Diffusion Behavior of Hexane in Diamine Chain-Extended Hydroxyterminated Polybutadiene Based Polyurethanes

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ABSTRACT: A new method of edge correction has been formulated to calculate the near true diffusion coefficient of hexane in thin polyurethane and polyurethaneurea sheets. The method involves the calculation of time-average thickness during the diffusion of hexane in hydroxyterminated polybutadiene-based polyurethane and polyurethaneurea sheets. The precision of the method has been tested by the iteration of data. The diffusion coefficient increases with the increase of diamine chain extender in polyurethaneureas. The variation of activation parameters and enthalpy of diffusion of hexane with diamine chain extender in polyurethaneurea also have been studied. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 90–97, 2002

Key words: diffusion; polybutadiene; polyurethaneurea

INTRODUCTION

The sorption of organic solvents by polyurethane elastomers has been of some interest in determining stability and ultimate use of this membrane in several environments.[1] Hydroxyterminated polybutadiene (HTPB)-based polyurethane is hydrophobic in nature,[2] and hence, organic nonpolar solvents are expected to diffuse through the matrix. Polyurethane elastomers are used as seals and gaskets in contact with petroleum fluids and solvents as well as membranes for separation by pervaporation. Diffusion parameters are dependent on temperature, sample geometry, and nature of both diffusing species and matrix. Although thin membranes are used in some applications, measurement of their diffusion parameters by gravimetric techniques leads to erroneous results due to evaporation loss during measurement. On the contrary, diffusion measurements using thick sheets/films also give erroneous diffusion parameters due to edge effects. To avoid such limitations people have developed methods of correcting diffusion coefficients arising out of edge effects from gravimetric data.[3–5] Shen and Springer[3] mainly recommended a geometric correction. But the assumption that the sample geometry remains unchanged during diffusion holds good only for short exposure time. Rothwell and Marshall[4] treated the problem of edge effects in a complex way. Grayson[5] used a three-dimensional diffusion equation and substituted the correction factor to sorption equation, which relates one-dimensional flow through poly (aryl-ether-ether-ketone). But this method is also tedious, as rigorous calculations are needed for each set of gravimetric data. Diffusion and pervaporation studies with organic solvents in polyurethanes have been made earlier without considering the influences of edge effects.[6–10] Although the diffusion of organic solvents through polyurethane elastomers has been studied,[11,12] the variation of their diffusion coefficients with a segmental concentration has not been studied. The concentration of polar moiety in HTPB-based crosslinked polyurethane is supposed to influence the diffusion kinetics of nonpolar penetrant. In this communication we, therefore, report the effects of diamine concentration in the diamine chain-extended polyurethane (polyurethaneurea) on the diffusion parameters of hexane and measurement of near true values of diffusion parameters using a new and simple method of edge correction based on time average thickness of sample within a moderate time span.

EXPERIMENTAL

Materials

Hydroxyterminated polybutadiene (HTPB) obtained from VSSC, India, with a number-average molecular weight of 2580 and average functionality of 2.4 was used as received. 2,4-Toluene diisocyanate (TDI) (Fluka AG) was used as received. 4,4′-Diaminodiphenyl sulfone (DADPS) (Fluka AG) was exposed to vacuum at 80°C for overnight followed by sublimation prior to use. Dibutyltindilaurate (DBTDL) (Fluka AG) was used without purification. Tetrahydrofuran (THF)

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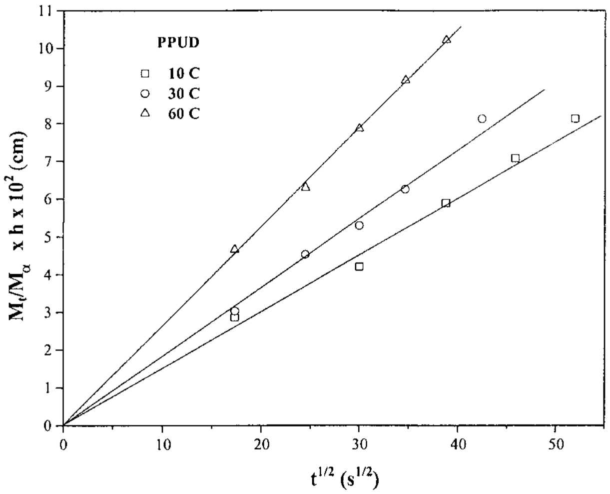

Figure 1 Variation in M_t/M_α of PPUD with the square root of time at different temperatures.

