

# Diffusion and Sorption of Organic Liquids Through Polymer Membranes. I. Polyurethane versus *n*-Alkanes

R. S. KHINNAVAR and T. M. AMINABHAVI\*

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

## SYNOPSIS

Sorption and diffusion studies of *n*-alkanes through a commercial polyurethane membrane have been investigated in the temperature interval of 25–60°C. Liquid diffusivity through polyurethane was measured by using the immersion/weight gain method and the diffusion mechanism was explained in terms of the Fickian model. The activation energies of sorption and diffusion processes have been estimated and used to investigate the thermodynamic interactions between polyurethane chains and *n*-alkanes. Furthermore, sorption data were used to estimate the molar mass between crosslinks of the network polymer.

## INTRODUCTION

Elastomeric polyurethane (PU) membranes are known to exhibit unique mechanical properties as a result of two-phase morphology.<sup>1</sup> These elastomers 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 (ester or ether). The hard and soft segments are chemically incompatible and microphase separation of the hard segments into domains dispersed in a matrix of soft segments can occur in varying degrees.<sup>2,3</sup> In view of the importance of PU as a barrier material in engineering applications,<sup>4</sup> it is essential to know its transport characteristics with respect to common organic solvents. Thus, a knowledge of the transport phenomenon due to sorption and diffusion of organic liquids in a PU matrix is helpful for establishing the relationships between structures and properties under extreme service conditions.

Previous research from our laboratory was concerned about the transport properties of PU versus a number of organic solvents.<sup>5–10</sup> In continuation of this program, we now present additional data on sorption and diffusion of hexane, heptane, octane, nonane, and decane at 25, 44, and 60°C through PU

membrane. It is expected that a systematic change in solvent properties would lead to transport results which could be interpreted by considering the possible interactions with the soft and hard segments of PU. From a temperature dependence of transport properties, attempts have been made to evaluate the Arrhenius activation parameters. Furthermore, the calculated results are discussed in terms of the thermodynamic interactions between PU and solvents.

## EXPERIMENTAL

### Reagents and Materials

Polyurethane used was procured from PSI, Austin, TX in sheets of 0.147 cm thickness. The base PU is a Vibrathane B600 (Uniroyal) which was obtained from the reaction of polypropylene oxide and 2,6-toluene diisocyanate (TDI). The base polymer was cured with 4,4'-methylene-bis-(*o*-chloroaniline), i.e., MOCA, to give the PU. Thus, the two-phase morphology of PU consists of polyether diol as the soft segment and the aromatic diisocyanate acting as the hard segment. The driving force for the phase separation is the incompatibility of the hard and soft segments. The molecular structure of the PU used was given earlier.<sup>4</sup>

Some representative engineering properties of PU are: tensile strength, 387 kg/cm<sup>2</sup> (5500 psi); modulus for 300% elongation, 155 kg/cm<sup>2</sup> (2200 psi);

\* To whom correspondence should be addressed.

tear strength, 5 kg/cm<sup>2</sup> (70 psi) (ASTM D-470); and specific gravity, 1.101. Its  $T_g$  as determined by differential scanning calorimetry (DuPont, Model 951) was found to be -43°C. The solvents used are of reagent grade and double distilled before use.

### Diffusion Experiments

Polyurethane elastomers were cut into uniform size circular pieces (diameter = 1.9 cm) using a specially designed, sharp-edged, steel die, and dried overnight in a desiccator before use. The thickness of the sample was measured at several points using a micrometer (precision  $\pm 0.001$  cm) and the mean value was taken as 0.147 cm. Dry weights of the cut samples were taken before immersion into the air-tight, metal-capped test bottles containing the liquid. After immersion into the respective liquids, the bottles were placed in a thermostatically controlled oven (Mettler, Germany).

At periodic intervals, the samples were removed from the bottles; the wet surfaces were dried between Kimwipes and weighed immediately to the nearest 0.05 mg by placing the samples on a covered watch glass within the chamber of the balance. The samples were placed back into test bottles and were transferred to the oven. The experiments were performed at 25, 44, and 60°C. A possible source of error in this method is that the sample has to be removed from the liquid to allow weighing. If this is done quickly (say within the first 30–50 s) compared to the time a sample spent in the liquid in between consecutive weighings, the sample exerts a negligible effect. While the experiments were in progress, any changes in thickness and diameter of the sample were determined by means of a micrometer and vernier calipers, respectively.

