Diffusion and Sorption of Organic Liquids through Polymer Membranes. 5. Neoprene, Styrene–Butadiene–Rubber, Ethylene–Propylene–Diene Terpolymer, and Natural Rubber versus Hydrocarbons (C_8–C_{16})

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ABSTRACT: Diffusion and sorption of four long-chain hydrocarbons, namely, 2,2,4-trimethylpentane, dodecane, tetradecane, and hexadecane, through four commercial polymer membranes has been studied in the temperature interval of 25–60 °C by conventional weight gain experiments. The diffusion results have been analyzed in terms of the simple Fickian model. The slightly anomalous transport behavior of the polymer–solvent systems has been attributed to a slow leaching out of the indigenous elastomer compounds and/or additives during solvent immersion. The dependence of diffusion coefficient and other related parameters on the size and shape of the penetrant molecule has been discussed. It was found that the transport parameters decreased with an increase in penetrant molecular size. A temperature dependence of transport parameters was used to estimate the Arrhenius activation energies for the process of sorption, diffusion, and permeation. The estimated activation energies of diffusion and permeation in the temperature interval of 25–60 °C showed an increase with increasing penetrant size. Furthermore, the sorption results have been interpreted in terms of the semiquantitative estimates of the kinetic rate constants and enthalpy of sorption. Experimental results and the predicted quantities have been used to study the nature of polymer–solvent interactions in terms of polymer structure and solvent power.

Introduction

The transient diffusion of low molecular weight organic liquids, aqueous salt solutions, and gases through polymer membranes has been of great interest in such diverse areas of technology as drug and pesticide delivery, protective clothing, ion-exchange chromatography, and toxic waste disposal.[1-3] We are currently interested in the study of sorption, diffusion, and permeation of organic liquids through polymer membranes of commercial importance.[4-7] Many diffusion studies have been made to quantify species diffusion rates; the best allow for a simultaneous determination of the diffusion and sorption coefficients of the species in the barrier medium from a single experiment. On the other hand, permeation coefficients have been either directly measured[8] or can be predicted from sorption and diffusion data.[9]

In engineering applications, the barrier properties of polymeric materials are often determined by the chemical structure of the chain and the system morphology. The parameters derived from chemical structure, such as degree of polarity, interchain forces, ability to crystallize, and chain stiffness, are essentially determined by the selection of the particular polymer. Dimensional stability and integrity of the polymeric materials in the presence of aggressive liquid environments is essential for their successful application. The aggressive environments can be broadly classified into two categories: solvents and nonsolvents. The former class of liquids actually solvates the polymer and induces extensive swelling, leading sometimes to degradative reactions. The nonsolvents, on the other hand, do not attack the polymer chemically, solvate it, or produce any recognizable effect other than to bring about material failure, which would not occur in a reasonable period of time under the same stress conditions and the absence of the environment. When no stresses are present, these agents do not have any readily discernible effect on the polymer. The present study deals with this latter category of solvents. Here, we will focus on how molecular structure influences the barrier properties of polymers including molecular orientation and chain stiffness. However, it must be recognized that the range in which these quantities can be manipulated will depend on polymer chemical structure.

In our earlier studies,[10,11] the influence of size and shape of the penetrant molecules on diffusion of lower members of hydrocarbons (C_6–C_{10}) into several commercial polymer membranes was reported. It was established that (i) the diffusion coefficient decreases with increasing penetrant size and (ii) a linear relationship exists between log D and the molar volume of the penetrant. However, these findings were limited to penetrants of relatively small size. Further investigation of the diffusion of large-size molecules into polymer membranes would be of considerable interest.

In continuation of this research and as a part of our ongoing data-gathering program on liquid transport through polymer membranes, we now present diffusion, sorption, and permeation results of the probe molecules belonging to higher hydrocarbons, namely, 2,2,4-trimethylpentane (TMP), dodecane, tetradecane, and hexadecane (i.e., ranging carbon atoms from C_8 to C_{16}) through four commercial polymer membranes, namely, neoprene (CR), styrene–butadiene–rubber (SBR), ethylene–propylene–diene terpolymer (EPDM), and natural rubber (NR). The transport parameters were calculated for each polymer–solvent system from the weight gain experiments. A study of the temperature dependence of these coefficients allowed us to predict the activation parameters and heats of sorption. The experimental results and the computed quantities were used to study the extent of polymer–solvent interactions.

Experimental Section

Molded sheets of CR, SBR, EPDM, and NR in dimensions of $^1/_{16}$ in. × 6 in. × 6 in. were procured from Utex Inc., Weimer, TX (courtesy of Mr. A. Kutac). During sample fabrication, 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. Polymer compositions and some representative engineering properties are given in Table I.

Reagent grade solvents, namely, 2,2,4-trimethylpentane, dodecane, tetradecane, and hexadecane, were double distilled before use to ensure purity. Their measured physical properties such

Table I
Elastomer Compositions and Their Properties

compounds	CR	SBR	EPDM	NR
Neoprene W[a]	100.0			
SBR 1500[b]		100.0		
EPDM 585[c]			100.0	
NR (RSS-2)				100.0
zinc oxide	5.0	5.0	5.0	5.0
carbon black, N550	50.0	50.0	50.0	50.0
stearic acid	0.5	1.0	1.0	2.0
sulfur		2.0	2.0	2.5
Agerite Resin D[d]		2.0	2.0	
Agerite Stallite S[e]				2.0
Aranox[f]	2.0			
Bonogen[g]				2.0
CBTS[h]		1.0	1.0	1.0
END-75[i]	0.7			
magnesium oxide	4.0			
totals	162.2	161.0	161.0	164.5
specific gravity	1.42	1.15	1.09	1.14
hardness (Shore A)	78	65	75	62
ultimate elongation, %	200	420	310	600
ultimate tensile, psi	3320	2840	2050	3510
T_g, °C	−36	−42	−37	−57

[a] Du Pont. [b] Ameripol Synpol. [c] Polysar. [d] Polymerized 1,2-dihydro-2,2,4-trimethylquinoline. [e] Octylated diphenylamine. [f] *N*-Phenyl-*N'*-(*p*-toluenesulfonyl)-*p*-phenylenediamine. [g] Sulfonic acid–oil blend. [h] *N*-Cyclohexyl-2-benzothiazolesulfenamide. [i] Ethylene thiourea 75%.

as density and refractive index at 25 °C agreed well with the literature. The perfectly dried polymer samples were cut circularly (diameter 1.94 cm) by means of a sharp-edged steel die. The thicknesses of the membranes were measured at several points with an accuracy of ±0.001 cm by using a micrometer screw gauge. An average of several values was taken as the initial thickness, *h*, of the polymer samples.

