



Sorption and diffusion of chlorinated aliphatic hydrocarbon penetrants into diol chain extended polyurethane membranes

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Abstract

Sorption and diffusion of a number of chlorinated alkanes through a diol chain extended polyurethane (PU) membranes have been investigated at 25, 40 and 60 °C, based on an immersion weight gain method. From the sorption result, the diffusion (D) and permeation (P) coefficients of halogenated hydrocarbon penetrants have been calculated. Molecular transport data depends on membrane–solvent interactions, size of the penetrants, temperature and also morphology of the chain extended PUs. The temperature dependence of the transport coefficient has been used to estimate the activation parameters for the process of diffusion (E_D) and permeation (E_P) from the Arrhenius plots. Furthermore, the sorption results have been interpreted in terms of the thermodynamic parameters such as enthalpy and entropy.

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1. Introduction

Polyurethane (PU) elastomers are known to exhibit unique mechanical properties, primarily as a result of two phase morphology [1]. These materials are alternating block copolymers made of hard segments of aromatic groups from the diisocyanate/chain extender and soft segments of aliphatic chains from the diol (ether or ester). The hard and soft segments are chemically incompatible and microphase separation of the hard segments into domains dispersed in a matrix of soft segment can occur in varying degrees.

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The transport behaviour of various organic solvents and gases through polymers are of great technological importance, since now-a-days the polymer membranes are increasingly used in various barrier applications. During the last few decades, the importance of polymer blends have increased, as it is possible to achieve desirable properties by simple blending of polymers. Among the different types of polymer blends, thermoplastic elastomers (TPEs) have their own advantages. Hence, it is necessary to analyse the transport behaviour of the thermoplastic elastomers in detail. The transport of small molecules through polymers have been widely studied by various research [2–7] groups. It is found that the transport of solvents through polymer is influenced by the physical and chemical structure of polymer, the cross link density, the size of solvent molecules and temperature.

In view of the versatility of PU as a barrier material in several engineering area [8,9], it is important to know its transport characteristics with respect to common organic solvents. Thus, the knowledge of transport mechanisms as manifested by sorption, diffusion and permeation of organic liquid penetrants in a PU matrix is helpful for establishing the relationships between structure and properties under severe application conditions.

A detailed literature survey reveals that, the diol chain extended PU systems have not been studied for sorption, diffusion and swelling characteristics. In view of the importance of PU membrane as coating, and barrier material in several engineering areas [10,11], it is important to know its swelling behaviour with respect to common organic solvents. This prompted us to undertake an investigation to study the interaction of chlorinated alkane penetrants with different diol chain-extended PUs.

This research article reports the experimental sorption and diffusion results of butane diol (BD)- and hexane diol (HD)-based chain extended PUs with methylene chloride (CH_2Cl_2), chloroform (CHCl_3) and carbon tetra chloride (CCl_4). The results are discussed interms of the nature of polymer–solvent interaction. The discussion is made on the correlation of the thermodynamic quality of the solvents and its structure with the molecular transport properties of chlorinated penetrant—PU membrane systems. Recently, authors published the structure property relationship and swelling behaviour of diamine chain extended PUs [12,13].

2. Experimental procedure

2.1. Specimen preparation

A series of castor oil-based chain extended PUs were prepared using different diisocyanates like methylene diisocyanate (MDI), toluene diisocyanate (TDI) and hexane methylene diisocyanate (HMDI) as cross linkers and diols like 1,4-butane diol and 1,6-hexane diol as chain extenders as per procedure reported elsewhere [14]. Structure property relationship of diol chain extended PUs have been reported [15]. The samples were cut circularly (1.76 cm diameter) using a sharp edged steel die. Initial thickness of the specimens was measured at several points and are ranged from 0.2 to 0.26 cm (Mitutoyo, Japan with a precision of ± 0.001 cm). The specimens were dried in desiccator before being used. Weights of the cut samples were taken before immersion into air tight, metal capped test bottles containing halogenated penetrants. The AR grade penetrants like CH_2Cl_2 , CHCl_3 and CCl_4 were

Table 1
Some physical properties of chlorinated probe liquids at 25 °C

Penetrants	Mol. vol. (cm ³ /mol)	Boiling point (°C)	Density (g/cm ³)	Sol. parameter (cal cm ⁻³) ^{1/2}	Dipole moment (debye)	Polarisability (10 ⁻²⁴ cm ⁻¹)
Methylene chloride	64.5	42	1.324	9.70	1.36	3.31
Chloroform	80.7	61	1.487	9.20	1.02	4.77
Carbon tetrachloride	97.1	77	1.592	7.28	0.00	6.34

obtained from s.d. fine Chemicals (India) and were used after distillation. Some physical properties of the chlorinated penetrants are given in Table 1.

2.2. Sorption experiments

Sorption experiments at 25, 40 and 60 °C were performed by immersing the cut specimens in the test solvents taken in screw tight metal capped bottle maintained at the desired constant temperature (± 0.5 °C) in a thermostatically controlled oven. At specified intervals of time, membranes are removed from the containers, surfaces were dried in between smooth filter paper wraps and were weighed immediately using analytical balance. The specimen was then placed back immediately in the test liquid and transferred to the temperature controlled oven. The total time spent by the membrane outside the solvent was kept minimum (say 30–50 s), so as to minimise the experimental error. This error was negligible when the time spent by the membrane outside the test bottle was compared to the time spent in the solvent. The weighing of the samples continued until the maximum (saturation) value was reached. The time taken for the attainment of equilibrium sorption for different liquids varies from 70 to 90 h.

