

Diffusion and Sorption of Organic Liquids Through Polymer Membranes. II. Neoprene, SBR, EPDM, NBR, and Natural Rubber versus *n*-Alkanes

S. B. HAROGOPPAD and T. M. AMINABHAVI*

Department of Chemistry, Karnatak University, Dharwad, 580 003, India

SYNOPSIS

Diffusion and sorption of *n*-alkanes (C_6 – C_{10}) through commercial polymer membranes such as neoprene, styrene butadiene rubber, ethylene propylene diene terpolymer, nitrile butadiene rubber, and natural rubber have been studied from 25 to 60°C. The diffusion results have been explained in terms of the size of liquid molecules and the diffusion mechanism was found to follow the Fickian trend. Nitrile butadiene rubber and neoprene showed much smaller values of diffusivities and sorption constants than the other polymer membranes. Arrhenius parameters for the activated diffusion process and the thermodynamic quantities for the process of equilibrium sorption have been estimated.

INTRODUCTION

Sorption and transport of organic solvents through elastomeric polymer membranes have been studied extensively in our laboratory over the past several years.^{1–4} In Part I of this series of papers,¹ we have investigated the transport characteristics of polyurethane membrane versus *n*-alkanes (C_6 – C_{10}). It was observed that the diffusion mechanism followed the Fickian trend and the kinetics of sorption was of the first order. In continuation of this study, we now present more data on the transport characteristics of neoprene (CR), styrene butadiene rubber (SBR), ethylene propylene diene terpolymer (EPDM), and natural rubber (NR). Sorption and diffusion of *n*-alkanes, namely, hexane, heptane, octane, nonane, and decane have been studied at 25, 44, and 60°C by the use of the immersion/weight gain method.^{5,6} From a temperature dependence of transport coefficients, activation parameters for diffusion and the thermodynamic quantities have been estimated.

EXPERIMENTAL

Reagents and Materials

Molded sheets of SBR, NBR, CR, EPDM, and NR in dimensions of $\frac{1}{16} \times 6 \times 6$ in. were supplied from Weimer, UTEX, Texas (Courtesy of Mr. A. 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. Rubber compositions and some representative engineering properties are given respectively, in Tables I and II.

Reagent grade solvents, namely, hexane, heptane, octane, nonane, and decane were double distilled before use. The polymer samples were cut circularly (diameter = 1.94 cm) by means of a sharp-edged steel die. The thickness measurements were made at several points on the membranes using a micrometer screw gauge with an accuracy of ± 0.001 cm.

Sorption Experiments

Sorption experiments were performed on cut polymer samples by immersing them in test bottles containing the solvent maintained at the desired tem-

* To whom correspondence should be addressed.

Table I Elastomer Compositions in phr

Compounds/Fillers	SBR	EPDM	CR	NR	NBR
SBR 1500 ^a	100.00	—	—	—	—
EPDM 585 ^b	—	100.0	—	—	—
Neoprene W ^c	—	—	100.0	—	—
NR (RSS-2)	—	—	—	100.0	—
Hycar 1051 ^d	—	—	—	—	100.0
Zinc oxide	5.0	5.0	5.0	5.0	5.0
Carbon black, N550	50.0	50.0	50.0	50.0	50.0
Stearic acid	1.0	1.0	0.5	2.0	1.0
Sulfur	2.0	2.0	—	2.5	2.0
Agerite resin D ^e	2.0	2.0	—	—	2.0
CBTS ^f	1.0	1.0	—	1.0	1.0
Magnesium oxide	—	—	4.0	—	—
Aranox ^g	—	—	2.0	—	—
END-75 ^h	—	—	0.7	—	—
Bonogen ⁱ	—	—	—	2.0	—
Agerite stallite S(j)	—	—	—	2.0	—
Totals	161.0	161.0	162.2	164.2	161.0

