298 J. Chem. Eng. Data 1990, 35, 298-303

Diffusivity, Permeability, and Sorptivity of Aliphatic Alcohols through Polyurethane Membrane at 25, 44, and 60 °C

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Diffusivity, permeability, and sorptivity of eight aliphatic alcohols through a commercially available polyurethane membrane at 25, 44, and 60 °C have been determined. Thermodynamic quantities such as enthalpy and entropy changes for sorption processes have been calculated from equilibrium sorption data. The Arrhenius parameters for the process of diffusion, permeation, and sorption have also been estimated. The experimental results and computed quantities are discussed in terms of the nature of polymer–penetrant interactions.

Introduction

The interactions between organic solvents and polymer membranes have been studied for almost half a century; nevertheless, a complete understanding of the transport mechanism, namely, sorption, diffusion, and permeation, at the molecular level is still not well understood (*1*). The interest in the accumulation of a large body of coherent and accurate experimental data on diffusion coefficients (D), permeability coefficients (P), and sorption coefficients (S) of solvent molecules through polymer membranes is attributed to a number of important engineering applications that depend wholly or partly on such phenomena. These include protective coatings, paints, and varnishes (*2*, *3*), electronic devices and cable sheathing materials (*4*, *5*), packaging goods for food and beverages (*6–8*), selective barriers for the separation of liquid mixtures (*9*, *10*), biomedical devices (*11*, *12*), etc.

In view of the importance of polyurethane as a membrane in engineering applications (*13*), we found it necessary to explore its interactions with several alcohols. In this paper, we will present some useful engineering data on sorption, diffusivity, and permeability of a number of aliphatic alcohols, which have some relevance in industry and engineering.

Experimental Section

Materials. Eight aliphatic alcohols, namely, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, and isoamyl alcohol, have been used as penetrants for the study. The liquids were obtained in their highest purity and were further purified before use (*14*). Table I lists some of the important physical properties of these alcohols.

The polyurethane (PU) used was obtained as a thin membrane of uniform thickness from PSI, Austin, TX. The base polymer was Vibrathane B600 cured with 4,4′-methylenebis(*o*-chloroaniline).

Table I. Some Physicochemical Properties of Solvents at 25 °C

	bp, °C		density, g/cm^3			
solvents	obsd	lit.[a]	obsd	lit.[a]	mol vol, cm^3/g	ΔH_v,[b] kcal/mol
methanol	65	64.70	0.7870	0.7866	40.75	9.3772
ethanol	78	78.29	0.7847	0.7850	58.68	9.6739
1-propanol	97	97.20	0.7796	0.7998	75.14	11.2988
2-propanol	82	82.26	0.7820	0.7813	76.92	10.0635
1-butanol	118	117.66	0.8058	0.8060	91.97	10.9705
2-butanol	99	99.55	0.8025	0.8026	92.35	10.7123
2-methyl-1-propanol	108	107.66	0.7999	0.8025	92.91	10.9360
isoamyl alcohol	131	130.50	0.8083	0.8071	109.22	12.4979

[a] Reference 14. [b] Reference 28.

Sorption Experiments. Sorption experiments were performed on uniformly cut circular polyurethane samples of diameter 1.9 cm, by the immersion/weight gain method (*15–17*). Initially, the samples were dried overnight in a vacuum desiccator, the original weights were taken, and the thicknesses were measured within ±0.001 cm at several places. The average thickness was found to be 0.250 cm. The polymer samples were solvent-submerged in specially designed airtight bottles, which were kept in a thermostatically controlled oven (Memmert, West Germany) at the desired temperature (25, 44, and 60 °C). At regular intervals, the test samples were removed, and the surfaces were dried between filter paper wraps, weighed immediately to the nearest 0.5 mg, and placed back into the test bottles at the desired constant temperature.

Results and Discussion

The percentage weight gain, $Q(t)$, of the soaked PU membranes was calculated by using eq 1, where M_i is the initial weight of the membrane and M_t, the weight at time t. Plots

$$Q(t) = \frac{M_t - M_i}{M_i} 100 \qquad (1)$$

of $Q(t)$ versus the square root of time ($t^{1/2}$) at 25 °C are given in Figures 1 and 2; however, the temperature dependence of $Q(t)$ versus $t^{1/2}$ curves for some typical penetrants is depicted in Figures 3–6. Among all the penetrants, at room temperature, 2-propanol exhibits the lowest value of $Q(t)$ whereas 1-butanol shows the highest value for $Q(t)$. However, there is no systematic variation of $Q(t)$ with temperature. In all cases, sorption curves exhibit initially a linear portion followed by a plateau region at longer times. Thus, the concentration-independent diffusion coefficients were computed (*15–17*) by using eq 2, where θ is the slope as obtained from a least-squares

$$D = \pi \left[\frac{h\theta}{4M_m} \right]^2 \qquad (2)$$

analysis of the straight-line portion of $Q(t)$ versus $t^{1/2}$ curves, before 50% completion of sorption, h is the thickness of the membrane, and M_m is its maximum weight gain at equilibrium. The sorption coefficients were computed as the gram of the solvent sorbed per gram of the polymer after complete equil-

