

Diffusion and sorption of organic liquids through polymer membranes: 10. Polyurethane, nitrile-butadiene rubber and epichlorohydrin *versus* aliphatic alcohols (C₁–C₅)

Tejraj M. Aminabhavi* and Rajashekhar S. Khinnavar

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

(Received 16 December 1991; revised 18 May 1992)

Diffusion and sorption of eight aliphatic alcohols — namely methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-pentanol and 3-methyl-1-butanol — into three engineering polymer membranes has been studied in the temperature range 25–60°C to investigate the kinetics of the transport mechanism. The results have been analysed in terms of the Fickian diffusion equation. The anomalous transport behaviour of rubber–alcohol systems is attributed to a leaching out of the polymer systems during solvent immersion. The dependence of transport coefficients and activation parameters, as obtained from a temperature dependence of these coefficients, have been discussed in terms of the polymer–solvent interactions and their effect on the size, shape and type of penetrant molecules. Furthermore, the transport results have been interpreted in terms of enthalpy and entropy contributions. Dependence of the transport parameter on penetrant concentration has also been investigated.

(Keywords: diffusion; sorption; membrane)

INTRODUCTION

The sorption and diffusion of small organic molecules in polymer matrices is a subject of great technological importance from the viewpoint of both processing and useful properties. Understanding the mobility of small organic molecules in polymer systems is crucial to the optimization of polymerization rates, mixing of additives, devolatilization, and other barrier properties of the resulting materials. Solvent diffusivity can be influenced profoundly by relatively minor changes in the chemical structure of the diffusant molecules and of the polymer. Diffusion in polymers has been reviewed by Crank and Park¹ and by Aminabhavi *et al.*². The pioneering works of Barrer^{3,4}, Meares⁵, Bueche⁶, Brandt⁷, and DiBenedetto and Paul^{8,9} are of special prominence. Several other theories, notably the work of Vrentas and Duda^{10–12}, have proved to be generally valid within their intended realm of application.

For molecules of low solubility, the polymer matrix is unaffected by the diffusant so that diffusion is expected to follow Fick's laws. For one-dimensional diffusion, the rate of mass transport across unit area of polymer in the *x*-direction is given by Fick's first law:

$$dm/dt = -D(dC/dx) \quad (1)$$

and the rate of change of concentration at any point is given by Fick's second law:

$$dC/dt = D(d^2C/dx^2) \quad (2)$$

where *D* is the diffusion coefficient. Solutions to equations (1) and (2) have been discussed by Crank¹³ for relevant boundary conditions, and have been used to compute uptake or loss of solvent if *D* is known precisely. Conversely, methods of measuring *D* are all based on Fick's laws. In principle, the diffusion coefficient can be determined by measuring the total sorption of the solvent or by monitoring the concentration profile as it evolves. A variety of techniques have been devised and used for this purpose^{14–20}.

In earlier papers from this laboratory^{21–34}, transport of small molecules into elastomer membranes was investigated; several aspects of diffusion anomalies were investigated for a wide range of solvent type into a variety of polymer systems. It was found that though diffusion in elastomers follows Fickian kinetics, in some cases non-Fickian behaviour was also observed. In previous studies concerning the transport of aliphatic alcohols²³ and of *n*-alkanes^{26,29,30,33} into elastomer membranes, it was realized that diffusion coefficients vary inversely with the size of the penetrant molecules. In continuation of these studies and as a further contribution towards an extensive data-base on sorption and diffusion of aliphatic alcohols (C₁–C₅) into polymer membranes, we have now undertaken a comprehensive investigation on the transport characteristics of polyurethane (PU), nitrile-butadiene rubber (NBR) and epichlorohydrin (ECH).

PU is a versatile engineering polymer which exhibits interesting physico-mechanical properties in view of its two-phase morphology. It is highly resistant to water but less resistant to organics. Generally, the polyester-based

* To whom correspondence should be addressed

PU elastomers exhibit excellent toughness with good oil and chemical resistance. NBR is a copolymer of acrylonitrile and butadiene with properties dependent mainly on the composition of the monomer units. NBR with high acrylonitrile content, i.e. 40–50%, generally exhibits high resistance to hydrocarbons, abrasion and low permeability to gases. Its oil resistance increases with increasing content of acrylonitrile. NBR is noted for its high strength and resistance to water, oil and heat. ECH has a good resistance to swelling in oils, good heat resistance and temperature flexibility. It is used in the automotive industry for seals, diaphragms and hoses.

Data on the solvent transport properties of these polymers are virtually non-existent in the literature. In this paper, we will present diffusion, sorption and permeation results for probe molecules, namely methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol and their branched analogues, namely 2-propanol, 2-methyl-1-propanol and 3-methyl-1-butanol. The alcohols are selected in increasing order of size and chain-length so as to study their effects on solvent transport properties. The transport parameters have been calculated for each of the polymer-solvent systems using the gravimetric method. 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 have been used to study the extent of polymer-solvent interactions. The phenomenon of the kinetics of sorption has been studied in terms of the kinetic rate constants and the activation parameters. A study of the concentration dependence of diffusivity has also been attempted.

EXPERIMENTAL

Polymer sheets of ECH and NBR with dimensions of 1.6 mm × 15.24 cm × 15.24 cm were moulded at UTEX, Weimer, TX, USA. During sample fabrication, a 30.48 cm laboratory mill was used to mix and prepare the rubber compounds for moulding; the ECH polymer sheets were press-cured at 176°C for 30 min and NBR was press-cured at 160°C for 20 min. The compositions and some engineering properties of ECH are given in Table 1; the properties and compositions of NBR membranes have been given previously³⁰. The PU (trade name Pellathane) was obtained from Dow Chemical Company, Midland, MI, USA. It is a 2102 series elastomer which combines excellent resistance to fuels and oils with good hydrolytic stability. Elastomers in this series have been used for making seals, gaskets, belting and other fabricated products. The PU is based on a polyester polycaprolactone. The physical and engineering property data of this series of PU are available from the manufacturer.

All the reagent grade solvents, namely methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 2-propanol, 2-methyl-1-propanol, and 3-methyl-1-butanol, were doubly distilled before use to ensure purity. Their measured physical properties such as refractive index and density at 25°C agreed well with the literature³⁵. The polymer samples were dried thoroughly in a desiccator before use and were cut into circles (diameter 1.96 cm) by means of a sharp-edged steel die. The membrane thicknesses were measured at several points with an accuracy of ±0.001 cm by using a micrometer screw gauge. The average of several values was taken to be the initial thickness, *h*, of the polymer samples and this was

Table 1 Composition and properties of ECH membrane

Compound	Phr	Properties	
Hydrin ^a	100	Specific gravity ^c	1.44
Carbon black	40 ^b	Hardness (shore A) ^d	62
Zinc stearate	1	Tensile strength (psi) ^e	1890
Dibasic lead phosphate	5	Ultimate elongation (%) ^e	440
Dibasic lead phthalate	7	E50 modulus (psi) ^e	220
75% ethylene thiourea	1	E100 modulus (psi) ^e	410
in EPR		E200 modulus (psi) ^e	950
Total	154.0	E300 modulus (psi)	1460

^aZuri Chemical

^bN550

^cASTM D792

^dASTM D2240

^eASTM D412

used in all calculations. The other experimental details are the same as given previously^{21–33}.

RESULTS AND DISCUSSION

The sorption plots (i.e. mol% uptake of solvent³⁶ by the polymer membrane *versus* square root of time, $t^{1/2}$) at 25°C for the polymer-solvent systems are given in Figures 1–3. The maximum values of sorption, Q_{∞} , at 25, 44 and 60°C are summarized in Table 2. In general, the mol% uptake of alcohols by PU is higher than that of NBR and ECH membranes. NBR exhibits mol% uptake values intermediate between those of PU and ECH membranes for all the penetrants except methanol. However, the differences in the maximum sorption values of NBR and ECH membranes are not greatly significant. The higher solvent uptake by the PU membrane may be attributed to the specific interactions between polar groups of PU segments and the hydroxy groups of alcohols. In all cases, the uptake values increase with temperature; this suggests the availability of free volume in the polymer matrices thereby facilitating higher solvent uptake. With increase in the size of alcohol molecules, i.e. from methanol (C_1) to 1-pentanol (C_5), their transport becomes more sluggish so that uptake values decrease. The branched alcohols such as 2-propanol and 2-methyl-1-propanol, due to their restricted movements, show lower uptake values than their linear homologues namely, 1-propanol and 1-butanol. In general, the Q_{∞} values for straight-chain alcohols (C_1 – C_5) show a systematic decrease with an increase in the number of carbon atoms.

