Molecular transport of methyl- and methoxy-substituted benzenes into bromobutyl rubber, chlorosulfonated polyethylene and epichlorohydrin membranes

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The diffusion and sorption of monocyclic aromatics such as benzene, toluene, *p*-xylene, 1,3,5-trimethylbenzene and methoxybenzene into bromobutyl rubber, chlorosulfonated polyethylene and epichlorohydrin membranes was investigated over the temperature range 25–60°C using a sorption gravimetric technique. The anomalous behaviour of some polymer–solvent systems was attributed to the greater relaxation of polymer chain segments than the movement of solvent molecules within the polymer matrices. Transport results were analysed using the Fickian model. A decrease in transport coefficients with an increase in diffusant size was observed. Arrhenius activation parameters were calculated from the temperature dependence of transport coefficients. Experimental and computed results were used to study polymer–solvent interactions in terms of polymer structures and the nature of solvent molecules.

(Keywords: molecular transport; bromobutyl rubber; polyethylene)

INTRODUCTION

The diffusion and sorption of small organic molecules into heterophase polymer media is a complex process with many technologically important applications[1–3]. Studies of this process are important for the understanding of polymer properties ranging from processing and production to end use and shelf-life. Understanding the mobility and distribution of organic solvent molecules in polymeric systems is crucial to the optimization of polymerization rates, mixing of additives, devolatilization and the overall barrier properties of the resulting materials. Improvements in the control of mass transport into and out of polymer membranes used as barrier materials is important in many packaging industries[4]. Solvent transport into polymer matrices is influenced by relatively small changes in the chemical structure and size of the diffusing molecule, in addition to morphological characteristics of the membrane materials. The effect of diffusant structure on the diffusion coefficient is important in the design of additives/plasticizers for industrial polymers[5].

In practical applications, polymeric materials undergo swelling when placed in contact with aggressive solvents. Several organic solvents, including aromatic hydrocarbons, oils, alkanes and ketones, are known to cause the swelling of a variety of polymers. A high degree of swelling of a polymer matrix immersed in a given solvent indicates that the polymer is not suitable for use in that environment, because the solvent causes the polymeric bonds to be weakened leading to failure[6–8]. However, in spite of its importance, there have been few studies on the swelling behaviour of unfilled rubbers[9,10]. In practice, fillers like carbon black and other additives are incorporated into the polymer network structure to enhance mechanical strength and durability. With filled polymeric systems, the penetration of solvent molecules takes place through co-operative movement by the so-called micro-Brownian motion of the polymer segments[11]. Hence, in addition to polymer–solvent interactions[12], the rate of diffusion of solvent into the polymer matrix is generally controlled by the molecular mobility of the chain segments.

In earlier papers[13–27], we investigated the molecular transport of organic liquids into polymer membranes of commercial interest. As a continuation of this research, we now present sorption and diffusion results of methyl- and methoxy-substituted benzenes into bromobutyl rubber (BIIR), chlorosulfonated polyethylene (CSM) and epichlorohydrin (ECO) membranes. Hardly any solvent sorption data are available in the literature for these membranes.

Bromobutyl rubber has low gas permeability with good weather and ozone resistivity. It is used mainly for inner tubes of tubeless tyres. It is also blended with other rubbers for use in linings, belts, hoses and seals. Chlorosulfonated polyethylene is good for hot-air ageing resistance. It has good flame retardance, abrasion and weather resistance. Epichlorohydrin has good resistance to swelling in oils,

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good heat resistance and excellent temperature flexibility. It is used in the automotive industry for making seals, diaphragms and hoses. In all these applications, the membranes are likely to come into contact with aromatic hydrocarbons and other liquids.

In this paper, we will present diffusion, sorption and permeation results of benzene, toluene, *p*-xylene, 1,3,5-trimethylbenzene (mesitylene) and methoxybenzene (anisole) into BIIR, CSM and ECO membranes. The transport parameters are calculated for each of the polymer–solvent systems using a sorption gravimetric method. From a study of the temperature dependence of these parameters, the energy of activation and heats of sorption for the transport processes in question are computed. The experimental results and the computed quantities are used to study the extent of polymer–solvent interactions.