The percentage weight gain Q_t of the soaked membrane was calculated as:

$$Q_t = \frac{M_t - M_i}{M_i} \times 100 \quad (1)$$

where M_i is the initial weight of the membrane and M_t the weight t , of the membrane at time t .

3. Results and discussion

Sorption curves expressed as percent penetrant uptake (Q_t) versus square root of time, for 25, 40 and 60 °C are displayed in Fig. 1a–c, respectively, for CO + TDI + BD membrane for all chlorinated aliphatic hydrocarbon penetrants. A perusal of the sorption curves given in Fig. 1 suggests a systematic trend with respect to molecular volume of penetrants. The sorption and diffusion processes are influenced by the factors such as molecular size, degree of interaction between the polymer and solvent and the solubility parameters of the PU membrane and the solvent. Here, sorption (S) increases with increase in molecular size of the penetrant. There is a competition between size of the penetrant and the interaction between polymers and the solvents [16–18]. This is attributed due to solubility parameter factor. Difference in solubility parameters overcomes the molecular size and hence, influence

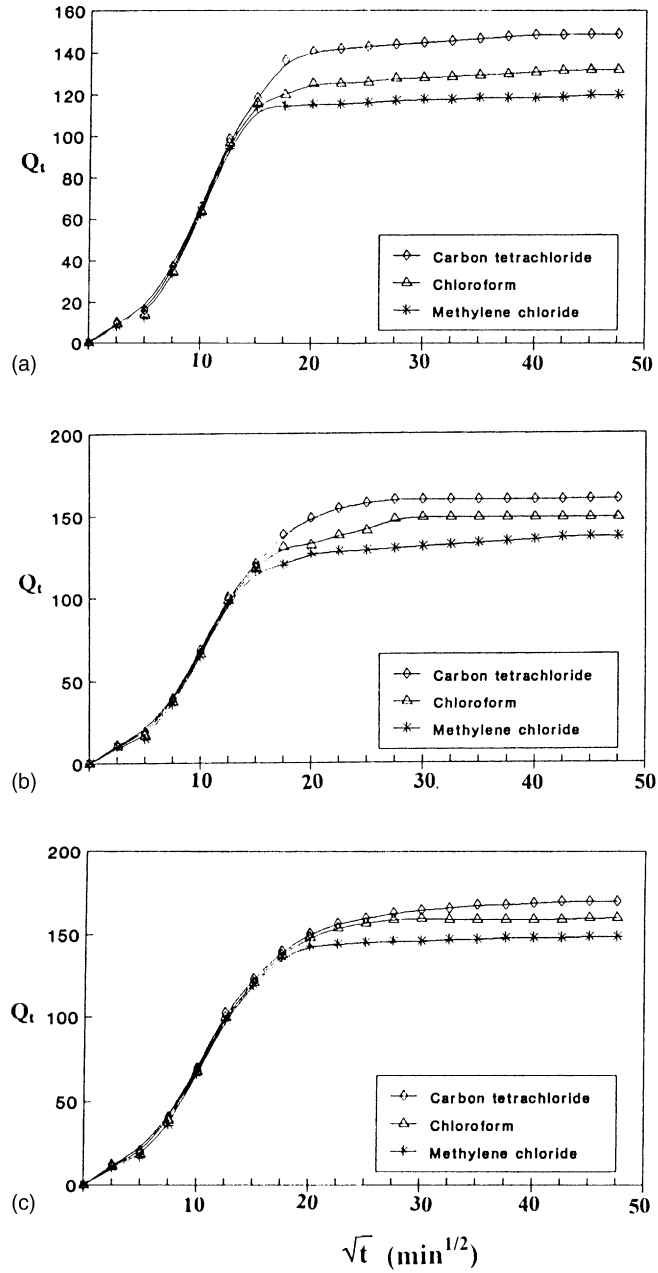


Fig. 1. Percent mass uptake (Q_t) of the PU (CO + TDI + BD) vs. $t^{1/2}$ with different alkanes at (a) 25 °C, (b) 40 °C and (c) 60 °C.

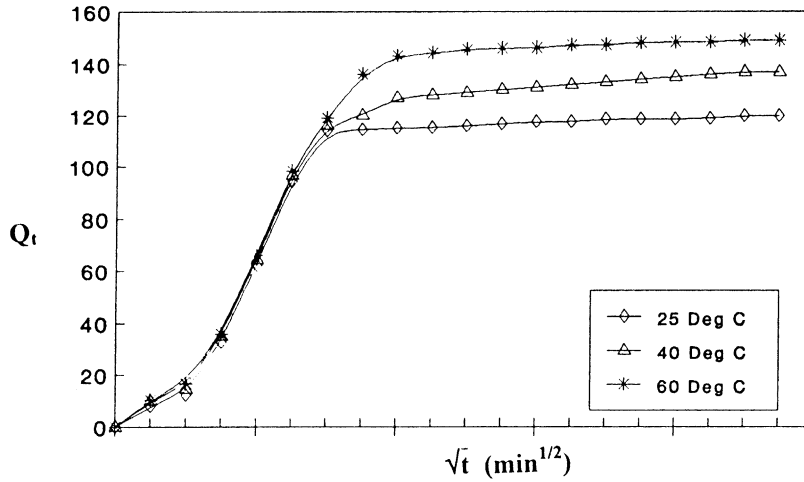


Fig. 2. Percent mass uptake (Q_t) vs. $t^{1/2}$ for CO + TDI + BD in CCl_4 .

the sorption [19]. The sorption process of all the penetrants follow the sequence; carbon tetrachloride > chloroform > methylene chloride.