Close observation of the sorption curves in Figures 1–3, indicates that different times are required for attainment of equilibrium saturation; this depends on the nature of the polymer segments and also of the penetrant molecules. Considering the smallest penetrant, namely methanol with PU membrane, it is found that the equilibrium saturation time is about 10 h; however, with NBR + methanol it is about three times longer, i.e. 30 h. With ECH + methanol it takes about 15 h to reach complete equilibrium. With an increase in the chain length of the alcohol, the time required to reach equilibrium also increases considerably. This can be seen for the sorption of 1-pentanol (C_5) with PU membrane, for which the equilibrium time is about 3.5 days as compared to 10 h for PU + methanol. For branched alcohols, the time required to attain equilibrium sorption is very much longer than for the linear homologues. For instance, with NBR + 3-methyl-1-butanol, about 25 days

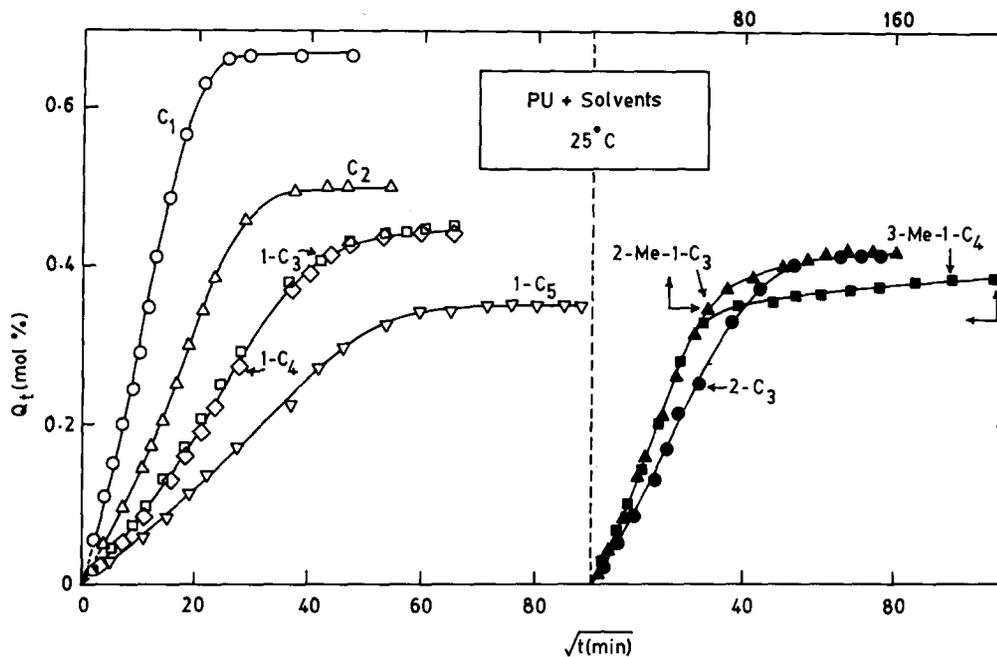


Figure 1 Solvent uptake (mol%) for PU and solvents at 25°C

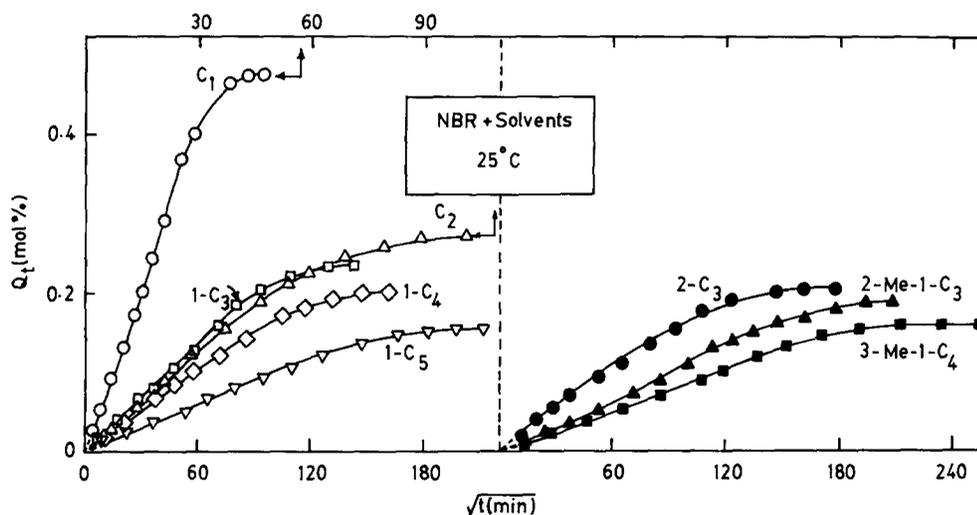


Figure 2 Solvent uptake (mol%) for NBR and solvents at 25°C

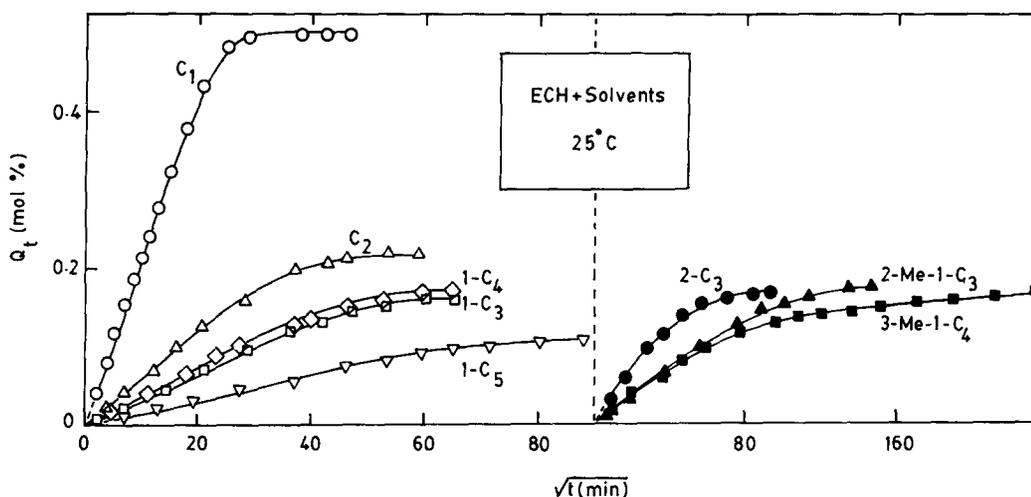


Figure 3 Solvent uptake (mol%) for ECH and solvents at 25°C

are required to attain equilibrium saturation, whereas for NBR + 2-propanol the equilibrium time is about 15 days. This further supports the conjecture that branched alcohols move considerably more slowly than the linear alcohols. In general the attainment of equilibrium sorption with PU and ECH membranes is slower than with NBR.

Sorption behaviours of PU, NBR and ECH membranes for all the penetrants at 25°C are given in Figures 4–7. It is observed that in all cases, sorption follows the Fickian mechanism, showing a linear increase in Q_t with $t^{1/2}$ up to about 50% equilibrium, and later levels off showing the attainment of complete equilibration. With

Table 2 Equilibrium sorption data and kinetic rate constants of polymer–solvent systems

Solvent	Temp. (°C)	Q_∞ (mol%)			$k \times 10^3$ (min ⁻¹)		
		PU	NBR	ECH	PU	NBR	ECH
Methanol	25	0.665	0.476	0.503	4.84	1.96	4.42
	44	0.732	0.542	0.559	9.44	4.44	8.57
	60	0.782	0.596	0.627	13.95	7.70	9.88
Ethanol	25	0.502	0.273	0.221	2.36	0.71	1.84
	44	0.565	0.321	0.276	5.11	2.02	4.35
	60	0.653	0.371	0.323	7.91	5.10	7.87
1-Propanol	25	0.449	0.236	0.161	1.30	0.22	1.11
	44	0.529	0.281	0.222	3.24	1.15	2.59
	60	0.628	0.353	0.285	5.45	2.80	5.54
2-Propanol	25	0.416	0.208	0.168	1.17	0.18	1.19
	44	0.471	0.249	0.202	2.75	1.09	2.55
	60	0.534	0.303	0.262	4.85	2.37	4.95
1-Butanol	25	0.444	0.196	0.169	1.14	0.20	1.16
	44	0.495	0.235	0.213	2.84	1.03	2.61
	60	0.551	0.284	0.264	5.13	2.39	4.45
2-Methyl-1-propanol	25	0.418	0.190	0.176	0.50	0.08	0.23
	44	0.425	0.222	0.167	1.68	0.43	1.71
	60	0.488	0.271	0.211	3.45	1.71	3.59
1-Pentanol	25	0.351	0.156	0.108	0.83	0.10	0.51
	44	0.381	0.176	0.137	2.20	0.70	1.79
	60	0.449	0.223	0.190	3.99	1.80	4.53
3-Methyl-1-butanol	25	0.385	0.160	0.171	0.57	0.07	0.25
	44	0.384	0.181	0.149	1.89	0.35	1.53
	60	0.421	0.218	0.191	2.50	1.23	2.51

PU membrane, the sorption curves are somewhat sigmoidal as compared to NBR and ECH membranes. This suggests that PU, being a phase-segregated membrane, consists of both hard and soft segments. Sorption takes place initially in the soft core of the membrane and later, due to the slow relaxation of the PU segments in the presence of the alcohol molecules, the sorption increases. Solvent uptake by the polymer depends on the experimental temperature in addition to other factors such as chain morphology, solvent type, etc. Figures 8 and 9 show temperature-dependent sorption plots for two typical systems, namely elastomers + methanol and elastomers + 2-propanol, respectively. It is observed that at higher temperatures (i.e. 60°C), due to increased interactions between polymer chain segments and solvent molecules, the sorption mechanism tends to deviate from the normal Fickian mode, as evidenced by the slight deviations from the linear relation between Q_t versus $t^{1/2}$ before attainment of 50% equilibrium. With ECH and NBR membranes in the presence of methanol, sorption tends to decrease at higher temperatures (i.e. at 44 and 60°C) suggesting a leaching out of the additives from the rubber compounds. However, this is not observed for higher alcohols.