EXPERIMENTAL

Materials

Polymer sheets of BIIR, CSM and ECO (0.15 cm × 15 cm × 15 cm) were moulded. During sample fabrication, a 30 cm laboratory mill was used to mix and prepare the rubber compounds for moulding. The ECO polymer sheets were press-cured at 176°C for 30 min and the CSM and BIIR membranes were press-cured, respectively, at 155 and 165°C for 30 min. The compositions and some representative engineering properties of the membranes are given in *Table 1*.

All the reagent grade solvents, namely benzene, toluene, *p*-xylene, 1,3,5-trimethylbenzene and methoxybenzene, were distilled twice before use to ensure purity. Their measured physical properties, such as refractive index and density at 25°C, agreed well with literature values[28].

Table 1 Elastomer compositions and their properties

Compound	BIIR	CSM	ECO
Bromobutyl X-2[a]	100.0	–	–
Hyphalon 20[b]	–	100.0	–
Hydrin[c]	–	–	100.0
Carbon black	50.0[d]	40.0[d]	40.0[e]
Sulfur	0.5	1.0	–
Zinc oxide	5.0	–	–
Benzothiazyl disulfide	1.25	–	–
90% Litharge in polymeric binder	–	27.0	–
Tetramethylthiuram monosulfide	–	2.0	–
Zinc stearate	–	–	1.0
Dibasic lead phosphite	–	–	5.0
Dibasic lead phthalate	–	–	7.0
75% Ethylene thiourea in EPR	–	–	1.0
Totals	156.75	170.0	154.0
Specific gravity[f]	1.13	1.44	1.44
Hardness (Shore A)[g]	50.0	75.0	62.0
Tensile strength (MPa)[h]	9.3103	18.9655	13.0345
Ultimate elongation (%)[h]	540.0	170.0	440.0
E 50 modulus (MPa)[h]	0.6897	3.3104	1.5172
E 100 modulus (MPa)[h]	0.9655	8.8280	2.8276
E 200 modulus (MPa)[h]	2.0000	–	6.5517
E 300 modulus (MPa)	3.8621	–	10.0670

[a] From Polysar
[b] From Du Pont
[c] From Zuri Chemical
[d] N774
[e] N550
[f] ASTM D792
[g] ASTM D2240
[h] ASTM D412

The polymer samples were dried for several days in a desiccator prior to use and were cut into circles (diameter 1.96 cm) using a sharp-edged steel die. The membrane thicknesses were measured at several points to 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 samples and this value is used in all the calculations. The other experimental details are the same as those previously reported[13–20].

RESULTS AND DISCUSSION

The equilibrium sorption results are expressed in terms of mole per cent uptake[29] (C_x) of the solvent by the polymer membranes. Data are given in *Table 2* for various polymer–solvent systems for the temperature interval 25–60°C. The sorption plots, i.e. mole per cent increase (C_t) *versus* the square root of time ($t^{1/2}$) for ECO, CSM and BIIR membranes at 25°C are presented in *Figures 1–3*, respectively. For the sake of clarity, the sorption curves at higher temperatures, namely 44 and 60°C, are not shown. However, the same pattern is also observed at these temperatures.

