

# Molecular Transport of Some Industrial Solvents Through a Polyurethane Membrane

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## SYNOPSIS

Sorption and transport studies of several industrial solvents have been investigated through a Uralite 3142 polyurethane. Diffusion coefficients have been measured for the preswollen and fully swollen polyurethanes. For majority of solvents, non-Fickian transport mode was observed and these results have been interpreted in terms of polymer-penetrant interactions. Temperature-dependent diffusion parameters followed the Arrhenius relation from which energy of activation have been obtained. The Flory-Rehner equation, in spite of its limitations, has been found to be useful to estimate the molar mass between crosslinks of the network polyurethane.

## INTRODUCTION

Polyurethane block copolymers are heterophase systems composed of alternating aromatic urethane and macroglycol segments. The macroglycol segments are usually a polyether or a polyester. Since thermodynamic incompatibility between the chemically dissimilar blocks prevents formation of a homogeneous mixture, the urethane and macroglycol segments cluster into separate domains and electron microscopic studies have proved the existence of two phases in polyurethanes.<sup>1</sup> At room temperatures, the macroglycol segments are above their glass transition ( $T_g$ ) and are designated as the soft segment; the aromatic isocyanates which are below their  $T_g$  form the hard segments. Thus, at temperatures below the  $T_g$  of the hard segments, the hard domains can act as filler particles and as crosslinks to restrain the motion of soft segment chains. This is the mechanism responsible for the enhanced mechanical properties of polyurethane. The mobility of chains within the hard domains increases as the temperature is increased and the crosslinking effectiveness of the hard domains decreases. The effects of hard

domain softening are apparent even at temperatures well below the hard segment  $T_g$ .

The structure-property relations of polyurethane have been the subject of extensive investigation.<sup>2,3</sup> Schneider et al.<sup>4-6</sup> studied the effects of structural variations on transport in polyurethanes. In a number of other studies, transport of organic solvents through polyurethane has been investigated.<sup>7-9</sup> All these studies have suggested that diffusion in polyurethanes is actually governed by an Arrhenius temperature dependence and the hard domains tend to produce more tortuous route for the diffusing molecules. As a further contribution in this area, our efforts have been directed to study the transport of some industrially important organic solvents through a commercial polyurethane available under the trade name, Uralite 3142 from Hexcel Chemical Products (U.S.A.). The solvents ranged from aromatics and hydrocarbons to alcohols. The transport of these solvents has been studied from sorption experiments to deduce transport parameters like diffusivity ( $D$ ), permeability ( $P$ ), and sorption coefficients ( $S$ ) over the temperature interval of 25–60°C. For some liquids, sorption experiments were performed at room temperature. Furthermore, the Arrhenius factors involved in the transport processes have been estimated to deduce the nature of polyurethane-solvent interactions. The swelling data have been discussed in terms of the Flory-Rehner

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model<sup>10</sup> to estimate the molar mass between cross-links of the network polymer.

## EXPERIMENTAL

### Materials

Polyurethane samples, Uralite 3142, used in this research were procured from Hexcel Chemical Products (U.S.A.). The technical data bulletin reveals its uses as abrasion resistant pads and bumpers, molds and mold facings, rollers and castings, flexible gaskets, electrical potting, and in encapsulation areas.

Some representative engineering properties of the elastomer as determined by the ASTM D 412-68 method are: tensile strength, 149 kg/sq cm (2,120 psi); elongation 500%; tensile modulus, at 100% elongation, 67 kg/sq cm (950 psi) and at 300% elongation, 125 kg/sq cm (1780 psi). The density of the polymer as determined by ASTM D 792-66 is 1.037 g/cm<sup>3</sup> (0.037 lb/cm<sup>3</sup>). The  $T_g$  of the polymer as determined by DSC (DuPont thermal analyzer 9900) is -63.95°C (see Fig. 1). Solvents used were all of reagent grade and double-distilled before use.