Following our earlier suggestions³⁷, efforts have been made to investigate the kinetics of sorption in terms of the first-order kinetic model. Thus, from the sorption results of polymer–solvent systems, the first-order kinetic rate constants have been evaluated by using:

$$dC/dt = k(C_\infty - C_t) \quad (3)$$

where k is the first-order rate constant (min⁻¹). Integration of equation (3) gives:

$$kt = 2.303 \log [C_\infty / (C_\infty - C_t)] \quad (4)$$

Here, C_t and C_∞ represent, respectively, the concentration at time t and at infinite time (i.e. equilibrium saturation) and these have the same meanings as Q_t and Q_∞ , respectively, as discussed above. These results are also included in Table 2. Generally, it is observed that k tends to decrease with an increase in the size of the

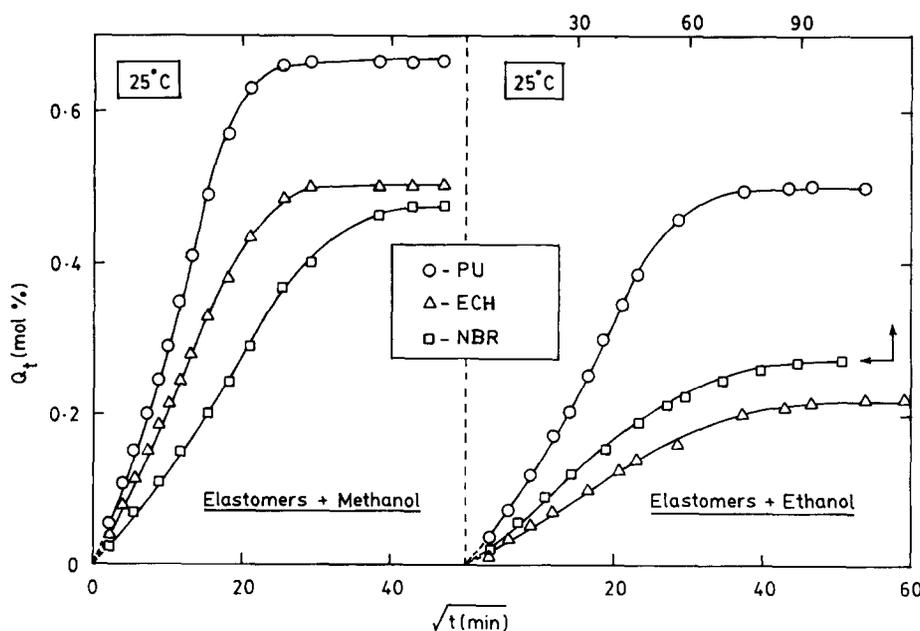


Figure 4 Solvent uptake (mol%) for methanol and ethanol with elastomers at 25°C

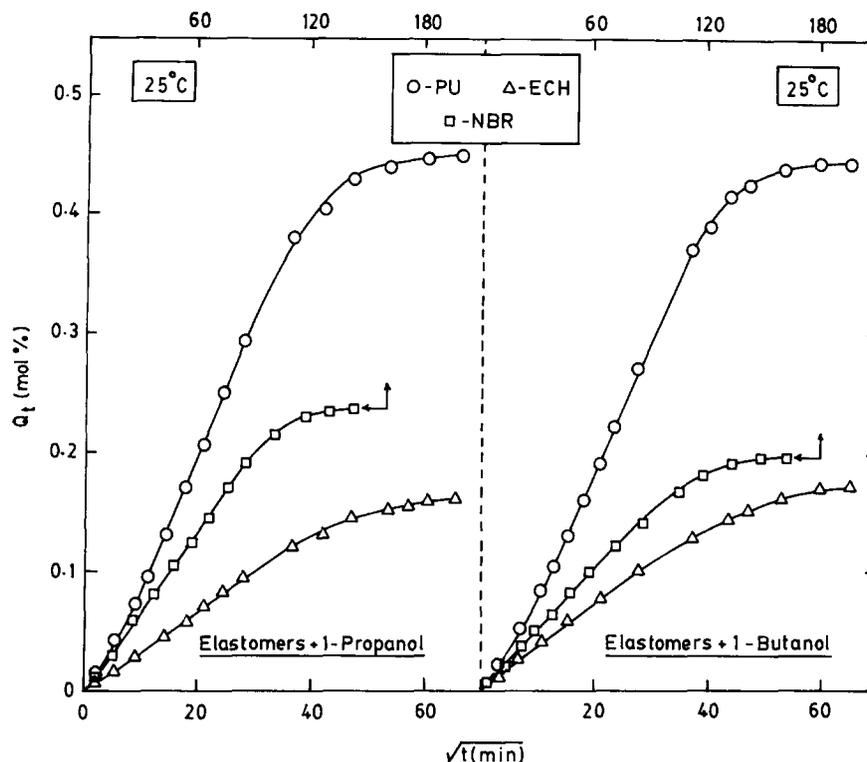


Figure 5 Solvent uptake (mol%) for 1-propanol and 1-butanol with elastomers at 25°C

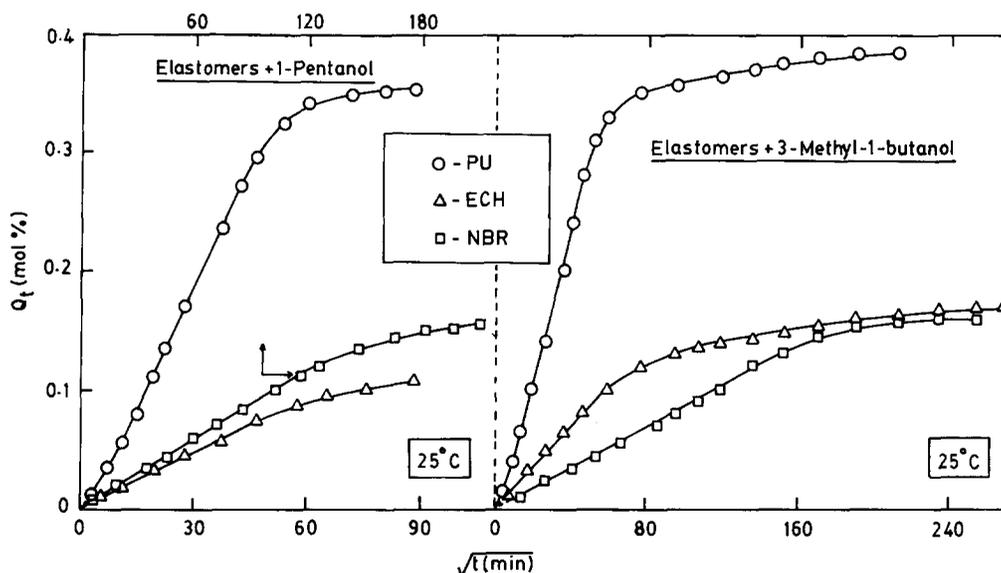


Figure 6 Solvent uptake (mol%) for 1-pentanol and 3-methyl-1-butanol with elastomers at 25°C

alcohols, but increases with temperature. In general, the values of rate constants are higher for PU and ECH membranes than for NBR for all penetrant molecules and at all temperatures.

In order to investigate further whether the sorption mechanism follows Fickian mode or not, the dynamic sorption results for short times (i.e. $Q_t/Q_\infty \leq 0.6$) have been fitted to the empirical expression^{38,39}:

$$Q_t/Q_\infty = Kt^n \quad (5)$$

where Q_t is the mass uptake of solvent at time t , Q_∞ is the mass uptake at equilibrium and K is a constant characteristic of the polymer-solvent system. For a polymer with slab geometry, a value of $n=0.5$ indicates the Fickian mode of transport while $n=1.0$ indicates case

II (relaxation-controlled) transport; values of n between these limits define anomalous transport²². The least-squares estimation of n and K from equation (5), at 95% confidence level, are given in Table 3. In the case of PU membrane, the values of n vary from 0.55 to 0.59, whereas with ECH and NBR membranes the n values are generally closer to 0.50 but in some cases increase to a maximum of 0.57. For a majority of polymer-solvent systems an increase in temperature shows an increase in the values of n (more so with PU than NBR or ECH membranes).