For all the penetrant–polymer systems, initially sorption increases linearly up to ~50% equilibrium saturation and later levels off. The equilibrium saturation curves are characterized by the sorption coefficients (*S*). As mentioned earlier[13–16,30], the sorption coefficients are to be regarded as the true equilibrium thermodynamic sorption constants (K_s). With the ECO and CSM membranes, there is a systematic decrease in *S* or K_s values from benzene to 1,3,5-trimethylbenzene at all the temperatures studied. However, methoxybenzene, with a molecular size somewhat closer to toluene, exhibits intermediary equilibrium sorption between benzene and toluene for ECO membrane. In the case of BIIR, sorption decreases systematically from toluene to methoxybenzene. However, as compared to toluene, benzene exhibits smaller *S* values at 25 and 44°C but higher values at 60°C. However, BIIR membrane in the presence of methoxybenzene shows the smallest *S* values as compared to the other polymers, and this value varies from 0.308 to 0.564 mol%. This trend is indicative of the dependence of the size of the penetrant molecule on sorption in the case of BIIR membrane. Generally, BIIR exhibits higher sorption than CSM and ECO for the selected methyl-substituted benzenes. However, the presence of the methoxy group (as in methoxybenzene) seems to hinder movement within BIIR yielding the smallest *S* value. This is not the case for methoxybenzene with CSM and ECO membranes. For the latter membranes, the sorption of methoxybenzene is considerably higher. For benzene, sorption follows the trend: ECO > BIIR > CSM and for toluene the trend is BIIR > ECO > CSM. However, in the case of *p*-xylene and 1,3,5-trimethylbenzene, the sorption shows the trend: BIIR > CSM > ECO. On the other hand, methoxybenzene shows a reverse trend, i.e. its *S* values decrease from ECO to CSM to BIIR. This clearly indicates the effect of backbone structures on the transport behaviour of penetrant molecules. Conversely, the sorption properties of the membranes are greatly influenced by the presence of methyl groups on the parent benzene molecule.

From the sorption plots given in *Figures 1–3* and the data given in *Table 2*, it is found that for CSM and ECO membranes sorption decreases with increasing

Table 2 Thermodynamic sorption constants (S), n and K ($g\,g^{-1}\,min^{-n}$) for polymer–solvent systems at different temperatures

Temp. (°C)	S (mol%)			BIIR		CSM		ECO	
	BIIR	CSM	ECO	n	K ($\times 10^2$)	n	K ($\times 10^2$)	n	K ($\times 10^2$)
Benzene									
25	1.505	1.057	1.780	0.58	2.64	0.65	2.76	0.64	2.15
44	1.831	1.079	1.780	0.62	2.95	0.66	3.74	0.66	2.79
60	2.128	1.105	1.740	0.63	3.46	0.64	4.83	0.66	3.34
Toluene									
25	1.753	0.951	1.197	0.61	2.53	0.64	3.08	0.62	2.22
44	1.940	0.940	1.240	0.63	2.99	0.65	3.94	0.64	3.06
60	2.066	0.957	1.238	0.65	3.33	0.66	4.17	0.65	3.67
p-Xylene									
25	1.719	0.790	0.575	0.61	2.29	0.64	2.44	0.55	2.32
44	1.827	0.767	0.678	0.62	2.90	0.63	3.25	0.59	2.80
60	1.941	0.787	0.708	0.64	3.20	0.63	3.78	0.60	3.24
1,3,5-Trimethylbenzene									
25	1.654	0.652	0.331	0.63	1.67	0.63	1.45	0.54	1.88
44	1.727	0.647	0.411	0.63	2.30	0.63	2.37	0.57	2.44
60	1.809	0.669	0.640	0.62	2.69	0.62	2.63	0.60	1.92
Methoxybenzene									
25	0.308	0.815	1.686	0.50	2.15	0.61	2.33	0.63	1.89
44	0.441	0.834	1.674	0.50	3.46	0.61	3.11	0.64	2.44
60	0.564	0.882	1.695	0.56	3.33	0.62	3.40	0.65	2.99

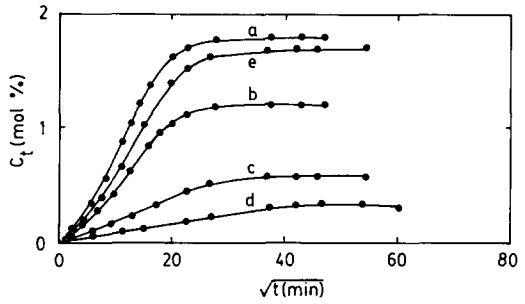

Figure 1 Mole per cent sorption *versus* the square root of time for ECO with solvents at 25°C: (a) benzene; (b) toluene; (c) *p*-xylene; (d) 1,3,5-trimethylbenzene; (e) methoxybenzene