Sorption data also serve as a guide to study the effect of temperature on the observed transport behaviour. Temperature variation (25–60 °C) on sorption curves for carbon tetrachloride penetrant is shown in Fig. 2 for chain extended PU (CO + TDI + BD) system. The effect of nature of the diisocyanate on the sorption behaviour of PUs have been studied. Sorption curves for 1,4-butane diol chain extended PU membranes with different diisocyanates is shown in Fig. 3 for CCl_4 penetrant at 40 °C. From the figure it was observed

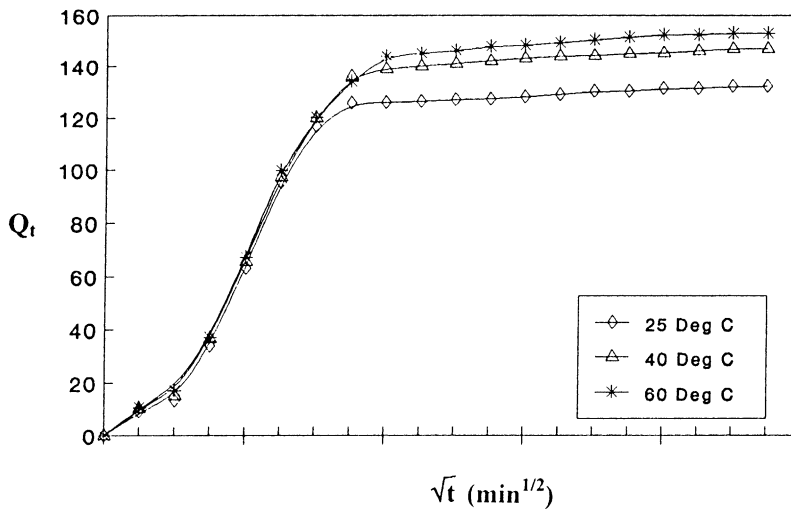


Fig. 3. Percent mass uptake Q_t vs. $t^{1/2}$ for chain extended PUs with different diisocyanates in CCl_4 at 40 °C.

that higher mass uptake for HMDI-based PUs followed by TDI- and MDI-based Systems. This result implies that higher the soft segment higher will be the mass uptake. The MDI PU membrane system possesses high degree of hard segment, which acts as a tortuous [20] path for the diffusion process and hence, the uptake is less. However, as the concentration of hard segment decreases, the size of crystalline spherulite also decreases. As soft segment increases, the contact between soft domains increases and this leads to the high uptake. The soft domains forms the continuous phase. The diffusion process is continuous through soft phase (amorphous) and hence, a sharp increase in uptake is observed. In almost all cases, the shapes of sorption curves at 25 °C are similar to those at the two higher temperatures, although the change in slope is more pronounced between 25 and 40 °C than between 40 and 60 °C. The equilibrium sorption increases with increase in temperature. This effect follows the conventional wisdom that, at higher temperature the increase in free volume occurs due to increased movement of the chain segments of the membrane [21].

For a Fickian behaviour, the plots of Q_t versus $t^{1/2}$ should increase linearly up to about 50% sorption. Deviations from the Fickian sorption are associated with the time taken by the polymer segments to respond to swelling stress and rearrange themselves to accommodate the solvent molecules [17]. This usually results in the sigmoidal shapes of the sorption curves. Thus, non-Fickian diffusion involves the tension between swollen (soft segments) and unswollen (hard segments) parts of PU as the latter tend to resist further swelling. However, during early stages of sorption, the samples may not reach the true equilibrium concentration of the penetrant and thus, the rate of sorption builds up slowly to produce slight curvatures as shown in Figs. 1–3. This is an indicative of the departure from the Fickian mode and is further confirmed from an analysis of sorption data.

In order to investigate the type of diffusion mechanism, attempts were made to estimate the values of ‘ n ’ and ‘ k ’ from the following relation [22,23];

$$\log \frac{M_t}{M_\infty} = \log K + n \log t \quad (2)$$

where K and n are empirical parameters, M_t and M_∞ are mass uptake values at time t and at equilibrium t_∞ , respectively. The magnitude of n decides the transport mode, for instance, a value of $n = 0.5$ suggests the Fickian mode and for $n = 1$, a non-Fickian diffusion mode is predicted. However, the intermediate values ranging from $n = 0.5$ to unity suggest the presence of anomalous transport mechanism.

In order to determine K and n , plots of $\log(M_t/M_\infty)$ versus $\ln t$ were constructed, and it is given in Fig. 4. The values calculated of the empirical parameters n and K are given in Table 2. The average uncertainty in the estimation of n and K are around ± 0.01 and ± 0.008 , respectively. The value of n does not indicate any systematic variation with temperature. However, a general variation of n from a minimum value of 0.50 to a maximum of 0.59 indicates that the anomalous type transport mechanism is operative and the diffusion is slightly deviated from the Fickian trend. This fact can be further substantiated from the curvature dependencies of Q_t versus $t^{1/2}$ plots shown in Figs. 1–3. Such observations are also evident from the work of Nicolais et al. [24] for n -hexane transport in glassy polystyrene (PS).