The results of weight uptake of the liquid by the polymer were expressed as moles of liquid sorbed by 100 g of the polymer film material. This way of expressing mol % concentration was found to be more convenient for comparison of sorption data by different penetrant molecules than the weight gain results. This practice has also been followed in the literature<sup>11–13</sup> and, thus, we prefer to use the mol % concept for discussing the sorption data.

## RESULTS AND DISCUSSION

The room temperature sorption curves expressed as mol uptake  $Q_t$  of the liquid by 100 g of the polymer versus square root of time,  $t^{1/2}$ , are displayed in Figure 1. It is found that  $Q_t$  increases linearly within

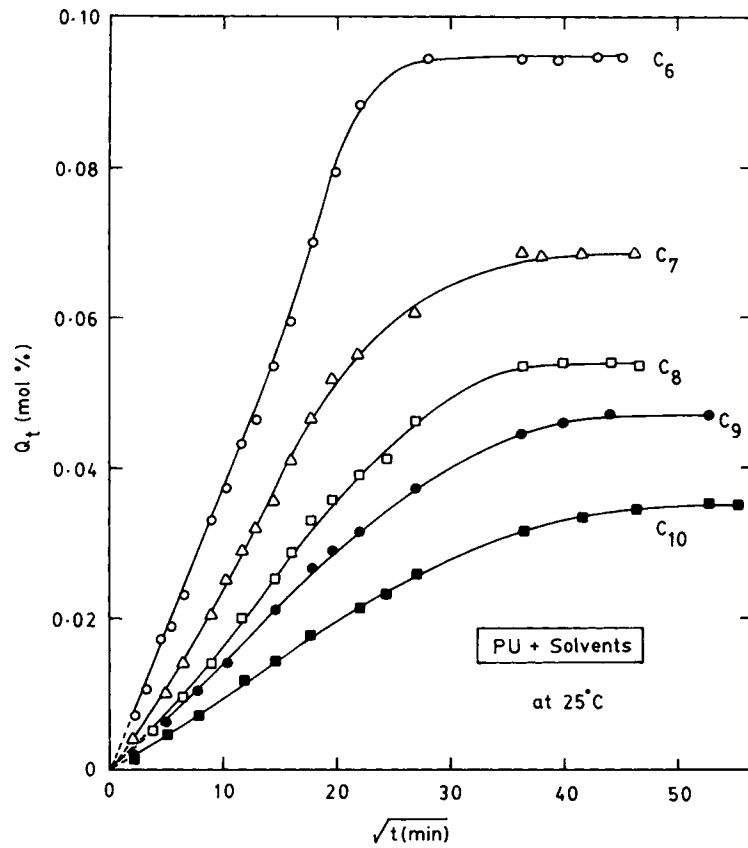
the first 10 min and then levels off. This suggests that the PU chains respond almost instantaneously (elastically) to the presence of liquid molecules. This is suggestive of the Fickian transport mechanism and that sorption is diffusion controlled with constant boundary conditions. It may be noted that, for *n*-hexane, the sorption phenomenon deviates slightly from the regular Fickian trend. The sorption curves for such systems can be rationalized in terms of polymer segmental motions relative to the concurrent liquid diffusivity. Several conclusions can be drawn from the sorption curves presented in Figure 1. First of all, there is a systematic trend in the sorption behavior of alkanes; for example, with an increase in the length of alkyl chain, there is a decrease in  $Q_t$  values. If hexane exhibits a maximum solubility of about 0.095 mol %, decane shows only about 0.035 mol % and the intermediate values are exhibited by heptane, octane, and nonane.

Sorption data also serve as an excellent guide to study the effect of temperature on the observed transport behavior. Temperature variation of sorption curves for hexane and decane are given in Figures 2 and 3. The sorption pattern of hexane in PU is almost identical in the temperature interval of 25–60°C; it may, however, be noted that sorption increases with increase in temperature and this is true of all the PU + *n*-alkane systems. In case of PU + decane system, the sorption pattern at 44 and 60°C are nearly identical, although, at 25°C, it is somewhat different in that it takes a longer time for equilibrium saturation (see Fig. 3). This is not prevalent with the other lower homologues and this effect is attributed to lower solubility of higher alkanes (e.g., decane). For the other alkanes namely, C<sub>7</sub>–C<sub>9</sub>, the sorption curves are not presented graphically so as to minimize the number of figures; but their temperature dependent  $Q_t$  vs.  $t^{1/2}$  curves are essentially identical to those of hexane.