Sorption experiments were performed by placing the previously weighed polymer test samples into the respective liquid containers maintained at the desired temperature in a thermostatically controlled electric oven (Memmert, Germany). At periodic intervals, the test samples were removed from the liquid containers, and the wet surfaces were dried between Kimwipe wraps and weighed immediately to the nearest 0.05 mg by placing the samples on a covered watch glass within the balance chamber. The samples, after weighing, were placed back into the original test bottles, which were then transferred to the electric oven. The sorption experiments were performed at 25, 44, and 60 °C with an accuracy of ±0.5 °C. A likely source of error in this method is that the sample has to be removed from the liquid container to allow weighing. If this is done quickly within 30–40 s, compared to the time the sample spent in the liquid container in between consecutive weighings, the sample exerts a negligible effect.

The results of mass uptake of the liquid by the polymer samples were expressed as moles of liquid sorbed per 100 g of the membrane material. This way of expressing the mole percent increase in sorption, M_t, was found to be very convenient for comparing the sorption results of various liquid–polymer systems. This practice has also been followed in the literature,[12,13] and thus, we prefer to use the mole percent concept for discussion of the sorption data rather than percent weight gains.

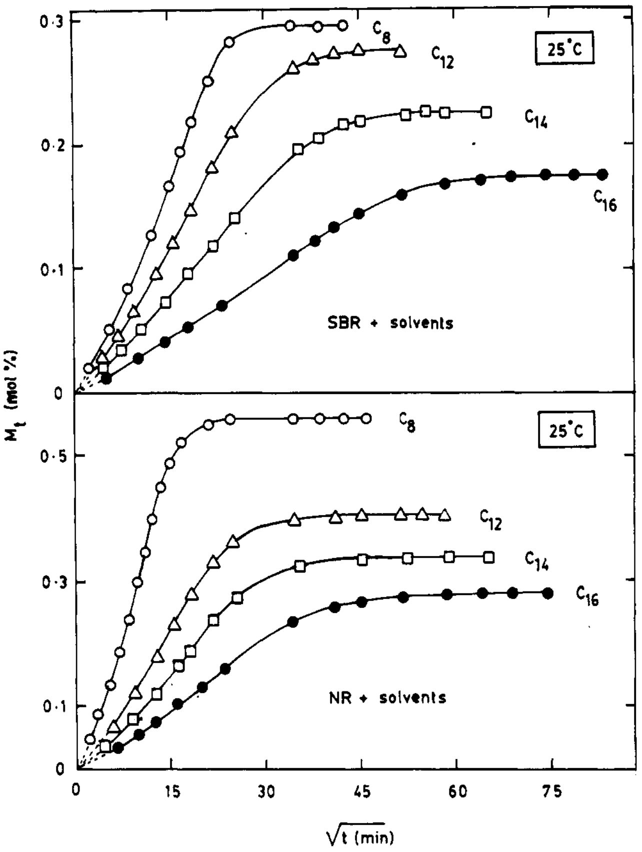

Figure 1. Mole percent solvent uptake at 25 °C for SBR and NR membranes with (○) 2,2,4-trimethylpentane, (△) dodecane, (□) tetradecane, and (●) hexadecane.

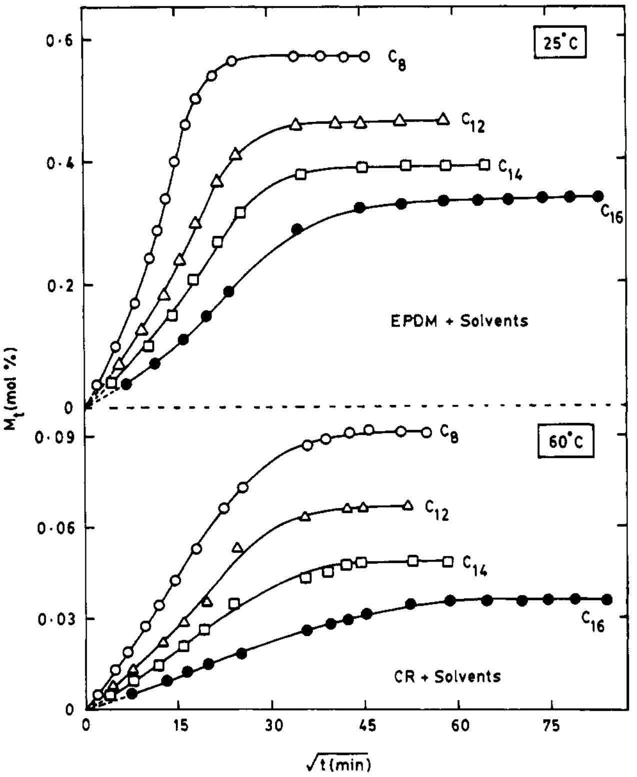

Figure 2. Mole percent solvent uptake for EPDM at 25 °C and CR at 60 °C with liquids shown in Figure 1.

Results and Discussion

The sorption plots (i.e., mole percent versus square root of time, $t^{1/2}$) at 25 °C for all the membrane–solvent systems are given in Figures 1 and 2. All the curves show initially almost a linear increase up to ~50% of equilibrium and later tend to level off. The plateau regions of these curves give the maximum sorption values; after attainment of equilibrium sorption, experiments were continued for longer times to ensure complete equilibration. The maximum sorption data, i.e., M_∞, for all the polymer–solvent systems in mole percent units are compiled in Table II. Similar sorption plots have been obtained at other temperatures but not displayed graphically. The overall sorption rate tends to decrease with increasing molecular weight of the penetrant. All of the sorption curves appear to be position-dependent anomalous transport, although hexadecane sorbed at a slower rate than the others. The

Table II
Equilibrium Sorption Data of Polymer–Solvent Systems

solvent	molar vol, cm^3/mol	temp, °C	$10^2 M_\infty$, mol %			
			CR	SBR	EPDM	NR
TMP (C_8H_{18})	166.1	25	8.33	29.46	56.98	56.19
		44	8.79	30.81	54.76	55.52
		60	9.13	31.20	54.25	54.82
dodecane ($C_{12}H_{26}$)	228.6	25	5.30	27.23	46.43	40.78
		44	5.86	30.29	44.59	42.19
		60	6.66	31.67	44.37	45.20
tetradecane ($C_{14}H_{30}$)	261.1	25	3.86	22.47	38.97	33.89
		44	4.26	24.29	38.27	34.78
		60	4.83	25.79	38.21	36.08
hexadecane ($C_{16}H_{34}$)	293.4	25	2.45	17.48	33.84	28.16
		44	3.25	19.57	32.70	29.45
		60	3.61	21.03	32.33	33.58

decreased sorption rate might be the consequence of lower equilibrium penetrant molar concentrations and consequently lower osmotic stresses.