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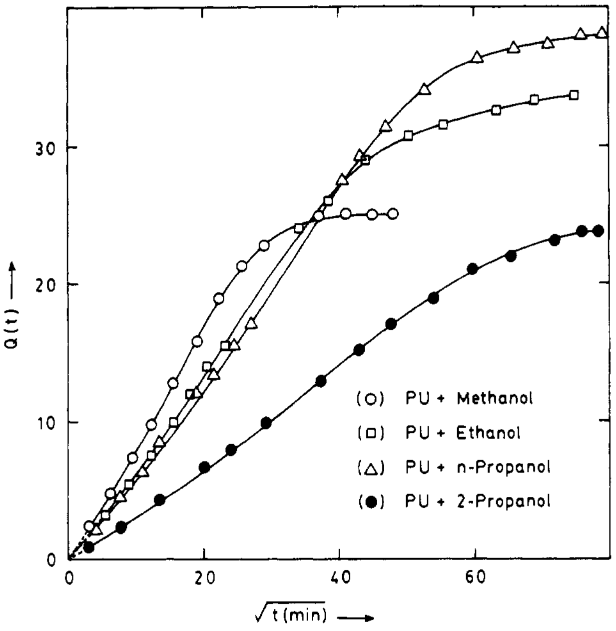


Figure 1. Percentage mass uptake $Q(t)$ of polyurethane versus square root of time ($t^{1/2}$) at 25 °C for (○) methanol, (□) ethanol, (△) 1-propanol, and (●) 2-propanol.

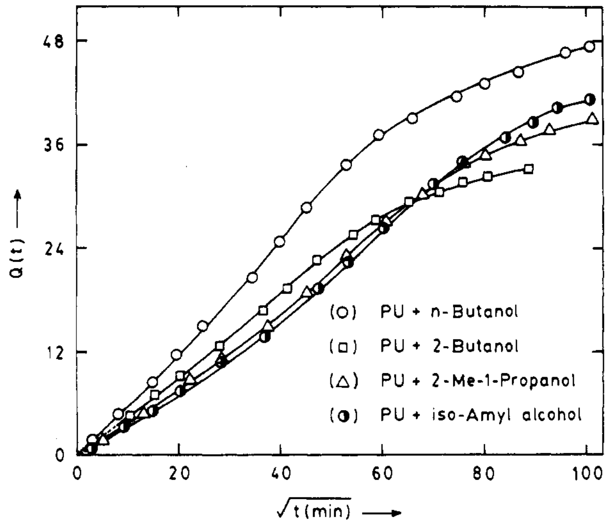


Figure 2. Percentage mass uptake $Q(t)$ of polyurethane versus square root of time ($t^{1/2}$) at 25 °C for (○) 1-butanol, (□) 2-butanol, (△) 2-methyl-1-propanol, and (◑) isoamyl alcohol.

ibration was attained. The estimated error in D as calculated from eq 2 is about ±0.003 unit. The permeability coefficients were then obtained by using the empirical relationship (*18*):

$$P = DS \tag{3}$$

The results of P, D, and S as obtained at 25, 44, and 60°C are summarized in Table II. For all the penetrants, P, D, and S tend to increase with a rise in temperature; additionally, diffusion and permeation data suggest an inverse dependence with their molar volumes. For instance, values of D and P decrease systematically from methanol to 1-butanol. Since the molar volumes of 1-butanol, 2-butanol, and 2-methyl-1-propanol are almost identical, thus, their transport properties should be more or less identical. This is indeed the case with 1-butanol and 2-butanol for which D values at 25 °C are respectively 3.5×10^{-8} and 3.9×10^{-8} cm^2/s. However, lower values of D and P as shown by 2-methyl-1-propanol could be attributed to the presence of a bulkier methyl group, which hinders the penetrant movement through polyurethane matrix. Isoamyl alcohol, which has the largest molar volume of all the penetrants considered here, exhibits lower P and D than 2-methyl-1-propanol. This is, however, true only at 25 °C. On the other hand at 44 and 60 °C, the magnitudes of D and P for isoamyl alcohol are larger than those of 2-methyl-1-propanol. From the dependence of D on the number of carbon atoms, as shown in Figure 7, it is found that D varies inversely with an increase in the number of carbon atoms. This also shows a clear effect of $-CH_2$ group contribution on diffusivity.