(E. Merck, India) was purified as per standard procedure.[13] Hexane (E. Merck, India) was double distilled before use.[14]

Synthesis of prepolyurethane and polyurethaneureas

Prepolyurethane (PPUD) was prepared by mixing 10.37 g HTPB and 1.37 mL TDI (maintaining NCO: OH = 2 : 1) in 60 mL of THF in presence of 0.5 wt % DBTDL as a catalyst. The reaction was run for 45 min at 30°C to obtain a viscous liquid. A thin sheet of prepolyurethane was cast from the viscous liquid on a clean plane glass plate and left overnight for moisture curing followed by heating at 80°C for 7 h.[7]

Polyurethaneureas, PUUSD 20, PUUSD 50, and PUUSD 100 were prepared by adding 20, 50, and 100-mol % DADPS (with respect to HTPB), respectively, after 40 min of the start of prepolyurethane synthesis. Polyurethaneurea sheet was cast and cured in the same way as done for prepolyurethane.[7]

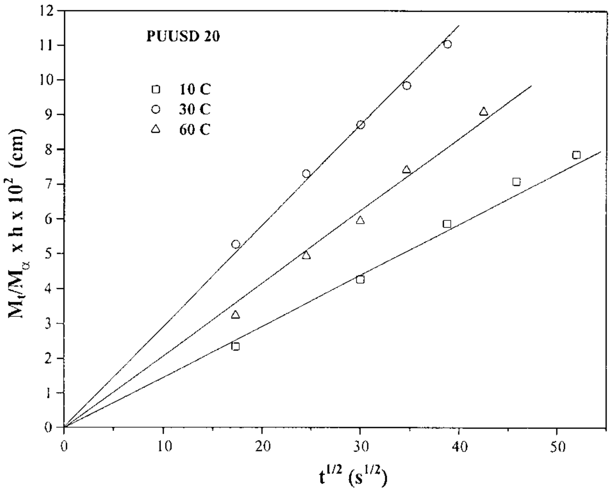

Figure 2 Variation in M_t/M_α of PUUSD 20 with the square root of time at different temperatures.

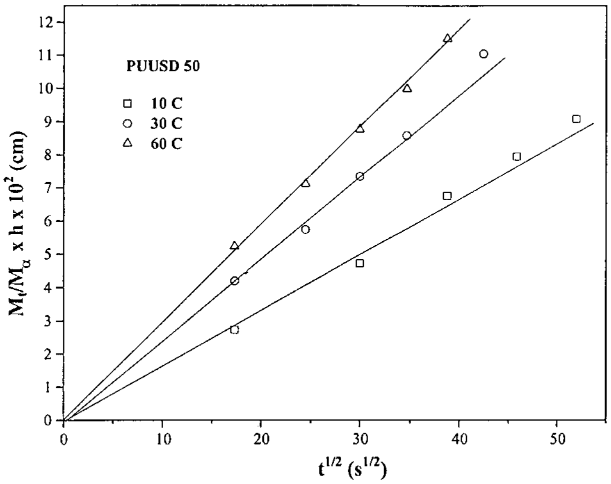

Figure 3 Variation in M_t/M_α of PUUSD 50 with the square root of time at different temperatures.

Sample preparation

The samples (1.2 × 1.2 cm) were cut by a sharp steel die from a cured polymer sheet; having an average thickness of 0.15 cm.