The major observation from our study is that, as the temperature of swelling increased, the penetrant uptake decreased for EPDM plus all the solvents and NR plus branched hydrocarbon, viz., 2,2,4-trimethylpentane. This effect, which is shown in Figure 3, is not an experimental artifact but may be the result of induced crystallinity at higher temperatures in the presence of penetrants. The induced crystallinity reduces the free energy of mixing, thereby decreasing the solvent uptake.[14]

To gain further insight into the transport mechanism, the sorption results were fitted to the heuristic expression[15,16]

$$M_t/M_\infty = kt^n \tag{1}$$

Here, M_t is the mole percent of the penetrant sorbed per weight of the polymer at time t, M_∞ represents the same quantity at long times, and k is a constant that is characteristic of the system. A value of $n = 0.50$ implies Fickian diffusion, a value of $n = 1.00$ implies case II transport, and for values of n greater than 1.0 supercase II transport is observed. Values of n of $0.50 < n < 1.00$ are indicative of anomalous transport behavior. It is usually stipulated that this equation is only valid for short times and for $M_t/M_\infty < 0.50$. The least-squares estimations of n and k obtained at the 95% confidence limit are presented in Table III.

In the majority of cases, the values of n lie between 0.50 and 0.60, indicating that the transport mechanism deviates slightly from the Fickian mode and may thus be classified as anomalous. This fact is also supported by the slightly sigmoid shaped sorption curves, indicating the behavior that is observed follows pretty much what would be expected of a nearly (but not completely) ideal "Fickian" process in elastomers well above their glass transition temperatures. In order to determine if the anomalous behavior is due to swelling-induced breakup of an agglomerate–filler structure similar to that commonly observed during the first mechanical deformation of a molded, filled elastomer sample (Mooney softening[17]), we have repeated[18] the sorption experiments (in a few cases) of the desorbed samples to see if subsequent sorption showed the same anomalous character or not. To our surprise, the same anomalous behavior was observed. However, the pattern of the initial portion of the sorption curves (before 50% equilibrium) was quite identical although the final equilibrium data differed to some extent; i.e., some of the indigenous compounds of the rubber were extracted during the first cycle of the sorption. However, we could not observe any systematic dependence of n on temperature. On the other hand, the values of k appear to increase systematically with a rise in temperature in all the cases.

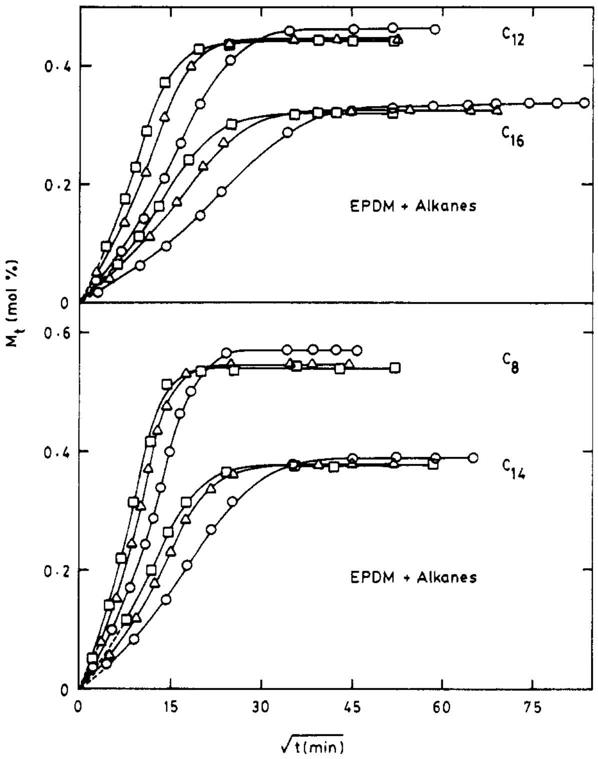

Figure 3. Temperature dependence of mole percent sorption for EPDM + solvents. Symbols: (○) 25 °C, (△) 44 °C, (□) 60 °C.

Moreover, the k values increase systematically from C_8 to C_{16} penetrants with CR, while a decreasing tendency is seen for SBR, EPDM, and NR membranes.

In view of what has been said above and due to no significant swelling, surface corrugation, etc., the effective diffusivity, D, of the polymer–solvent systems has been calculated by using the Fickian model

$$D = \pi(h\theta/4M_\infty)^2 \tag{2}$$

where θ is the slope of the nearly linear portion of the plot of M_t vs $t^{1/2}$ before attainment of 50% equilibrium and it was estimated by fitting the experimental sorption data before 50% sorption to a least-squares procedure. However, the slight sigmoidal sorption-rate curves were analyzed by using the model of Joshi and Astarita,[19] 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 resulting from application of eq 2, ignoring the initial slight curvature, for EPDM + solvent systems and for elastomers + TMP systems are given, respectively, in Figures 4 and 5. The diffusion coefficients go through maxima with concentration and the results from this analysis are only slightly higher than those obtained from eq 2. Similar findings can be also observed from the work of Waksman et al.[20] for toluene diffusion in natural rubber.

The diffusion data of all the polymer–solvent systems are given in Table IV. It is found that the decrease in diffusion coefficient on going from TMP to hexadecane is relatively smaller in the case of CR than the other polymer membranes and this is attributed to the greater flexibility of long-chain hexadecane (in comparison to other penetrants) in the presence of a somewhat rigid macromolecular chain like CR. Such effects have also been observed for hydrocarbon solvent transport into a number of polymer membranes. For instance, diffusion of hydrocarbons (C_8–C_{36}) into a number of cross-linked rubbers

Table III
Analysis of Sorption Results of Polymer–Solvent Systems

		CR		SBR		EPDM		NR	
solvent	temp, °C	n	10^2k, g/g min^n	n	10^2k, g/g min^n	n	10^2k, g/g min^n	n	10^2k, g/g min^n
TMP	25	0.55	0.96	0.54	2.88	0.63	2.09	0.62	3.03
	44	0.58	1.26	0.55	3.62	0.64	2.70	0.66	3.15
	60	0.56	2.33	0.58	3.68	0.63	3.49	0.61	4.18
dodecane	25	0.50	1.24	0.57	1.95	0.60	1.86	0.58	2.15
	44	0.51	1.95	0.54	2.73	0.59	2.82	0.58	2.97
	60	0.54	2.14	0.55	3.42	0.61	3.35	0.59	3.78
tetradecane	25	0.50	1.55	0.55	1.73	0.58	1.76	0.57	1.98
	44	0.51	1.64	0.55	2.16	0.59	2.30	0.58	2.53
	60	0.54	2.08	0.58	2.60	0.56	3.11	0.58	2.84
hexadecane	25	0.53	0.80	0.54	1.34	0.58	1.28	0.54	1.64
	44	0.50	1.78	0.54	2.02	0.57	2.01	0.57	2.19
	60	0.50	2.03	0.57	2.22	0.58	2.36	0.58	2.44