^a Ameripol Synopl.^b Polysar.^c E. I. DuPont.^d B. F. Goodrich.^e Polymerized 1,2-dihydro-2,2,4-trimethylquinoline.^f *N*-cyclohexyl-2-benzothiazolesulfenamide.^g *N*-phenyl-*N'*-(*p*-toluene sulfonyl)-*p*-phenylene diamine.^h 75% ethylene thiourea.ⁱ Sulfonic acid-oil blend.^j Octylated diphenylamine.

perature of an electric oven (Memmert, Germany). The experimental details are the same as described in Part I (Ref. 1). The output from a sorption experiment is the percent fractional weight gain versus square root of time, $t^{1/2}$, profile, for different values of the initial thickness h of the polymer samples. The sorption curves plotted in Figures 1–4 show an initial linear region which goes through the origin as expected for Fickian behavior. However, with some polymer–solvent systems, the sorption curves initially showed slightly curvature tendencies suggesting a mild concentration dependent diffusion, the diffusion coefficient increasing with the concen-

tration.⁷ For a Fickian diffusion, the sorption curves are independent of the material thickness. Assuming a negligible concentration dependence of diffusivity over the concentration interval studied in a sorption experiment (i.e., before attainment of 50% equilibrium saturation); a value of the mutual diffusion coefficient D can be calculated from the initial slope θ of the sorption curve as

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

where Q_∞ represents the maximum mol equilibrium uptake of the solvent by 100 g of the polymer sample.

Table II Some Representative Engineering Properties of Polymer Membranes

Property	SBR	EPDM	CR	NR	NBR
Specific gravity	1.15	1.09	1.42	1.14	1.21
Hardness (Shore A)	65	75	78	62	74
Ultimate elongation (%)	420	310	200	600	370
Ultimate tensile (psi)	2840	2050	3320	3510	3320
T_g (°C)	–42	–37	–36.21	–57	–10

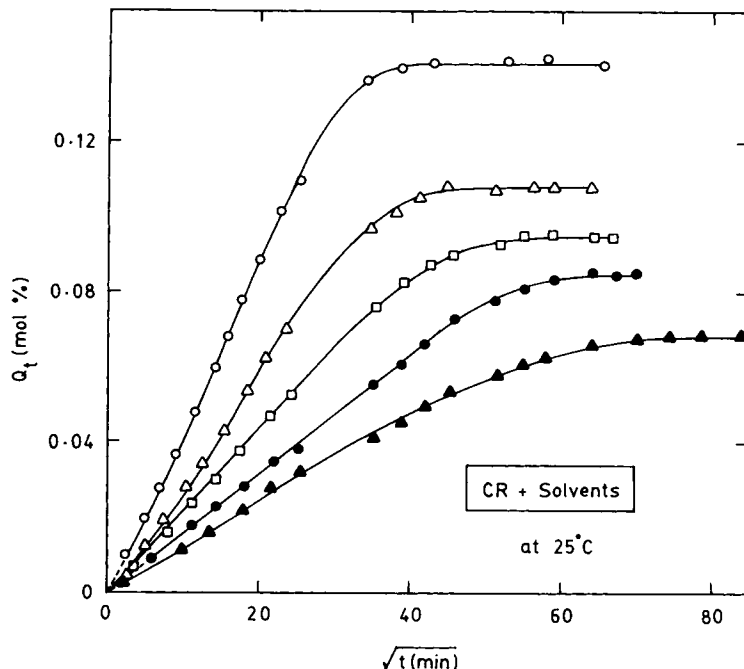


Figure 1 Mole percent solvent uptake for neoprene membrane at 25°C. (○) hexane; (△) heptane; (□) octane; (●) nonane; (▲) decane.

