

# Sorption and diffusion of organic solvents in polyurethane elastomers

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Sorption and diffusion of low-molar-mass organic solvents in polyurethane membranes has been studied via an immersion/weight-gain method. The experiments have been conducted at 25, 44 and 60°C. The solvents were chosen to have varying polarity, molecular size, solvent power and interacting groups. The temperature dependence of transport parameters has been used to estimate the activation parameters in addition to enthalpy and entropy of activation. Furthermore, the classical Flory–Rehner swelling model has been used in the thermodynamic analysis of sorption data. The experimental results are discussed in terms of the nature of the interacting solvent molecules.

(Keywords: sorption; diffusion; organic solvent; polyurethane; elastomers)

## INTRODUCTION

Thermoplastic polyurethanes (PU) are block copolymers consisting of alternating hard and soft segments. At service temperatures the soft segment is in the rubbery state while the hard segment is in a glassy or semicrystalline state. The soft segment provides elastomeric character for the polymer, while the hard segment provides dimensional stability by acting as a thermally reversible multifunctional crosslink and also as a reinforcing filler. The unusual properties of PU are directly related to their two-phase morphology wherein the soft segments are commonly low-molar-mass (600–3000) polyether or polyester macroglycols. The hard segments usually consist of an aromatic diisocyanate, which is chain-extended with a low-molar-mass diol to produce blocks with a distribution of molar masses. The driving force for phase separation in PU is the incompatibility of the two segment types. A wide spectrum of physicomechanical properties has been observed depending upon the composition, processing history and chemical architecture of the hard and soft segments<sup>1–3</sup>.

The sorption of organic solvents by PU elastomer has been of some interest in determining the stability and ultimate use of this membrane in severe environments. The solubility of water in thin membranes of polyurethane has been reported to be small<sup>4,5</sup> (approximately 1%) and no extensive data on diffusion of organic solvents have been reported. In this paper, a number of polar solvents with varying polarity and interacting groups have been used. We have performed the sorption experiments using the immersion/weight-gain method<sup>6–8</sup> to investigate solvent transport through a commercially available PU membrane. The liquid sorption was studied at temperatures ranging from 25 to 60°C. From the temperature dependence of transport coefficients, attempts were made to predict the activation parameters, Flory–Huggins type interaction parameter ( $\chi$ ) and molar mass between crosslinks ( $M_c$ ) of the polymer,

## EXPERIMENTAL

### Materials and solvents

Polyurethane used was obtained from PSI Austin, Texas, in sheets of 0.250 cm thickness. The base polymer used is a Vibrathane B600 (Uniroyal), which was prepared from the reaction of polypropylene oxide and toluene diisocyanate (TDI). This base polymer was cured with 4,4'-methylenebis(*o*-chloroaniline) (MOCA) to give the PU elastomer. Thus, the two-phase morphology of PU consisted of polyether diol as the soft segment with molar mass ranging from 300 to 6000 and the aromatic diisocyanate acting as hard segment with molar mass of around 500–3000. The driving force for phase segregation is the incompatibility of the hard and soft segments.

Some of the representative engineering properties of PU used are: tensile strength, 387 kg cm<sup>-2</sup> (5500 psi); maximum percentage elongation, 430; modulus for 300% elongation, 155 kg cm<sup>-2</sup> (2200 psi); tear strength, 5 kg cm<sup>-2</sup> (70 psi) (ASTM D-470); specific gravity, 1.1016; bell brittle point, -62°C; and Bayshore rebound (resilience), 42%.

All the solvents used were of reagent grade and were doubly distilled before use<sup>9</sup>. The PU sample was cut circularly (diameter = 1.94 cm) using a sharp-edged steel die; the thickness measurements were made at several points on the membrane using a micrometer with an accuracy of  $\pm 0.01$  cm.