Measurement of diffusion parameters

Diffusion coefficient (D_m) was measured by gravimetric method. The polymer sample was immersed in hexane in a stoppered conical flask kept at the specified temperature in a thermostatically controlled bath. The sample was taken out from the flask time to time to measure the weight and thickness and returned to

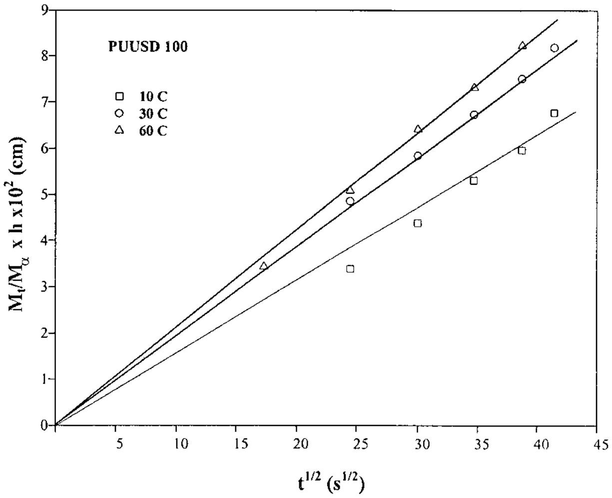

Figure 4 Variation in M_t/M_α of PUUSD 100 with the square root of time at different temperatures.

TABLE I
Diffusion Coefficients, Sorptivity (*S*), and Permeability (*P*) of Hexane in Polyurethane and Polyurethaneurea

Sample code	Temperature (°C)	Diffusion coefficient $\times 10^7$ cm^2/s		Sorptivity (*S*) gg^{-1}	Permeability (*P*) $\times 10^7$ cm^2/s
		D_m	D_a		
PPUD	10	4.30	2.42	0.513	1.24
	30	6.25	3.65	0.587	2.14
	60	13.22	6.76	0.590	3.95
PUUSD 20	10	4.04	2.56	0.564	1.44
	30	8.09	4.66	0.565	2.62
	60	15.67	7.68	0.567	4.35
PUUSD 50	10	5.50	3.50	0.531	1.85
	30	12.04	5.37	0.571	3.07
	60	17.69	8.79	0.598	5.26
PUUSD 100	10	4.92	3.08	0.533	1.70
	30	7.13	4.29	0.641	2.75
	60	8.82	5.15	0.682	3.51

the system within 30 s to avoid incorporation of error due to solvent evaporation. The value of D_m was obtained from the slope [$m_f = 4\sqrt{D_m/\pi}$] of the plot of $\{(M_l/M_\alpha) \times h\}$ against the square root of diffusion time $\sqrt{t}$, where M_t and M_α are fractional weight gains of sample at time t and at equilibrium, respectively, and h is the initial sample thickness.[15] The near actual diffusion coefficient value (D_a) was obtained through multiplying D_m by an average edge correction factor (R_{ac}) proposed in this investigation based on the time average thickness measurement. Hence,

$$D_a = D_m \times R_{ac} \tag{1}$$

Sorptivity (*S*), the measure of fractional solvent absorption by the polymer at equilibrium, is expressed as the gram of solvent absorbed per gram of polymer.

Permeability (*P*) is calculated from the product of near actual diffusion coefficient and sorptivity.

Activation energy of diffusion and permeation

Activation energy of diffusion (E_d) and activation energy of permeation (E_p) were calculated from the Arrhenius relationship. E_d and E_p were obtained from the slope of the plot of ln D vs. $1/T$ and ln P vs. $1/T$, respectively.

Enthalpy of diffusion H was obtained from the difference of E_p and E_d.

RESULTS AND DISCUSSION

Method of edge correction for polyurethane sheet to obtain D_a

The diffusion coefficient is a kinetic parameter, which depends on the mobility of polymer chain segments. To get the diffusion coefficient D_m, $[(M_t/M_\alpha) \times h]$ was plotted against $\sqrt{t}$ for prepolyurethane (PPUD) and polyurethaneureas (PUUSD 20, PUUSD 50, and PUUSD 100) at three different experimental temperatures 10°, 30°, and 60°C (Fig. 1–4). The values of D_m are included in Table I.