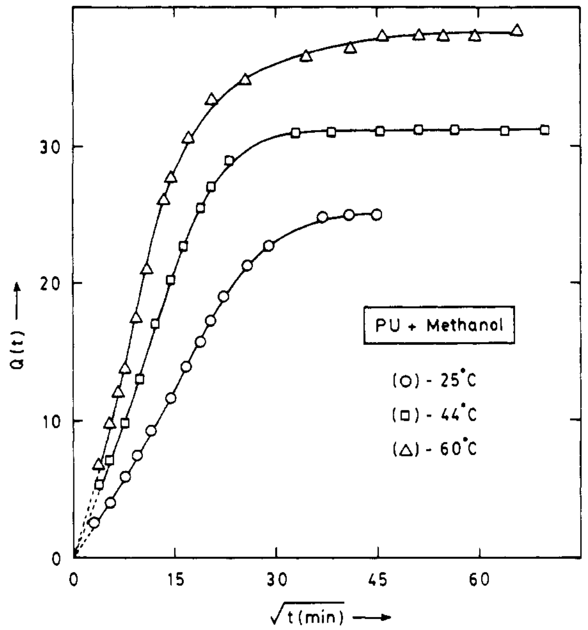


Figure 3. Temperature dependence of $Q(t)$ versus $t^{1/2}$ for the polyurethane + methanol system. Symbols: (○) 25, (□) 44, and (△) 60 °C.

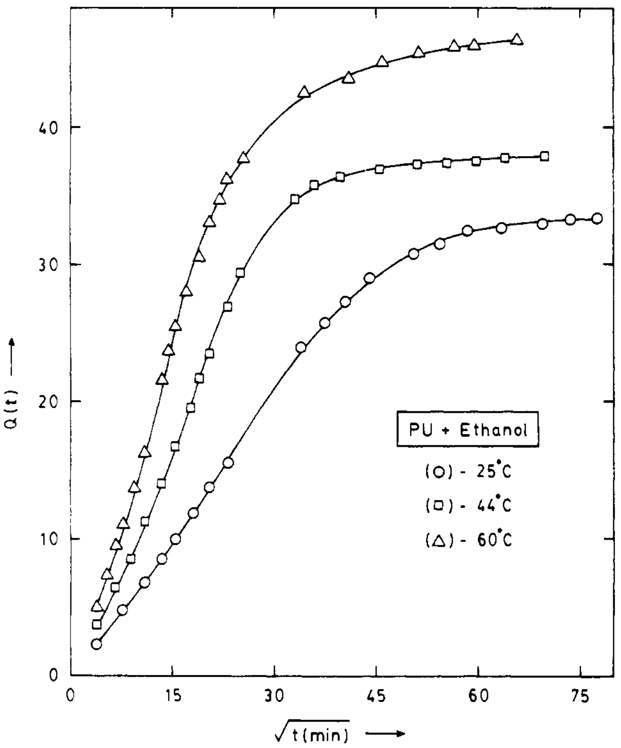


Figure 4. Temperature dependence of $Q(t)$ versus $t^{1/2}$ for the polyurethane + ethanol system. Symbols have the same meanings as those in Figure 3.

Of the three branched alcohols, namely, 2-propanol, 2-butanol, and isoamyl alcohol, the latter exhibits lower diffusivity than either 2-propanol or 2-butanol. This may be due to its larger cross-sectional area thereby hindering its passage

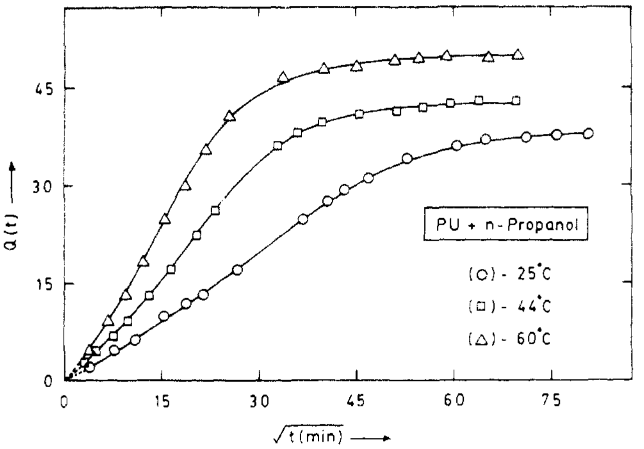


Figure 5. Temperature dependence of $Q(t)$ versus $t^{1/2}$ for the polyurethane + 1-propanol system. Symbols have the same meanings as those in Figure 3.