### Immersion/weight-gain assays

Sorption experiments at 25, 44 and 60°C were performed by immersing the cut PU samples in about 15–20 ml of solvents previously taken in screw-tight metal-capped test bottles kept in a thermostatically controlled oven ( $\pm 0.5^\circ\text{C}$ ) at the desired temperature. The samples were periodically removed from the test bottles, surface liquid was removed by using smooth filter papers, and samples were weighed on a Mettler balance ( $\pm 0.05$  mg). The samples spent no longer than 30–40 s outside the temperature-controlled oven and thus the errors introduced due to solvent evaporation, etc., were minimal.

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The procedure was continued until the membranes attained maximum swelling. The raw data were transferred to a PC-XT or AT personal computer for analysis, graphic display and storage. The gravimetric data were edge-corrected for finite dimensions of the sample by the procedures suggested in the literature<sup>10</sup>. For the case of a constant diffusion coefficient  $D$  ( $\text{cm}^2 \text{s}^{-1}$ ) in the direction normal to the surface, the following relation was used<sup>11</sup>:

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

where  $\theta$  is the slope of the straight-line fit to a plot of percentage weight gain  $Q(t)$  versus square root of time  $t^{1/2}$ ;  $h$  is the sample thickness; and the limiting quantity  $M_\infty$ , for  $t \rightarrow \infty$ , can be related directly to the equilibrium solubility. The foundation for interpreting sorption data for concentration-dependent  $D$  was laid by the pioneering investigations of Crank<sup>11</sup>, who showed that equation (1) also provides the same average of the concentration-dependent diffusion coefficient.

## RESULTS AND DISCUSSION

The sorption data for all the penetrants at 25°C are displayed in Figures 1 and 2; the temperature variation of sorption profiles for a few representative PU-solvent systems is presented in Figures 3 and 4. From the sorption results presented in Figure 1, acetonitrile exhibits an  $M_\infty$  value of about 18%, and it reached equilibrium saturation earlier than nitromethane and nitroethane; the latter exhibited the highest  $M_\infty$  values (~46%) among the penetrants included in Figure 1. The attainment of sorption equilibrium is very slow in the case of n-hexane, for which  $M_\infty$  is about 8%; on the other hand, cyclohexane did not reach equilibrium even after a period of about 10 days. However, results up to only 4 days of immersion are shown in Figure 1. Therefore, experiments with cyclohexane were discontinued. Also, the transport parameters were not calculated for cyclohexane.

Sorption data for some of the highly penetrating liquids are included in Figure 2. Here, the only solvent that reached equilibrium saturation ( $M_\infty \sim 51\%$ ) within a reasonable amount of time is ethyl acetate. On the other hand, ethyl benzoate did not reach true equilibrium even after 10 days of continuous immersion, and thus the transport parameters were not estimated for ethyl benzoate. However, the sorption behaviour of dimethyl-

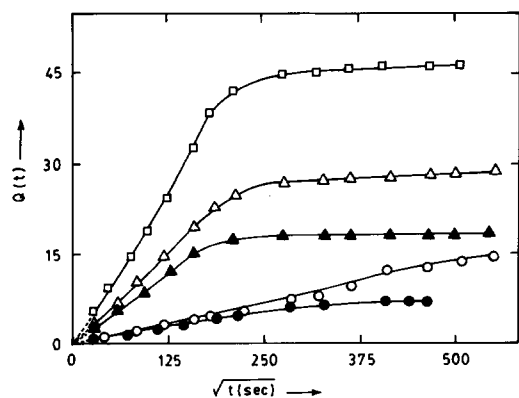


Figure 1 Percentage mass uptake of solvent  $Q(t)$  versus square root of time  $t^{1/2}$  at 25°C: (□) nitroethane; (△) nitromethane; (▲) acetonitrile; (○) cyclohexane; (●) n-hexane