RESULTS AND DISCUSSION

Sorption results are interpreted in terms of mol increase in concentration per 100 g of the polymer sample versus square root of time, $t^{1/2}$. Some typical plots at 25°C for CR and EPDM polymers versus n -alkanes are given in Figures 1 and 2, respectively. With EPDM, the attainment of equilibrium was quicker than CR + n -alkane system. However, with all the polymers, the mol % increase in concentration and the times required to attain equilibrium saturation were found to be inversely proportional to the size of the solvent molecules. The increase in maximum sorption values (as obtained from the plateau regions of sorption curves) with various polymer + solvent systems followed the sequence: CR < SBR < EPDM < NR, and there is a systematic increase in solvent sorptivities with a rise in temperature.

The sorption plots shown in Figures 1 and 2 appear to show linearities in the beginning suggesting the transport mechanism to be of Fickian type. The sorption behavior of different polymers versus hexane and decane are presented respectively, in Figures 3 and 4. There is some similarity in the sorption behavior of EPDM and NR membranes in the presence of both hexane and decane. However, neoprene appears to take longer times than EPDM to attain equilibrium saturation in the presence of both hex-

ane and decane. It is found from the data given in Figures 3 and 4 that the sorption behavior of SBR is intermediate to those of EPDM and neoprene in the presence of both hexane and decane; this is also

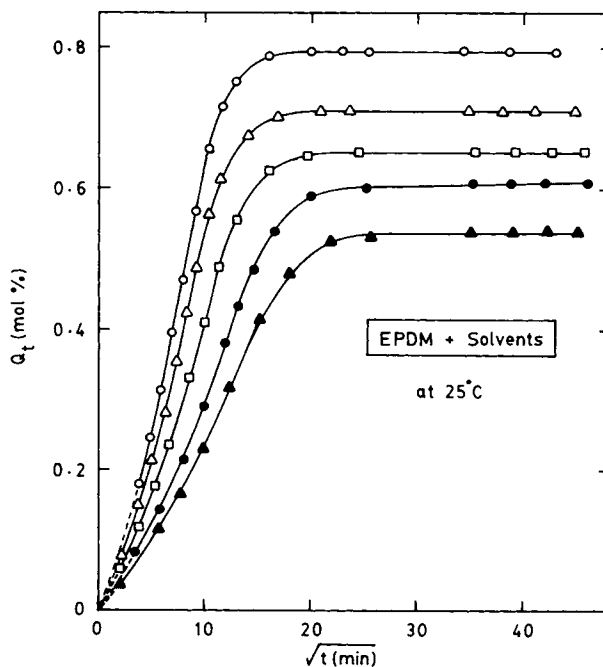


Figure 2 Mole percent solvent uptake for EPDM membrane at 25°C. Symbols have the same meaning as in Figure 1.

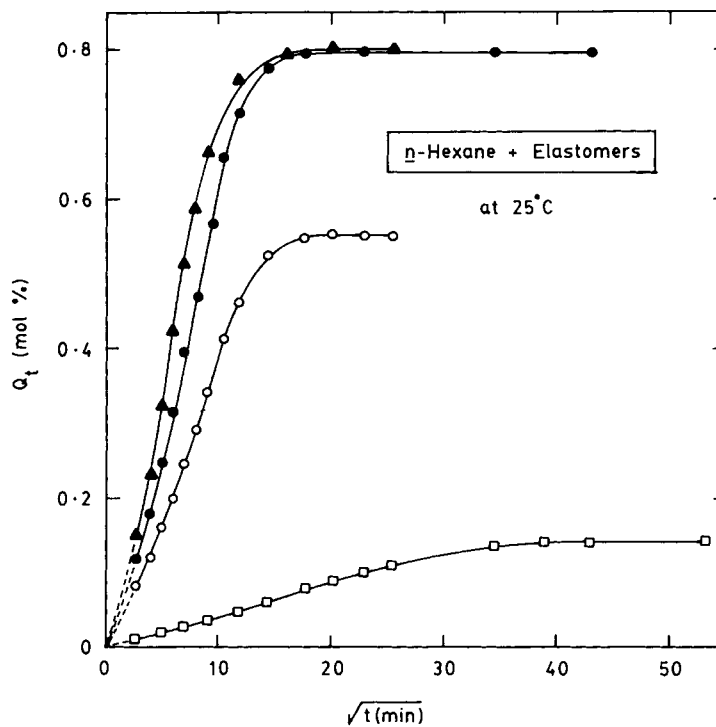


Figure 3 Mole percent solvent uptake for hexane + polymer membrane systems at 25°C: (○) SBR; (●) EPDM; (▲) NR; (□) CR.