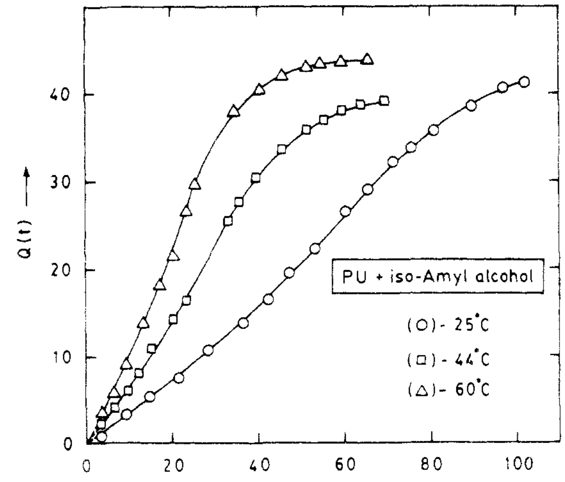


Figure 6. Temperature dependence of $Q(t)$ versus $t^{1/2}$ for the polyurethane + isoamyl alcohol system. Symbols have the same meanings as those in Figure 3.

Table II. Experimental Results on Polyurethane + Penetrant Systems at 25, 44, and 60 °C

penetrant	temp, °C	S, g/g	10^8D, cm²/s	10^8P, cm²/s	K_s, mmol/g	n (eq 8)	10^2k
methanol	25	0.249	22.5	5.60	7.772	0.557	2.394
	44	0.312	43.5	13.57	9.738	0.495	4.330
	60	0.384	57.4	22.04	11.985	0.534	4.129
ethanol	25	0.334	8.18	2.73	7.250	0.535	1.598
	44	0.379	19.90	7.54	8.227	0.560	2.263
	60	0.465	23.80	11.07	10.093	0.525	2.561
1-propanol	25	0.380	5.75	2.19	6.323	0.534	1.345
	44	0.431	11.10	4.78	7.171	0.574	1.619
	60	0.502	18.90	9.48	8.353	0.558	2.168
2-propanol	25	0.251	3.84	0.96	4.176	0.527	1.138
	44	0.329	12.63	4.16	5.474	0.565	1.578
	60	0.324	22.93	7.43	5.391	0.577	2.079
1-butanol	25	0.473	3.49	1.65	6.382	0.526	1.061
	44	0.451	11.0	4.96	6.085	0.552	1.650
	60	0.484	18.26	8.84	6.530	0.570	1.874
2-butanol	25	0.333	3.90	1.30	4.493	0.542	1.043
	44	0.375	10.30	3.86	5.059	0.545	1.691
	60	0.383	16.70	6.40	5.167	0.539	2.392
2-methyl-1-propanol	25	0.389	2.34	0.91	5.248	0.537	0.797
	44	0.385	6.70	2.58	5.194	0.544	1.420
	60	0.422	13.47	5.68	5.693	0.547	1.819
isoamyl alcohol	25	0.414	1.95	0.81	4.697	0.538	0.703
	44	0.393	7.30	2.87	4.458	0.551	1.338
	60	0.441	13.10	5.78	5.003	0.555	1.689

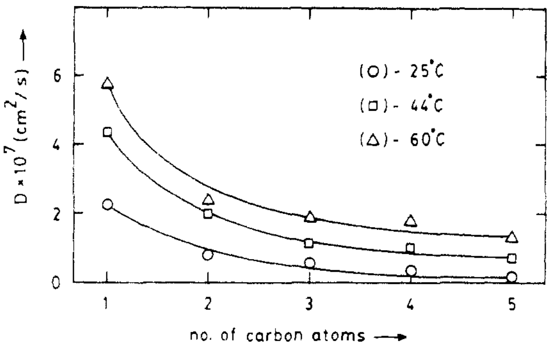


Figure 7. Dependence of diffusivity on the number of carbon atoms. Symbols: (○) 25, (□) 44, and (△) 60 °C.

Chart I. Possible Hydrogen Bond Formation between Alcohols and Polyurethane Segments

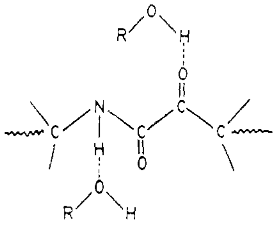
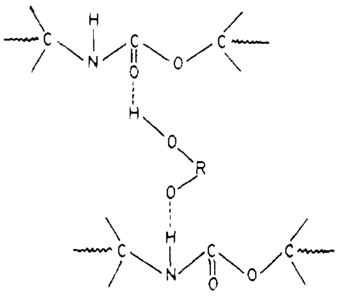


Chart II. Intermolecular Interaction Forces through Double Hydrogen Bonds between Branched Alcohol and Polyurethane Segments



through PU segments. Additionally, it appears that the hydrogen-bond-type interactions between the –OH group of the branched alcohols and the polar groups of PU segments may be responsible for the slower diffusivity. The possible hydrogen bond interactions between the branched alcohols and polyurethane is shown in Chart I. On top of this, there is also a possibility that the secondary forces such as hydrophobic bond interactions may contribute toward the overall diffusion pattern. Thus, the two –OH groups might form double hydrogen bonds as shown in Chart II.