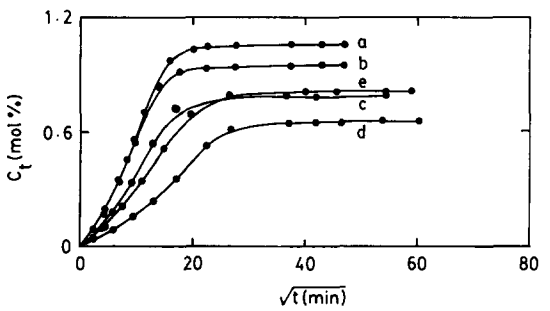

Figure 2 Mole per cent sorption *versus* the square root of time for CSM with solvents at 25°C. Curves a–e as in *Figure 1*

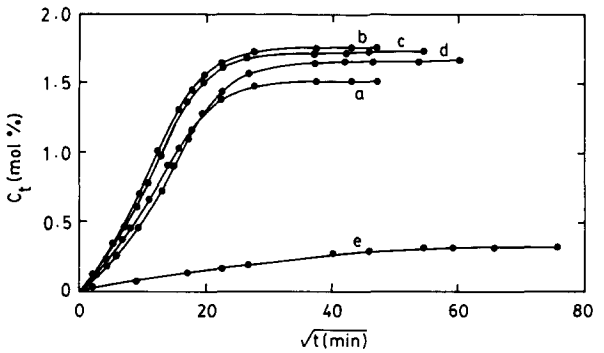

Figure 3 Mole per cent sorption *versus* the square root of time for BIIR with solvents at 25°C. Curves a–e as in *Figure 1*

molecular size of the penetrant molecules. However, with BIIR, benzene shows lower sorption than toluene but *p*-xylene, 1,3,5-trimethylbenzene and methoxybenzene exhibit systematically lower S values than toluene. The decreased sorption rate might be due to lower equilibrium penetrant molar concentrations and, consequently, lower osmotic stresses. With ECO and CSM membranes, the time required to attain equilibrium sorption is directly related to the molecular size of the penetrants (*Figures 1* and *2*), suggesting the exceedingly open structure of these membranes. However, with BIIR the equilibrium times do not show any direct relationship with the penetrant size. For instance, with BIIR, except for methoxybenzene (which requires a long time for equilibrium saturation), the solvents all require similar times. This further confirms that the size of the penetrant molecule does not bear any direct relationship with the time to attain equilibrium saturation when BIIR is considered as the barrier material (*Figure 3*).

An interesting observation of the present study is that as the temperature increases, sorption generally increases but, in some systems, there is no systematic trend. For instance, for the ECO and benzene system, S decreases with an increase in temperature. This effect (*Figure 4*) is

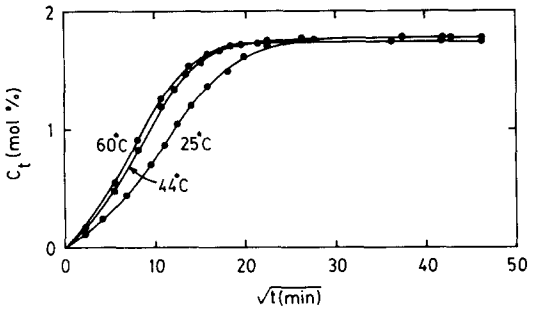

Figure 4 Temperature dependence of mole per cent sorption *versus* the square root of time for ECO with benzene

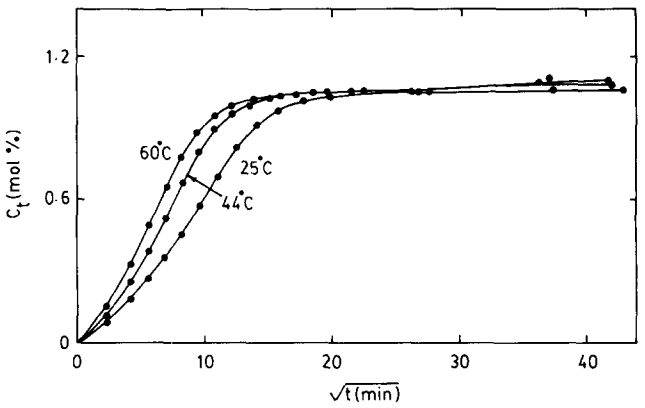

Figure 5 Temperature dependence of mole per cent sorption *versus* the square root of time for CSM with benzene