A temperature dependence of K suggests that it increases with increase in temperature for all the penetrants [21,25], except CO + HMDI + BD sample. Furthermore, K appears to depend on structural characteristics of the penetrant molecules, i.e. it decreases successively

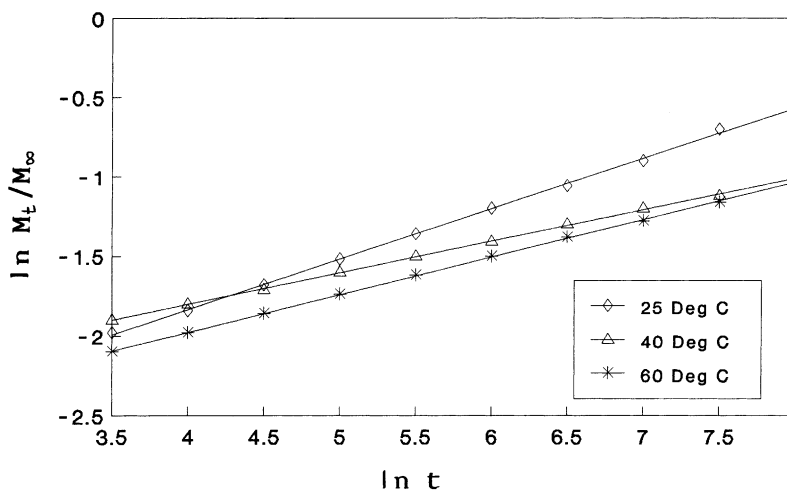


Fig. 4. A plot of $\ln M_t/M_\infty$ vs. $\ln t$ for CO + TDI + 1,4 BD at different temperatures.

from methylene chloride to carbon tetrachloride. Thus, it appears that K not only depends on the structural characteristics of the polymer and penetrant molecules, but also on solvent interactions with the PU chains. Methylene chloride and chloroform are polar solvents and possibly due to dipole–dipole type interactions with the polymer segments, exhibits higher K than CCl_4 . A close observation of the results of K presented in Table 2 shows the following sequence; $\text{CH}_2\text{Cl}_2 > \text{CHCl}_3 > \text{CCl}_4$ over the investigated range of temperature for all PU membranes.

Another striking feature of the sorption data, of all PUs is that sorption increases with increase in the size of chlorinated alkanes. Thus, the sorption data are found to vary according to the sequence; $\text{CCl}_4 > \text{CHCl}_3 > \text{CH}_2\text{Cl}_2$. (Molecular volume = molecular weight/

Table 2
Sorption data for diols chain extended PUs in chlorinated aliphatic hydrocarbon penetrants

Penetrants	Temperature (°C)	$n (\pm 0.01)$						$K (\times 10^2 \text{ g/g min}) (\pm 0.008)$					
		A	B	C	D	E	F	A	B	C	D	E	F
CH_2Cl_2	25	0.502	0.533	0.516	0.506	0.504	0.515	4.06	4.61	4.92	7.99	5.50	4.00
	40	0.504	0.542	0.507	0.539	0.546	0.506	9.52	5.39	6.83	8.78	6.75	8.61
	60	0.500	0.505	0.503	0.503	0.508	0.533	15.8	8.18	9.40	10.52	4.46	9.33
CHCl_3	25	0.508	0.528	0.511	0.533	0.502	0.542	3.32	2.81	3.72	3.80	5.19	3.28
	40	0.519	0.508	0.525	0.519	0.502	0.504	4.79	5.84	4.61	4.62	6.74	4.98
	60	0.505	0.500	0.513	0.504	0.519	0.561	8.01	5.91	5.75	8.72	4.31	5.31
CCl_4	25	0.590	0.590	0.504	0.506	0.568	0.513	2.00	2.21	3.21	3.72	6.28	3.24
	40	0.514	0.513	0.503	0.508	0.537	0.502	3.92	4.54	4.60	4.50	4.69	3.99
	60	0.520	0.522	0.508	0.516	0.537	0.502	7.99	5.07	5.62	8.08	4.28	4.81

A = CO + TDI + BD; B = CO + TDI + HD; C = CO + MDI + BD; D = CO + MDI + HD; E = CO + HMDI + BD; F = CO + HMDI + HD.

density \times Avagadro number). The higher S values of 200×10^{-2} g/g for CO+HMDI+HD at 60 °C, in carbon tetrachloride may be due to the presence of more soft segment (methylene group) in the HMDI as well as in the 1,6-hexane diol chain extender. Lower S value of 87×10^{-2} g/g for CO + MDI + BD at 25 °C in methylene chloride penetrant may be due to the presence of more hard segment (phenyl group) content in methylene diisocyanate.

From the slope, θ of the initial linear portion of the sorption curves, i.e. Q_t versus $t^{1/2}$, the diffusion coefficients, have been calculated by using the equation;

$$D = \pi \left[\frac{h\theta}{4M_\infty} \right]^2 \quad (3)$$

where h is thickness of the material and M_∞ the mass uptake at infinite time. The values of D determined in this manner can be regarded as independent of concentration and are thus applicable for Fickian mode of transport. A triplicate evaluation of D from sorption curves gave us D values with an error of ± 0.003 units at 25 °C, ± 0.004 units at 40 °C and ± 0.005 units at 60 °C for all polymer-penetrant systems (Table 3). These uncertainty estimates regarding diffusion coefficients suggest that the half times were very reproducible.

The diffusion coefficient (D) decreases with increase in molecular volume of the penetrant, from CH_2Cl_2 to CCl_4 . The dependence of D on molecular volume with halogenated alkanes proves in conjecture that larger molecules in a related series of liquids occupy large free volumes leading to hindered diffusivities through the polymer matrix [26]. The values of sorption coefficient, S , are given in Table 3, which are obtained as computed from the plateau regions of sorption curves and permeability coefficient, P as calculated [27] from the simple relation; $P = DS$, also follow the same trend as that of diffusivities.