### Sorption Experiments

Sorption experiments were performed by soaking the circularly cut samples of diameter = 1.94 cm, thickness = 0.325 cm, and initial weight ~ 1.0 g, in about 15–20 mL of the solvent taken in sorption bottles. The bottles were closed tightly and kept in thermostatically controlled oven (Memmert, Germany) for specified lengths of time. At regular intervals, these samples were taken out, weighed to the nearest fraction of a milligram, and placed back into the containers. Sorption experiments were conducted at 25, 44, and 60°C with benzene, toluene, acetonitrile, *n*-hexane, and cyclohexane solvents. For solvents which required long times to reach equilibrium saturation, only room temperature data were taken. In each case, the moles of solvent sorbed per 100 g of the polymer were calculated from the weight gain measurements and these results were used in the discussion.

### Diffusion Coefficients

Diffusion of a liquid in a polymer matrix is described by the Fick's laws. The first law states that, in one dimension, rate of mass transfer ( $F$ ) of a penetrant through a unit area of polymer is proportional to

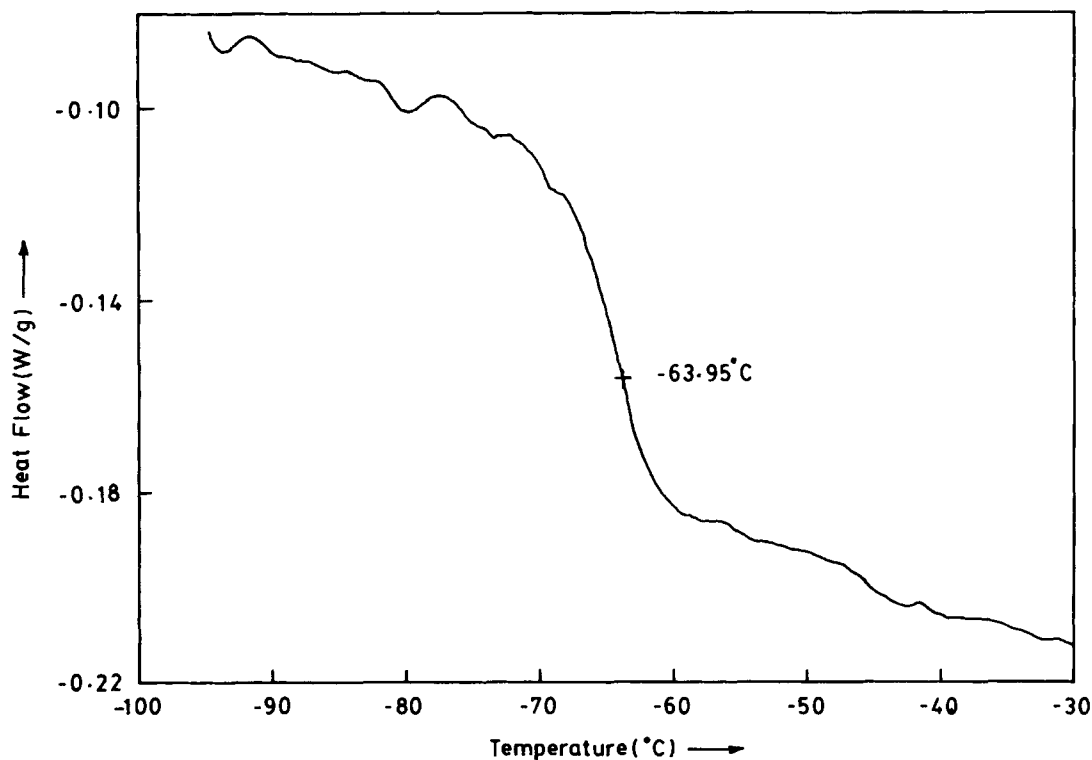


Figure 1 DSC tracing of polyurethane.

concentration gradient ( $\partial c/\partial z$ ), normal to materials surface,<sup>11</sup>

$$F = -D_z \left( \frac{\partial c}{\partial z} \right) \quad (1)$$

where the constant of proportionality is the diffusion coefficient  $D_z$ . According to Fick's second law in one dimension, we have

$$\frac{\partial c}{\partial t} = - \frac{\partial F}{\partial t} = - \frac{\partial}{\partial t} \left( D_z \frac{\partial c}{\partial z} \right) \quad (2)$$