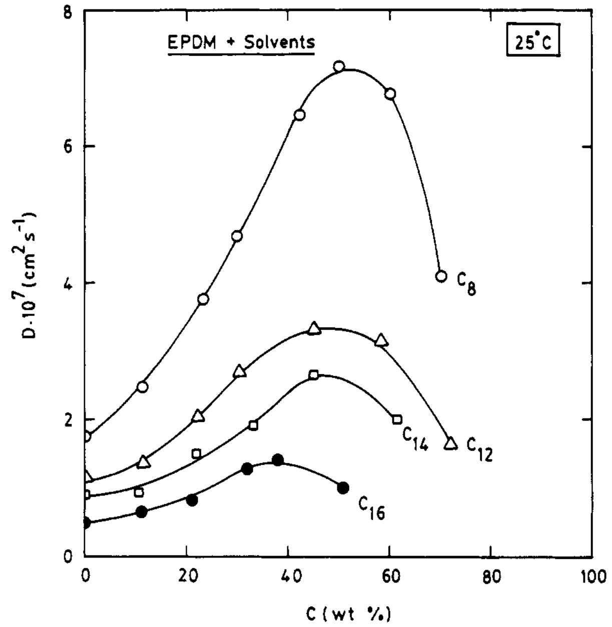

Figure 4. Diffusion coefficient versus concentration for EPDM membrane. Symbols have the same meaning as in Figure 1.

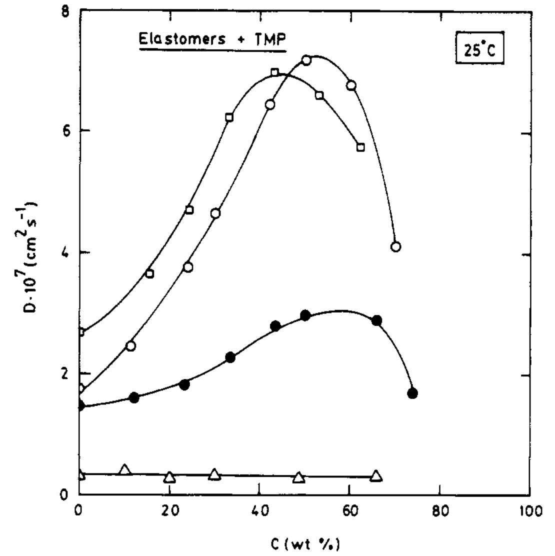

Figure 5. Diffusion coefficient versus concentration for elastomers with TMP. Symbols: (○) EPDM, (△) CR, (□) NR, (●) SBR.

Table IV
Diffusion Coefficients of Polymer–Solvent Systems

		10^7D, cm^2/s			
solvents	temp, °C	CR	SBR	EPDM	NR
TMP	25	0.33	2.01	3.43	4.10
	44	0.95	3.31	4.98	5.52
	60	1.83	4.95	6.87	7.34
dodecane	25	0.24	1.29	1.96	2.06
	44	0.80	2.29	3.33	3.34
	60	1.46	3.62	4.67	4.70
tetradecane	25	0.19	0.92	1.43	1.46
	44	0.67	1.56	2.35	2.32
	60	1.32	2.71	3.45	3.95
hexadecane	25	0.19	0.50	0.77	0.84
	44	0.41	1.14	1.73	1.77
	60	0.78	1.82	2.72	2.32

has been studied at 51 °C by the pulsed field gradient spin-echo method.[21] In another study by Koszinowski,[22] diffusion and sorption of n-alkanes from carbon atom numbers 12 to 32 were determined by a permeation method (pouch method) for the polyolefin membranes, namely, LDPE, HDPE, PP copolymer, and PP homopolymer at room temperature. In both of these studies, we find observations similar to that seen by us in this study. The effect of microstructure on the diffusion of n-hexadecane into poly(1,4-butadienes) has also been investigated.[23] In addition to these, several other investigators[24-34] studied different aspects of the hydrocarbon transport into polymer membranes wherein such a behavior was prevalent. Because of the differences in chemical structures and physical homogeneity of our membrane materials, it is somewhat difficult to give a nearly unified interpretation of the transport data in terms of a difference in polymer molecular structure; however, the trend is consistent with what one would expect from a variation in polymer structures, at least in qualitative terms. In any case, our present diffusion results conform to the principle that diffusion coefficients depend inversely on the penetrant molecular size and a linear relationship exists between log D and the molar volume of the solvent.

The variation in diffusivity at 25 °C with the size of the diffusing molecule and/or number of carbon atoms is shown in Figure 6 for all the penetrants and the polymer membranes. Similar plots have been obtained at other temperatures (not displayed graphically). For each of these membranes, D decreases as the penetrant size increases. This effect is much less for neoprene than for other elastomers, and also, the values of D are much less for the CR membrane; the greater effect of molecular size on D in polymers having low D values agrees with the observations in other polymers.[28] It can be clearly seen from our data that the decrease in diffusion coefficient on going from TMP to hexadecane is relatively smaller in the case of the CR membrane than the others. This may well be caused by the flexibility of the hexadecane molecule. Unfortunately, no extensive data base is available in the literature on the types of polymers used in this research, and hence, we could not directly compare our results with the literature findings. At any rate, all the elastomers

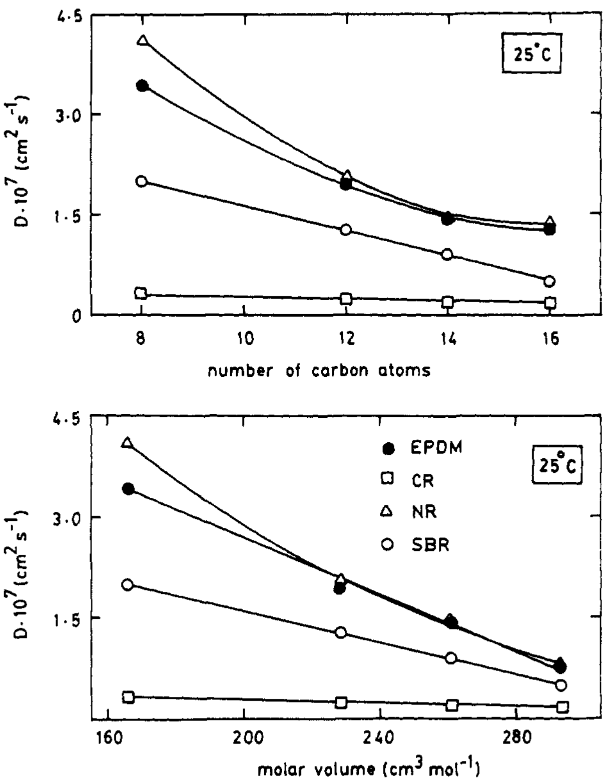

Figure 6. Dependence of diffusion coefficient on number of carbon atoms and on molar volume of solvents at 25 °C.

used in this study seem to behave in a manner similar to most other rubbery polymeric materials well above their glass transition temperatures.