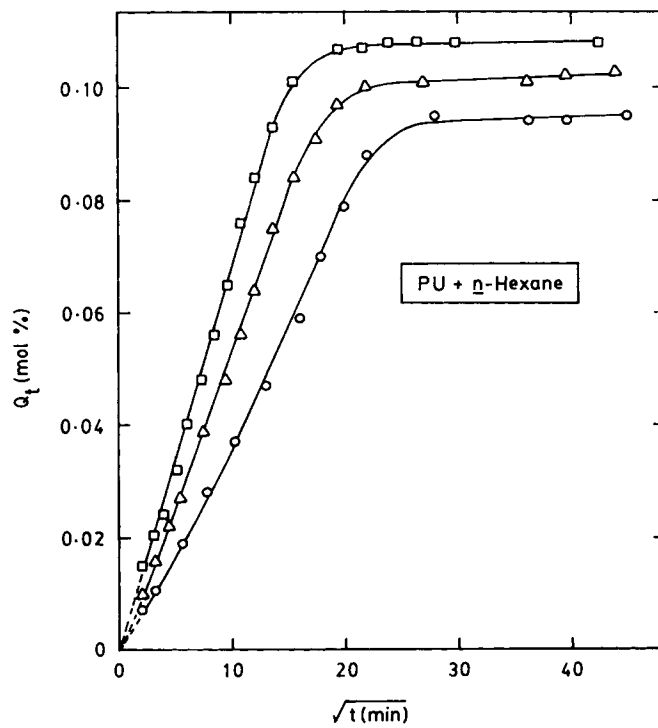
In order to study the type of transport phenomenon, the dynamic swelling results have been fitted to the empirical relation<sup>14,15</sup>

$$\log(Q_t/Q_\infty) = \log k + n \log t \quad (1)$$

where  $k$  is a constant which depends on the structural characteristics of the barrier material in addition to its interaction with the solvent molecules and  $Q_t$  and  $Q_\infty$  are the mol % increases in sorption at time  $t$  and at equilibrium, respectively. The value of  $n$  gives an indication about the type of transport mechanism and, for most rubbery polymer-solvent systems,  $n$  varies between 0.5 and unity. If  $n = 0.5$ , then the diffusion mechanism follows the regular



**Figure 1** Mole percent solvent uptake of polyurethane at 25°C: (○) hexane; (△) heptane; (□) octane; (●) nonane; (■) decane.



**Figure 2** Temperature dependence of mol % solvent uptake for polyurethane + hexane at (○) 25°C, (△) 44°C, and (□) 60°C.

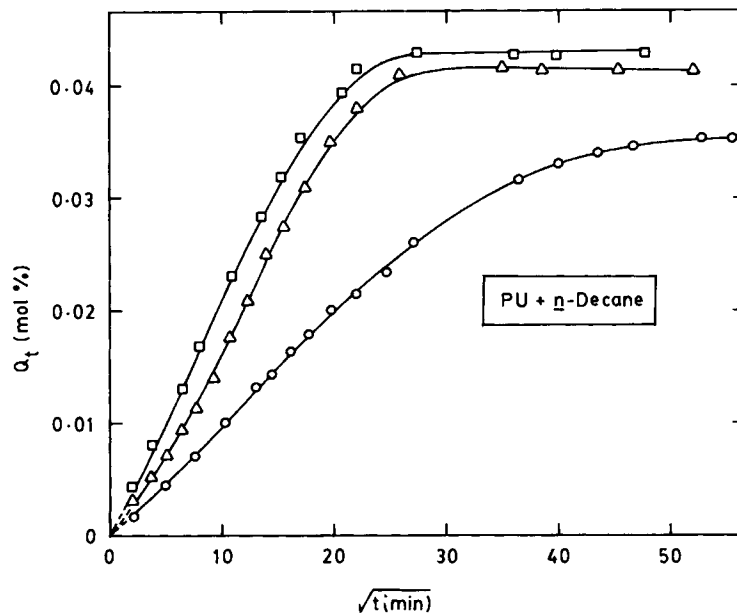


Figure 3 Same as in Figure 2 for polyurethane + decane system.