A polymer-liquid system is said to be Fickian if both the laws are obeyed. Furthermore, if the diffusion coefficient is independent of concentration and time, then diffusion follows the Fickian Case I mechanism; for Case I, the integrated Fick's equation yields

$$\frac{M_t}{M_\infty} = \frac{4}{\pi^{1/2}} \left( \frac{D_z t}{h} \right)^{1/2} \quad (3)$$

where  $M_t$  and  $M_\infty$  are, respectively, the mole percent sorbed concentrations at time  $t$  and at equilibrium saturation;  $h$  is sample thickness. Equation (3) is valid for sorption time shorter than the time required to sorb 50% of the equilibrium uptake of penetrant. Furthermore, eq. (3) predicts that mole percent uptake plotted as a function of square root of time will yield a sorption curve and the values of  $D_z$  can be determined from the slope  $G$ , of the straight line portion before 50% of sorption, by using eq. (4) if Fickian Case I is applicable<sup>12</sup>:

$$D_z = \frac{\pi}{16} \left( \frac{hG}{M_\infty} \right)^2 \quad (4)$$

If the polymer/penetrant system under study does not follow the Case I diffusion, then the values of  $D_z$  thus obtained are not the true values of diffusion coefficient but can be regarded as apparent diffusivities. Thus, in a Fickian diffusion, the rate of diffusion is much less than that of relaxation due to mechanical, structural, etc., modes of the polymer-solvent system. In the other extreme, i.e., Case II transport, diffusion is very rapid compared to other relaxation processes. Departure from Fickian diffusion can occur for many reasons. If sorption equilibrium cannot be achieved at a film surface due to appreciable surface evaporation rate, sorption curves exhibit sigmoidal shapes. Such sorption curves are described, more generally, as non-Fickian or anomalous sorption curves. In addition to surface con-

centration changes, non-Fickian or anomalous sorption curves are also observed when the diffusion and relaxation rates are comparable.<sup>13</sup> Thus, the three modes of transport processes can be distinguished by fitting the fractional uptake data to an empirical relation of the type<sup>14</sup>

$$\frac{M_t}{M_\infty} = kt^n \quad (5)$$

where the value of exponent  $n = \frac{1}{2}$  for Case I (Fickian) diffusion, whereas, for Case II,  $\frac{1}{2} < n < 1$  suggests the non-Fickian (or anomalous) diffusion. The constant  $k$  is indicative of the extent of polymer-solvent interaction. The estimated error in the evaluation of  $n$  is found to be  $\pm 0.005$  units, and we have rounded the values to second decimal place.

## RESULTS AND DISCUSSION

### Sorption and Diffusion

Sorption data shown in Figures 2 and 3 show that the sorbed concentration increases rapidly from zero time until at least 50% of equilibrium sorption. The slight sigmoidal shapes of the curves during early stages of sorption are indicative of the deviation from the true Fickian transport. These curves can be rationalized on the basis of polymer chain segmental motions relative to the concurrent penetrant diffusion rate. The rate of relaxation is very fast for small molecules whereas more extensive cooperative chain segmental motions are needed to accommodate larger penetrant molecules. When the polymer relaxation and diffusion rates are comparable, then non-Fickian anomalies are observed. Departure from the Fickian behavior is further seen from the estimated values of  $n$  of eq. (5) given in Table I. For almost all penetrants,  $n$  varies from 0.51 to 0.68 and thus, we classify diffusion process to be anomalous.

The sorption data of several penetrants shown in Figure 2 exhibit sorption behavior typical of sorption of moderately swelling penetrants in elastomers. Mole percent sorption of chlorobenzene is highest and, for  $n$ -hexane, it is lowest. However, intermediate sorptivities are observed for benzene and methyl-substituted benzenes, and these penetrants follow the sequence: benzene > toluene > *m*-xylene > mesitylene. Figure 3 indicates that the amount of ethanol sorbed into the polymer at equilibrium is the same as that of methanol. Also, sorption of methanol is higher than those of acetonitrile and