The diffusivities as obtained from eq 2 were further used to generate the theoretical sorption profiles on a computer with the modified Fick's relation (*19*)

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp[-D(2n+1)^2\pi^2 t/h^2] \qquad (4)$$

Here, the symbol M_∞ has the same meaning as M_m. Comparisons between the theoretical and experimental profiles are shown in Figures 8–10 for some representative alcohols. Fair agreement between the simulated and experimental sorption curves over the entire time scale of the sorption experiment suggests the validity of eq 2 used to compute D.

Considering the diffusion and permeation to be an activated process, attempts were also made to estimate the activation parameters of diffusion E_D, as well as for permeation E_P, using the standard Arrhenius relationship (*18*)

$$\log X = \log X_0 - E_x/2.303RT \qquad (5)$$

where X refers to either D or P; X_0 is a constant representing

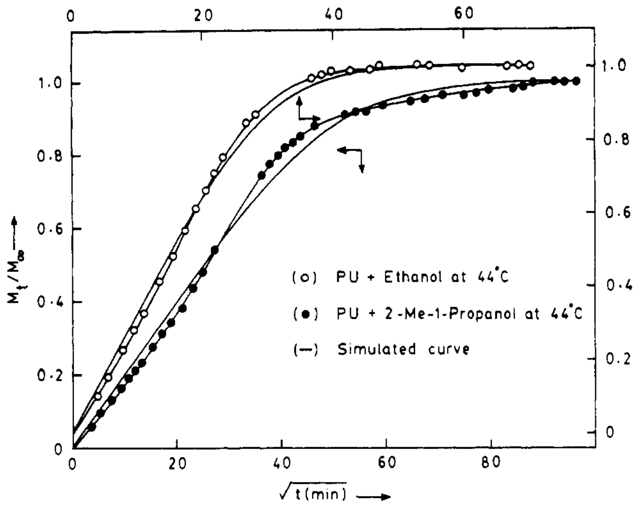


Figure 8. Comparison between experimental and simulated sorption profiles for polyurethane + solvent systems. Symbols: (○) ethanol at 44 °C, (●) 2-methyl-1-propanol at 44 °C, and (—) simulated data.

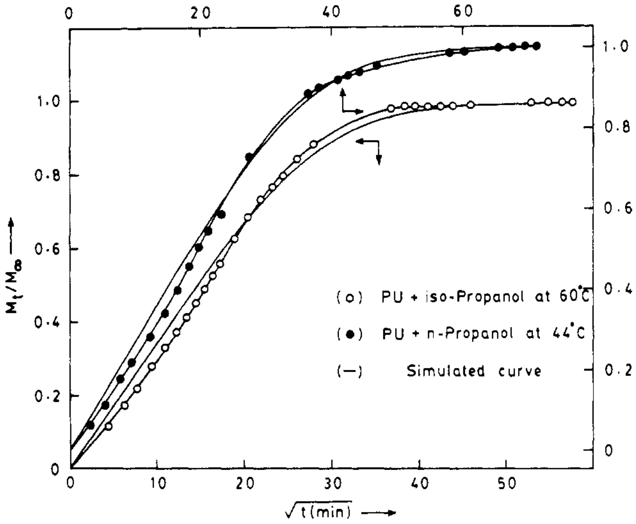


Figure 9. Comparison between experimental and simulated sorption profiles for polyurethane + solvent systems. Symbols: (○) 2-propanol at 60 °C, (●) 1-propanol at 44 °C, and (—) simulated data.

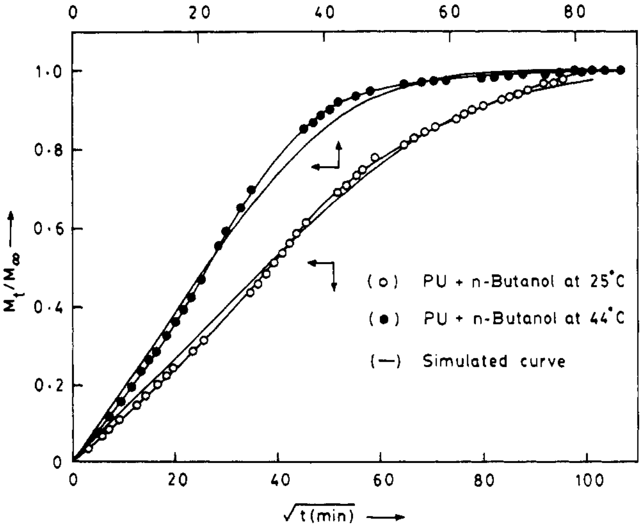


Figure 10. Comparison between experimental and simulated sorption profiles for polyurethane + solvent systems. Symbols: (○) 1-butanol at 25 °C, (●) 1-butanol at 44 °C, and (—), simulated data.