The results for K , as obtained from equation (5), increase systematically with temperature, suggesting increased molecular interactions between polymer chain segments and solvent molecules. This is also supported

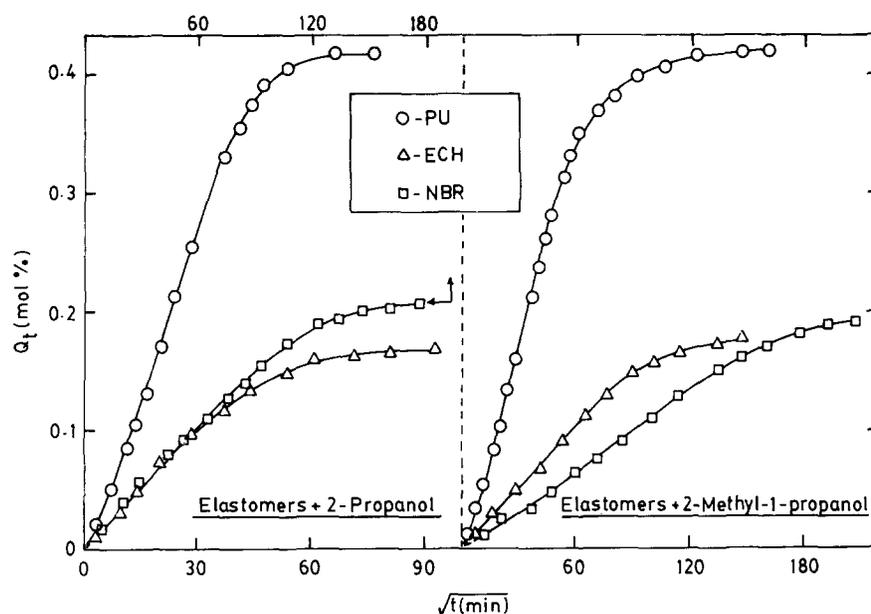


Figure 7 Solvent uptake (mol%) for 2-propanol and 2-methyl-1-propanol with elastomers at 25°C

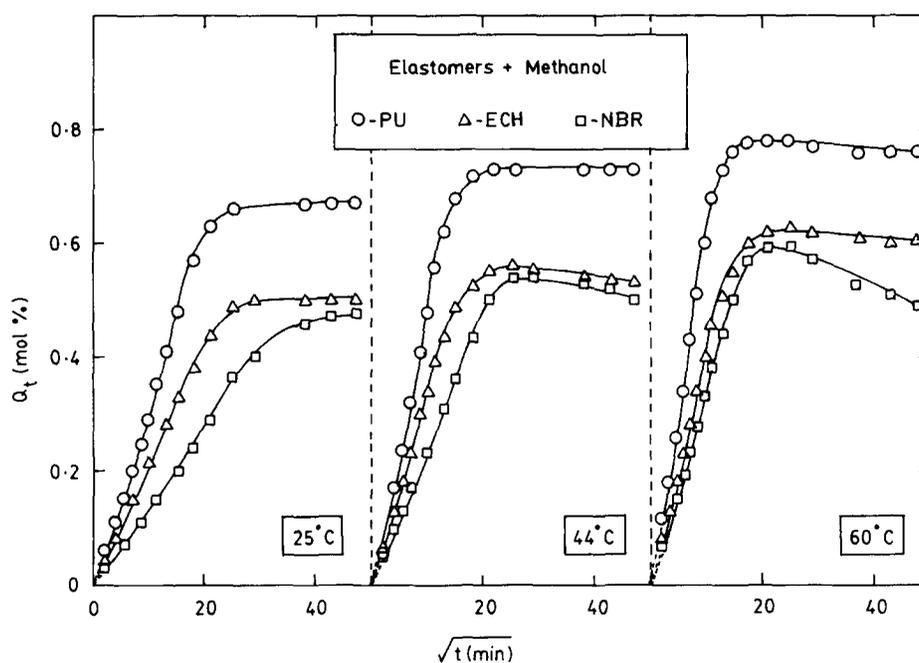


Figure 8 Solvent uptake (mol%) for methanol with elastomers at 25, 44 and 60°C

by the slightly sigmoidal shapes of the sorption curves; the observed behaviour is that expected of a nearly (but not completely) Fickian mode process in elastomers well above their glass transition temperatures. In order to determine whether the observed anomalous behaviour is due to swelling-induced morphological changes of the filled elastomer samples, similar to the case of Mooney-softening⁴⁰, we repeated the sorption experiments for some of the already desorbed polymer samples, to test whether or not subsequent sorption showed the same anomalous behaviour⁴¹. The anomalous behaviour persisted during the sorption experiments of the desorbed samples. Although the manner in which the initial sorption curves vary remained the same initially, the final equilibrium data decreased by about 1–2%. This further suggests that some of the indigenous compounds (addi-

tives, fillers, etc.) of the rubber samples might have been leached out of the rubber membranes during the first cycle of sorption.

Elastomers are normally considered to have sufficiently rapid segmental relaxation times that relaxation effects are absent and diffusion follows Fickian kinetics. However, diffusion in phase-segregated elastomers and natural rubbers has shown evidence of non-Fickian behaviour⁴². In these materials, the relaxation must result from the interaction of the solvent with the hard segment phase and this behaviour is most likely related to a control of the polymer relaxation by the hard segment domains functioning as physical crosslinks.

The dynamic swelling properties of a polymer film include the solvent sorption rate, the rate of approach to equilibrium swelling, the solvent front velocity, and

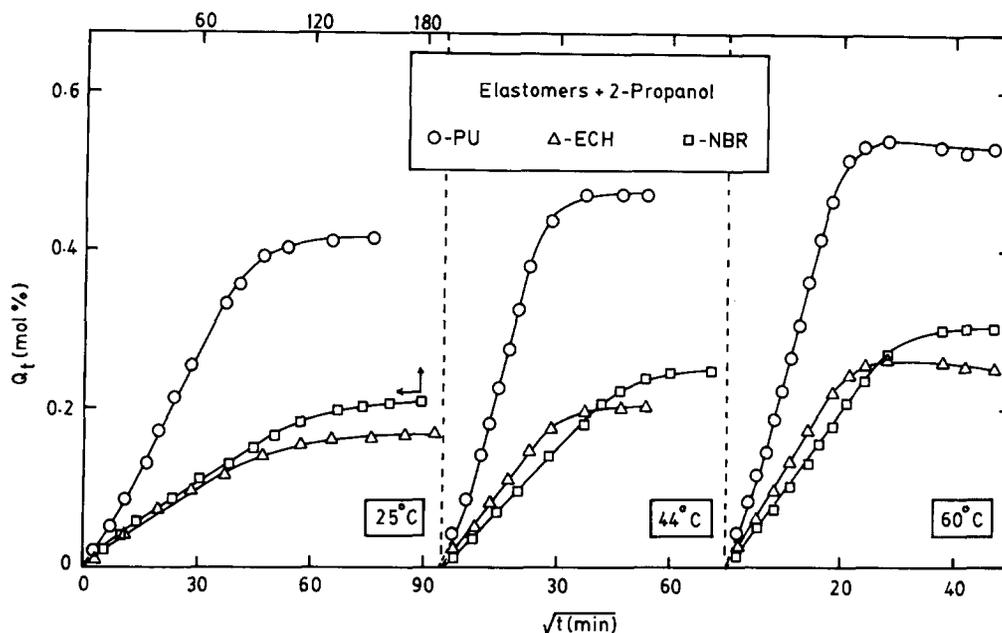


Figure 9 Solvent uptake (mol%) for 2-propanol with elastomers at 25, 44 and 60°C

the transport mechanism controlling solvent sorption. The solvent sorption rate indicates the solvent uptake per unit time and is directly related to the degree of equilibrium swelling of the polymer. For a Fickian mechanism, the rate of approach to equilibrium can be characterized by a diffusion coefficient. For ordinary diffusion, Fick's law is the appropriate constitutive equation for the mass transfer flux and a mutual diffusion coefficient can be defined, related to the polymer-fixed frame of reference^{39,42}. For a plane geometry of the polymer sheet, the diffusion coefficient D , can be calculated from¹³:

$$Q_t/Q_\infty = 1 - \sum_{n=0}^{\infty} [8/(2n+1)^2\pi^2] \exp[-(2n+1)^2\pi^2(Dt/h^2)] \quad (6)$$

where t is time and h is the initial thickness of the polymer sheet. Although this equation can be solved readily, it is instructive to examine the short-time limiting expression as well¹³:

$$Q_t/Q_\infty = [4/\pi^{1/2}][Dt/h^2]^{1/2} \quad (7)$$

From a plot of Q_t versus $t^{1/2}$, a single master curve (referred to as a diffusion plot) is obtained, which is initially linear. Thus, D can be calculated³⁰⁻³⁴ from a rearrangement of equation (7) as:

$$D = \pi \left[\frac{h\theta}{4Q_\infty} \right]^2 \quad (8)$$

where θ is the slope of the initial linear part of the graph of Q_t versus $t^{1/2}$.