The experimentally obtained gravimetric data M_t and M_α are utilized for obtaining diffusion coefficient D_m by substituting the value of m_f, which is the slope of the plot of the product of fractional weight gain ratio (M_t/M_α) and initial sample thickness (h) as function of $\sqrt{t}$, in the equation

$$D_m = \frac{1}{16}\,\pi(m_f)^2 \tag{2}$$

Ficks law predicts that the linearity of the plot of (M_t/M_α) against $\sqrt{t}$ would be valid within the range $0 \le M_t/M_\alpha \le 0.6$.[15] Actually, the samples used in the gravimetric analysis are of finite size and are three-dimensional. Hence, the diffusion of the penetrant in the real sample occurs through the sample edges in addition to the major surfaces. As a result, the diffusion coefficient D_m, determined from gravimetric measurement, for real samples is higher over the near actual value D_a representing diffusion through major surfaces. One way to minimize the diffusion is decreasing the film thickness. But in many cases it is not possible to control the sample thickness. Hence, a correction factor is necessary to obtain a value very close to near actual diffusion coefficient D_a.

Here, we report a method for the calculation of D_a eliminating the effects of diffusion through the edges using the experimental data of diffusion of hexane in the polymer matrix. This is simpler than the existing methods,[3–5] because only one average edge correction factor R_{ac} is used for the full set of data obtained within a moderate diffusion time span <45 min. Shen and Springer[3] considered the initial geometry of the sample (at the start of the diffusion) to calculate the correction factor. But the thickness, length, and width of the sample changes with time as the solvent pene-

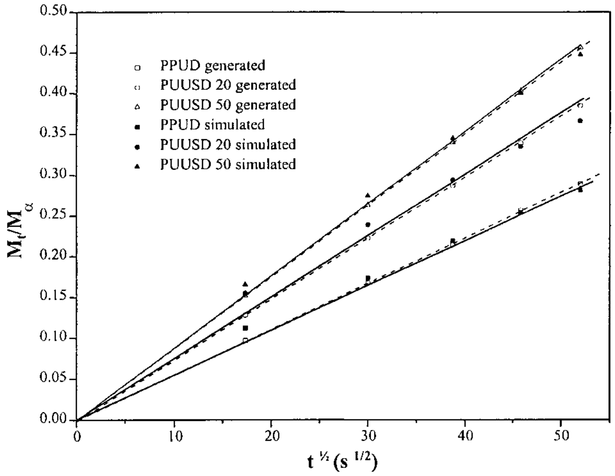

Figure 5 Iteration of M_t/M_α values for hexane diffusion in polyurethane at 10°C.

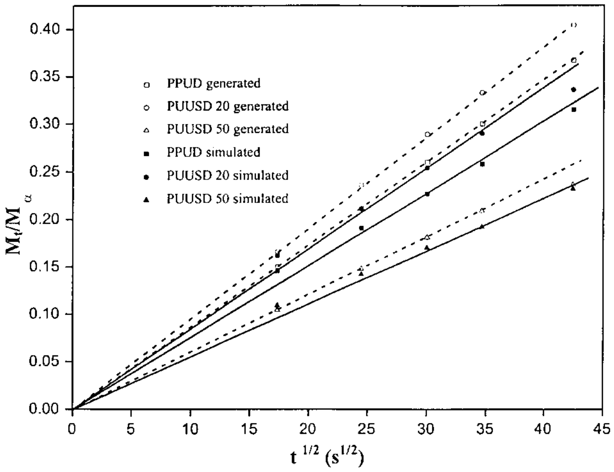

Figure 7 Iteration of M_t/M_α values obtained by the Shen and Springer method for hexane diffusion in polyurethane at 30°C.

trates inside. It is not practically possible to measure the changes of all dimensions at every measurement in a diffusion experiment with a fast diffusing solvent. Some error will be incorporated due to solvent loss on exposure to air during the measurement. The use of a thin sheet with a high length and breadth is a remedy to nullify the error. But even in a thin film, change in thickness occurring during diffusion incorporates error. The use of time average thickness (h_{av}) instead of initial thickness (h) used by Shen and Springer to calculate the correction factor, will average out the effect of the change in thickness with time for the data taken in a moderate time span of diffusion experiment. The time average thickness of the sample used in this investigation within the experimental range is formulated as