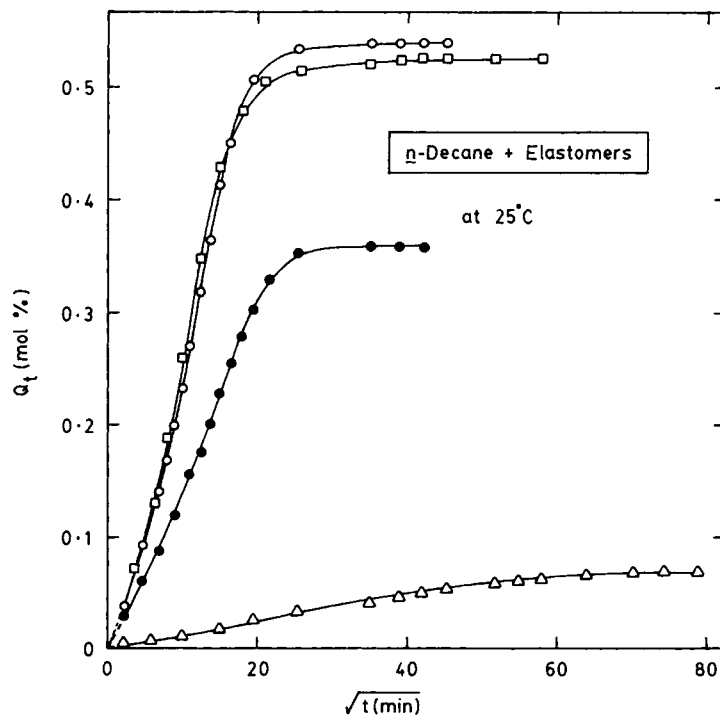


Figure 4 Mole percent solvent uptake for decane + polymer membrane systems at 25°C: (○) EPDM; (Δ) CR; (□) NR; (●) SBR.

Table III Analysis of Sorption Data of *n*-Alkanes and Polymer Membranes Using Eq. (2) at Different Temperatures

<i>n</i> -Alkanes	<i>T</i> (°C)	CR		SBR		EPDM		NR	
		<i>n</i>	<i>k</i> × 10 ² (g/g min ^{<i>n</i>})	<i>n</i>	<i>k</i> × 10 ² (g/g min ^{<i>n</i>})	<i>n</i>	<i>k</i> × 10 ² (g/g min ^{<i>n</i>})	<i>n</i>	<i>k</i> × 10 ² (g/g min ^{<i>n</i>})
Hexane	25	0.53	2.47	0.61	4.16	0.66	3.73	0.67	4.59
	44	0.55	3.06	0.59	5.30	0.64	4.94	0.64	5.72
	60	0.56	3.70	0.57	6.80	0.63	5.80	0.63	6.77
Heptane	25	0.56	1.85	0.59	3.90	0.64	3.76	0.62	4.49
	44	0.55	2.70	0.61	4.49	0.64	4.74	0.62	5.65
	60	0.58	3.81	0.59	5.62	0.66	5.28	0.63	6.37
Octane	25	0.53	1.88	0.59	3.46	0.63	3.31	0.61	4.19
	44	0.56	2.31	0.59	4.25	0.63	4.14	0.62	4.72
	60	0.53	3.43	0.58	5.47	0.57	5.69	0.62	5.58
Nonane	25	0.50	1.81	0.55	3.30	0.61	2.84	0.63	3.01
	44	0.53	2.35	0.59	3.89	0.61	3.90	0.60	4.45
	60	0.54	2.86	0.57	4.72	0.56	5.36	0.61	4.90
Decane	25	0.51	1.57	0.54	3.14	0.61	2.57	0.61	2.96
	44	0.51	2.16	0.56	3.49	0.61	3.31	0.60	3.73
	60	0.52	2.82	0.57	4.12	0.57	4.37	0.59	4.60

true for other alkanes, namely, heptane, octane, and nonane and these data are not displayed graphically.