not an experimental artifact but is a result of the induced crystallinity of the polymer chain segments at higher temperatures in the presence of benzene. The induced crystallinity reduces the free energy of mixing thereby leading to a decrease in solvent uptake. Such effects have also been studied earlier by Harogoppad and Aminabhavi[31] and by Barr-Howell *et al.*[32]. On the other hand, for CSM with toluene, *p*-xylene or methoxybenzene, we could not observe any systematic variation of S with temperature. Also, the increase in S at higher temperatures is not considerable for the CSM and benzene system (*Figure 5*). However, for the BIIR and benzene system clearly separated equilibrium sorption data could be seen at different temperatures (*Figure 6*). For BIIR, the sorption of 1,3,5-trimethylbenzene is quite different compared to the other solvents in that its behaviour drastically changes at higher temperatures. At lower temperatures (i.e. 25 and 44°C), the sorption more closely resembles a Fickian mechanism. However, at 60°C, the sorption did not seem to reach equilibrium even after 1 week of continuous liquid immersion. This suggests that chemical degradation of BIIR has occurred in the presence of 1,3,5-trimethylbenzene. This was also confirmed by the deep coloration of the surrounding solvent after prolonged exposure. However, such effects did not occur with ECO and CSM membranes and both these membranes remained intact.

In order to gain a deeper understanding of the transport mechanism, sorption results have been fitted to the empirical relation[13–15]:

$$\log\left(\frac{C_t}{C_\infty}\right) = K + n\log t \qquad (1)$$

where K is a characteristic constant of the polymer–solvent system and the value of n indicates the nature of the transport mechanism. From a least-squares procedure, the values of K and n have been estimated for each of the polymer–solvent systems (*Table 2*). The values of n are accurate to within ± 0.01. Generally, an increase in K is observed with temperature but we could not observe any systematic dependence of n on temperature. The n values for the systems vary from 0.50 to 0.66 indicating the transport mechanism to be of anomalous type but not necessarily Fickian or non-Fickian. This fact is also supported by the slightly sigmoidal shapes of the sorption curves, indicating the behaviour that is observed follows roughly what could be expected of a nearly, but not completely, ideal 'Fickian' mechanism in elastomers well above their glass transition temperatures. This anomalous behaviour was confirmed by repeated measurements on the desorbed polymer samples and slight leaching from the polymer membranes did not seem to affect the sorption results significantly.

As a further test in the understanding of the molecular transport and in view of no significant swelling of the polymer membranes in the presence of the solvents used, the effective diffusion coefficients (D) of polymer–solvent systems have been calculated as[33]:

$$D = \pi(h\theta/4C_\infty)^2 \qquad (2)$$

where h is the polymer sample thickness and θ is the slope of the linear portion of the C_t *versus* $t^{1/2}$ curves. The estimated diffusion coefficients are accurate to within ± 0.005 but are given to two decimal places in *Table 3*. Permeability coefficients (P) were calculated using the simple empirical relation: $P \equiv DS$ (*Table 3*). Except for BIIR and benzene, for the other polymer membranes, the values of D and P decrease systematically with increase in size of the penetrant molecules. The variation of D and K_s at 25°C with molar volume of the methyl-substituted benzenes is given in *Figure 7*. Similar dependences are observed at other experimental temperatures (not shown).