$$h_{av} = \frac{\sum_{n=1}^{n} h_n t_n}{\sum_{n=1}^{n} t_n} \tag{3}$$

where, h_n is the thickness of the sample at time t_n. The average edge correction factor is obtained by replacing h by h_{av} in Shen and Springers[3] geometrical correction as

$$R_{ac} = \left[1 + \frac{2h_{av}}{L}\right]^{-2} \tag{4}$$

where, L is the length of the side of the square. The near actual diffusion coefficient is obtained by substituting the eqs (3) and (4) in eq. (1):

$$D_a = D_m\left[1 + \frac{2h_{av}}{L}\right]^{-2}$$

$$\text{or, } D_a = D_m\left[1 + \frac{2\sum_{n=1}^{n} h_n t_n}{L\sum_{n=1}^{n} t_n}\right]^{-2} \tag{5}$$

Validity and precision of the method

To verify the precision of the method applied, the values of D_a, thickness (h) and time (t) related to 10 and 30°C were fed to one-dimensional sorption equation

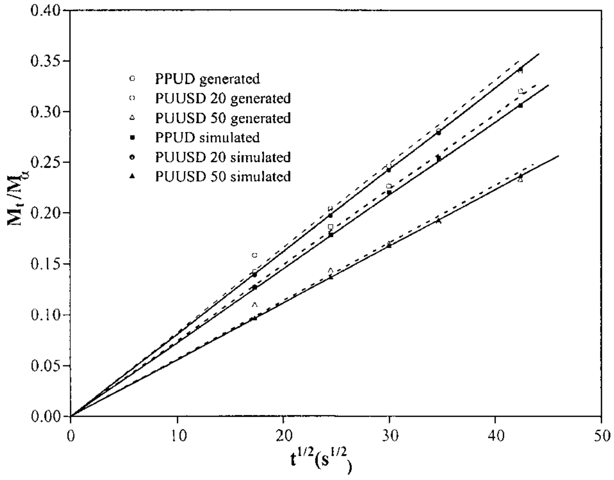

Figure 6 Iteration of M_t/M_α values for hexane diffusion in polyurethane at 30°C.

TABLE II
Comparison of Methods for the Calculation of Near Actual Value of Diffusion Coefficient (D_a) by One-Step Iteration

		Our Method				Shen and Springer			
Sample Code	Temp. (°C)	D_m	R_{ac}	D_a	Error[a] (%)	D_m	R_c	D_a	Error[a] (%)
PPUD	10	4.30	0.562	2.42	+3.60	4.30	0.594	2.55	−22.47
	30	6.25	0.584	3.65	+5.23	6.25	0.619	3.86	−31.20
	60	13.22	0.511	6.76	+3.36	13.22	0.550	7.21	−27.90
PUUSD 20	10	4.04	0.633	2.56	+4.70	4.04	0.694	2.86	−56.25
	30	8.09	0.576	4.66	+3.20	8.09	0.615	4.97	−29.50
	60	15.67	0.490	7.68	+1.70	15.67	0.538	8.43	−36.50
PUUSD 50	10	5.50	0.636	3.50	+2.88	5.50	0.673	3.70	−31.50
	30	12.04	0.446	5.37	+2.35	12.04	0.447	5.38	−13.36
	60	17.69	0.497	8.79	+3.05	17.69	0.537	9.49	−27.00
PUUSD 100	10	4.92	0.626	3.08	−2.27	4.92	0.670	3.30	−21.21
	30	7.13	0.601	4.29	−1.39	7.13	0.670	4.77	−34.38
	60	8.82	0.584	5.15	+5.63	8.82	0.668	5.90	−39.15

[a] Calculated for single-step iteration of generated M_t/M_α values. D_a and D_m $\times 10^7$ cm^2/s.

$$\frac{M_t}{M_\alpha} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\alpha}(2n+1)^{-2} \times \exp[-D(2n+1)^{-2}\pi^2 t h^{-2}] \quad (6)$$

to generate a new set of M_t/M_α. Generated M_t/M_α values were iterated and plotted against $\sqrt{t}$ (Fig. 5 and 6) to estimate the validity and precision of the method.

From the plots in Figures 5 and 6 it is clear that a good agreement between generated M_t/M_α values and simulated (iterated) M_t/M_α values is obtained with a slight deviation at the early stage of diffusion experiment.