The diffusion coefficients of all the hydrocarbon + polymer membrane systems appear to increase according to the sequence NR > EPDM > SBR > CR. As seen in Table I, all these rubbers contain additives and fillers, the presence of which might cause tortuosity in the diffusion pathway; i.e., they behave as randomly scattered obstacles that cause the diffusion pathway to become larger than it would have been otherwise. However, there still appears to be no clearcut foolproof way to extract tortuosity information from the morphological studies.[29] Additionally, our diffusion data given in Table IV suggest that as the size of the penetrant molecule increases, its displacement depends upon rotation of chain segments and the availability of voids larger than the penetrant size.[30] As a result, the small change in the penetrant size can result in a substantial change in diffusivity. As the temperature increases, the amplitude of segmental oscillations of polymer chains also increases. Greater segmental motion results in an increase in the size of free volume[35] and subsequent increase in diffusivity as the temperature is increased.

Table V
Permeation Coefficients of Polymer–Solvent Systems

		$10^8 P$ ($\equiv DS$), cm^2/s			
solvent	temp, °C	CR	SBR	EPDM	NR
TMP	25	0.314	6.764	22.326	26.318
	44	0.954	11.648	31.150	35.008
	60	1.909	17.642	42.573	45.963
dodecane	25	0.217	5.983	15.502	14.311
	44	0.798	11.816	25.295	24.005
	60	1.656	19.530	35.296	36.185
tetradecane	25	0.146	4.101	11.057	9.817
	44	0.566	7.518	17.844	16.008
	60	1.265	13.867	26.155	28.275
hexadecane	25	0.106	1.979	5.901	5.357
	44	0.302	4.920	12.811	11.687
	60	0.638	8.667	19.913	17.641

The mechanism by which small molecules permeate through rubbery or glassy amorphous polymers has been described by many authors.[31-36] Because a solution–diffusion process is involved, the permeability coefficient, P, of amorphous polymers is the product of the effective diffusion, D, and solubility, S, coefficients (i.e., $P = DS$). The calculated results are listed in Table V. Here, the values of S are taken as gram of liquid sorbed per gram of the polymer. Over a reasonable temperature range, the apparent solubility coefficient can be expressed in terms of a van't Hoff relationship and a preexponential factor, S_0, as

$$S = S_0 \exp(-\Delta H_s/RT) \qquad (3)$$

Here, the heat of sorption, ΔH_s, is a composite parameter involving both the Henry's law and the Langmuir (hole-filling) type sorption mechanisms. The Henry's law mode requires both the formation of a site and the dissolution of the species into that site. The formation of a site involves an endothermic contribution to this process. With the Langmuir mode, the site already exists in the polymer matrix, and consequently, sorption by hole filling yields more exothermic heats of sorption. In a form of Fick's law that describes diffusion of liquids through the amorphous polymer matrix, the diffusion coefficient has been observed to follow an Arrhenius relationship, characteristic of an activated process:

$$D = D_0 \exp(-E_D/RT) \qquad (4)$$

Here, E_D is the activation energy required to create an opening between polymer chains large enough to allow the penetrant molecule to pass. Thus, E_D is a function of the inter- and intrachain forces that must be overcome in order to create the space for a unit diffusional jump of the penetrant. Molecular models include these characteristics largely to describe the Arrhenius behavior of diffusion coefficients observed experimentally. It may be noted that a correlation is found between E_D and the molecular diameter of the penetrant, but no theoretical expression for D has been obtained with molecular models.[37] The E_D value will be greater the larger the penetrant molecule, the stronger the polymer cohesive energy, and the more rigid the chains. By substitution of eqs 3 and 4 into the $P = DS$ relation, the permeability can also be expressed in terms of an Arrhenius-type relationship:

$$P = P_0 \exp(-E_P/RT) \qquad (5)$$

where $E_P = E_D + \Delta H_s$. The activation energy of diffusion is considered to be the energy required to complete the unit diffusion process of 1 mol of the diffusing molecule. Some representative Arrhenius diffusion plots are shown in Figures 7 and 8, while similar plots for permeation data are given in Figures 9 and 10. The estimated Arrhenius quantities, viz., E_P, E_D, and the derived heats of sorption are compiled in Table VI.

Heats of sorption and activation energies for the sorption processes provide additional information about the transport process. As seen in Table VI, the heats of sorption are higher for CR and SBR membranes than for NR and EPDM, suggesting thereby that the sorption mechanism in these systems is dominated by the Henry's law dissolution process. Since the values of ΔH_s are calculated from the difference $E_P - E_D$, an alternative explanation for the high heats of sorption could be a lower apparent activation energy of diffusion than that of permeation as caused by the transport along the boundaries of the polydomain morphology. Given the rigid nature of the CR and SBR polymer chains, somewhat lower equilibrium sorption values as compared to EPDM and NR, and the

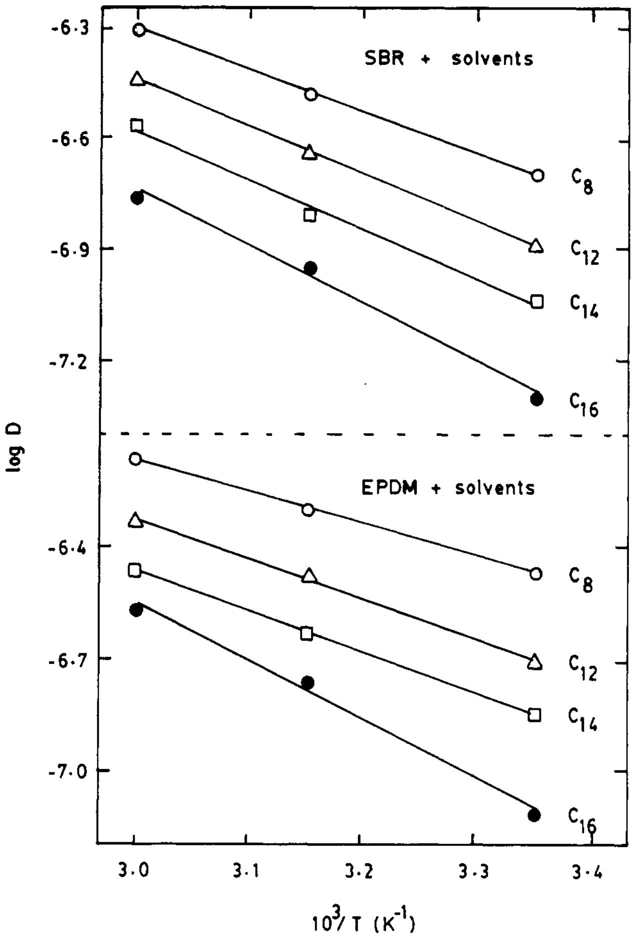

Figure 7. Arrhenius plots of diffusivity for SBR and EPDM membranes with solvents. Symbols have the same meaning as in Figure 1.