Fickian trend and for  $n = 1$ , the non-Fickian mode is predicted. It may be noted that eq. (1) can be used to analyze the sorption data before attainment of 50% equilibrium saturation. The values of  $n$  and  $k$  have been estimated from the least-squares analysis of eq. (1). The values of  $n$  and  $k$  are given in Table I. The estimated errors in the computation of  $n$  are around 0.008 units, and, hence, the results are approximated to second decimal place.

The values of both  $k$  and  $n$  show a dependence on temperature. With the increase in temperature,  $k$  values also tend to increase, suggesting the increase in the PU-solvent interactions with the temperature. This increase is quite significant as we go from lower to higher members of  $n$ -alkanes. Such increases in the values of  $k$  with temperature have also been observed earlier.<sup>5-8</sup> The values of  $n$  are found to decrease with the increase in temperature for all the

PU + liquid systems. The magnitude of  $n$  from a minimum of 0.5–0.6 is further supportive of the probable Fickian diffusion mechanism operative in most of our experimental systems.

From the initial linear portions of the sorption plots, the solvent diffusivity  $D$  into polyurethane membrane was calculated<sup>5,8</sup> by using

$$D = \pi(h\theta/4Q_{\infty})^2 \quad (2)$$

where  $h$  is the membrane thickness and  $\theta$  is slope of the linear portion of sorption curves before attainment of 50% equilibrium. The calculated values of  $D$  at 25, 44, and 60°C along with the maximum mol % expressed as sorption constant,  $K_s$ , at equilibrium saturation are compiled in Table II for each  $n$ -alkane + PU pair. Since no significant swelling was observed for all the systems, the diffusivities as

Table I Analysis of Sorption Data for PU +  $n$ -Alkane Systems from Eq. (1)

$n$ -Alkanes	$k \times 10^2$ (g/g min <sup><math>n</math></sup> ) at (°C)			$n$ at (°C)		
	25	44	60	25	44	60
Hexane	3.37	4.23	5.72	0.53	0.53	0.51
Heptane	2.48	4.61	5.28	0.57	0.51	0.51
Octane	1.87	3.17	4.51	0.60	0.56	0.55
Nonane	2.48	4.10	6.41	0.54	0.51	0.50
Decane	1.93	2.65	4.78	0.57	0.58	0.50

**Table II** Diffusion Coefficients and Sorption Constants of PU + *n*-Alkanes

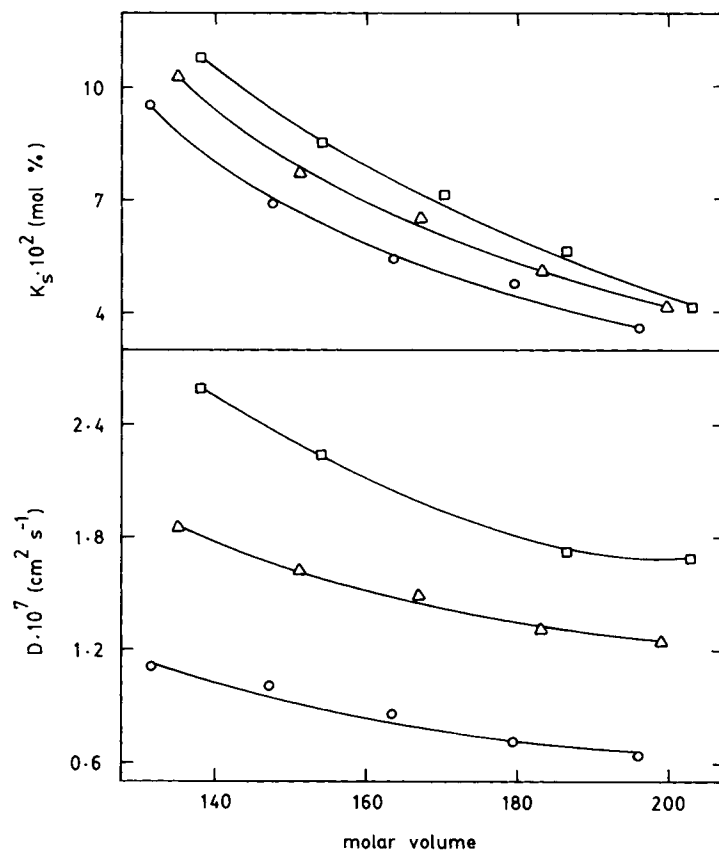
<i>n</i> -Alkanes	$D \times 10^7$ (cm <sup>2</sup> /s) at (°C)			$K_s \times 10^2$ (mol %) at (°C)		
	25	44	60	25	44	60
Hexane	1.114	1.851	2.591	9.496	10.297	10.830
Heptane	1.024	1.619	2.243	6.871	7.613	8.550
Octane	0.859	1.496	2.489	5.420	6.483	7.085
Nonane	0.709	1.307	1.716	4.730	5.080	5.636
Decane	0.637	1.251	1.689	3.538	4.139	4.285