The transport of small molecules through polymers generally occurs through a solution diffusion mechanism. That is the penetrant molecules are first sorbed by the polymer followed by the diffusion through polymer membrane [18]. The net diffusion through the polymer depends on the amount of penetrant molecules between the two surfaces. Variation of P values with respect to temperature for different penetrants are shown in Fig. 5 for CO + MDI + BD membrane.

3.1. Thermodynamic and activation parameters

Attempts have also been made to calculate the equilibrium sorption constants, K_S , from consideration on the equilibrium process occurring in the liquid phase at constant temperature and pressure.

$$K_S = \frac{\text{number of moles of penetrant sorbed}}{\text{unit mass of the polymer}} \quad (4)$$

The variation in K_S and D values with molar volume of halogenated penetrants are shown in Figs. 6 and 7, respectively. Thus, Figs. 6 and 7 show that the dependence of K_S and D on penetrant molecular volume at 25, 40 and 60 °C. A systematic decrease in K_S or D values with increase in molecular volume of penetrant suggests an inverse dependence of K_S or D on molecular volume of probe molecules. This may be more logical as larger molecules tend to occupy more free volume in the amorphous regions of PU chains than smaller molecules. This could be attributed to the structural and polarity similarities of the solvents. Another

Table 3

Diffusion (D), sorption (S), thermodynamic sorption constant (K_S) and permeation (P) coefficients of different diols chain extended PUs in chlorinated aliphatic alkane penetrants

PU samples	Temperature (°C)	Methylene chloride				Chloroform				Carbon tetrachloride			
		D ($\times 10^7$ cm ² /s)	K_S ($\times 10^{-2}$)	S ($\times 10^2$ g/g)	P ($\times 10^7$ cm ² /s)	D ($\times 10^7$ cm ² /s)	K_S ($\times 10^{-2}$)	S ($\times 10^2$ g/g)	P ($\times 10^7$ cm ² /s)	D ($\times 10^7$ cm ² /s)	K_S ($\times 10^{-2}$)	S ($\times 10^2$ g/g)	P ($\times 10^7$ cm ² /s)
A	25	3.25	1.41	120	3.90	2.06	1.10	132	2.71	1.83	0.96	149	2.72
	40	3.98	1.61	137	5.45	2.23	1.24	149	3.32	2.02	1.04	161	3.25
	60	4.12	1.75	149	6.13	2.56	1.33	160	4.09	2.25	1.11	172	3.87
B	25	3.64	1.55	132	4.80	2.42	1.21	145	3.50	2.18	1.01	156	3.40
	40	4.15	1.72	147	6.10	2.75	1.32	158	4.34	2.62	1.09	168	4.40
	60	4.35	1.8	153	6.65	3.04	1.37	164	4.98	2.82	1.16	179	5.04
C	25	2.05	1.02	87	1.78	1.91	0.77	95	1.81	1.87	0.66	102	1.90
	40	2.32	1.09	93	2.15	2.05	0.88	106	2.17	2.00	0.77	119	2.38
	60	2.52	1.18	101	2.54	2.35	0.97	117	2.74	2.18	0.81	126	2.74
D	25	2.48	1.08	92	2.28	2.16	0.86	103	2.22	2.07	0.76	118	2.44
	40	2.72	1.21	103	2.80	2.27	0.99	119	2.70	2.11	0.81	125	2.63
	60	2.98	1.31	112	3.33	2.48	1.07	128	3.17	2.37	0.88	137	3.16
E	25	4.48	1.85	158	7.07	4.30	1.40	168	7.22	4.12	1.13	175	7.21
	40	4.78	1.91	163	7.79	4.51	1.45	174	7.84	4.23	1.20	185	7.82
	60	4.95	2.02	172	8.51	4.72	1.54	185	8.73	4.59	1.27	196	8.99
F	25	4.83	1.90	162	7.82	4.70	1.43	172	8.08	4.52	1.17	181	8.18
	40	4.93	2.01	175	8.43	4.84	1.50	180	8.71	4.69	1.24	192	9.00
	60	5.12	2.05	175	8.96	5.00	1.58	189	9.45	4.83	1.29	200	9.66

A = CO + TDI + BD; B = CO + TDI + HD; C = CO + MDI + BD; D = CO + MDI + HD; E = CO + HMDI + BD; F = CO + HMDI + HD.

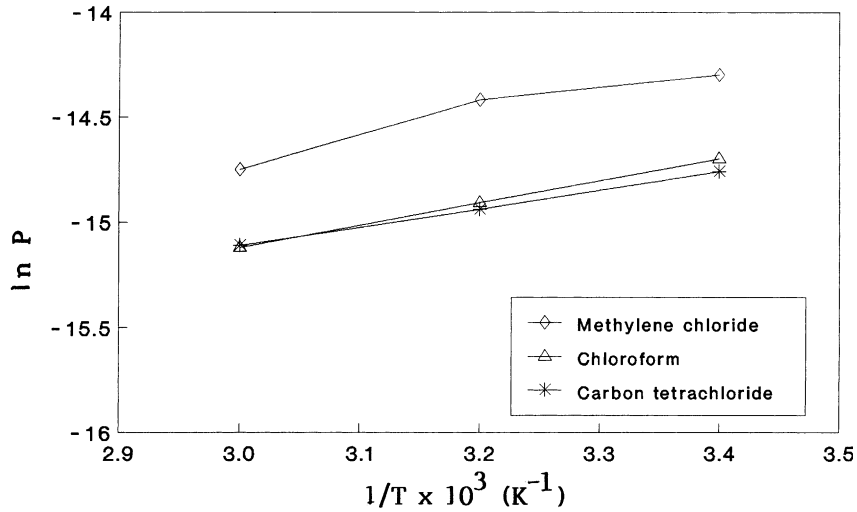


Fig. 5. A plot of $\ln P$ vs. $1/T$ for CO + TDI + 1,4 BD.

factor might be the affinity of these solvents towards PU. Following the generalisation “like absorbs like”, this explanation is consistent with our experimental results.