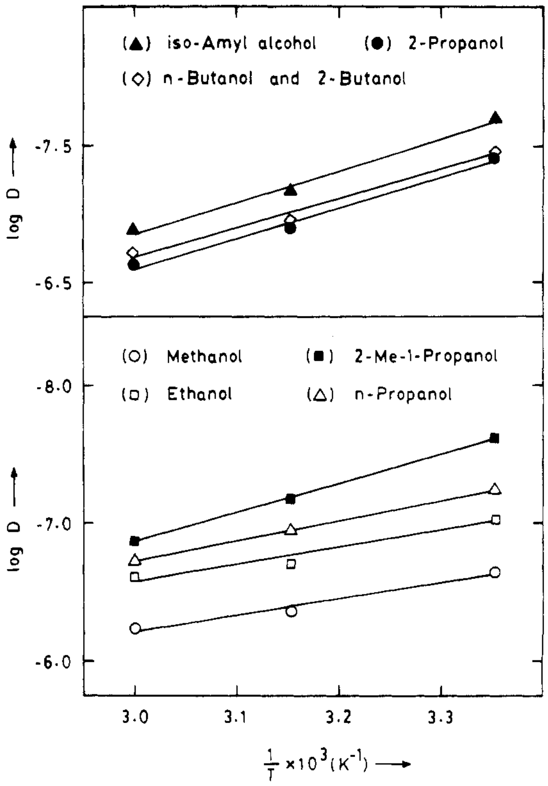


Figure 11. Arrhenius plots for diffusivity. Symbols: (○) PU + methanol, (□) PU + ethanol, (△) PU + 1-propanol, (■) PU + 2-methyl-1-propanol, (▲) PU + isoamyl alcohol, (●) PU + 2-propanol (◇) PU + 1-butanol, and PU + 2-butanol.

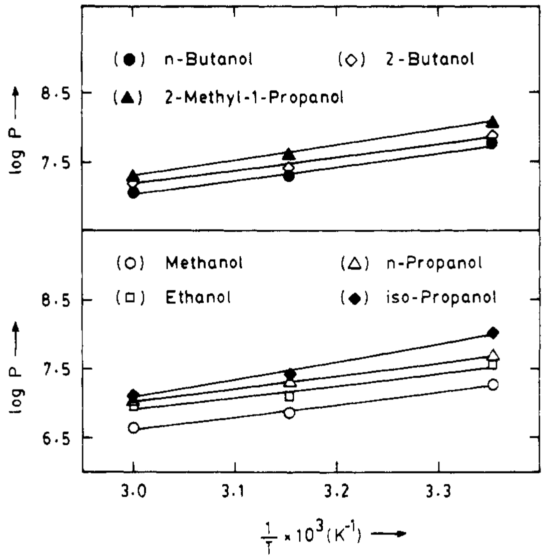


Figure 12. Arrhenius plots for permeability. Symbols: (○) PU + methanol, (□) PU + ethanol, (△) PU + 1-propanol, (♦) PU + 2-propanol, (●) PU + 1-butanol, (◇) PU + 2-butanol, and (▲) PU + 2-methyl-1-propanol.

Table III. Activation Parameters and Thermodynamic Quantities for Polyurethane + Penetrant Systems at 25, 44, and 60 °C

penetrant	activation parameters, kcal/mol				
	E_D	E_P	ΔH_s	$\Delta S°$, eu	$\Delta H°$, kcal/mol
methanol	5.3216	7.7440	2.4224	12.1847	2.4213
ethanol	6.1393	7.9652	1.8259	10.0280	1.8266
1-propanol	6.6714	8.2183	1.5469	8.8259	1.5440
2-propanol	10.1212	11.6162	1.5950	7.9239	1.4969
1-butanol	9.3956	9.4930	0.0974	3.9759	0.0974
2-butanol	8.2378	9.0423	0.8045	5.7068	0.8046
2-methyl-1-propanol	9.8562	10.2849	0.4287	4.6975	0.4278
isoamyl alcohol	10.8142	11.1201	0.3059	4.0630	0.3098