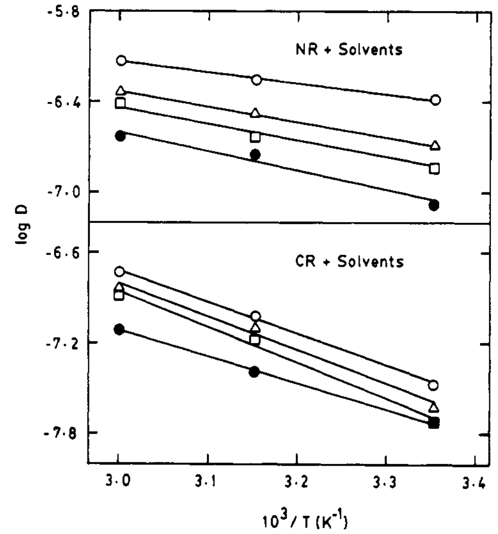

Figure 8. Arrhenius plots of diffusivity for NR and CR membranes with solvents. Solvents have the same symbols as shown in Figure 1.

lack of macroscopic directional order in these materials, the foregoing hypothesis seems justifiable. It may further be noted that for all the solvents with EPDM and 2,2,4-trimethylpentane with NR, negative ΔH_s values are found; this suggests that the Langmuir mode of sorption might be operative in these systems. A plausible explanation for this anomaly would be the result of induced crystallinity of the polymer matrix materials showing inverse effect of sorption on temperature resulting in an increased E_D as compared to E_P (see Figure 3). Unlike sorption, the effects of crystallinity on the effective diffusivity intimately involve the details of the polymer morphology. Because of the chain immobilization effect, crystallinity might cause an increase in E_D. The more detailed aspects of transport in heterogeneous media have been given in excellent reviews of the topic by Barrer[37] and Petropoulos.[38] The apparent activation energies, E_D, for CR range from 32 to 46 kJ/mol, whereas these values are quite small for NR and range from 13 to 24 kJ/mol. Thus, in the majority of cases, E_D values follow the sequence CR > SBR > EPDM > NR for all the hydrocarbon solvents. This trend is also true for E_P data. The high values of activation energy further suggest the relaxation of large polymer segments at the advancing boundary and this would be expected for the rigid nature of the backbone systems.

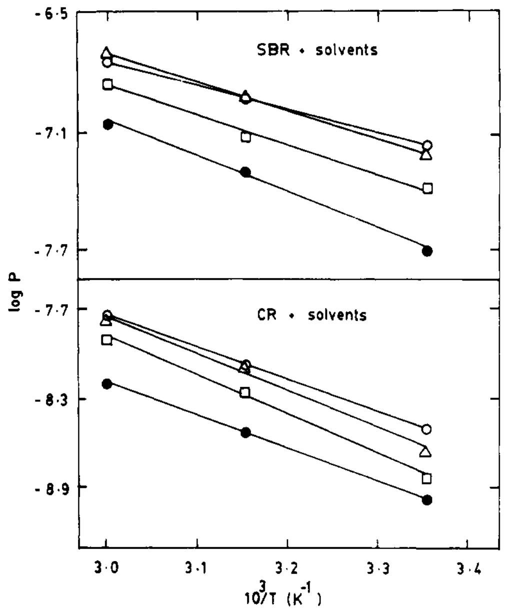

Figure 9. Arrhenius plots of permeability for SBR and CR membranes with solvents. All symbols have the same meaning as in Figure 1.

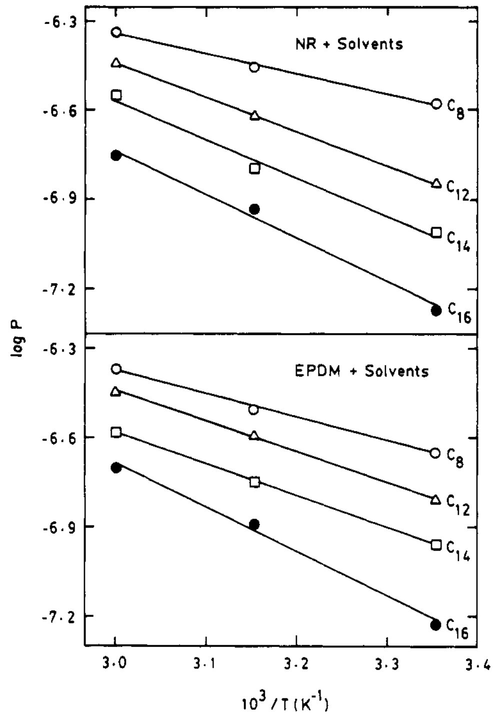

Figure 10. Arrhenius plots of permeability for NR and EPDM membranes with solvents. Symbols have the same meaning as in Figure 1.

Table VI
Activation Parameters and Thermodynamic Quantities for Polymer–Solvent Systems

solvent	param, kJ/mol	polymer membrane			
		CR	SBR	EPDM	NR
TMP	E_a	42.32	17.62	18.32	9.96
	E_D	40.45	21.25	16.36	13.64
	E_P	42.55	22.64	15.17	13.10
	ΔH_s	2.10	1.39	−1.19	−0.54
dodecane	E_a	39.57	20.16	24.21	23.59
	E_D	43.30	24.43	20.66	19.59
	E_P	48.35	27.96	19.48	21.88
	ΔH_s	5.05	3.53	−1.18	2.29
tetradecane	E_a	44.56	23.22	19.32	17.51
	E_D	45.95	25.47	20.85	23.26
	E_P	51.36	28.58	20.31	24.73
	ΔH_s	5.41	3.11	−0.54	1.47
hexadecane	E_a	34.38	28.05	23.23	22.44
	E_D	31.99	30.57	29.92	24.40
	E_P	42.57	35.04	28.91	28.38
	ΔH_s	10.58	4.47	−1.01	3.98