To verify the precision of our method the generated and simulated M_t/M_α values (after a single step of iteration) were plotted against $\sqrt{t}$ following the correction method of Shen and Springer[3] using the same number of iteration (Fig. 7). A wide deviation between the generated and simulated (M_t/M_α) values is observed with the increase in sorption time in Shen and Springer method. The correction factors and average errors (%) involved in one-step iteration of generated M_t/M_α values in this method and Shen and Springer method are given in Table II. The errors involved in our correction method appear much less compared to that of Shen and Springer.[3] The generated and simulated M_t/M_α values related to diffusion of hexane in

TABLE III
Simulation of M_t/M_α Data for PUUSD 100

			Our Method			Shen and Springer		
Diffusion temp (°C)	Time (s)	Thickness (cm)	$D_a \times 10^7$ cm^2 s^{-1}	M_t/M_α[a]	M_t/M_α[b]	$D_a \times 10^7$ cm^2 s^{-1}	M_t/M_α[a]	M_t/M_α[b]
10	0	0.133	3.08	0	0	3.30	0	0
	600	0.148		0.207	0.205		0.255	0.192
	900	0.154		0.244	0.241		0.282	0.225
	1200	0.158		0.275	0.271		0.306	0.254
	1500	0.160		0.303	0.299		0.330	0.280
	1800	0.163		0.326	0.322		0.350	0.301
30	0	0.133	4.29	0	0	4.77	0	0
	600	0.165		0.219	0.219		0.266	0.188
	900	0.170		0.261	0.261		0.299	0.223
	1200	0.173		0.296	0.296		0.329	0.253
	1500	0.176		0.325	0.325		0.355	0.277
	1800	0.178		0.352	0.352		0.380	0.301
60	0	0.132	5.15	0	0	5.90	0	0
	300	0.162		0.174	0.178		0.235	0.147
	600	0.172		0.230	0.237		0.278	0.193
	900	0.180		0.269	0.277		0.310	0.225
	1200	0.188		0.298	0.306		0.335	0.249
	1500	0.194		0.323	0.332		0.357	0.269

[a] Denotes generated data.
[b] Denotes simulated data.

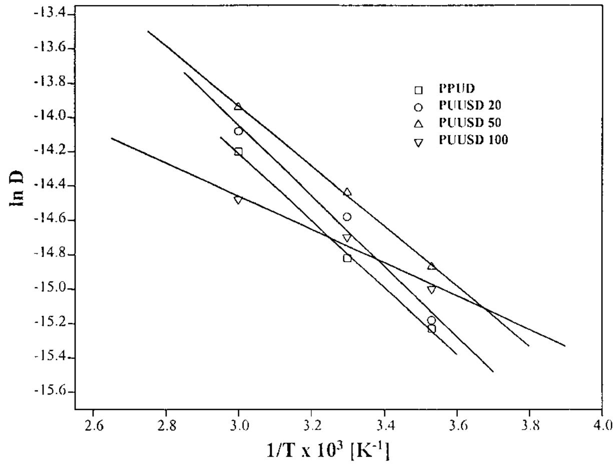

Figure 8 Arrhenius plots of diffusion coefficient of hexane in prepolyurethane and polyurethaneureas.

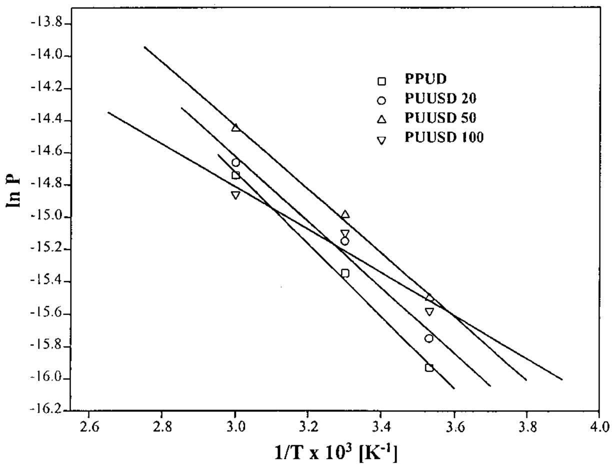

Figure 9 Arrhenius plots of permeation of hexane in prepolyurethane and polyurethaneureas.