calculated from eq. (2) may be regarded as concentration-independent values.

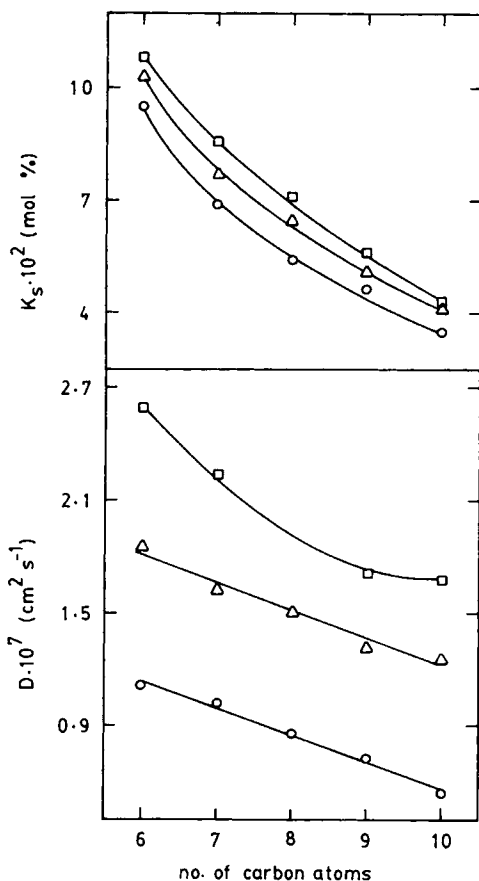
In a study by Schneider et al.,<sup>16</sup> a series of linear chloroalkanes have been used in addition to heptane and other aromatic chlorocompounds to study diffusion into a segmented polyurethane elastomer. Our value of diffusion coefficient for PU + heptane at 25°C is  $10.24 \times 10^{-8}$  cm<sup>2</sup>/s, whereas Schneider et al.<sup>16</sup> found a value of  $7.3 \times 10^{-8}$  cm<sup>2</sup>/s at 20°C. This difference could be the result of the morphological

differences between the PU membrane used in this work and that of Schneider et al.<sup>16</sup>

Transport data given in Table II reveal a systematic increase with the rise in temperature and decrease systematically with an increase in the chain length of alkanes. This fact is demonstrated in Figures 4 and 5 wherein we observe a systematic decrease in  $K_s$  and  $D$  values with the increase in either molar volume (Fig. 4) or the number of carbon atoms (Fig. 5) of the members of the alkane series. Further,



**Figure 4** Dependence of sorption equilibrium constant ( $K_s$ ) and diffusion coefficient ( $D$ ) on molar volume of *n*-alkanes at (○) 25°C, (△) 44°C, and (□) 60°C.



**Figure 5** Dependence of sorption equilibrium constant and diffusion coefficient on number of carbon atoms of *n*-alkanes at (○) 25°C, (△) 44°C, and (□) 60°C.

this observation is true over the investigated temperature range of 25–60°C. Such an inverse dependence of  $D$  or  $K_s$  on the size of the liquid molecule has also been observed earlier<sup>8</sup> for PU + methyl-substituted benzenes.