Continuing our discussion further and realizing the fact that sorption follows nearly Fickian behavior, we have attempted to analyze the sorption data in terms of the first-order kinetic model. To do this, it was tacitly assumed that sorption and desorption of a solvent by a polymer membrane is one of the possible structural changes that can accompany the liquid transport. Naturally, these structural changes require a rearrangement of the polymer segments that can dominate the kinetic behavior, which in turn are considered to be affected by the total free volume and its distribution in the polymer system. Thus, sorption depends on solvent mobility within the polymer in addition to the availability of its free volume.[39] In rubbery polymers, well above their glass transitions, a greater propensity of polymer chains to adjust quickly to the presence of penetrants does not cause diffusion anomalies. If sorption is controlled by the rate of polymer expansion, then a more reasonable suggestion is that sorption rate will be proportional to the difference in osmotic pressure inside and outside the polymeric materials.[40,41] As a first approximation, we can relate this to simple vapor pressure, and if up to the equilibrium point the vapor pressure of liquid in the polymer is proportional to its concentration, the following first-order kinetic equation may be used:

$$dC/dt = k'(C_\infty - C_t) \tag{6}$$

where k' is first-order rate constant (min^{-1}). Integration of eq 6 gives

$$k't = 2.303 \log [C_\infty/(C_\infty - C_t)] \tag{7}$$

Here, C_t and C_∞ represent, respectively, the concentrations at time t and at infinite time (i.e., equilibrium saturation) and these have the same meaning as M_t and M_∞, respectively, discussed before. Some typical plots of log $(C_\infty - C_t)$ versus time are given in Figures 11 and 12, while the estimated rate constants for all the polymer–solvent systems are presented in Table VII. The estimated energy of activation data, E_a, from a temperature dependence of rate constant are included in Table VI. It may be noted that in almost all cases the results of E_a are somewhat lower than the E_D data and the rate constants follow the same trend as those of diffusion coefficients. The E_P data are higher than E_D for CR, SBR, and NR membranes, but a reverse tendency was observed in case of EPDM.

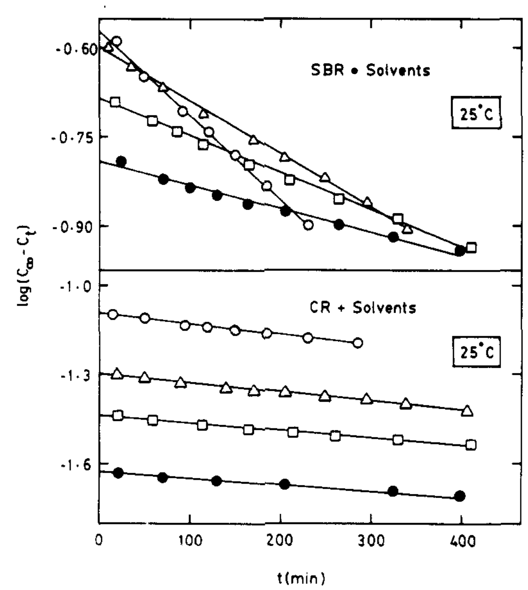

Figure 11. Plots of log $(C_\infty - C_t)$ versus time for SBR and CR membranes at 25 °C. Symbols have the same meaning as in Figure 1.

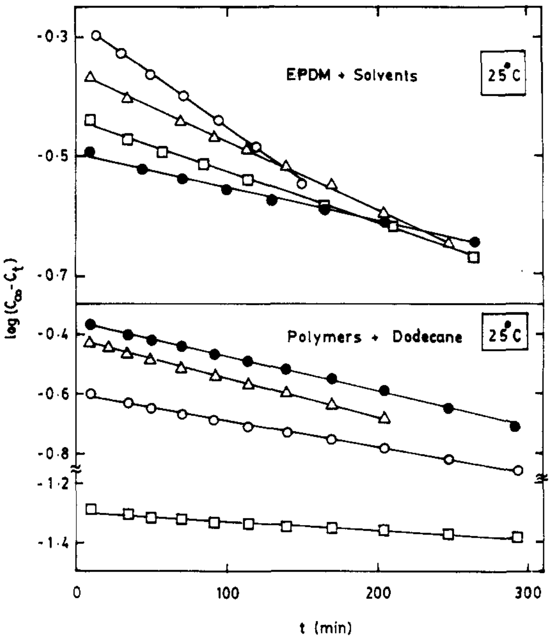

Figure 12. Plots of log $(C_\infty - C_t)$ versus time for EPDM + solvents and all polymers + dodecane. Symbols for polymers are the same as in Figure 6. Symbols for solvents are as in Figure 1.

Table VII
Rate Constants (k') of Polymer–Solvent Systems

solvent	temp, °C	$10^3k'$, min^{-1}			
		CR	SBR	EPDM	NR
TMP	25	0.39	3.33	4.49	7.50
	44	1.06	5.60	7.22	9.88
	60	2.36	6.96	9.72	11.39
dodecane	25	0.34	2.07	2.69	2.99
	44	1.19	3.08	5.12	4.82
	60	1.74	4.89	7.44	8.19
tetradecane	25	0.28	1.42	2.06	2.24
	44	1.01	2.17	3.59	3.85
	60	1.77	3.84	4.63	4.65
hexadecane	25	0.23	0.86	1.30	1.40
	44	0.55	1.70	2.50	2.66
	60	0.97	2.83	3.44	3.57

Concluding Remarks

The barrier properties of rubbery polymers may be seriously impaired by the presence of organic liquids that penetrate the polymer. It would therefore be useful to forecast conditions and penetrants that might cause polymer degradation and to predict their consequences on transport behavior. The complex and anomalous equilibrium and kinetic behavior of small organic molecules in rubbery polymers has long been recognized, but there are few correlations allowing predictions of transport behavior from material properties. These correlations seem to provide a basis for at least qualitatively useful predictions of sorption equilibria and diffusion kinetics.

In the present investigation, we have used structurally different elastomer membranes to gain some further insight into the dependence of polymer structure on variations in the length of the penetrant molecules. It was found that sorption, diffusion, and permeation of the selected hydrocarbons in these membrane systems are influenced by the nature of the penetrant molecule and the polymer. Those factors determine the chain segmental mobility and interactions that control the sorption magnitude and penetrant molecular mobility within the polymer. Transport of relatively noninteracting penetrant molecules in a polymer seemed to follow the classical behavior predicted by Fick's law relationships with a constant (or nearly so) diffusion coefficient. An increase in generalized interactions (van der Waals, etc.) leads to increased sorption of the penetrant such that the diffusion process often becomes concentration dependent. Then, depending upon the relative rates of polymer relaxation processes concurrent with the sorption–diffusion process, the overall transport phenomenon may exhibit Fickian behavior with a simple concentration-dependent diffusion coefficient or it may deviate significantly from that behavior due to complicating relaxation effects. The sorption curves can be accurately fitted by the Joshi–Astarita analysis of combined diffusion, and relaxation effects might be involved in the swelling behavior. Relaxation might arise from slow response of the network structure to the swelling stresses. In view of the low amounts of liquid sorption and no significant swelling of the membranes, the diffusion results have been analyzed in terms of the simple Fickian model. The transport results of this study confirm the results of various authors on hydrocarbon–polymer systems as studied by using other experimental techniques. Future work will include a variety of functional groups to study the specific interactions of polymer and penetrant.