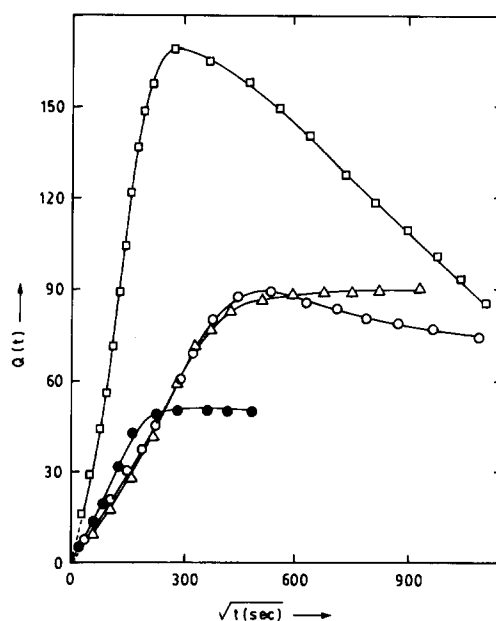


Figure 2 Percentage mass uptake of solvent  $Q(t)$  versus square root of time  $t^{1/2}$  at 25°C: (○) dimethylsulphoxide; (□) dimethylformamide; (△) ethyl benzoate; (●) ethyl acetate

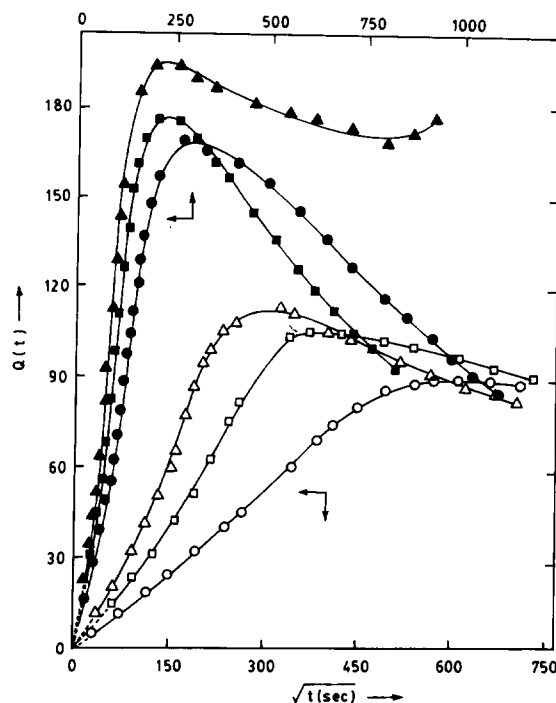
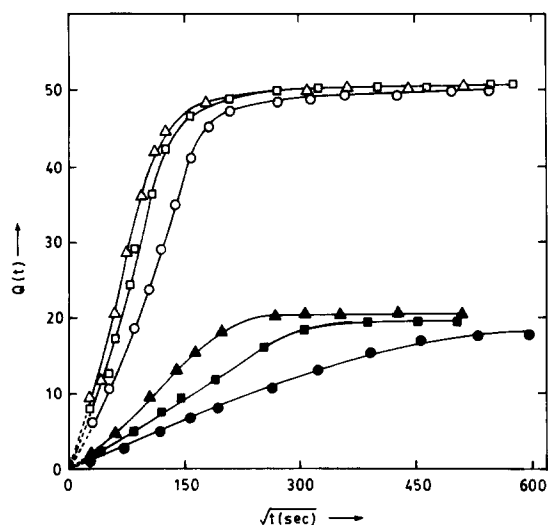


Figure 3 Temperature dependence of sorption:  $Q(t)$  versus  $t^{1/2}$  curves for polyurethane-dimethylformamide (full symbols) and polyurethane-dimethylsulphoxide (open symbols) at 25°C (circles), 44°C (squares) and 60°C (triangles)

formamide (DMF) and dimethylsulphoxide (DMSO) is quite different. DMF rapidly reached a maximum of ~170% and then showed a sudden decrease with time. On the other hand, DMSO showed a maximum sorption of ~90% after a somewhat longer time than DMF and then showed a steady decline in  $Q(t)$  values over an extended period of time. We attribute this effect to the loss of low-molar-mass indigenous compounds in the presence of such aggressive solvents as DMF or DMSO. Such loss of material was checked by drying the sample at the end of an experiment and weighing. In order to



**Figure 4** Temperature dependence of sorption:  $Q(t)$  versus  $t^{1/2}$  curves for polyurethane-ethyl acetate (open symbols) and polyurethane-cyclohexane (full symbols) at 25°C (circles), 44°C (squares) and 60°C (triangles)

see whether such an effect is systematic or not, we also performed experiments with DMF and DMSO at 44 and 60°C, and these results are presented in *Figure 3*, together with the values at room temperature. Such plots indicate that the indigenous low-molar-mass compounds in PU leached out more quickly at higher temperatures than at room temperature for DMSO. However, for DMF, this effect is more rapid at 44°C than at 25 or 60°C.