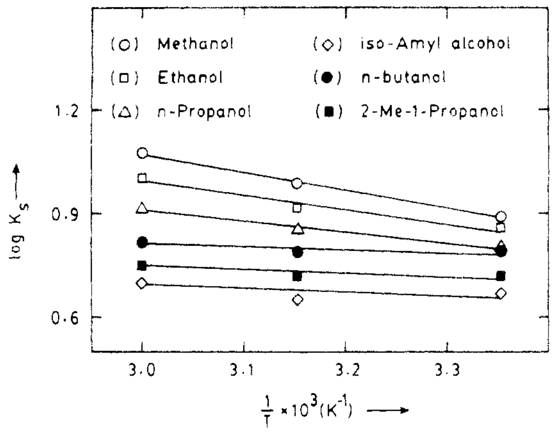


Figure 13. van't Hoff plots for polyurethane + solvent systems. Symbols: (○) methanol, (□) ethanol, (△) 1-propanol, (●) 1-butanol, (■) 2-methyl-1-propanol, and (◇) isoamyl alcohol.

D_0 or P_0; and E_x gives the value of either E_D or E_P, depending upon the process under consideration. From a least-squares fit of the linear plots of log X versus $1/T$, as shown in Figures 11 and 12 for diffusivity and permeability, respectively, the E_D and E_P values have been calculated. These results are given in Table III. The uncertainties in the values of E_D or E_P vary from 0.002 to 0.003. The heat of sorption, ΔH_s was calculated as

$$\Delta H_s = E_P - E_D \tag{6}$$

From the results given in Table III, it is obvious that both E_D and E_P vary systematically with the size and shape of the diffusing molecules. For instance, E_D for methanol is about 5 kcal/mol, which increases steadily up to about 10 kcal/mol for 2-propanol. For the three penetrants, namely, 1-butanol, 2-butanol, and 2-methyl-1-propanol, both E_D and E_P values are more or less in the same order of magnitude (i.e., around 8–10 kcal/mol). This is expected because the size of these penetrants is almost identical. For isoamyl alcohol, either E_D or E_P values are higher as compared to other penetrants (i.e., E_D = 10.8 and E_P = 11.1 kcal/mol). This proves the conjecture that larger molecules require more energy to create what are known as "Eyring holes" within the polymer matrix (*20*). The ΔH_s values are all positive but small, and these vary from 0.1 kcal/mol for 1-butanol to 2.42 kcal/mol for methanol. Similar magnitudes for ΔH_s can be found in the literature (*21–25*).

One other observation, while performing sorption experiments, was that of membrane swelling due to penetration of solvent molecules into the preexisting pores of the polymer matrix. According to the theory of Flory and Rehner (*26*), the swelling behavior of a cross-linked network such as the PU membrane can be described by a balance between mixing and elastic free energies. Usually, the entropy of mixing acts as the driving force for swelling. Thus, it is of interest to know the values of standard entropy, $\Delta S°$, and enthalpy changes, $\Delta H°$, for sorption of each penetrant–polymer pair. Following the procedure suggested by Hung (*22*), we have calculated the equilibrium sorption constant, K_s, as millimoles of solvent sorbed per gram of the polymer (see Table II). Further, by making use of the van't Hoff relationship (*27*),

$$\log K_s = \frac{\Delta S°}{2.303R} - \frac{\Delta H°}{2.303R}\left(\frac{1}{T}\right) \tag{7}$$

we have estimated the values of $\Delta S°$ and $\Delta H°$ from the intercept and slope, respectively, of the linear plots of log K_s versus $1/T$. Such plots are displayed in Figure 13, and the results are included in Table III. Again, the uncertainties in the estimations of $\Delta H°$ and $\Delta S°$ are in the third decimal place. It is heartening to note that there is an excellent agreement between ΔH_S and $\Delta H°$ values, although these are obtained differently. However, the $\Delta S°$ values are small but still significant and vary systematically, depending on the nature of the penetrant. For instance, they decrease successively from 12.19 eu for methanol to about 3.98 eu for 1-butanol. For 2-butanol, 2-methyl-1-propanol, and isoamyl alcohol, $\Delta S°$ varies in the range of 4.0–5.7 eu.

A comparison of heat of vaporization ΔH_v, listed in Table I, to E_D values, given in Table III, suggests an approximate correlation for several penetrants except methanol, ethanol, and 1-propanol. This suggests that the interactions of higher alcohols with polyurethane are similar to the intermolecular bonding such as, for example, hydrogen bonding of the alcohols in the liquid state. Any deviation in the E_D and ΔH_v values for some of the penetrants like methanol, ethanol, and 1-propanol implies that their interactions with polyurethane may also be due to other secondary interactions such as hydrophobic bonding. Further qualitative evidence for the hydrophobic interactions comes from the sorption data given in Table II. For instance, with the exception of 2-propanol, solubility increases from methanol to 1-propanol. A decrease in the values of S for 2-propanol, 2-butanol, and isoamyl alcohol (even as compared to 1-butanol) may be due to the fact that the free volume available in the polymer to accommodate the larger cross-sectional molecules is less than for the lower homologues of alcohol.