PUUSD 100 are given in Table III to show the precision of the two methods.

Diffusion coefficient (D_a), sorptivity, and permeability

The values of D_a of polymer samples are given in Table I. It is evident from the results that with the increase in temperature, diffusion coefficients increase for all the polymers. At a specific temperature the diffusion coefficient (D_a) of hexane increases from PPUD to PUUSD 50. This is due to the increase in looseness of the crosslinked network after chain extension and branching. The chain extension generates more free space through branching for hexane diffusion. But in the case of PUUSD 100, a decrease in diffusion coefficient of hexane has been observed due to the very high concentration of polar hard segment. Permeability (P) and sorptivity (S) were also measured and given in Table I.

Permeation is a collective process of diffusion and sorption and, hence, the permeability of solvent molecules in polymer depends on both the diffusion and solubility.[16] Permeability is the product of actual diffusion coefficient (D_a) and sorptivity. The value of S is taken as a gram of solvent absorbed per gram of polymer at equilibrium swelling. The sorptivity increases with increase in temperature for a specific polymer. Permeation coefficient P also increases with temperature following the same trend of diffusion coefficient (Table I).

Activation parameters of diffusion

It is evident from the Figures 1–4 that the slopes of the linear curves increase with increase in temperature, indicating that the diffusion process is temperature dependent. This follows the Arrhenius relationships for diffusion as well as permeation as

$$D_a = D_0 \exp^{-E_D/RT} \quad \text{and} \quad P = P_0 \exp^{-E_p/RT} \tag{7}$$

where, E_D is the activation energy required to create opening between the polymer chains to permit penetrant molecules to pass. E_D is the function of inter- and intrachain forces. E_D values obtained from the Arrhenius plots in Figure 8 do not show much variation with the increase in diamine concentration up to PUUSD 50, but has shown more of a decrease in PUUSD 100 due to higher concentration of hard segments (Table IV).

To obtain activation energy of permeation E_p, ln P was plotted against $1/T$ in Figure 9. The activation energies of permeation of hexane in polyurethanes are

TABLE IV
Activation Parameters of Diffusion of Hexane in Polyurethane

Sample code	Activation energy of diffusion (E_D) kJ mol^{-1}	Activation energy of permeation (E_p) kJ mol^{-1}	Enthalpy of diffusion (ΔH) kJ mol^{-1}
PPUD	16.96	17.61	0.65
PUUSD 20	16.62	17.30	0.68
PUUSD 50	14.63	15.50	0.87
PUUSD 100	7.89	10.22	2.24

TABLE V
Variation of Rate Constant of Penetration (k) of Hexane and Fickian Index (n) with Diamine Concentration and Temperature in Polyurethane Thin Sheets

Sample code	Temperature (°C)	$k \times 10^2 (gg^{-1}\ min^{-1})$	n (Fickian index of equation 8)
PPUD	10	4.44	0.494
	30	5.47	0.504
	60	6.31	0.518
PUUSD 20	10	5.62	0.495
	30	6.03	0.505
	60	6.12	0.517
PUUSD 50	10	5.40	0.497
	30	5.62	0.564
	60	6.29	0.587
PUUSD 100	10	7.87	0.562
	30	7.94	0.563
	60	9.39	0.569

given in Table IV. E_p decreases with increase in diamine concentration.

Table IV shows the increase in enthalpy of diffusion of hexane (H) with the increase in diamine concentration for the increase in the polarity of the system.