The temperature dependence of sorption for cyclohexane and ethyl acetate is shown in *Figure 4*. For ethyl acetate, the sorption equilibrium was reached somewhat quicker than for cyclohexane; moreover, the sorption curves of ethyl acetate reached plateau regions with  $M_\infty$  values varying within a narrow range, i.e. 50–51% over the investigated temperature interval. On the other hand, cyclohexane attained the sorption plateau regions at longer times at 44 and 60°C; at 25°C no equilibrium was reached even after about 6 days, and different values of  $M_\infty$  are seen over the investigated temperature interval.

#### Sorption kinetics

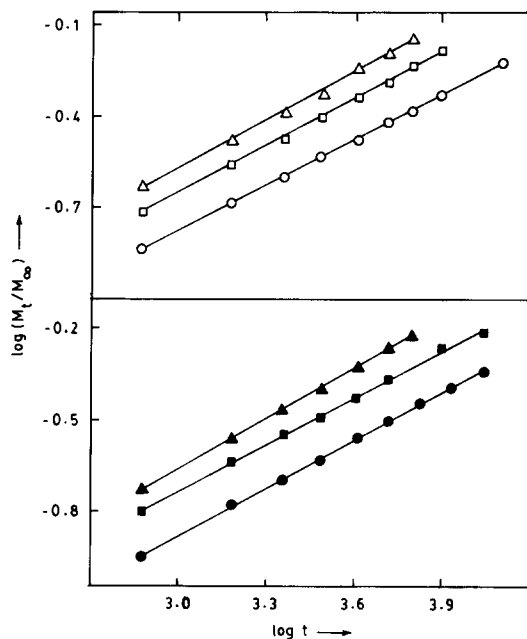
In order to establish the type of diffusion mechanism, the  $(M_t/M_\infty)$  data have been analysed using the equation:

$$\log(M_t/M_\infty) = \log k + n \log t \quad (2)$$

Here,  $M_t$  represents the solvent uptake at time  $t$ ; the parameters  $k$  and  $n$  of equation (2) have been estimated from a least-squares fit of the experimental  $\log(M_t/M_\infty)$  values versus  $\log t$ . Some representative plots for acetonitrile and nitroethane are given in *Figure 5*. The estimated values of  $k$  and  $n$  are included in *Table 1* along with other quantities. In all cases, at all temperatures, the magnitude of  $n$  varies from a minimum of 0.50 to a maximum of 0.64. This suggests that the diffusion process deviates slightly from the normal Fickian behaviour but is not completely non-Fickian; it may thus be classified as anomalous<sup>12,13</sup>. There is no systematic variation of  $n$  with temperature for any of the penetrants considered here. However, the magnitude of  $k$  showed a systematic increase with rise in temperature for all the penetrants except DMF and DMSO.

#### Transport coefficients

Of the three transport coefficients, namely, diffusivity  $D$ , solubility  $S$  and permeability  $P$ , diffusivity was obtained by using equation (1). The penetrant solubility in polyurethane was determined from the plateau regions as the amount of solvent sorbed per gram of PU. The permeability can be calculated<sup>14</sup> from the product of  $D$



**Figure 5**  $\log(M_t/M_\infty)$  versus  $\log t$  curves for polyurethane-nitroethane (full symbols) and polyurethane-acetonitrile (open symbols). Symbols have the same meaning as in *Figures 3* and *4*