Diffusion coefficients for benzene and toluene increase according to the sequence: CSM > ECO > BIIR; for *p*-xylene the trend is CSM > BIIR > ECO; for 1,3,5-trimethylbenzene the sequence is BIIR > CSM > ECO; and with methoxybenzene the trend is ECO > CSM > BIIR. However, the trends for permeation coefficients are slightly different. As can be seen from *Table 1*, all the polymers contain fillers and additives to different extents, the presence of which seems to cause tortuosity in the diffusion pathways. Thus, solvent diffusion within polymer matrices is dependent on the nature of the

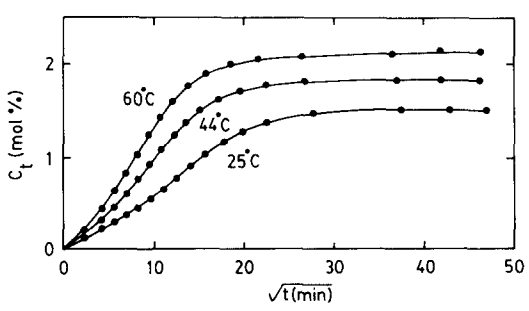

Figure 6 Temperature dependence of mole per cent sorption *versus* the square root of time for BIIR with benzene

Table 3 Diffusion coefficients (D) and permeation coefficients (P) of solvents into polymer membranes at different temperatures

Solvent	Temp. (°C)	D ($\times 10^7$) ($cm^2\ s^{-1}$)			P ($\times 10^7$) ($cm^2\ s^{-1}$)		
		BIIR	CSM	ECO	BIIR	CSM	ECO
Benzene	25	3.17	5.28	4.75	3.73	4.36	6.60
	44	5.64	8.51	7.91	8.07	7.17	11.01
	60	7.26	10.94	11.38	12.07	9.44	15.47
Toluene	25	3.93	5.17	4.20	6.35	4.53	4.63
	44	6.66	8.75	6.49	11.91	7.58	7.41
	60	8.41	11.11	8.39	16.01	9.80	9.57
p-Xylene	25	3.36	3.79	2.18	6.13	3.18	1.33
	44	5.21	5.78	4.18	10.11	4.71	3.01
	60	7.57	7.25	6.03	15.59	6.06	4.53
1,3,5-Trimethylbenzene	25	2.46	1.72	0.98	4.90	1.35	0.39
	44	4.12	3.25	2.27	8.55	2.53	1.12
	60	4.99	4.47	2.41	10.84	3.59	1.85
Methoxybenzene	25	0.79	2.82	3.14	0.26	2.48	5.72
	44	2.20	4.50	5.68	1.05	4.06	10.29
	60	3.86	6.50	8.09	2.36	6.20	14.82

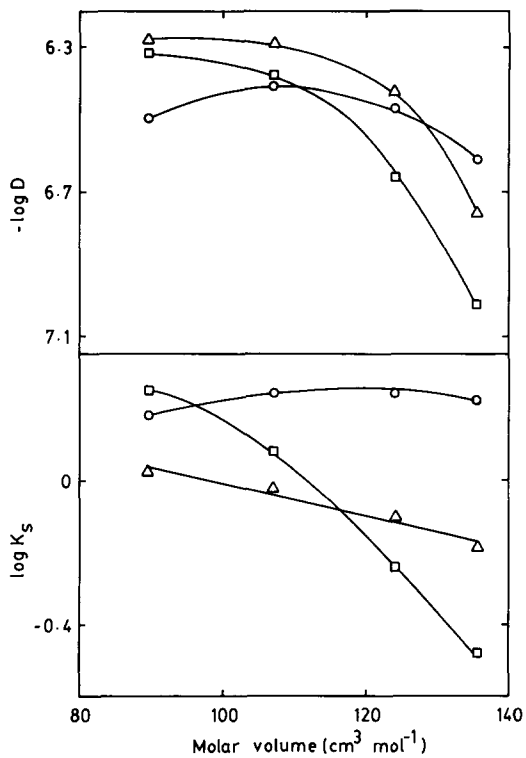

Figure 7 Dependence of log D and log K_s on molar volume of solvents at 25°C: (○) BIIR; (△) CSM; (□) ECO