Penetrant transport mechanism

In liquid penetration experiment, where a penetrant front advancing into the polymer is observed, a simple descriptive way is to quantify the penetration rate by using the relationship[17–19]

$$\frac{M_t}{M_\alpha} = kt^n \tag{8}$$

where, M_t and M_α are fractional weight gains of sample at time t and at equilibrium respectively. k is a constant that depends on the structure of the polymer and its interaction with solvent. The magnitude of the Fickian index n denotes the transport mode. For the Fickian mode of transport, the rate of polymer chain relaxation is higher compared to the diffusion of the penetrant, and the corresponding value appears very close to 0.5. The estimated values of k and n obtained from the plot of log (M_t/M_α) values (after edge correction) against log t are included in Table V. The values of n near about 0.5 for sorption experiment in hexane suggest a Fickian behavior for PPUD and PUUSD 20 at the three experimental temperatures (10, 30, and 60°C). For PUUSD 50, although the penetration follows Fickian mechanism at a lower temperature (10°C), at higher temperatures (30 and 60°C) a slight deviation is observed as the value of n increases. For PUUSD 100, a higher deviation of n is observed at the three experimental temperatures. This can be explained on the basis of increase in polar rigid hard segment dispersed in the polybutadiene matrix with an increase in diamine concentration. As the hard segment concentration is maximum for PUUSD 100 in the series, the penetrant experiences a Fickian mode in the polybutadiene matrix and a non-Fickian mode of transport in the polar hard segment. The phenomenon is prominent at higher temperature with high diffusion rate.

CONCLUSION

The diffusion parameters of hexane in HTPB-based polyurethane and polyurethaneureas thin sheets have been studied and near actual diffusion coefficients have been calculated following an easy mathematical method of edge correction. A good correlation between the simulated and generated diffusion coefficient values has been obtained with much less error over that of Shen and Springer[3] reported earlier. The corrected diffusion coefficient increases with the increase in the diamine chain extender in polyurethaneureas. The activation energy of diffusion of hexane is found to be decreased with the increase in the diamine chain extender. The diffusion of nonpolar hexane followed Fickian behavior in polyurethaneurea with a low diamine chain extender followed by a gradual shifting towards non-Fickian character with the increase in the chain extender concentration.

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References

1. Aithal, U. S.; Aminabhavi, T. M. Polymer 1990, 31, 1757.
2. Zawadzki, S. F.; Akcelrud L. Polym Int 1997, 42, 422.
3. Shen, C.; Springer, G. S. J Comp Mater 1976, 10, 2.
4. Rothwell, W. S.; Marshall, H. P. In Analysis of Experimental Transport Data: Diffusion in Water in EPDM, LMSC-0566642, 1977.
5. Grayson, M. A. J Polym Sci Polym Phys Ed 1986, 24, 1747.

6. Sreenivasan, K. J Polym Sci Polym Phys Ed 1993, 31, 1083.
7. Gupta, T.; Adhikari, B. J Polym Sci Part A Polym Chem 2001, 39, 2978.
8. Lee, K. R.; Teng, M. Y.; Hsu T. N.; Lai, J. Y. J Membr Sci 1999, 162, 173.
9. Chen, S. H.; Yu, K. C.; Houng, S. L.; Lai, J. Y. J Membr Sci 2000, 173, 99.
10. Yang, J. M.; Lai, W. C.; Lin, H. T. J Membr Sci 2001, 183, 37.
11. Aminabhavi, T. M.; Cassidy, P. E. Polym Commun 1986, 27, 254.
12. Cassidy, P. E.; Aminabhavi, T. M.; Manjeshwar, L. S.; Balundgi, R. H. J Sci Ind Res 1986, 45, 244.
13. Perrin, D. D.; Armarego, W. L. F. In Purification of Laboratory Chemicals; Pergamon: Oxford, 1988, p. 284, 3rd ed.
14. Riddick, J. A.; Bunger, W. B. In Techniques of Chemistry, Vol. II, Organic Solvents; Wiley Interscience: New York, 1970.
15. Cranks, J. In The Mathematics of Diffusion; Clarendon: Oxford, 1975, p. 48, 248, 2nd ed.
16. Mateo, J. L.; Bosch, P.; Serrano, J.; Calvo, M. Eur Polym J 2000, 36, 1903.
17. Aithal, U. S.; Aminabhavi, P. E. J Membr Sci 1990, 50, 225.
18. Frason, N. M.; Peppas, N. A. J Appl Polym Sci 1983, 28, 1299.
19. Chiou, J. S.; Paul, D. R. Polym Eng Sci 1986, 26, 1228.