**Table 1** Analysis of penetrant transport at various temperatures

Penetrant	Molar volume (cm <sup>3</sup> mol <sup>-1</sup> )	Temp. (°C)	Equation (2)	
			Exponent $n$	$k \times 10^2$ (g g <sup>-1</sup> h <sup>-1</sup> )
Acetonitrile	52.9	25	0.51	4.62
		44	0.52	4.73
		60	0.53	5.48
Nitromethane	54.0	25	0.52	2.68
		44	0.53	3.93
		60	0.52	5.05
Dimethylsulphoxide	71.3	25	0.50	1.74
		44	0.60	1.37
		60	0.56	2.28
Nitroethane	71.9	25	0.54	2.63
		44	0.53	3.83
		60	0.56	4.16
Dimethylformamide	77.4	25	0.59	1.83
		44	0.61	2.23
		60	0.64	2.08
Ethyl acetate	98.5	25	0.55	2.78
		44	0.59	3.05
		60	0.59	3.66
Cyclohexane	108.8	25	0.51	1.71
		44	0.55	1.90
		60	0.57	2.32
n-Hexane	131.6	25	0.50	2.91
		44	0.55	3.18
		60	0.54	4.12
Ethyl benzoate	144.0	25	0.57	1.04
		44	0.57	1.49
		60	0.53	2.36

**Table 2** Solubility  $S$ , equilibrium sorption constant  $K_s$ , diffusivity  $D$  and permeability  $P$  of polyurethane-penetrant system at various temperatures

Penetrant	Temp. (°C)	$S$ (g g <sup>-1</sup> )	$K_s$ (mmol g <sup>-1</sup> )	$D \times 10^7$ (cm <sup>2</sup> s <sup>-1</sup> )	$P \times 10^7$ (cm <sup>2</sup> s <sup>-1</sup> )
Acetonitrile	25	0.184	4.48	3.04	0.56
	44	0.197	4.80	5.63	1.11
	60	0.205	4.98	9.22	1.89
Nitromethane	25	0.302	4.95	2.10	0.63
	44	0.299	4.90	4.47	1.34
	60	0.317	5.19	6.68	2.12
Nitroethane	25	0.463	6.17	2.22	1.03
	44	0.465	6.19	3.83	1.78
	60	0.485	6.46	6.84	3.32
Ethyl acetate	25	0.506	5.75	2.70	1.37
	44	0.508	5.77	5.44	2.77
	60	0.506	5.74	8.22	4.16
Cyclohexane	44	0.194	2.31	1.44	0.28
	60	0.208	2.47	2.66	0.55
n-Hexane	25	0.077	0.89	1.68	0.13
	44	0.082	0.95	3.30	0.27
	60	0.083	0.97	5.24	0.44

and  $S$  (i.e.  $P=DS$ ). These data are summarized in Table 2. It may be noted that diffusivities were obtained only for those penetrants for which we observed complete sorption equilibrium (i.e. perfect plateau regions) over an extended period of time.

Looking at the data given in Tables 1 and 2, it appears that there is no correlation between molar volume and penetrant solubility. For example, acetonitrile, which has the lowest molar volume (52.9 cm<sup>3</sup> mol<sup>-1</sup>) of all the penetrants, shows about 18% maximum sorption; cyclohexane, with a molar volume of about 108.8 cm<sup>3</sup> mol<sup>-1</sup>, also exhibits the same value for  $M_\infty$ . However, n-hexane, even though it has a large molar volume (~132 cm<sup>3</sup> mol<sup>-1</sup>), exhibits as little as 8% maximum sorption, whereas ethyl benzoate, with a molar volume of about 144 cm<sup>3</sup> mol<sup>-1</sup>, shows a maximum solubility of about 90%. Acetonitrile exhibits the highest value of  $D$ , but lower solubility and permeability than nitromethane, even though the molar volume of the latter is almost identical to that of acetonitrile.