In continuation of the discussion of penetrant transport through PU membrane, the type of diffusion mechanism was established by fitting the sorption data to an empirical equation of the type (*1*)

$$M_t/M_\infty = kt^n \tag{8}$$

where k is a constant that depends on the structural characteristics of the polymer and its interaction with solvent. The value of the exponent n decides the type of transport mechanism. For example, n = 0.5 suggests the Fickian case I diffusion; n = 1.0 indicates departure from Fickian case I, but is usually referred to as Fickian case II, while the intermediate values of n (i.e., n = 0.5–1.0) suggest the anomalous transport behavior (*1*). Transforming eq 8 into logarithmic form, we get

$$\log (M_t/M_\infty) = \log k + n \log t \tag{9}$$

The least-squares estimates of k and n from the intercept and slope, respectively, of the straight lines of the plots of log (M_t/M_∞) versus log t are also included in Table II. Some typical plots for ethanol and 1-propanol are presented in Figure 14. In the present investigation, the value of n varies between 0.50 and 0.58 for all the penetrants, suggesting that the transport mechanism deviates only slightly from the Fickian case I mode. However, the values of k depend on the temperature: k increases systematically with increases in temperature. Furthermore, the values of k are almost of the same order of magnitude for all the polymer–penetrant systems. This suggests that the majority of alcohols studied here interact more or less in the same manner with the PU membrane.

Conclusions

Diffusivity, sorptivity, and permeability of eight aliphatic alcohols into polyurethane membrane have been studied at 25, 44, and 60 °C. From the temperature dependence of these quantities, Arrhenius parameters were computed for the transport processes under consideration. The van't Hoff relationship was used to calculate entropy and enthalpy of sorption, and these were used in the discussion of penetrant–polymer interactions. In general, none of the chosen alcohols interacted strongly with the polymer membrane, as evidenced by insignificant swelling or no signs of degradation. However, the activation parameters for diffusion and permeation are higher for

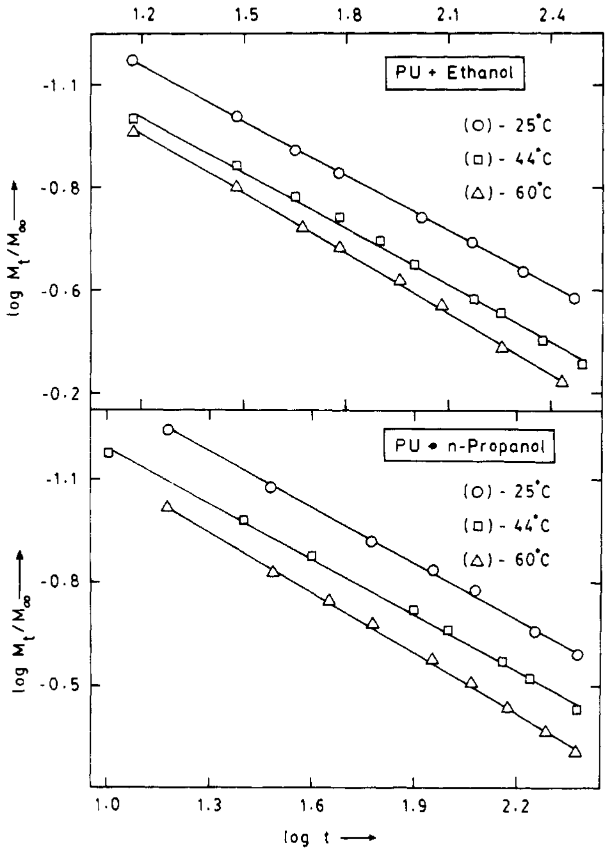


Figure 14. log (M_t/M_∞) versus log t for polyurethane + ethanol and polyurethane + 1-propanol systems. Symbols: (○) 25, (□) 44, and (△) 60 °C.

larger molecules while their diffusivities are smaller. On the whole, the transport data were affected if the branched alcohols were used as penetrants.

Acknowledgment

We thank Dr. John Idoux and Dr. Keith Hansen of Lamar University for their interest, and Dr. Patrick E. Cassidy of Southwest Texas State University for providing a polyurethane sample.

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Received for review April 7, 1989. Revised November 22, 1989. Accepted March 29, 1990. We thank the University Grants Commission (UGC), New Delhi, India, for financial support under a UGC major scheme (No. F.12-55/88-SR-III) and also for the award of a teacher fellowship to U. S. Aithal to study at Karnatak University. T.M.A. and S.S.S. thank the Robert A. Welch Foundation, Houston, TX, for partial support of this study.