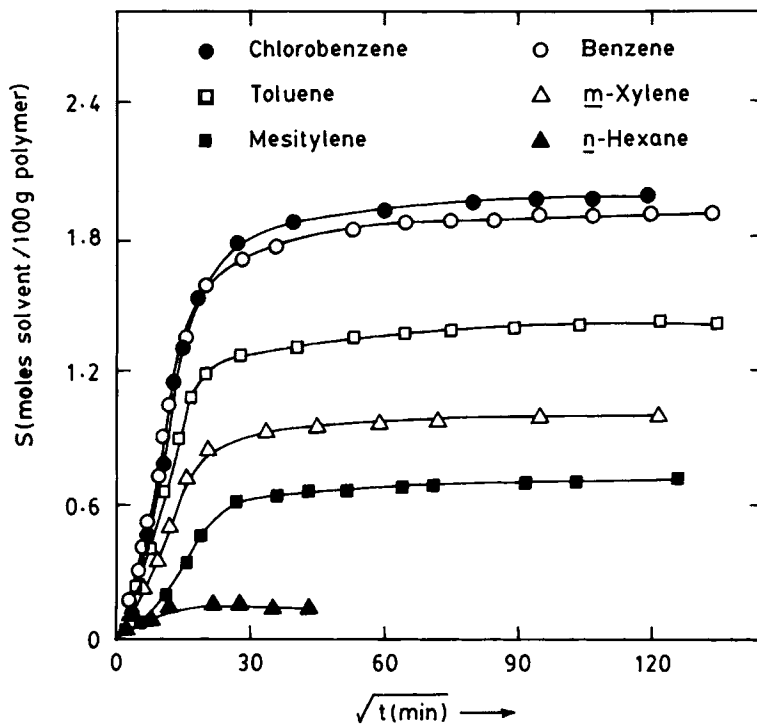


Figure 2 Sorption vs. square root of time at 25°C for benzene (○), toluene (□), *m*-xylene (△), mesitylene (■), chlorobenzene (●), and *n*-hexane (▲) in polyurethane.

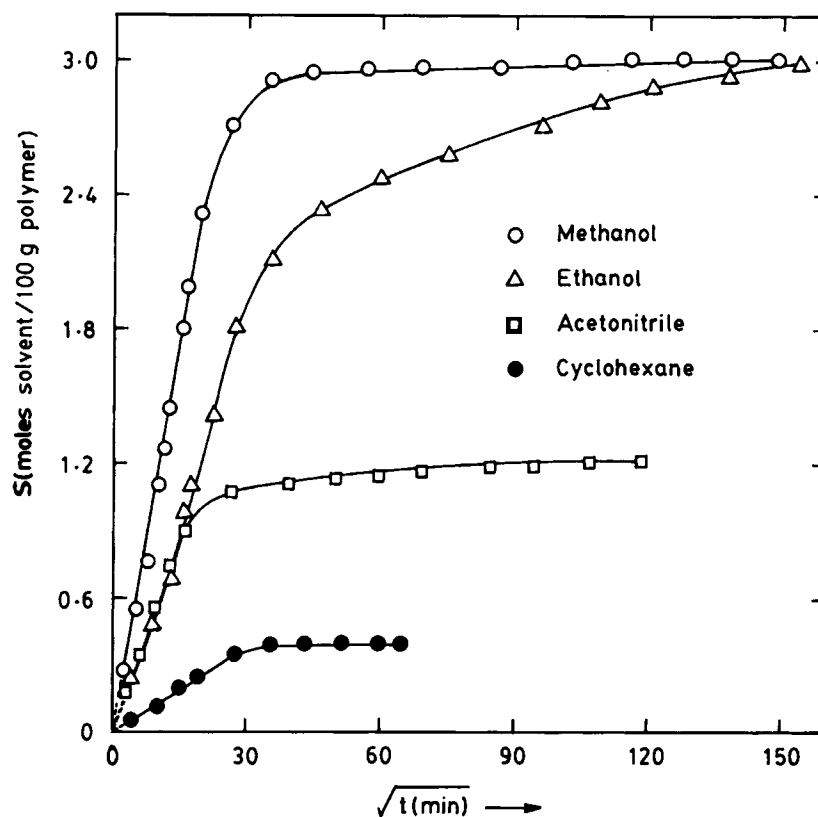


Figure 3 Sorption vs. square root of time at 25°C, for methanol (○), ethanol (△), acetonitrile (□), and cyclohexane (●) in polyurethane.