In order to investigate the type of diffusion mechanism, the sorption data of all the penetrant-polymer systems have been fitted to the following relation^{8,9}:

$$\log(Q_t/Q_\infty) = \log k + n \log t \quad (2)$$

where Q_t and Q_∞ represent the mole percent increase in concentration at time t and at equilibrium time.

The values of n tell us something about the type of transport mechanism. A value of $n = 0.5$ represents the Fickian mechanism and $n = 1$ indicates the non-Fickian transport. The constant k depends on the structural characteristics of polymer network in addition to its interaction with the solvent.

From a least-squares analysis of the $\log(Q_t/Q_\infty)$ data versus $\log t$, the values of k and n have been obtained and these are included in Table III. The average uncertainty in the estimation of n is ± 0.01 . For all polymer + n -alkanes, the values of n vary

Table IV Diffusion Coefficients of *n*-Alkanes into Polymer Membranes at Different Temperatures

Polymer	Temp (°C)	$D \times 10^7$ (cm ² /s) for				
		Hexane	Heptane	Octane	Nonane	Decane
CR	25	1.71	1.37	0.98	0.65	0.61
	44	3.39	2.72	2.16	1.49	1.04
	60	5.09	4.09	3.30	2.63	1.83
SBR	25	6.89	5.29	4.04	2.61	2.04
	44	9.34	8.06	6.49	4.28	3.28
	60	11.77	10.82	8.42	6.00	4.70
EPDM	25	10.55	8.15	6.05	3.93	3.00
	44	13.99	12.48	8.19	6.37	4.89
	60	18.82	16.43	11.07	8.42	6.88
NR	25	11.55	8.48	6.82	4.41	3.25
	44	14.77	10.96	8.81	5.94	4.85
	60	17.76	14.48	11.24	8.48	6.23

Table V Thermodynamic Sorption Constants (K_s) of n -Alkanes + Polymer Membrane Systems at Different Temperatures

Polymer	Temp (°C)	$K_s \times 10^2$ (mol %) for				
		Hexane	Heptane	Octane	Nonane	Decane
CR	25	14.18	10.81	9.55	8.51	6.88
	44	14.90	11.98	10.14	9.24	7.72
	60	15.67	12.46	10.96	10.19	8.16
SBR	25	55.09	48.52	44.82	40.86	35.85
	44	55.57	49.20	45.53	42.16	36.66
	60	55.22	48.26	46.52	42.66	38.06
EPDM	25	79.57	71.15	65.30	60.71	53.93
	44	75.98	67.65	63.48	58.62	52.72
	60	74.09	65.56	61.27	58.46	52.05
NR	25	80.66	71.81	64.75	60.69	52.57
	44	79.66	71.75	66.14	60.70	53.32
	60	78.94	70.78	66.65	61.61	55.25

from 0.5 to 0.6, and, thus, the transport mechanism is not strictly of Fickian type. However, we could not observe any systematic dependence of n on temperature, but k increases systematically with temperature, suggesting an increase in segmental motion with the rise in temperature, a fact that was observed earlier also.^{3,4} The values of k are found to be low for CR and high for NR; however, the general trend in these values for all the n -alkanes follow the sequence: NR > SBR > EPDM > CR. This sequence

also suggests the strength of solvent interactions with the polymer backbones. Generally, the extent of interaction appears to be less as we go from lower members of the homologous series to higher members.

