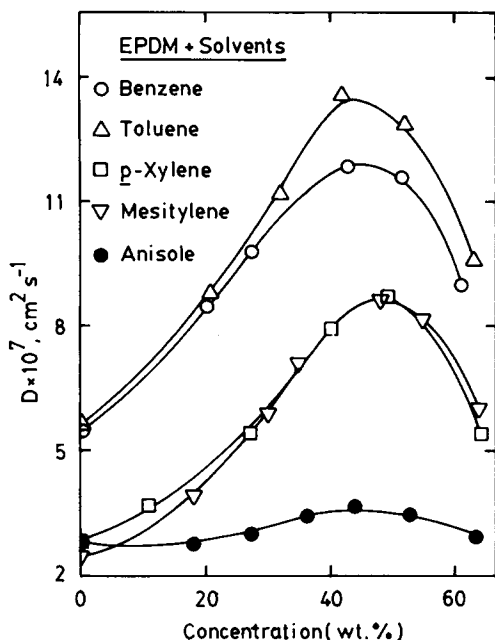


Figure 6 Concentration dependence of diffusion coefficient for mesitylene + elastomers at 25°C.



**Figure 7** Concentration dependence of diffusion coefficient for EPDM + solvents at 25°C.

from the data of the amounts of liquids sorbed by the membranes.

As one can see from Figures 6 and 7, the diffusion coefficients go through maxima for those polymer-solvent systems that exhibit high concentration dependencies of diffusivity. Furthermore, the diffusivities seem to depend on the concentration for those membranes which showed significant swelling. However, the almost linear variation of  $D$  with concentration in case of mesitylene + NBR (Fig. 6) and EPDM + anisole (Fig. 7) suggest that  $D$  values in these systems are not highly concentration-dependent. For NBR + mesitylene shown in Figure 6, diffusivity is almost independent of solvent concentration, whereas, for mesitylene with other rubbers, sharp maxima are observed. The swelling of SBR is highest for mesitylene, thus showing sharp maximum in the  $D$  versus  $C$  plots, whereas CR shows an almost linear behavior with a slight increase in  $D$  with  $C$ . Similar observations have also been found in our earlier work<sup>16</sup> on diffusion of higher alkanes ( $C_8$ - $C_{16}$ ) into these rubber membranes and that of Waksman et al.<sup>23</sup>

## CONCLUSIONS

The barrier properties of rubbery polymers may seriously be impaired by the presence of organic liquids that penetrate into them. It would be useful to fore-

cast conditions under which liquids might cause polymer degradation. In this paper, we have used some structurally different polymer membranes to gain further insight into the dependence of polymer structure on variations with the solvent properties. It is found that swelling and diffusion of the selected solvents in these membranes are influenced by the nature of the solvent molecules as well as the polymer.

Transport of relatively noninteracting liquid molecules in a polymer seems to follow the classical behavior predicted by Fick's law with constant (or nearly so) diffusion coefficients. An increase in generalized interactions (van der Waals, etc.) leads to increased swelling of the membranes so that diffusion becomes concentration-dependent. The results of this study indicate that swelling of EPDM is very small as compared to SBR for the aromatic hydrocarbons used. However, compared to NR, NBR appears to be a better barrier material. In summary, none of the polymers used are destroyed by any of the solvents. On the whole, EPDM appears to be a better barrier material to hydrocarbons than the rubbers used here.

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