**Table I Sorption and Diffusivity Data on Polyurethane + Solvent Systems**

Liquid	Temp (°C)	Molar Volume (cm <sup>3</sup> /mol)	S (mol %)	Exponent <i>n</i>	<i>D</i> × 10 <sup>7</sup> (cm <sup>2</sup> /s)	$\bar{D}$ × 10 <sup>7</sup> (cm <sup>2</sup> /s)
Benzene	25	89.4	1.903	0.62	8.01	16.16
	44		1.933	0.66	14.79	29.84
	60		1.964	0.68	20.40	41.35
Toluene	25	106.9	1.414	0.58	6.14	12.34
	44		1.438	0.61	11.97	24.04
	60		1.469	0.66	18.85	37.85
Acetonitrile	25	52.9	1.227	0.51	8.00	15.87
	44		1.247	0.57	12.00	23.81
	60		1.356	0.59	16.91	33.55
<i>n</i> -Hexane	25	131.6	0.156	0.55	10.66	20.46
	44		0.168	0.59	13.93	26.74
	60		0.201	0.57	19.07	36.61
Cyclohexane	25	108.8	0.405	0.58	3.12	6.03
	44		0.520	0.64	6.03	11.67
	60		0.583	0.59	7.12	13.78
Chlorobenzene	25	102.2	1.975	0.64	8.44	16.42
	44		1.988	0.65	11.68	22.71
	60		2.109	0.64	13.33	25.93
Methanol	25	40.7	2.368	0.52	3.67	7.54
Ethanol	25	58.7	2.430	0.56	1.24	2.36
<i>m</i> -Xylene	25	123.5	0.872	0.58	5.11	9.51
Mesitylene	25	139.6	0.604	0.62	2.64	5.15

cyclohexane. However, ethanol did not reach sorption equilibrium even after 15 days of continuous immersion and therefore experiments were discontinued. The increase in sorption as a function of molecular size of the penetrants can be accounted in terms of solubility parameter theory.<sup>15</sup> It is observed that an approximate linear relation exists between sorption and solubility parameter of penetrants (excepting acetonitrile). Thus, sorption is governed not only by the differences in solubility parameters but that the structure of polymer and penetrant size per se also play roles in determining sorption levels. It is seen in Figure 3 that, for methanol (the smallest penetrant), the sorption levels off, whereas this is not true for ethanol. This suggests that hindered chain segmental mobility of polyurethane not only affects the ease for diffusion depending on the size of penetrant, but also contributes to the sorption process in addition to thermodynamic considerations. With an increase in temperature, sorption coefficient also increases (see Table I). For some solvents, given in Table I, the sorption data have not been collected at higher temperatures.

Diffusion coefficients as determined from the slopes of the initial linear part of the sorption curves calculated from eq. (4) are summarized in Table I. These diffusion coefficients ( $D_z$ ) are to be considered

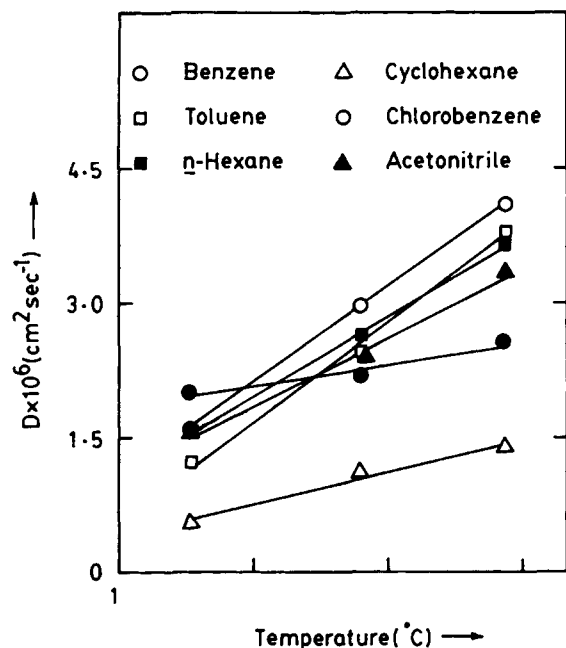
as parameters for preswollen polyurethane assuming that Fickian transport is operative. However, during sorption experiments we found significant swelling of polyurethane for a majority of solvents. In order to account for such spatial distribution of solvent molecules within the polymer matrix, we have attempted to make corrections to diffusivities under swollen conditions. Thus, following the procedure developed earlier,<sup>16</sup> we propose to calculate diffusion coefficient  $\bar{D}$ , by considering changes in the thickness as well as diameter of the polymer sample.