Similarly, the temperature dependent equilibrium sorption constant K_S values may be fitted to the Vant Hoff’s relation, to estimate the enthalpy (i.e. heat of sorption) ΔH and standard entropy, ΔS of sorption process.

$$\text{Log } K_S = \left(\frac{\Delta S}{2.303R} \right) - \left(\frac{\Delta H}{2.303R} \right) \times \left(\frac{1}{T} \right) \quad (5)$$

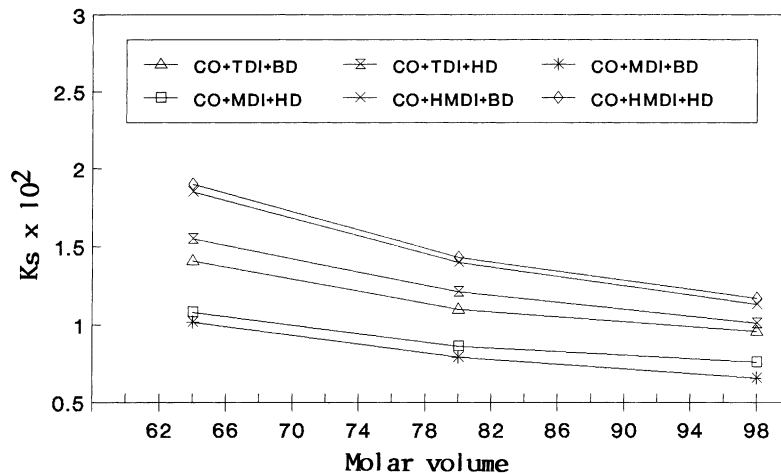


Fig. 6. Variation of K_S with molar volume for different systems.

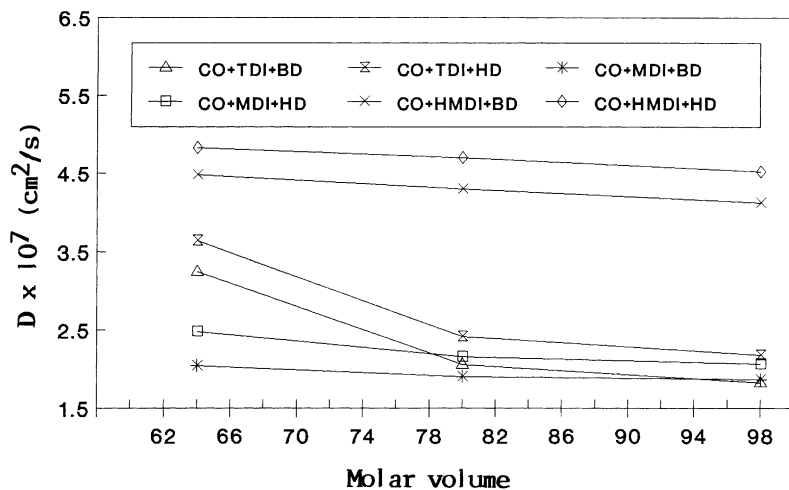


Fig. 7. Dependence of diffusivity (D) on molar volume of the penetrants.

The estimated values of ΔH and ΔS are given in Table 3. The average estimated error in ΔH is about ± 1 J/mol whereas, for ΔS is about ± 1 J/(mol K). ΔH values are low for CO + HMDI + HD, suggesting that, there exists a strong specific interaction between the penetrant and the polymer matrix. However, the higher values of ΔH for CO + TDI + HD confirms the conjecture that there exists a mild interaction of the penetrant with the polymer matrix giving a high endothermic heat of sorption. For all liquids, the values of ΔH were positive, suggesting that sorption is an endothermic process and it is dominated by Henry's law mode, i.e. the sorption proceeds through the creation of new sites or pores in the polymer. The plots of $\ln K_S$ versus $1/T$ for 1,4-butane diol chain extended PUs is shown in Fig. 8 for

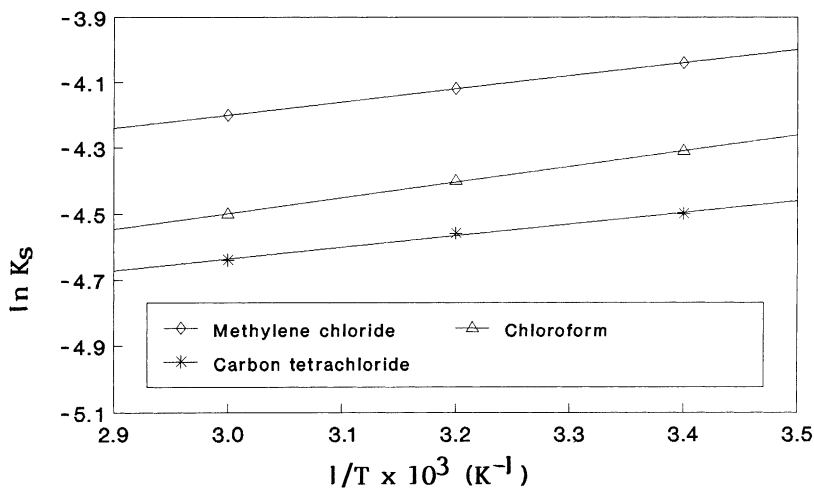


Fig. 8. Van't Hoff plots of $\ln K_S$ vs. $1/T$ for CO + TDI + 1,4 BD for different penetrants.