The diffusive trends of n-hexane and cyclohexane (for the latter, data are obtained only at 44 and 60°C) are quite different. Even though the molar volume of n-hexane is greater than that of cyclohexane, the latter exhibits lower  $D$  than n-hexane. However,  $S$  for n-hexane is smaller by an order of magnitude compared to cyclohexane; both penetrants show very close  $P$  values. The transport coefficients for nitromethane and nitroethane are quite comparable. For ethyl acetate,  $P$ ,  $D$  and  $S$  are all higher than for the remaining penetrants. Thus, it is clear that the magnitudes of  $P$ ,  $D$  and  $S$  depend to a great extent on the nature of the penetrant molecules in addition to their sizes. The coefficients appear to be sensitive to fluctuations in temperature, although generally these are found to increase with a rise in temperature.

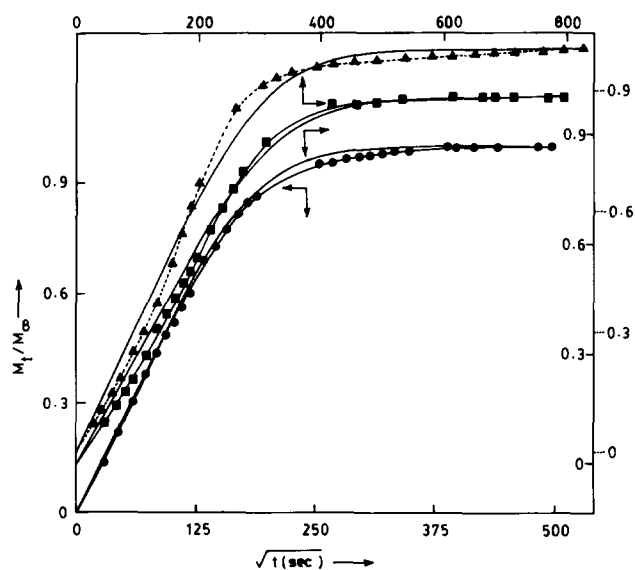
To carry our analysis further, attempts have also been made to analyse the diffusion data in terms of the sorption equation:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} (2n+1)^{-2} \exp[-D(2n+1)^2 \pi^2 t h^{-2}] \quad (3)$$

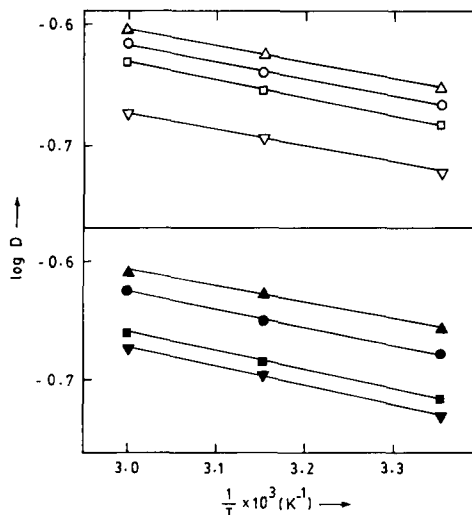
The values of  $D$  obtained from equation (1) along with other relevant parameters have been fed as input parameters to solve equation (3) iteratively and to generate theoretical values of  $(M_t/M_\infty)$ . A comparison between the theoretically calculated curves and those of the experimental sorption profiles for a few representative penetrants is displayed in Figure 6. In the majority of cases, good agreement is observed between the simulated and experimental curves for all the systems. However, the poor fit for ethyl benzoate at 44°C may be attributed to the errors involved in the computation of  $D$  values calculated from equation (1).

#### Arrhenius activation parameters

From the temperature dependence of diffusivity shown in Figure 7, the energy of activation  $E_D$  for the process



**Figure 6** Comparison between experimental and simulated (—) sorption profiles for polyurethane-solvent systems: (●) n-hexane at 44°C; (▲) ethyl benzoate at 44°C; (■) cyclohexane at 60°C. For ethyl benzoate a broken curve is drawn through the experimental points, which refers to the right-hand scale outside the vertical axis. In the case of n-hexane and cyclohexane, the scale on the inside of the vertical line is applicable