During sorption experiments significant swelling anomalies were not observed with any of the polymer membranes. Thus, the diffusion coefficients calcu-

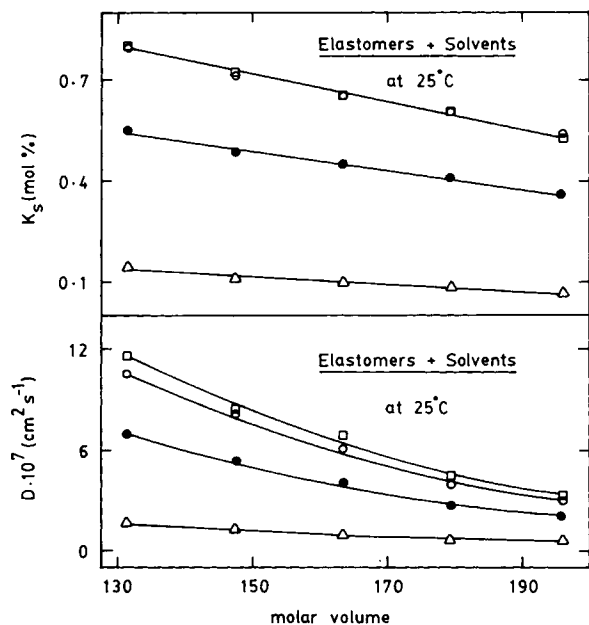


Figure 5 Dependence of equilibrium sorption constant (K_s) and diffusivity (D) on molar volume of n -alkanes at 25°C. Symbols have the same meaning as in Figure 4.

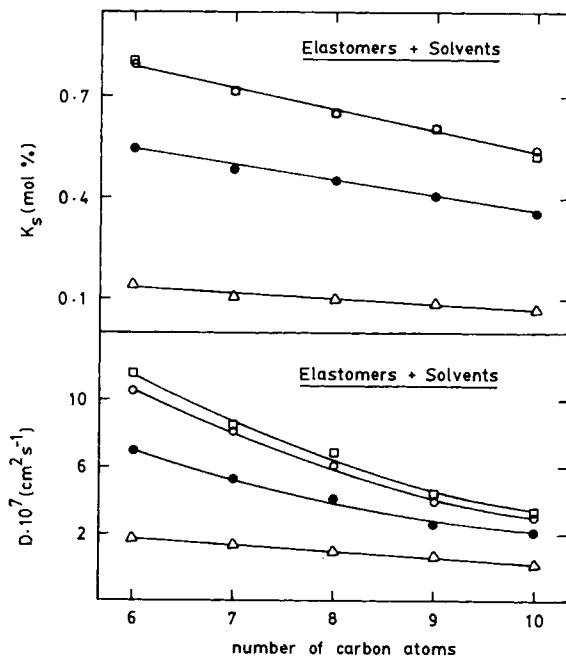


Figure 6 Dependence of equilibrium sorption constant (K_s) and diffusivity on number of carbon atoms of n -alkanes at 25°C. Symbols have the same meaning as in Figure 4.

Table VI Activation Parameters [E_D (kJ/mol); ΔH_s (kJ/mol); ΔS (J/mol/°C)] for Polymer + n -Alkanes Systems

n -Alkanes	Parameter	CR	SBR	EPDM	NR
Hexane	E_D	25.93	12.64	13.58	10.16
	ΔH_s	2.066	0.07	-1.70	-0.51
	$-\Delta S$	41.20	43.00	55.82	41.82
Heptane	E_D	26.08	16.93	16.62	12.55
	ΔH_s	3.367	-0.087	-1.95	-0.33
	$-\Delta S$	45.52	44.67	47.70	42.12
Octane	E_D	28.95	17.46	14.19	11.71
	ΔH_s	6.212	0.86	-1.49	0.696
	$-\Delta S$	37.2	42.12	46.82	39.6
Nonane	E_D	32.89	19.76	19.54	16.38
	ΔH_s	4.21	1.03	-0.92	0.335
	$-\Delta S$	44.70	42.30	45.67	41.40
Decane	E_D	25.77	19.73	19.64	15.43
	ΔH_s	4.086	1.39	-0.84	1.14
	$-\Delta S$	46.8	42.2	46.3	39.8