Table 4

Activation energy for diffusion (E_D , kJ/mol), activation energy for permeation (E_P , kJ/mol), enthalpy of sorption (ΔH (kJ/mol) ± 4) and entropy of sorption (ΔS (J/mol) ± 1) for diol chain extended PUs

Samples	Activation parameters	CH ₂ Cl ₂	CHCl ₃	CCl ₄
F	E_P	13.24	12.64	15.38
	E_D	7.12	9.26	12.01
	ΔH	50.00	33.25	12.47
	$-\Delta S$	31.01	34.00	36.91
D	E_P	18.54	19.36	20.88
	E_D	12.46	15.19	17.28
	ΔH	58.19	37.41	29.09
	$-\Delta S$	31.09	34.41	37.08
E	E_P	14.39	17.54	18.34
	E_D	9.88	11.90	13.08
	ΔH	62.35	41.52	33.25
	$-\Delta S$	31.06	34.25	36.99
B	E_P	12.06	14.08	15.95
	E_D	6.89	8.49	9.42
	ΔH	78.98	45.72	41.57
	$-\Delta S$	31.50	34.75	37.46
C	E_P	18.65	19.25	21.04
	E_D	13.08	14.86	16.23
	ΔH	70.66	24.92	24.90
	$-\Delta S$	31.63	35.16	37.74
A	E_P	14.80	15.67	17.36
	E_D	7.68	9.12	10.60
	ΔH	66.51	24.94	62.38
	$-\Delta S$	32.05	35.25	37.99

A = CO+TDI+BD; B = CO+TDI+HD; C = CO+MDI+BD; D = CO+MDI+HD; E = CO+HMMDI+BD; F = CO + HMMDI + HD.

all penetrates. From the figure it was noticed that the plots are linear within the temperature interval of 25–60 °C (Table 4).

The calculated ΔS values are negative for the all the systems. This suggests that, the solvent molecules are retained in the sorbed state. For methylene chloride, ΔS is about -31.01 J/(mol K) and it progressively decreases upto carbon tetrachloride for which ΔS is about -36.91 J/(mol K).

The Arrhenius activation parameters, viz. E_D and E_P for the processes of diffusion and permeation have been computed from a consideration of the temperature variation of P and D , respectively. The corresponding Arrhenius plots are given in Figs. 5 and 9 for 1,4-butane diol chain extended PUs (TDI).

The value of E_D lies in the range 6.89–17.28 kJ/mol, while those of E_P lie in the range 12.06–21.04 kJ/mol. These values are within the range expected for rubbery polymers (PUs) well above their glass transition temperatures. There is a systematic increase in E_D values with increase in chlorine atoms of the penetrants or molecular volume of the penetrants under investigation. These results could be explained on the basis of Eyring's hole theory

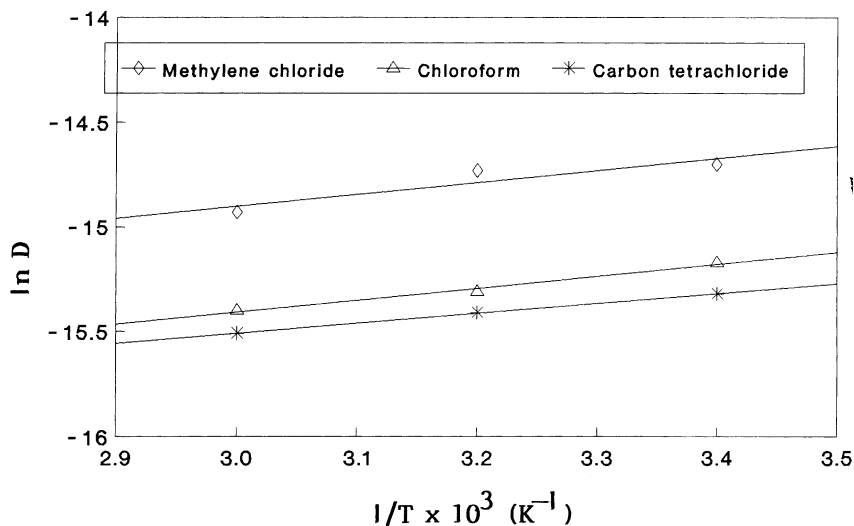


Fig. 9. Van't Hoff plots of $\ln D$ vs. $1/T$ for CO + TDI + 1,4 BD for different penetrants.

[28,29] according to which, the energy required to “open a hole” in the polymer matrix to accommodate a diffusing molecule bears a direct relationship with E_D . Thus, the larger molecules in a related series will have larger E_D value and smaller diffusion coefficients. This is in conformity with the experimental observations reported here.

Activation energy (E_P) will be greater compared to E_D for all penetrants, because of higher degree of cohesive energy in polymer chain. On the other hand, the heat of sorption is a composite parameter which involves contribution from Henry's law mode with the endothermic reaction contributions to Langmuir's (hole filling) type sorption giving exothermic heats of sorption. Those liquids which exhibit lower values of D have shown higher value of activation parameter E_D and vice versa. There was no systematic variation in E_P values with molecular volume.