**Figure 7** Arrhenius plots for diffusivity of solvents through polyurethane membrane: (△) acetonitrile; (○) nitromethane and nitroethane; (□) dimethylformamide; (▽) dimethylsulphoxide; (▲) ethyl acetate; (●) n-hexane; (■) cyclohexane; (▼) ethyl benzoate

**Table 3** Analysis of Arrhenius parameters and thermodynamic functions

Penetrant	$E_D$ (kJ mol <sup>-1</sup> )	$E_p$ (kJ mol <sup>-1</sup> )	$\Delta H_s$ (kJ mol <sup>-1</sup> )	$\Delta S$ (J mol <sup>-1</sup> k <sup>-1</sup> )	$-\Delta G$ (kJ mol <sup>-1</sup> )	$-\left(\frac{d\phi}{dT}\right) \times 10^4$	$\chi$	$M_c$
Acetonitrile	26.03	28.56	2.53	21.0	3.72	8.0	0.44	106
Nitromethane	27.39	28.43	1.03	16.7	3.94	4.8	0.36	110
Nitroethane	26.23	27.25	1.02	18.9	4.48	5.4	0.54	351
Ethyl acetate	26.30	26.28	-0.02	14.5	4.33	3.2	0.35	440
n-Hexane	26.74	28.77	2.03	5.8	-0.30	6.8	1.51	962
Ethyl benzoate	-	-	-	-	-	5.2	0.41	1320

of diffusion has been estimated. Arrhenius plots for the dependence of  $\log P$  versus  $1/T$  similarly yield values of the activation energy for the process of permeation (graphs not shown). From these results, the heat of solution  $\Delta H_s (=E_p - E_D)$  can be calculated, and these data are also included in Table 3. It may be noted that both  $E_D$  and  $E_p$  values are found to be around 26–29 kJ mol<sup>-1</sup>; furthermore, there is no direct relationship between the size of the diffusing solvent molecule and either  $E_D$  or  $E_p$ . The  $\Delta H_s$  value for ethyl acetate is small but negative, whereas for the other penetrants (namely, acetonitrile, n-hexane, nitroethane and nitromethane) the  $\Delta H_s$  values are all positive and vary in the order of 1–2.5 kJ mol<sup>-1</sup>.

#### Equilibrium sorption constants

Following the procedure of Hung<sup>15</sup>, the equilibrium sorption constant  $K_s$  was obtained from the ratio of millimoles of solvent sorbed per gram of PU membrane. These results are also included in Table 2. In all cases,  $K_s$  is found to increase systematically with increase in temperature. From the van't Hoff plots as given in Figure 8, the change in entropy  $\Delta S$  for the sorption process has been calculated<sup>16</sup> from the intercepts:

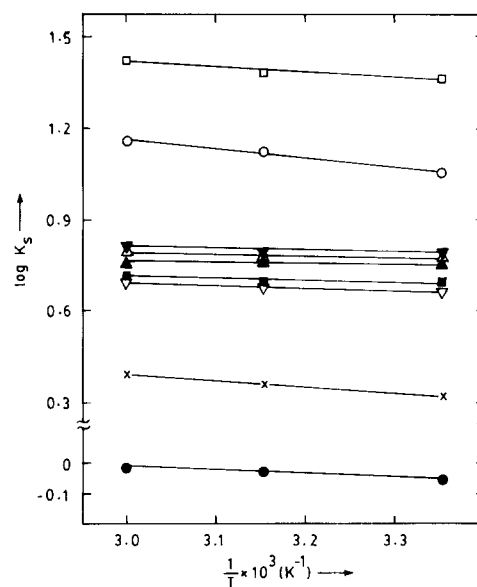
$$\log K_s = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \quad (4)$$

These values are then used to predict the Gibbs free energy  $\Delta G$  at 25°C for the sorption phenomenon for each PU–solvent pair using the standard Gibbs relation, i.e.  $\Delta G = \Delta H - T\Delta S$ . The calculated  $\Delta G$  values are negative for all the penetrants except n-hexane, which showed positive  $\Delta G$  values. The results for  $\Delta G$  at 25°C are also included in Table 3. However, an increase in temperature showed a systematic decrease in  $\Delta G$  values.