lated from eq. (1) can be regarded to be concentration-independent. The calculated diffusivity data for all the membranes are given in Table IV. In all the cases, it is found that diffusivity decreases with an increase in chain length of the n -alkanes; however, diffusivity values of all the systems are found to be increasing with an increase in temperature. The diffusivity data are found to vary according to the sequence: CR < SBR < EPDM < NR. This trend, which is similar to that of the maximum sorption discussed earlier in this paper, suggests that, for n -alkanes used here, neoprene may be a better barrier material than natural rubber.

The sorption coefficients of n -alkanes into polymer membranes as obtained from the plateau regions of the sorption curves may be regarded^{4,10} as thermodynamic equilibrium sorption constants (K_s). These data which are summarized in Table V also follow the same trend as those of diffusivities. The inverse dependence of D or K_s either on molar volume (Fig. 5) or on number of carbon atoms (Fig. 6) of n -alkanes proves the conjecture that larger molecules in a related series of liquids occupy larger free volumes leading to hindered diffusivities through the polymer matrix. The diffusion data from Table IV have been used to estimate the activation energy E_D for the process of diffusion from the Arrhenius relation of the type

$$D = D_0 \exp(-E_D/RT) \quad (3)$$

where D_0 is the preexponential factor, R is the molar gas constant, and T is the absolute temperature.

Similarly, the temperature-dependent K_s values from Table V may be fitted to the van 't Hoff relation to estimate the enthalpy ΔH_s and entropy ΔS of sorption. These data are summarized in Table VI

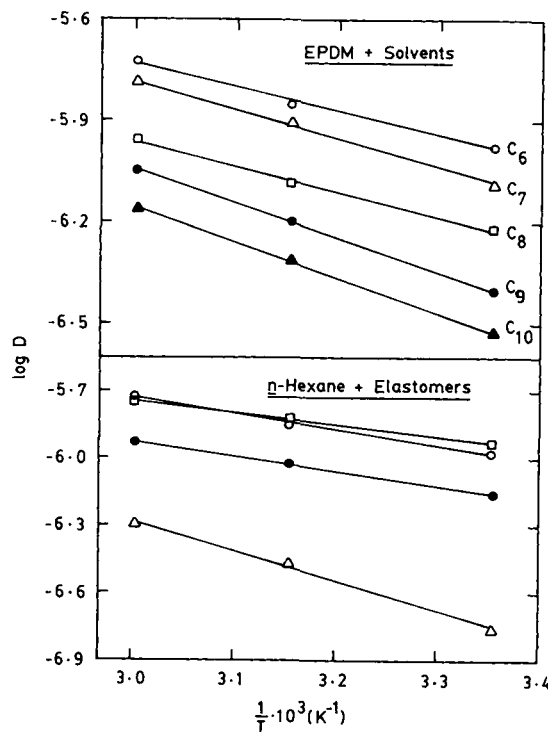


Figure 7 Arrhenius plots of $\log D$ vs. $1/T$ for EPDM + n -alkanes (upper portion) and for hexane + polymer membranes (lower portion). Symbols have the same meaning as in Figure 4 for the lower portion.

and some representative Arrhenius and van 't Hoff plots are given, respectively, in Figures 7 and 8. Here, only the data for EPDM with all the n -alkanes and n -alkanes with all the polymers are given as representative examples. Similar dependencies were also observed in case of other polymer + solvent systems; these data are not presented to avoid redundancy. In the majority of cases, ΔH_s data are positive and, with EPDM, ΔH_s values for all the liquids are negative. Similarly, NR also shows negative ΔH_s values for hexane and heptane. However, the calculated ΔS values are negative for all the systems. This suggests that the structure of the solvent molecules is retained even in the sorbed state.