4. Conclusions

In the present study, we have tried to identify the factors which limit the long time performance of chain extended PUs. The results of sorption and transport of chlorinated alkanes such as CH_2Cl_2 , CHCl_3 and CCl_4 into structurally different castor oil-based diol chain extended PUs are presented. From this study, it would be possible to forecast conditions and penetrant types which would cause degradation of polymer membrane performance or swelling as it would be possible to predict their consequences on molecular transport data. It was observed that factors such as solvent type, the chemical nature of the PU and their morphology seem to exert tremendous influence on the transport characteristics. The lower diffusion coefficient was observed for MDI-based PUs compared to HMDI. The values of n lie in the range 0.5–0.59 suggesting that the molecular transport is of Fickian

mode. The D , P and S values for all penetrants lie in the range 1.83×10^7 to 5.12×10^7 , 1.78×10^7 to $9.66 \times 10^7 \text{ cm}^2/\text{s}$ and 87×10^2 to $200 \times 10^2 \text{ g/g}$, respectively, in the temperature range 26–60 °C. The diffusion coefficient for all the PU membranes vary in the sequence $\text{CH}_2\text{Cl}_2 > \text{CHCl}_3 > \text{CCl}_4$. The ΔH and ΔS values for all PU-solvent systems lie in 12.47–78.98 kJ/mol and -37.99 to -31.00 J/mol , respectively. The negative values of ΔS suggest that the structure of solvent molecules are retained even in the sorbed state. The highest E_D and E_P values were observed for high hard domain containing PUs compared to higher soft segment PU.

References

- [1] K.E. Polmanteer, in: A.K. Bhowmick, H.L. Stephens (Eds.), *Handbook of Elastomers*, Marcell Dekkar, New York, 1988, p. 375.
- [2] K.T. Varughese, G.B. Nando, P.P. De, S.K. De, *J. Mater. Sci.* 23 (1988) 3894.
- [3] S.B. Harogopad, T.M. Aminabhavi, *Macromolecules* 24 (1991) 2598.
- [4] N.S. Schneider, J.L. Illinger, M.A. Cleaves, *Polym. Eng. Sci.* 26 (22) (1986) 1547.
- [5] D.C. Liao, Y.C. Chem, J.L. Han, K.H. Hseih, *J. Polym. Sci. B: Polym. Phys.* 35 (1995) 1747.
- [6] G. Unnikrishnan, S. Thomas, *J. Polym. Sci. B: Polym. Phys.* 35 (1997) 725.
- [7] A.P. Mathew, S. Pakirisamy, M.G. Kumaran, S. Thomas, *Polymer* 36 (26) (1995) 4935.
- [8] Z. Wirpsza, in: T.J. Kemp (Ed.), *Polyurethanes Chemistry, Technology and Applications*, Ellis Horwood, PTR Prentice-Hall, New York, 1993.
- [9] W. Neumuller, R.J. Bonant, *Macromol. Sci. Phys. Ed.* B21 (1982) 203–217.
- [10] P.E. Gibson, in: I. Goodman (Ed.), *Properties in Polyurethane Block Co-polymers Development in Block Copolymers*, Elsevier, London, 1982.
- [11] G. Trapps, in: J.M. Buist, H. Gudgeon (Eds.), *Advances in Polyurethanes Technology*, Wiley/Interscience, New York, 1968, p. 63.
- [12] B.K. Kendaganna Swamy, Siddaramaiah, T.M. Aminabhavi, *Polym. News* 1021 (2001).
- [13] B.K. Kendagannaswamy, Siddaramaiah, *J. Appl. Polym. Sci.* 84 (2002) 359–369.
- [14] B.K. Kendagannaswamy, Ph.D. thesis, University of Mysore, Mysore, 2001.
- [15] B.K. Kendagannaswamy, Siddaramaiah, R. Somashekar, *J. Mater. Sci.* 38 (2003) 451–460.
- [16] S.B. Harogopad, T.M. Aminabhavi, *Indian J. Chem.* 30A (1991).
- [17] S.B. Harogopad, T.M. Aminabhavi, *J. Appl. Polym. Sci.* 42b (1991) 2329.
- [18] S.B. Harogopad, T.M. Aminabhavi, *Macromolecules* 24 (1991) 259.
- [19] Siddaramaiah, S. Roopa, U. Premakumar, *Polymer* 39 (17) (1998) 3925–3933.
- [20] S. George, K.T. Varguhese, S. Thomas, *Polymer* 41 (2000) 579–594.
- [21] U.S. Aithal, T.M. Aminabhavi, *J. Chem. Ed.* 67 (1990) 82.
- [22] I.M. Lucht, N.A. Peppas, *J. Appl. Polym. Sci.* 33 (1987) 1557.
- [23] J.S. Chiou, D.H. Paul, *Polym. Engg. Sci.* 26 (1986) 1218.
- [24] L. Nicolais, E. Drioli, H.B. Hopfenberg, A. Apicella, *Polymer* 20 (1979) 459.
- [25] U.S. Aithal, T.M. Aminabhavi, P.E. Cassidy, *Polym. Prepr.* 307 (1) (1989) 17.
- [26] U.S. Aithal, T.M. Aminabhavi, P.E. Cassidy, *J. Am. Chem. Soc.* 19 (1990) 351–376.
- [27] P.E. Cassidy, T.M. Aminabhavi, C.M. Thompson, *Rubb. Chem. Tech. Rubb., Revs.* 556 (1983) 594.
- [28] B.J. Zwolinski, H. Eyring, C.E. Reese, *J. Phys. Colloid. Chem.* 53 (1949) 1426.
- [29] S. Glasstone, K.J. Laidler, H. Eyring, *Theory of Rate Processes*, McGraw-Hill, New York, 1941.