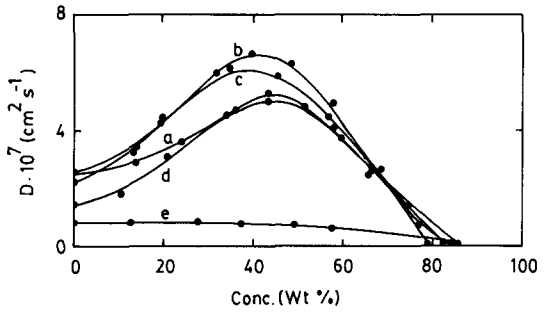

Figure 8 Dependence of diffusivity on penetrant concentration (wt%) for BIIR with solvents at 25°C. Curves a–e as in *Figure 1*

polymer chain segments in addition to the availability of free volume and the type of ingredient present. However, transport of penetrating molecules depends upon the rotation of chain segments. Thus, in the case of BIIR, due to the presence of polar groups on the backbone, a small change in the structure of penetrant molecules does not seem to have any significant effect on their diffusion properties. However, with somewhat loosely coiled polymer structures like CSM and ECO, even small changes in penetrant size have shown a substantial change in diffusivity. With an increase in temperature, the amplitude of segmental oscillations of the polymer chains also increases creating additional free volume with a subsequent increase in diffusion coefficients[34].

It may, however, be noted that the slight sigmoidal shapes in the observed sorption curves (*Figures 1–6*) are not indicative of the existence of a strict non-Fickian mechanism. The absence of complete non-Fickian transport was also supported by the fact that n in equation (1) was not equal to unity in any of the polymer–solvent systems studied. However, it is likely that the diffusion coefficients depend on penetrant concentration for most of the systems. Therefore, to study the concentration dependence of diffusivity, the procedure developed by Joshi and Astarita[35] was employed to calculate D as a function of penetrant concentration (in wt%). The computer-generated curves of BIIR, CSM and ECO membranes at 25°C are given in *Figures 8*, *9* and *10*, respectively. In almost all cases, the curves pass through maxima indicating a concentration dependence of the diffusion coefficients for the polymer–solvent systems studied. For the BIIR and methoxybenzene system (*Figure 8*), no

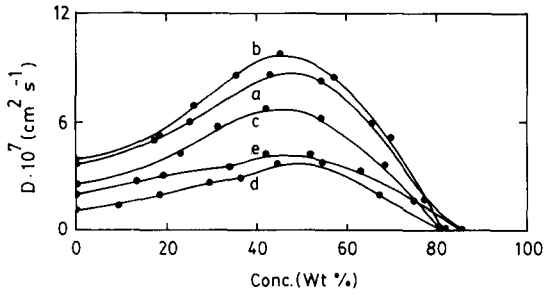

Figure 9 Dependence of diffusivity on penetrant concentration (wt%) for CSM with solvents at 25°C. Curves a–e as in *Figure 1*

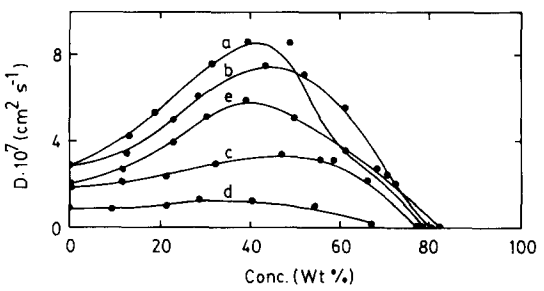

Figure 10 Dependence of diffusivity on penetrant concentration (wt%) for ECO with solvents at 25°C. Curves a–e as in *Figure 1*

Table 4 Activation parameters (E_D, E_P and ΔH_s) (in kJ mol^{-1}) for polymer–solvent systems

Solvent	Elastomer	E_D	E_P	ΔH_s
Benzene	BIIR	19.78	27.95	8.17
	CSM	17.36	18.38	1.02
	ECO	20.68	20.16	−0.52
Toluene	BIIR	18.18	22.08	3.90
	CSM	18.28	18.41	0.13
	ECO	16.44	17.27	0.83
p-Xylene	BIIR	19.14	21.99	2.85
	CSM	15.43	15.27	−0.16
	ECO	24.17	29.16	4.99
1,3,5-Trimethylbenzene	BIIR	16.90	18.99	2.09
	CSM	22.71	23.26	0.55
	ECO	21.96	37.18	15.21
Methoxybenzene	BIIR	37.68	52.00	14.32
	CSM	19.73	21.56	1.83
	ECO	22.49	22.59	0.24