#### Molar mass between crosslinks

The Flory–Rehner swelling model<sup>17–19</sup> has been used in the literature to predict the molar mass between crosslinks ( $M_c$ ). To do this we need to have accurate values of Flory–Huggins type interaction parameter  $\chi$ . Several researchers<sup>20–22</sup> have attempted to compute  $\chi$  from the solubility parameter concept as developed by Hildebrand<sup>23</sup>. This approach being strictly empirical sometimes leads to wrong predictions for  $\chi$ ; also, for some penetrants it would be cumbersome to find reliable literature data on solubility parameters of solvents. Instead, we suggest using an alternative phenomenological theory to calculate  $\chi$ . Thus, starting from the Flory–Rehner equation<sup>17–19</sup>, the temperature coefficient of volume fraction  $(d\phi/dT)$  may be obtained as:

$$\left(\frac{d\phi}{dT}\right) = \chi\phi T^{-1} \{2\chi\phi - \phi(1-\phi)^{-1} - [\ln(1-\phi) + \phi + \chi\phi^2]N\}^{-1} \quad (5)$$



**Figure 8** van't Hoff plots for polyurethane–solvent systems: (□) dimethylformamide; (○) dimethylsulphoxide; (▼) nitroethane; (△) ethyl benzoate; (▲) ethyl acetate; (■) nitromethane; (▽) acetonitrile; (×) cyclohexane; (●) n-hexane

where

$$N = \left(\frac{1}{3}\phi^{2/3} - \frac{2}{3}\right)\left(\phi^{1/3} - \frac{2}{3}\phi\right)^{-1} \quad (6)$$

Solving equation (5) for  $\chi$  we get:

$$\chi = \left[\phi(1-\phi)^{-1} + N \ln(1-\phi) + N\phi\right] \times [2\phi - \phi^2N - \phi^2T^{-1}(d\phi/dT)^{-1}]^{-1} \quad (7)$$

The molar mass between crosslinks can then be estimated as:

$$M_c = -\rho_p V_s \phi^{1/3} [\ln(1-\phi) + \phi + \chi\phi^2]^{-1} \quad (8)$$

where  $V_s$  is the molar volume of penetrant. The volume fraction  $\phi$  of the polymer in its swollen state may be computed as:

$$\phi = [1 + (\rho_p/\rho_s)(M_a/M_b) - (\rho_p/\rho_s)]^{-1} \quad (9)$$

where  $\rho_p (=1.1016 \text{ g cm}^{-3})$  and  $\rho_s$  are the densities of polymer and penetrant, respectively, and  $M_b$  and  $M_a$  are the masses of polymer before and after swelling, respectively.

Wide variations in the values of  $\chi$  and  $M_c$  were observed. For instance,  $\chi$  varied from a lowest value of 0.35 for nitromethane and ethyl acetate to a highest value of 1.51 for n-hexane. However, the lowest value of  $M_c$  (=106) was observed for acetonitrile and for ethyl benzoate  $M_c$  is 1320, which is the highest among the penetrants studied here. It may be noted that such variations of the  $M_c$  values indicate the serious limitations

of the Flory–Rehner model for the study of swelling of PU in the presence of organic solvents. However, the complexity of solvent interactions may probably affect, in various degrees, the hard- as well as the soft-segment phases of PU.

### CONCLUSIONS

The transport properties of nine organic solvents in polyurethane membranes were investigated by the immersion/weight-gain method in the temperature interval 25–60°C. The activation energies for the processes of diffusion and permeation varied from 26 to 29 kJ mol<sup>-1</sup>. Diffusion was found to follow an anomalous pattern. From the temperature dependence of the equilibrium sorption constant, the Gibbs energy and entropy changes were estimated. These results have been used in the discussion of thermodynamic interactions between polyurethane and penetrants. Attempts were made to estimate the molar mass between crosslinks of PU segments using the classical Flory–Rehner theory.

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