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References and Notes

(1) Aminabhavi, T. M.; Aithal, U. S.; Shukla, S. S. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1989**, *C29*, 319.
(2) Aithal, U. S.; Aminabhavi, T. M.; Shukla, S. S. *Polym. Plast. Technol. Eng.* **1989**, *28*, 567.
(3) Aithal, U. S.; Aminabhavi, T. M.; Balundgi, R. H.; Shukla, S. S. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1990**, *C30*, 43.
(4) Aithal, U. S.; Aminabhavi, T. M.; Cassidy, P. E. *Polym. Prepr.* **1989**, *30*, 17.
(5) Britton, L. N.; Ashman, R. B.; Aminabhavi, T. M.; Cassidy, P. E. *J. Appl. Polym. Sci.* **1989**, *38*, 227.
(6) Aithal, U. S.; Aminabhavi, T. M. *J. Chem. Educ.* **1990**, *67*, 82.
(7) Aithal, U. S.; Aminabhavi, T. M.; Cassidy, P. E. In *Barrier Polymers and Structures*; Koros, W. J., Ed.; ACS Symp. Ser. No. 423, American Chemical Society: Washington, DC, 1990; Chapter 19, p 351.
(8) Britton, L. N.; Ashman, R. B.; Aminabhavi, T. M.; Cassidy, P. E. *J. Chem. Educ.* **1988**, *65*, 368.
(9) Aminabhavi, T. M.; Thomas, R. W.; Cassidy, P. E. *Polym. Eng. Sci.* **1984**, *24*, 1417.
(10) Harogoppad, S. B.; Aminabhavi, T. M. *J. Appl. Polym. Sci.*, in press.
(11) Khinnavar, R. S.; Aminabhavi, T. M. *J. Appl. Polym. Sci.*, in press.
(12) Sfirakis, A.; Rogers, C. E. *Polym. Eng. Sci.* **1981**, *21*, 542.
(13) Harogoppad, S. B.; Aminabhavi, T. M. *Polymer*, in press.
(14) Barr-Howell, B. D.; Peppas, N. A.; Squires, T. G. *J. Appl. Polym. Sci.* **1986**, *31*, 39.
(15) Franson, N. M.; Peppas, N. A. *J. Appl. Polym. Sci.* **1983**, *28*, 1299.
(16) Chiou, J. S.; Paul, D. R. *Polym. Eng. Sci.* **1986**, *26*, 1218.
(17) MacKenzie, C. I.; Scarlan, J. *Polymer* **1984**, *25*, 559.
(18) Three sorption experiments were conducted on the same polymer samples after complete desorption. It was found that during the first sorption run some indigenous rubber compounds were leached out of the samples, as evidenced by slight coloration of the solvent at equilibrium and the loss in weight of the sample. The refractive indexes of the equilibrium solvent were measured in all cases, and these were subsequently higher than the solvents in their pure states. In the majority of cases, the difference in refractive index was around 0.01 unit. In any case, the loss of extractables did not show any great effect on our diffusion data.
(19) Joshi, S.; Astarita, G. *Polymer* **1979**, *20*, 455.
(20) Waksman, L. S.; Schneider, N. S.; Sung, N. H. In *Barrier Polymers and Barrier Structures*; Koros, W. J., Ed.; American Chemical Society: Washington, DC, 1990; Chapter 19.
(21) vonMeerwall, E.; Ferguson, R. D. *J. Appl. Polym. Sci.* **1979**, *23*, 3657.
(22) Koszinowski, J. *J. Appl. Polym. Sci.* **1986**, *32*, 4765.
(23) Jenkins, R. B.; Park, G. S. *J. Membr. Sci.* **1983**, *15*, 127.
(24) Asfour, A. F. A.; Saleem, M.; DeKee, D.; Harrison, B. H. *J. Appl. Polym. Sci.* **1989**, *38*, 1503.
(25) Aitken, A.; Barrer, R. M. *Trans. Faraday Soc.* **1955**, *51*, 116.
(26) Prager, S.; Long, F. A. *J. Am. Chem. Soc.* **1951**, *73*, 4072.
(27) Chen, S. P.; Ferry, J. D. *Macromolecules* **1968**, *1*, 270.
(28) Newns, A. C.; Park, G. S. *J. Appl. Polym. Sci.* **1969**, *22*, 927.
(29) Ottino, J. M.; Shah, N. *Polym. Eng. Sci.* **1984**, *24*, 153.
(30) Brown, W. R.; Park, G. S. *J. Paint Technol.* **1970**, *42*, 16.
(31) Stannett, V. T.; Hopfenberg, H. B.; Petropoulos, J. H. *Int. Rev. Sci.: Phys. Chem., Ser. 1* **1972**, *8*, 329.
(32) Crank, J., Park, G. S., Eds. *Diffusion in Polymers*; Academic: New York, 1968.
(33) Crank, J. *The Mathematics of Diffusion*, 2nd ed.; Oxford University: London, 1975.
(34) Rogers, C. E.; Machin, D. *CRC Crit. Rev. Macromol. Sci.* **1972**, 245.
(35) The concept of free volume has been of more limited use in the prediction of sorption coefficients, although Peterlin (Peterlin, A. *J. Macromol. Sci. Phys.* **1975**, *B11*, 57) has suggested that the sorption coefficient is directly proportional to the free volume available in the polymer matrix. In many respects, the free-volume expressions closely resemble the relationships developed in the activated-state approach. The usefulness of the free-volume model lies in the accessibility of the fractional free volume by the application of group contribution methods developed by Sugden (Sugden, S. *J. Chem. Soc.* **1927**, 1786) and Bondi (Bondi, A. In *Physical Properties of Molecular Crystals, Liquids and Glasses*; Wiley: New York, 1968; Chapters 3 and 4) for correlation of barrier properties of polymers of different chemical structures as demonstrated elegantly by Lee (Lee, W. M. *Polym. Eng. Sci.* **1980**, *20*, 1).
(36) Aminabhavi, T. M.; Aithal, U. S.; Shukla, S. S. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1988**, *C28*, 421.
(37) Barrer, R. M. In *Diffusion in Polymers*; Crank, J., Park, G. S., Eds.; Academic Press: New York, 1968; Chapter 6.
(38) Petropoulos, J. H. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1309.
(39) Rogers, C. E.; Bemaneik, J. R.; Kapur, S. In *Structures and Properties of Polymer Films*; Lenz, R. W., Stein, R. S., Eds.; Plenum: New York, 1973; p 297.
(40) Cosgrove, J. D.; Hurdley, T. G.; Lewis, T. J. *Polymer* **1982**, *23*, 144.
(41) Aminabhavi, T. M.; Harogoppad, S. B. *J. Chem. Educ.*, in press.

Registry No. TMP, 540-84-1; dodecane, 112-40-3; tetradecane, 629-59-4; hexadecane, 544-76-3.