significant dependence of D on concentration could be observed. Similarly, for 1,3,5-trimethylbenzene with CSM (*Figure 9*) and with ECO (*Figure 10*), sharp maxima are not observed suggesting no significant dependence of D on concentration. However, with CSM and ECO membranes, benzene, toluene or *p*-xylene exhibit concentration dependences of diffusivity as shown by the sharp maxima of the D *versus* concentration curves (*Figures 9* and *10*). This observation is supported by similar findings in the literature for solvent diffusion into rubbery polymer systems[36,37].

Over a reasonable temperature range, the transport coefficients (P, D and S) discussed above can be expressed in terms of an Arrhenius relationship:

$$X = X_0 \exp(-\Delta E_X/RT) \quad (3)$$

where $X = P$, D or S and the pre-exponential factor $X_0 = P_0$, D_0 or S_0. The term RT has its usual meaning and ΔE_X refers to the activation parameters for the process of permeation, diffusion or sorption. For sorption, the activation parameter, as evaluated from equation (3), represents the heat of sorption (ΔH_s). The latter quantity is a composite parameter involving both Henry's law and Langmuir-type sorption. Henry's law requires both the formation of a site and the dissolution of the species into that site; this involves an endothermic contribution to the sorption. However, the Langmuir mode involves sorption by a hole-filling mechanism and thus yields exothermic heat. Other terms such as E_D and E_P represent the activation energies for the process of diffusion and permeation. Since $P \equiv DS$, one may also obtain ΔH_S from the difference $E_P - E_D$. The estimated values of E_D, E_P and ΔH_S are given in *Table 4*.

The results of heats of sorption and activation energies (E_D and E_P) provide additional information about the transport of aromatic hydrocarbons into the chosen polymer membranes. As seen in *Table 4*, the heats of sorption are generally higher for BIIR than CSM and for both these membranes with all the solvents used, the ΔH_s values are positive. This suggests that the sorption mechanism in these systems is dominated by the Henry's law dissolution process. However, with CSM and *p*-xylene, ΔH_s is negative suggesting the presence of Langmuir-type sorption in this system. Similarly, for ECO with benzene, ΔH_s is negative. A plausible explanation for this anomaly could be the result of induced crystallinity of the polymer chains showing an inverse effect of sorption on temperature for these systems (*Table 2*). The values of E_D and E_P follow the same trend for all the systems. For instance, E_D for BIIR ranges between 17 kJ mol^{-1} and 38 kJ mol^{-1} and for ECO membrane, the E_D values range from 16 to 24 kJ mol^{-1}. In the case of CSM membrane, the range of E_D values is between 15 kJ mol^{-1} and 23 kJ mol^{-1}. The high values of E_D or E_P further suggest the exceedingly rigid structure of the membrane systems. From the present study, it may be inferred that the values of the activation parameters fall in the range as expected for the rubbery polymers well above their glass transition temperatures.

CONCLUSIONS

The effects of polymer backbone structure on the kinetics of sorption of methyl- and methoxy-substituted monocyclic aromatic hydrocarbons in elastomer membranes were investigated at 25, 44 and 60°C. In all cases, sorption and diffusion follow anomalous-type behaviour, which is an intermediate behaviour between Fickian and non-Fickian transport. However, in the initial stages of sorption, Fickian behaviour was more prevalent and hence, diffusion data were extracted from Fick's relation. The uptake behaviour of the penetrants was also examined to determine the effect of molecular size and penetrant affinity for network polymer on the uptake behaviour. Furthermore, the loss of equilibrium in the case of some polymer–solvent systems signifies that impurities such as low molar mass oligomers or additives have been removed from the original network. The transport parameters all increased with increasing temperature. The concentration dependence of these parameters appeared to become stronger with decreasing temperature or penetrant size. As expected, the diffusivities decreased with increasing penetrant size. However, more evidence is needed to support the molecular transport picture of small molecules into network polymer systems.

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