$$\bar{D} = D_z \left[ 1 + \frac{\bar{h}}{\bar{r}} \left( \frac{D_r}{D_z} \right)^{1/2} + \frac{\bar{h}}{2\pi\bar{r}} \left( \frac{D_\theta}{D_z} \right)^{1/2} \right]^2 \quad (6)$$

Here,  $\bar{h}$  and  $\bar{r}$  represent, respectively, average thickness and radius of the sample before and after swelling;  $D_r$  and  $D_\theta$  are, respectively, the diffusivities along the radial and angular directions. For isotropic diffusion under equilibrium conditions, we may assume  $D_z = D_r = D_\theta$  so that

$$\bar{D} = D_z \left( 1 + \frac{\bar{h}}{\bar{r}} + \frac{\bar{h}}{2\pi\bar{r}} \right)^2 \quad (7)$$

The calculated values of  $\bar{D}$  are also included in Table I.



**Figure 4** Variation of diffusion coefficient with temperature for benzene (○), toluene (□), acetonitrile (▲), *n*-hexane (■), cyclohexane (△), and chlorobenzene (○), in polyurethane.

Diffusion coefficients ( $D$  or  $\bar{D}$ ) of all the penetrants increase with a rise in temperature (see Fig. 4). At 25°C, benzene, toluene, *m*-xylene, and mesitylene show a regularly decreasing trend in  $\bar{D}$  with an increase in molar volume of the solvent. However, *n*-hexane having a molar volume of about 132 cm<sup>3</sup>/mol, exhibits higher diffusivity than mesitylene, although, for the latter, the molar volume is about 140 cm<sup>3</sup>/mol. Acetonitrile and benzene exhibit almost identical diffusivities at 25°C, but, at higher temperatures, benzene exhibits higher diffusivities than acetonitrile. Diffusivity of chlorobenzene is higher than benzene and its methyl-substituted homologues. We do not consider  $D$  or  $\bar{D}$  data for ethanol to be reliable as no true equilibrium was attained

within the laboratory period of investigation. Surprisingly, diffusivities of methanol and cyclohexane are comparable, though their molar volumes are widely different.

#### Arrhenius Parameters

From a temperature dependence of diffusivity, the activation energy  $E_D$  for the diffusion process has been calculated as

$$\log D = \log D_0 - E_D/2.303RT \quad (8)$$

The estimated values of  $E_D$  are compiled in Table II. The Arrhenius plots describing the temperature dependence of diffusivity for all the penetrants are linear as shown in Figure 5. It is observed that wide variations in  $E_D$  values are observed and these range from a minimum of about 11 kJ/mol for chlorobenzene to a maximum of 27 kJ/mol for toluene.

In order to compute heat of sorption,  $\Delta H_s$ , attempts were made to calculate the equilibrium sorption constant  $K_s$ , from considerations on the equilibrium process occurring in the liquid phase at constant temperature and pressure.<sup>17</sup> Thus,