The diffusion data derived from equation (8) are compiled in Table 4. The diffusion coefficients of linear alcohols into polymer membranes show a systematic decrease with an increase in the chain length. However, the branched alcohols (namely, 2-propanol, 2-methyl-1-propanol, and 3-methyl-1-butanol) did not show any systematic dependence of diffusivity on their molecular sizes. For all the polymer-solvent systems, diffusion increases with an increase in temperature, suggesting

the availability of increased free volume at higher temperatures. In general, the diffusion coefficients for ECH membrane with all penetrants are higher than for PU or NBR membranes (the latter exhibits the least diffusivity).

Hung and Autian⁴³ used a thermogravimetric method to obtain the diffusivity and solubility of a series of aliphatic alcohols in a PU membrane in the temperature range 24–50°C. In their study, the diffusion coefficients of the straight-chain alcohols increased with temperature and decreased with penetrant molecular weights. The branched-chain alcohols had diffusion coefficients lower than the non-branched isomers. This indicates that as the cross-sectional areas of the alcohols increase, greater hindrance is presented to their passage through the polymer. Similar results were reported by other investigators^{44,45} for different polymer-penetrant systems, and also for butyleneadipate PU membrane with monohydric alcohols⁴⁶. The permeability data, as calculated from the simple empirical relation $P \equiv DS$ given in Table 4, follow nearly the same pattern as those of diffusivities. This simple relation holds for the permeation process when D obeys Fick's diffusion law and S obeys Henry's law⁴⁷. For the penetrant-polymer systems used in this study, it is not certain to what degree one or both laws are obeyed. Thus, the P values presented in Table 4 are to be considered as estimates of the permeability coefficient.

The mean effective diffusion coefficient characterizing the sorption kinetics was estimated from the initial slope of normalized mass uptake versus square root of time (i.e. $0 \leq Q_t/Q_\infty \leq 0.5$). The corresponding plots of $\ln(1 - Q_t/Q_\infty)$ versus time using long-time sorption data (i.e. $Q_t/Q_\infty \geq 0.5$) were also constructed in order to compare the diffusivities obtained from short-time and long-time data. An example corresponding to Figure 1 is shown in Figure 10 for PU with linear alcohols from methanol to 1-pentanol. The diffusion coefficients determined by these two methods agreed within 10–15%. The intercept of the $\ln(1 - Q_t/Q_\infty)$ versus t plot was also determined to confirm that the intercept was close to the

Table 3 Analysis of sorption results of polymer-solvent systems

Solvent	Temp. (°C)	PU		NBR		ECH	
		<i>n</i>	$K \times 10^{2a}$	<i>n</i>	$K \times 10^{2a}$	<i>n</i>	$K \times 10^{2a}$
Methanol	25	0.56	3.36	0.54	2.23	0.55	3.29
	44	0.56	4.71	0.51	4.11	0.55	4.76
	60	0.57	5.84	0.55	4.65	0.55	5.30
Ethanol	25	0.57	2.07	0.55	1.17	0.51	2.56
	44	0.58	3.04	0.56	2.06	0.52	3.80
	60	0.58	3.81	0.54	3.41	0.55	4.45
1-Propanol	25	0.58	1.30	0.53	0.78	0.52	1.79
	44	0.59	2.21	0.54	1.63	0.54	2.67
	60	0.58	3.14	0.56	2.44	0.53	4.03
2-Propanol	25	0.56	1.39	0.51	0.86	0.55	1.62
	44	0.55	2.42	0.53	1.62	0.50	3.28
	60	0.56	3.15	0.55	2.40	0.53	3.91
1-Butanol	25	0.57	1.32	0.51	0.83	0.52	1.98
	44	0.58	2.20	0.53	1.61	0.53	2.96
	60	0.59	2.85	0.55	2.27	0.54	3.40
2-Methyl-1-propanol	25	0.56	0.89	0.50	0.57	0.50	1.00
	44	0.57	1.68	0.54	1.04	0.53	2.14
	60	0.58	2.30	0.57	1.56	0.53	3.19
1-Pentanol	25	0.57	1.10	0.50	0.75	0.50	1.56
	44	0.56	2.04	0.52	1.39	0.51	2.49
	60	0.57	2.74	0.56	1.75	0.53	3.74
3-Methyl-1-butanol	25	0.57	0.87	0.52	0.47	0.50	1.47
	44	0.58	1.69	0.51	1.22	0.53	2.12
	60	0.55	2.58	0.53	1.69	0.50	3.42

^a Values of *K* are expressed in g/g min^a

Table 4 Diffusion coefficients and permeation coefficients of polymer-solvent systems

Solvent	Temp. (°C)	$D \times 10^7$ (cm ² s ⁻¹)			$P \times 10^8$ ($\equiv DS$) (cm ² s ⁻¹)		
		PU	NBR	ECH	PU	NBR	ECH
Methanol	25	1.90	1.10	3.23	4.04	1.68	5.21
	44	3.69	2.99	6.00	8.66	5.19	10.76
	60	6.05	5.14	8.34	15.16	9.81	16.74
Ethanol	25	0.88	0.41	1.35	2.02	0.51	1.38
	44	1.94	1.41	3.26	5.06	2.09	4.14
	60	3.32	2.54	5.48	10.00	4.34	8.15
1-Propanol	25	0.47	0.12	0.71	1.27	0.17	0.69
	44	1.28	0.65	2.00	4.06	1.10	2.66
	60	2.18	1.92	3.63	8.21	4.07	6.22
2-Propanol	25	0.45	0.11	0.87	1.12	0.14	0.88
	44	1.05	0.59	1.85	2.96	0.88	2.24
	60	1.95	1.62	3.63	6.25	2.94	5.72
1-Butanol	25	0.42	0.12	0.66	1.39	0.18	0.83
	44	1.15	0.56	1.95	4.22	0.97	3.07
	60	2.12	1.56	3.72	8.68	3.29	7.27
2-Methyl-1-propanol	25	0.19	0.05	0.17	0.58	0.07	0.22
	44	0.67	0.29	1.24	2.10	0.48	1.53
	60	1.45	0.98	2.29	5.23	1.97	3.58
1-Pentanol	25	0.30	0.06	0.40	0.94	0.08	0.38
	44	0.87	0.36	1.44	2.91	0.56	1.74
	60	1.54	1.06	2.56	6.10	2.08	4.29
3-Methyl-1-butanol	25	0.22	0.04	0.18	0.73	0.06	0.27
	44	0.72	0.23	1.23	2.44	0.36	1.62
	60	1.67	0.64	1.66	6.19	1.22	2.80

value of $\ln(8/\pi^2)$ or -0.21 , predicted for Fickian sorption with a constant *D*. The diffusion coefficient decreases systematically in the case of linear alcohols from methanol to 1-pentanol; similarly, with the branched alcohols, *D* decreases from 2-propanol to 3-methyl-1-butanol (except for PU + 3-methyl-1-butanol).

The large diffusivities in ECH membrane are likely to be a direct consequence of the exceedingly open structure of the polymer. Presumably, the presence of the Cl group in conjunction with the long alkyl chain on the adjacent backbone carbon forces the polymer backbone into a conformation which confers rather extraordinary rigidity to the chain and loose interactive packing. The resulting polymer, with a large amount of excess volume, permits relatively easy passage of alcohol molecules without requiring significant cooperative movement of polymer chain segments.