From temperature dependence of diffusivity, attempts were made to estimate the activation parameter  $E_D$  for the process of diffusion. Since sorption constants obtained at equilibrium saturation represent the true values of thermodynamic equilibrium<sup>17</sup> sorption constants, we have employed the van't Hoff relation

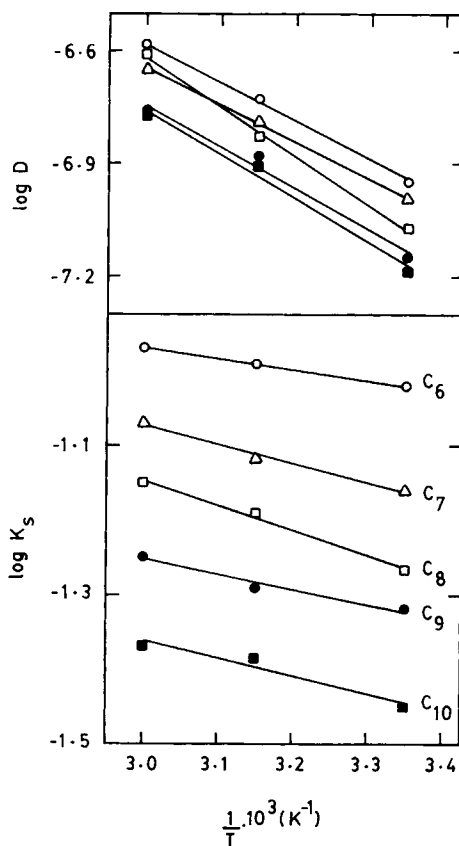
$$\log K_s = \frac{\Delta S}{2.303R} - \frac{\Delta H_s}{2.303R} \frac{1}{T} \quad (3)$$

to estimate the enthalpy  $\Delta H_s$  and entropy  $\Delta S$  of sorption from the slope and intercept, respectively, of the Arrhenius plots of  $\log D$  or  $\log K_s$  vs.  $1/T$  given in Figure 6. The estimated values of  $E_D$  from the diffusion data and those of  $\Delta H_s$  and  $\Delta S$  from

the sorption equilibrium data are compiled in Table III. The values of  $E_D$  fall in the range of 18–25 kJ/mol whereas heat of sorption values are in the range of 3–6 kJ/mol. The entropy of sorption data are negative in all cases, suggesting the retainment of liquid state structure of solvent molecules even in the sorbed state.

For a better understanding of the structure-property relationships of the PU membrane in the presence of a solvent, it is necessary to know the extent of polymer-solvent interaction. This can be studied in terms of Flory-Huggins type interaction parameter  $\chi$ . In our earlier paper,<sup>18</sup> we have developed a new procedure to estimate  $\chi$  in terms of volume fraction  $\phi$  of the swollen PU in the presence of a solvent. In that study,<sup>18</sup> the  $\chi$  was calculated as

$$\chi = \frac{(d\phi/dT) \{ [\phi/(1-\phi)] + N \ln(1-\phi) + N\phi \}}{[2\phi(d\phi/dT) - \phi^2 N(d\phi/dT) - \phi^2/T]} \quad (4)$$



**Figure 6** Arrhenius plots of  $\log D$  and  $\log K_s$  vs.  $1/T$  for polyurethane + *n*-alkane systems. Symbols have the same meaning as in Figure 1.

**Table III Arrhenius Parameters and Thermodynamic Functions for PU + *n*-Alkanes**

<i>n</i> -Alkanes	$E_D$ (kJ/mol)	$\Delta H_s$ (kJ/mol)	$\Delta S$ (J/mol/deg)	$\chi$	$M_c$
Hexane	19.99	3.114	-47.4	1.135	398
Heptane	18.57	5.118	-43.5	1.292	457
Octane	25.01	6.385	-41.05	1.971	<sup>a</sup>
Nonane	21.10	4.076	-50.06	1.438	542
Decane	23.31	4.632	-50.43	1.628	692

<sup>a</sup> Negative value found.

with

$$N = \frac{(\phi^{2/3}/3 - 2/3)}{(\phi^{1/3} - 2\phi/3)} \quad (5)$$

and

$$\phi = \left[ 1 + \frac{\rho_p}{\rho_s} \left( \frac{M_a}{M_b} \right) - \frac{\rho_p}{\rho_s} \right]^{-1} \quad (6)$$

where  $M_b$  and  $M_a$  are, respectively, the mass of the polymer before and after swelling,  $\rho_s$  is density of the solvent, and  $\rho_p$  is density of the polymer. Details of the computations have been given earlier.<sup>18</sup> Using the value of  $\chi$  as calculated from eq. (4), the molar mass  $M_c$  between crosslinks of the network polymer was estimated from the Flory-Rehner (FR) theory<sup>19-21</sup>:

$$M_c = \frac{-\rho_p V(\phi)^{1/3}}{[\ln(1 - \phi) + \phi + \chi\phi^2]} \quad (7)$$

where  $V$  is the molar volume of the solvent. The calculated  $\chi$  and  $M_c$  values are also included in Table III. It is found that, except octane, the  $\chi$  and  $M_c$  values are found to be increasing systematically from hexane to decane. For octane,  $\chi$  was somewhat higher than the other alkanes and thus, the calculated  $M_c$  for PU + octane system was found to be negative. It may, however, be noted that such negative values of  $M_c$  were also observed by Schneider et al.<sup>16</sup> for sorption of *o*-dichlorobenzene into a segmented polyurethane membrane. It can be said, on the basis of the present results, that the FR theory is applicable in an absolute sense. However, the smaller apparent values of  $M_c$  may be the result of only a soft segment swelling but not the hard segment part of the PU elastomer. Most of the solvents

selected in this research show only limited swelling of the soft segment structure and the sorption behavior in majority of the cases appears to be mostly Fickian. However, the only complication is the mild concentration dependence of the diffusion coefficient which is a formidable task.

We thank the University Grants Commission, New Delhi, for a major grant support, No. F.12-15/88 (SR-III) and to Professor P. E. Cassidy of Southwest Texas State University for a supply of polyurethane samples. The assistance of Mr. S. B. Harogoppad in this research is highly appreciated.

## REFERENCES

- S. L. Cooper and A. V. Tobolsky, *J. Appl. Polym. Sci.*, **10**, 1837 (1966).
- P. E. Gibson, M. A. Vallance, and S. L. Cooper, in *Developments in Block Copolymers*, I. Goodman, Ed., Elsevier, London, 1982.
- G. Trapps, in *Advances in Polyurethane Technology*, J. M. Buist and H. Gudgeon, Eds., Wiley-Interscience, New York, 1968, p. 63.
- U. S. Aithal, T. M. Aminabhavi, R. H. Balundgi, and S. S. Shukla, *J. Macromol. Sci. Rev. Macromol. Chem. Phys.*, **C30**(1), 43 (1990).
- U. S. Aithal and T. M. Aminabhavi, *J. Chem. Educ.*, **67**, 82 (1990).
- U. S. Aithal and T. M. Aminabhavi, *Indian J. Chem.*, **29A**, 270 (1990).
- U. S. Aithal and T. M. Aminabhavi, *Polymer*, **31**, 1757 (1990).
- U. S. Aithal, T. M. Aminabhavi, and P. E. Cassidy, *Polym. Prepr.*, **30**(1), 17 (1989).
- U. S. Aithal, T. M. Aminabhavi, and P. E. Cassidy, *J. Membr. Sci.*, **50**, 225 (1990).
- T. M. Aminabhavi and U. S. Aithal, *J. Appl. Polym. Sci.*, **41** (9-10), 2113 (1990).
- A. Sfirakis and C. E. Rogers, *Polym. Eng. Sci.*, **21**, 542 (1981).

12. S. B. Harogopad and T. M. Aminabhavi, *Polymer*, (1990), to appear.
13. S. B. Harogopad and T. M. Aminabhavi, *J. Chem. Educ.*, (1990), to appear.
14. L. M. Lucht and N. A. Peppas, *J. Appl. Polym. Sci.*, **33**, 1557 (1987).
15. J. S. Chiou and D. R. Paul, *Polym. Eng. Sci.*, **26**, 1218 (1986).
16. N. S. Schneider, J. L. Illinger, and M. A. Cleaves, *Polym. Eng. Sci.*, **26**, 1547 (1986).
17. G. W. C. Hung, *Microchem. J.*, **19**, 130 (1974).
18. U. S. Aithal, T. M. Aminabhavi, and P. E. Cassidy, *Barrier Polymers and Structures*, Am. Chem. Soc., Symp. Ser. 423, W. J. Koros, Ed., 197th National ACS Meeting, Dallas, TX, Am. Chem. Soc., Washington, DC, 1989, p. 351.
19. P. J. Flory and J. Rehner, Jr., *J. Chem. Phys.*, **11**, 521 (1943).
20. P. J. Flory, *J. Chem. Phys.*, **18**, 108 (1950).
21. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University, Ithaca, NY, 1953.

Received April 17, 1990

Accepted August 28, 1990