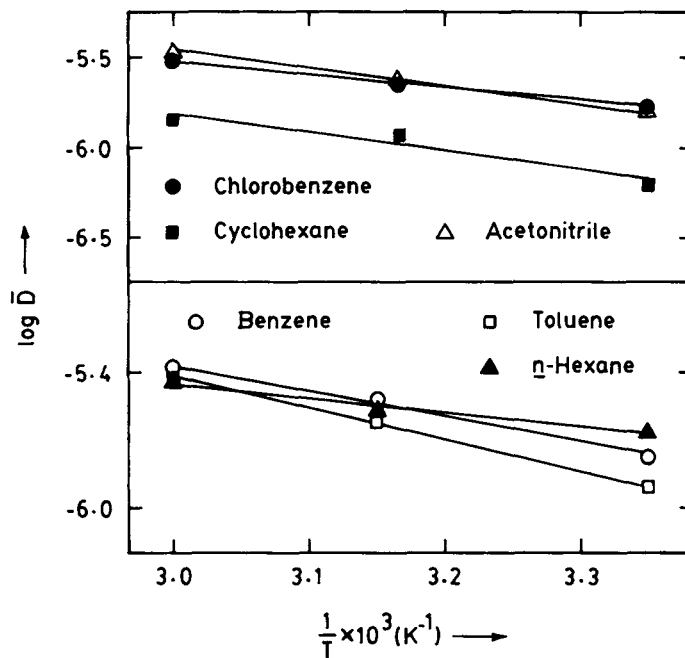
$$\begin{aligned} K_s &= \frac{\text{n mol penetrant sorbed}}{\text{mass polymer}} \\ &= \frac{\text{m mol penetrant}}{\text{g membrane}} \end{aligned} \quad (9)$$

Realizing the interrelationships between  $K_s$  and various thermodynamic quantities, we can calculate change in enthalpy (i.e., heat of sorption),  $\Delta H_s$ , and change in entropy of sorption  $\Delta S$ , by using van 't Hoff relationship<sup>7</sup>:

$$\log K_s = \frac{\Delta S}{2.303R} - \frac{\Delta H_s}{2.303R} \cdot \frac{1}{T} \quad (10)$$

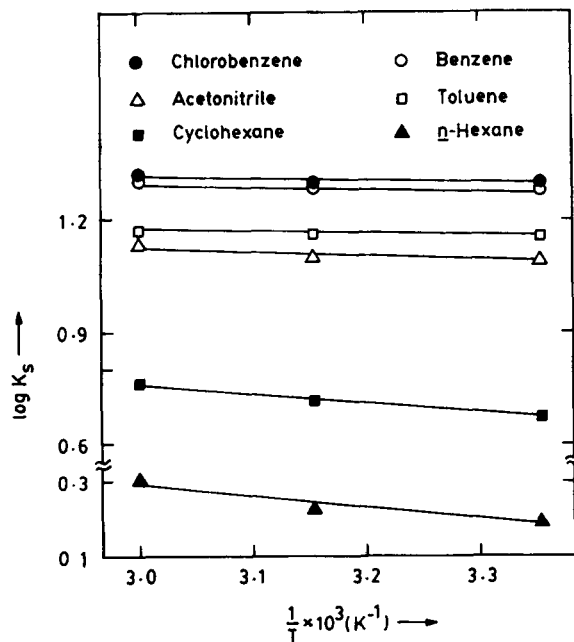
**Table II** Thermodynamic Quantities and Activation Parameters of Polyurethane + Solvent Systems

Liquid	$E_D$ (kJ/mol)	$\Delta H_s$ (kJ/mol)	$\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$-\Delta G$ (kJ/mol)
Benzene	22.304	0.738	26.97	7.300
Toluene	26.460	0.879	24.97	6.565
Chlorobenzene	10.907	1.417	29.51	7.399
Acetonitrile	17.580	2.266	28.36	6.214
<i>n</i> -Hexane	13.574	5.896	23.29	1.094
Cyclohexane	19.861	8.684	40.87	3.463



**Figure 5** Arrhenius plots of  $\log \bar{D}$  vs.  $1/T$  for benzene ( $\circ$ ), toluene ( $\square$ ), chlorobenzene ( $\bullet$ ), acetonitrile ( $\triangle$ ), cyclohexane ( $\blacksquare$ ), and *n*-hexane ( $\blacktriangle$ ) in polyurethane.