Of all the polymer membranes studied here, NBR exhibited the least sorption tendency towards all the n -alkanes even after longer times of experimentation. The sorption results for NBR + n -alkanes are included in Table VII. In view of the extremely small amount of sorption of the liquids by NBR, diffusion coefficients were not evaluated. More experiments on other n -alkane series of liquids are under study, and these results will be communicated in the near future.

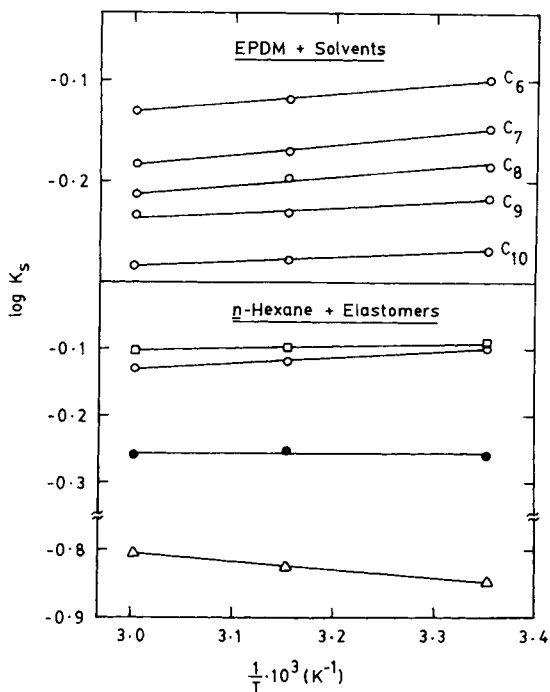


Figure 8 van't Hoff plots of $\log K_s$ vs. $1/T$ for EPDM + n -alkanes (upper portion). Symbols have the same meaning as in Figure 4 for the lower portion.

Table VII Sorption Results of Nitrile Butadiene Rubber + n -Alkanes at Different Temperatures

n -Alkanes	Temp (°C)	Time (h)	$K_s \times 10^2$ (mol %)
Hexane	25	32	0.88
	44	54	2.82
	60	30	3.18
Heptane	25	48	0.54
	44	48	1.43
	60	48	2.50
Octane	25	36	0.33
	44	44	0.82
	60	46	1.74
Nonane	25	49	0.37
	44	53	0.63
	60	45	1.39
Decane	25	45	0.32
	44	58	0.37
	60	51	0.87

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REFERENCES

1. R. S. Khinnavar and T. M. Aminabhavi, *J. Appl. Polym. Sci.*, (1990), submitted as Part I, to appear.
2. S. B. Harogopad and T. M. Aminabhavi, *Polymer*, (1990), to appear.
3. U. S. Aithal and T. M. Aminabhavi, *J. Chem. Educ.*, **67**, 82 (1990).
4. U. S. Aithal, T. M. Aminabhavi, and P. E. Cassidy, *Polym. Prepr.*, **30**(1), 17 (1989).
5. T. M. Aminabhavi and P. E. Cassidy, *Polym. Commun.*, **27**, 254 (1986).
6. L. N. Britton, R. B. Ashman, T. M. Aminabhavi, and P. E. Cassidy, *J. Chem. Educ.*, **65**, 368 (1988).
7. J. Crank, *Mathematics of Diffusion*, 2nd ed., Oxford University Press, London, 1975.
8. L. M. Lucht and N. A. Peppas, *J. Appl. Polym. Sci.*, **33**, 1557 (1987).
9. J. S. Chiou and D. R. Paul, *Polym. Eng. Sci.*, **26**, 1218 (1986).
10. G. W. C. Hung, *Microchem. J.*, **19**, 130 (1974).

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