The effect of diffusant structure on *D* is important in the design of additives for practical applications. Increasing the chain length of alcohols results in a decrease in *D*; this dependence is displayed in Figure 11 which shows the relationship between *D* and K_s with the molar volume of linear alcohols studied in the series. It is obvious that the curves of $\ln D$ or $\ln K_s$ versus molar volume show the same general variations, indicating that both K_s and *D* are directly correlated with each other and that their effects on molar volume of the penetrant

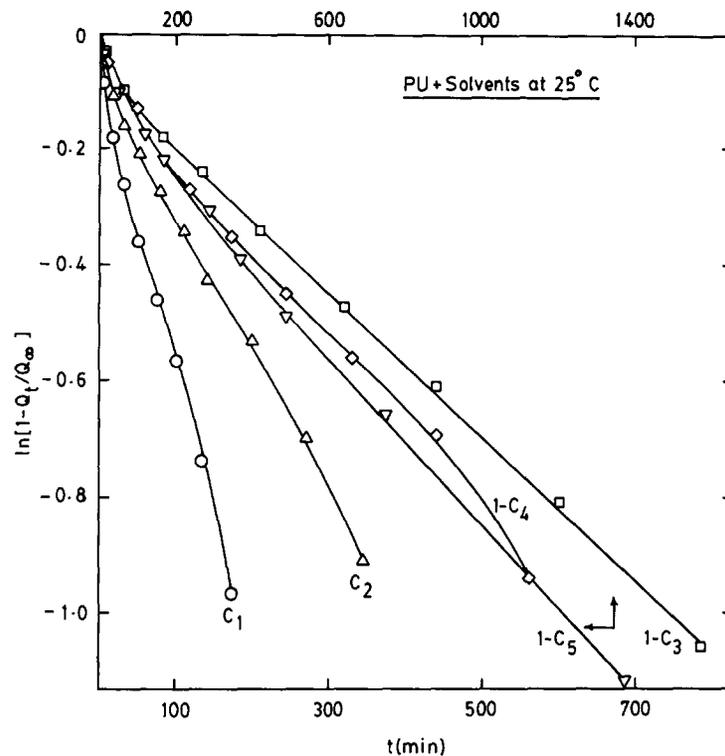


Figure 10 Long-time sorption plots for PU with solvents at 25°C

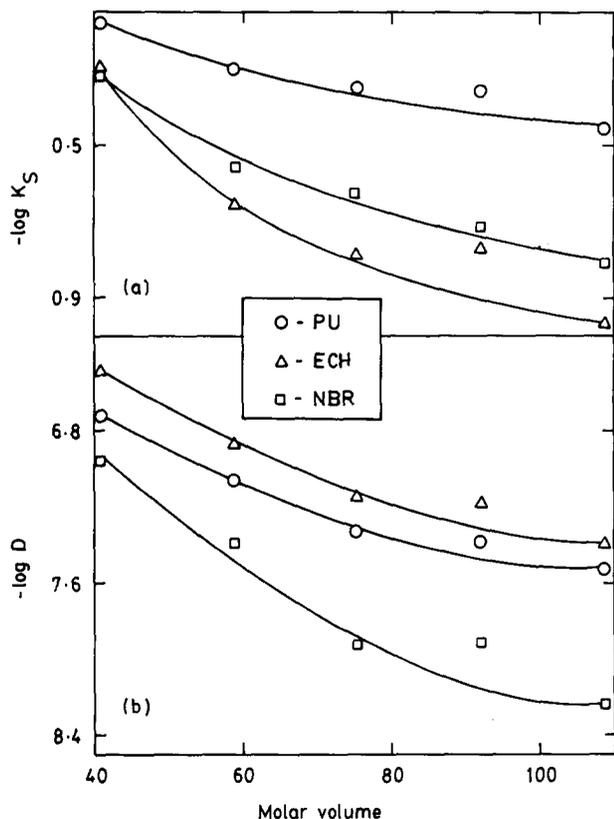


Figure 11 Dependence of (a) $\log K_s$ and (b) $\log D$ on molar volume of solvents for elastomer + solvent systems at 25°C

molecules in the heterogeneous solid-state polymer matrices are similar. The effect of chain length on diffusivity may be interpreted as a direct reflection of the molecular motion of the penetrant in the polymer matrix, while the effect of molar volume on diffusivity or sorptivity is generally correlated with the availability of

the free volume between polymer chains for the required transport.

There are two categories of compounds showing variable diffusion behaviours with respect to their molecular sizes. The first category contains larger molecules, such as 2-propanol, 2-methyl-1-propanol and 3-methyl-1-butanol, in which the polar hydroxy functional groups are attached to one terminal of each of the molecules. This group of compounds is found to exhibit slower diffusion rates. It seems that the interaction through hydrogen-bonding between the -OH group of these solvents and the polar groups of the polymer chains is responsible for the slower diffusion rates. However, it is also possible that other secondary forces, such as hydrophobic bonding, play an important role in the polymer-solvent interactions¹.

Diffusion coefficients, as calculated from the procedure of Joshi and Astarita⁴⁸ for alcohols in polymer membranes, are presented as a function of penetrant concentration in Figure 12 for PU + alcohols at 44°C. The sigmoidal shapes of the resulting curves are at variance not only with the concentration dependence of solvent molecules in rubbery polymers but also with the normally observed exponential increase of diffusion coefficient for most of the plasticizing penetrants in synthetic polymers¹. These data seem to reflect a competition between membrane plasticization and penetrant clustering, perhaps by association of the hydroxyl groups. It may be noted that at higher concentration of alcohols in the polymer membranes, the diffusion coefficients are lower. Diffusion increases considerably as penetrant concentration increases, and later falls off rapidly, probably due to the lack of a corresponding increase in polymer conformation. For lower alcohols, namely methanol and ethanol, the diffusivity passes through sharp maxima, indicating a considerable dependence of penetrant diffusivity on their concentrations. However, this effect is not so significant for higher alcohols.

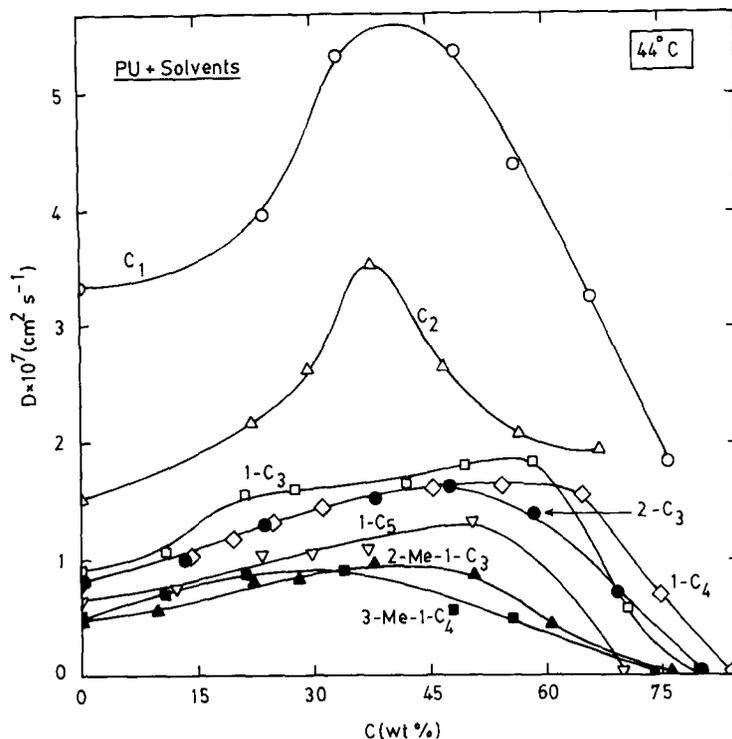


Figure 12 Dependence of diffusion coefficient, D , on concentration (wt%) for PU with solvents at 44°C

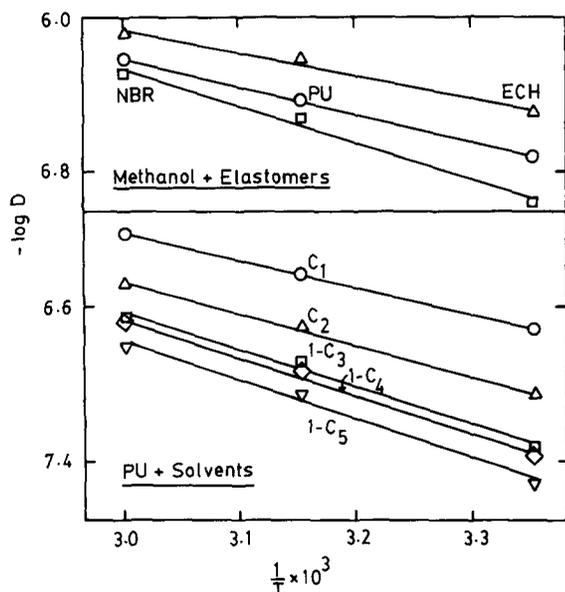


Figure 13 Arrhenius plots of diffusivity for methanol with elastomers and for PU with solvents

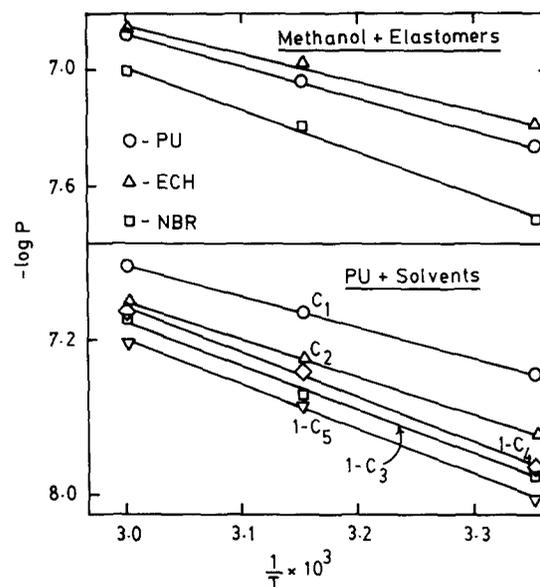


Figure 14 Arrhenius plots of permeability for methanol with elastomers and for PU with solvents

Considering the diffusion and permeation to be activated processes, attempts were also made to estimate the apparent activation parameters of diffusion E_D , as well as of permeation E_P , using the standard Arrhenius relationship:

$$\log X = \log X_0 - E_X/2.303RT \quad (9)$$

where X refers to either D or P ; X_0 is a constant representing D_0 or P_0 ; E_X gives the value of either E_D or E_P , depending upon the transport process under consideration. The mechanism by which small molecules permeate through rubbery or glassy amorphous polymers has been described by many authors⁴⁹⁻⁵³. From a

least-squares fit of the linear plots of $\log X$ versus $1/T$, as shown in Figures 13 and 14 for diffusivity and permeability respectively, the E_D and E_P values have been calculated. These results are given in Table 5. The uncertainties in the estimations of E_D or E_P vary from 0.02 to 0.03 units. The heat of sorption was calculated from the difference: $\Delta H_s = E_P - E_D$. The activation energy required to complete the unit diffusion jump of one mole of the diffusant molecule. From the representative plots given in Figures 13 and 14, straight lines are observed for all the polymer-solvent systems indicating the range of applicability of temperatures used in this investigation.