By assuming that  $\Delta H_s$  and  $\Delta S$  remain constant over the investigated temperature interval (25–60°C), a plot of  $\log K_s$  vs.  $1/T$  as shown in Figure 6 is found to be linear from which  $\Delta H_s$  and  $\Delta S$  have been ob-



**Figure 6** van't Hoff plots of  $\log K_s$  vs.  $1/T$  for benzene ( $\circ$ ), toluene ( $\square$ ), chlorobenzene ( $\bullet$ ), acetonitrile ( $\triangle$ ), cyclohexane ( $\blacksquare$ ), and *n*-hexane ( $\blacktriangle$ ) in polyurethane.

tained from the intercept and slope, respectively. These results are also included in Table II. The results of  $\Delta H_s$  are positive for all the penetrants and increase systematically from benzene all the way to cyclohexane, as shown in Table II. This suggests the increased endothermicity of the sorption phenomenon in the presence of series of solvents given in Table II. However, the positive  $\Delta S$  values range from 23 to 40 J mol<sup>-1</sup> K<sup>-1</sup>. The standard Gibbs energy of sorption,  $\Delta G$ , is negative at 25°C and suggests the spontaneous sorption process taking place for all polyurethane–solvent pairs.

#### Molar Mass between Crosslinks

When a polymer sample is immersed in a solvent medium, solvent molecules will diffuse into the solid polymer to produce a swollen membrane. Swelling continues until the elastic retraction of the network balances the osmotic pressure driving the solvent into the swollen polymer. Flory–Rehner theory<sup>10</sup> has been used to calculate the molar mass  $M_c$  between crosslinks. For a high degree of swelling the Flory–Rehner equation is expressed as

$$\frac{1}{V_e} = -V_s \phi^{1/3} / [\ln(1 - \phi) + \phi + \chi \phi^2] \quad (11)$$

where  $\phi$  is volume fraction of the polymer in swollen

**Table III Analysis of Swelling Results in Terms of the Flory–Rehner Model**

Liquid	$\delta_s$ (cal/cm <sup>3</sup> ) <sup>1/2</sup>	$\phi$	$\chi$	$M_c$
Benzene	9.2	0.362	0.35	1611
Toluene	8.9	0.390	0.41	1903
Acetonitrile	11.9	0.598	0.86	5967
<i>n</i> -Hexane	7.3	0.825	1.42	<sup>a</sup>
Cyclohexane	8.2	0.687	0.65	595
Chlorobenzene	9.5	0.323	0.34	2307
Methanol	14.5	0.440	2.06	<sup>a</sup>
Ethanol	10.0	0.368	0.37	1057
<i>m</i> -Xylene	8.8	0.435	0.44	1858
Mesitylene	8.8	0.496	0.45	1319

<sup>a</sup> Negative values are observed.

gel at equilibrium in solvent which is determined as<sup>18</sup>

$$\phi = \left[ 1 + \frac{\rho_p}{\rho_s} \left( \frac{M_a}{M_b} \right) - \frac{\rho_p}{\rho_s} \right]^{-1} \quad (12)$$

where  $M_b$  and  $M_a$  are masses of polymer before and after swelling,  $\rho_s$  and  $\rho_p$  are densities of solvent and polymer, and  $V_e$  is the number of polymer chains per unit volume, which is related to the apparent molar mass  $M_c$  between crosslinks by density as

$$V_e = \rho_p / M_c \quad (13)$$

To determine the polymer–solvent interaction parameter  $\chi$ , in eq. (11), the Bristow and Watson<sup>19</sup> semiempirical relation was used:

$$\chi = \beta + (V_s / RT) (\delta_s - \delta_p)^2 \quad (14)$$

Here  $\beta$  is the lattice constant, whose value is about 0.34, and  $V_s$  is the molar volume of the solvent;  $RT$  has the usual conventional meaning. The solubility parameter  $\delta_p$  of the polymer was obtained from a consideration of the corresponding parameter  $\delta_s$  of the solvent by a method suggested by Gee.<sup>20,21</sup>

Table III summarizes the results of these analyses. Here, results of  $\chi$  and  $M_c$  should be regarded as strictly approximate because due correction to include the compositional variation of soft and hard segments of polyurethane was not made; however, this information was also not available from the manufacturers. The wide variations in the values of  $M_c$  are attributed to the limitations of the Flory–

Rehner theory for a heterogeneous system and also to the fact that the complexity of solvent interactions affect in various degrees, the microdomain structure of polyurethane.

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