Table 5 Activation parameters and thermodynamic quantities for polymer-solvent systems

Solvent	Parameter ^a	Polymer membrane		
		PU	NBR	ECH
Methanol	E_a	25.12	32.41	19.47
	E_D	27.40	36.59	22.54
	E_p	31.22	41.91	27.71
	ΔH_s	3.82	5.32	5.17
	$-\Delta S$	28.85	26.62	26.70
Ethanol	E_a	28.78	46.49	34.44
	E_D	31.58	43.69	33.25
	E_p	37.75	50.98	42.18
	ΔH_s	6.17	7.29	8.94
	$-\Delta S$	23.41	24.69	20.84
1-Propanol	E_a	34.01	60.50	37.77
	E_D	36.50	66.27	38.74
	E_p	44.34	75.59	52.20
	ΔH_s	7.84	9.34	13.46
	$-\Delta S$	18.72	19.08	8.32
2-Propanol	E_a	33.62	62.08	33.49
	E_D	34.74	63.59	33.47
	E_p	40.60	72.40	43.79
	ΔH_s	5.86	8.80	10.31
	$-\Delta S$	25.98	21.91	18.69
1-Butanol	E_a	35.67	58.86	31.91
	E_D	38.39	59.97	40.98
	E_p	43.43	68.68	51.48
	ΔH_s	5.09	8.71	10.51
	$-\Delta S$	28.01	22.70	17.90
2-Methyl-1-propanol	E_a	46.04	71.26	65.49
	E_D	48.59	71.08	62.83
	E_p	52.12	79.40	66.76
	ΔH_s	3.53	8.31	3.93
	$-\Delta S$	33.88	24.36	39.92
1-Pentanol	E_a	37.34	68.67	51.77
	E_D	38.77	69.33	44.28
	E_p	44.42	77.62	57.44
	ΔH_s	5.64	8.30	13.17
	$-\Delta S$	28.21	26.10	12.83
3-Methyl-1-butanol	E_a	35.64	66.58	55.29
	E_D	48.50	66.26	54.16
	E_p	50.50	73.51	56.32
	ΔH_s	1.99	7.26	2.16
	$-\Delta S$	39.69	29.33	46.19

^a Values of E_a , E_D , E_p and ΔH_s are expressed in kJ mol^{-1} and ΔS in $\text{J mol}^{-1} \text{K}^{-1}$.

From the results given in Table 5 it is obvious that although the values of E_D and E_p generally vary systematically with the size of the diffusant molecules, some discrepancies are observed with higher alcohols. This may be the result of extensive hydrogen bonding between PU, NBR and ECH chains with the alcohol molecules. Such effects are shown earlier for a phase-segregated PU membrane in the presence of alcohols of the type used here^{23,43,46}.

A comparison of activation energies for diffusion is difficult because literature data are not available for ECH and NBR membranes. However, a comparison of the present E_D values with those of Hung and Autian⁴³ suggests that our E_D values are slightly lower, but are still comparable considering the different morphologies of the PU samples used in two different studies. For linear alcohols there is a systematic increase in E_D with chain length. Thus, E_D varies from 27.4 kJ mol^{-1} for methanol to 38.8 kJ mol^{-1} for 1-pentanol; however, with the branched alcohols, the apparent values of E_D are quite high and range from 34.7 kJ mol^{-1} for 2-propanol to as high as 48.5 kJ mol^{-1} for 3-methyl-1-

butanol. Similarly, for ECH, the E_D values range from 22.5 kJ mol^{-1} for methanol to $44.28 \text{ kJ mol}^{-1}$ for 1-pentanol. On the other hand, the E_D values for NBR are somewhat higher and range from 36.6 kJ mol^{-1} for methanol to 69.3 kJ mol^{-1} for 1-pentanol. The same dependences are shown by apparent activation energy values E_p , for the permeation process, and also by the E_a values as determined from the Arrhenius plots of $\log k$ versus $1/T$ (not displayed graphically).

Heats of sorption provide additional information about the molecular transport of liquids into the polymer membranes. The quantity ΔH_s is a composite parameter involving both Henry's law and Langmuir (hole filling) type sorption mechanisms. The Henry's law mode requires both the formation of a site in the polymer matrix and the dissolution of a species into that site. The formation of a site involves an endothermic contribution to this process. On the other hand, with the Langmuir mode the site already exists within the polymer matrix, and consequently the sorption by hole filling gives higher exothermic heats of sorption. For all the polymer-solvent systems, ΔH_s values are positive and increase systematically from methanol (C_1) to 1-propanol (C_3). However, for higher alcohols, i.e. C_4 to C_5 including the branched alcohols, the ΔH_s values vary within a narrow range. This is expected because the size of these penetrants is almost identical. For 3-methyl-1-butanol the ΔH_s values are smaller than those of methanol for PU and ECH membranes, whereas for ethanol or 3-methyl-1-butanol NBR gives identical ΔH_s values indicating similar sorption mechanisms for these penetrant-polymer systems.

From the data given in Table 5 it is obvious that higher values of E_D or E_p are observed for NBR, whereas for PU and ECH membranes these values are somewhat smaller. Moreover, an increase in the values of E_D or E_p corresponds to the increase in the size of the penetrants. This suggests that the larger molecules require more energy to create what are known as Eyring holes within the polymer matrix. The positive values of ΔH_s suggest that the sorption mechanism in these systems is dominated by Henry's law. Since the values of ΔH_s are calculated from the difference $E_p - E_D$, an alternative explanation for high heats of sorption may be the higher activation energy of permeation as compared to activation energy due to the diffusion processes; this may be caused by transport along the boundaries of the polymer domain morphology because of the rigid nature of the NBR membrane. With the lower equilibrium sorption values as compared to PU and ECH membranes, due to the lack of macroscopic directional order in these membrane materials, the foregoing hypothesis seems appropriate because of the chain immobilization effect. The high values of activation energy also suggest the relaxation of large polymer segments at the advancing boundary, and this has been generally accepted⁵⁰ for the rigid nature of the backbone system of NBR.

The equilibrium sorption as calculated²³ from the plateau regions of the sorption curves is regarded as a thermodynamic equilibrium sorption constant designated by the symbol K_s as shown typically in Figure 15. By using the van't Hoff equation:

$$\log K_s = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad (10)$$

we have calculated the standard enthalpy, ΔH° , and entropy, ΔS° , of sorption. As expected, the values of ΔH°

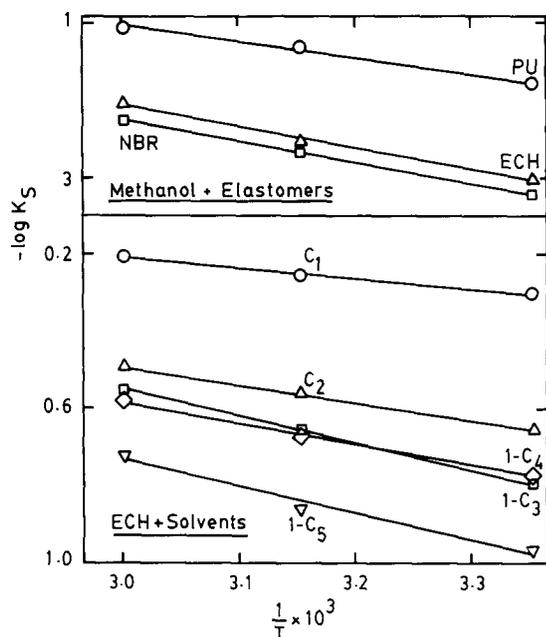


Figure 15 van't Hoff plots of sorption constant for methanol with elastomers and for ECH with solvents

calculated from the slope of equation (10) are in close agreement with the values calculated from the difference $E_p - E_D$. This further suggests that the molecular transport of organic solvents in rubbery polymer systems is controlled by a combination of sorption, diffusion and permeation mechanisms. The negative values of ΔS° , as observed for all the systems, indicates that the liquid state structure of alcohol molecules is retained even in the sorbed state within the polymer matrices.

CONCLUSIONS

Using a simple mass-uptake technique, the detailed analysis of sorption and diffusion of aliphatic alcohols in PU, NBR and ECH membranes has been carried out over the temperature range 25–60°C. By its very nature, the technique measures diffusion under kinetic rather than equilibrium conditions. Diffusion coefficients measured in this manner ranged from $4 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ to a maximum of $8 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$; this depends to a great extent on the type and nature of polymer backbones in addition to physico-chemical characteristics of the penetrant molecules. It was found that the temperature dependency of diffusion could be well fitted, within a relatively narrow range of temperatures, to an Arrhenius expression above the glass transition temperature, T_g , values of the polymer membranes. The activation energy for diffusion was found to vary from 23 to 71 kJ mol^{-1} depending on the polymer-solvent system.

In general, the diffusion of low molecular weight penetrants in rubbery polymers above T_g is believed to be facilitated by a temperature-dependent chain-segmental relaxation mechanism⁵⁴. The molecular structures of alcohols are considerably more complex than those of simple organic solvents in terms of conformation. Furthermore, in the associated form their molecular sizes are greater than those of most common polymer repeat units. For these reasons, a fundamental understanding of the unit flow event and its associated jump length involves a level of complexity beyond that required for simple

penetrants. Therefore, in future studies, it seems worthwhile to investigate the steric/conformational details of the penetrant molecule and to develop a concept of how its overall shape might be favourably incorporated into, and move through, a local array of polymer chains.

ACKNOWLEDGEMENTS

The authors are grateful to the Council of Scientific and Industrial Research, Extramural Research Division, New Delhi for a major grant support (No. 01 (1239)/92/EMR-II) to carry out this research.

REFERENCES

- 1 Crank, J. S. and Park, G. S. (Eds) 'Diffusion in Polymers', Academic Press, London, 1968
- 2 Aminabhavi, T. M., Aithal, U. S. and Shukla, S. S. *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* 1989, **C29**, 319
- 3 Barrer, R. M. 'Diffusion In and Through Solids', Cambridge University Press, New York, 1941
- 4 Barrer, R. M. *J. Phys. Chem.* 1957, **61**, 178
- 5 Meares, P. *J. Am. Chem. Soc.* 1954, **76**, 3415
- 6 Bueche, F. *J. Chem. Phys.* 1953, **21**, 1850
- 7 Brandt, W. W. *J. Phys. Chem.* 1959, **63**, 1080
- 8 DiBenedetto, A. T. *J. Polym. Sci. A*, 1963, **1**, 3477
- 9 Paul, D. R. and DiBenedetto, A. T. *J. Polym. Sci., C: Polym. Symp.* 1965, **10**, 17
- 10 Vrentas, J. S. and Duda, J. L. *J. Polym. Sci., Polym. Phys. Edn* 1977, **15**, 403; 417
- 11 Vrentas, J. S. and Duda, J. L. *Macromolecules* 1976, **9**, 785
- 12 Vrentas, J. S. and Duda, J. L. *J. Polym. Sci., Polym. Phys. Edn* 1979, **17**, 1085
- 13 Crank, J. S. 'The Mathematics of Diffusion', 2nd edn, Clarendon Press, Oxford, 1975
- 14 Weisenberger, L. A. and Koenig, J. L. *Macromolecules* 1990, **23**, 2454
- 15 Billingham, N. C., Calvert, P. D. and Uzuner, A. *Eur. Polym. J.* 1989, **25**, 839
- 16 Gall, T. P., Lasky, R. C. and Kramer, E. J. *Polymer* 1990, **31**, 1491
- 17 Sanopoulou, M. and Petropoulos, J. H. *J. Membr. Sci.* 1990, **52**, 325
- 18 McKenna, G. B., Flynn, K. M. and Chen, Y. *Polymer* 1990, **31**, 1937
- 19 Barson, C. A. and Dong, Y. M. *Eur. Polym. J.* 1990, **26**, 329
- 20 Leclerc, B., Conrath, G., Falson-Reig, F. and Couarraze, G. *Eur. Polym. J.* 1989, **25**, 1203
- 21 Aithal, U. S., Aminabhavi, T. M. and Cassidy, P. E. *Am. Chem. Soc. Symp. Ser.* 1990, **423**, 351
- 22 Aithal, U. S., Aminabhavi, T. M. and Cassidy, P. E. *J. Membr. Sci.* 1990, **50**, 225
- 23 Aithal, U. S., Aminabhavi, T. M. and Shukla, S. S. *J. Chem. Eng. Data* 1990, **35**, 298
- 24 Aithal, U. S. and Aminabhavi, T. M. *Polymer* 1990, **31**, 1757
- 25 Aminabhavi, T. M. and Aithal, U. S. *J. Appl. Polym. Sci.* 1990, **41**, 2113
- 26 Aminabhavi, T. M., Harogoppad, S. B. and Khinnavar, R. S. *Polym. Plast. Technol. Eng.* 1991, **30**, 453
- 27 Harogoppad, S. B. and Aminabhavi, T. M. *Polymer* 1990, **31**, 2346
- 28 Harogoppad, S. B. and Aminabhavi, T. M. *Polymer* 1991, **32**, 870
- 29 Harogoppad, S. B. and Aminabhavi, T. M. *J. Appl. Polym. Sci.* 1991, **42**, 2329
- 30 Harogoppad, S. B. and Aminabhavi, T. M. *Macromolecules* 1991, **24**, 2598
- 31 Khinnavar, R. S. and Aminabhavi, T. M. *Polym. Plast. Technol. Eng.* 1991, **30**, 529
- 32 Harogoppad, S. B. and Aminabhavi, T. M. *Polym. Commun.* 1991, **32**, 120
- 33 Khinnavar, R. S. and Aminabhavi, T. M. *J. Appl. Polym. Sci.* 1991, **42**, 2321
- 34 Aithal, U. S. and Aminabhavi, T. M. *J. Appl. Polym. Sci.* 1991, **42**, 2837
- 35 Riddick, J. A., Bunger, W. B. and Sakano, T. K. (Eds) 'Techniques of Chemistry, Vol. II, Organic Solvents', 4th edn, Wiley, New York, 1986

- 36 Sfrakis, A. and Rogers, C. E. *Polym. Eng. Sci.* 1981, **21**, 542
37 Aminabhavi, T. M. and Harogoppad, S. B. *J. Chem. Educ.* 1991, **68**, 343
38 Franson, N. M. and Peppas, N. A. *J. Appl. Polym. Sci.* 1983, **28**, 1299
39 Davidson, G. W. R. and Peppas, N. A. *J. Controlled Release* 1986, **3**, 243
40 Mackenzie, C. I. and Scarlan, J. *Polymer* 1984, **25**, 559
41 Harogoppad, S. B. PhD Thesis, Karnatak University, Dharwad, India, 1991
42 Korsmeyer, R. W., Meerwall, E. W. and Peppas, N. A. *J. Polym. Sci., Polym. Phys. Edn* 1986, **24**, 409
43 Hung, G. W. C. and Autian, J. *J. Pharm. Sci.* 1972, **61**, 1094
44 Huang, R. Y. M. and Lin, V. J. C. *J. Appl. Polym. Sci.* 1968, **12**, 2615
45 Huang, R. Y. M. and Jarvis, N. R. *J. Appl. Polym. Sci.* 1970, **14**, 2341
46 Hopfenberg, H. B., Schneider, N. S. and Votta, F. *J. Macromol. Sci. Phys.* 1969, **B3**, 751
47 Garbarini, G. R., Eaton, R. F., Kwei, T. K. and Tobolsky, A. V. *J. Chem. Educ.* 1971, **48**, 226
48 Joshi, S. and Astarita, G. *Polymer* 1979, **20**, 455
49 Stannett, V. T., Hopfenberg, H. B. and Petropoulos, J. H. *Int. Rev. Sci.: Phys. Chem., Ser. 1* 1972, **8**, 329
50 Rogers, C. E. and Machin, E. *CRC Crit. Rev. Macromol. Sci.* 1972, 245
51 Aminabhavi, T. M., Aithal, U. S. and Shukla, S. S. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* 1988, **C28**, 421
52 Petropoulos, J. H. *J. Polym. Sci., Polym. Phys. Edn* 1985, **23**, 1309
53 Billovits, G. F. and Durning, C. J. *Chem. Eng. Commun.* 1989, **82**, 21
54 Mauritz, K. A., Storey, R. F. and George, S. E. *Macromolecules* 1990, **23**, 441