Interaction of Some Highly Aggressive Solvents and Effect of Temperature on the Transport Characteristics of Polyurethane

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Synopsis

A number of highly interacting liquids have been used as penetrants to study their transport characteristics into a commercial polyurethane membrane. The penetrant-polyurethane interaction is strongly dependent on the nature of the interacting molecules. With tetrahydrofuran, dioxane, cyclohexanol, acetophenone, and benzyl alcohol the polymer swells greatly even at room temperature, and in such cases, sorption experiments were not carried out at higher temperatures. In a few other cases like pyridine, aniline, etc., the polymer loses its shape and physical integrity leading to chemical degradation reactions. Some of the otherwise normally behaving liquids like n-butanol, 1,4-dichlorobutane, anisole, toluene, chlorobenzene, and nitrobenzene did not reach equilibrium at high temperatures (70–90°C) even after prolonged exposure, making it difficult to interpret the sorption data. The results of this study may be useful to make an overall assessment about the application of polyurethane under extreme service conditions. Furthermore, concentration-independent diffusion coefficients have been calculated for those penetrant–polymer systems which exhibited the least amount of swelling. For highly swelling liquids, the transport mechanism deviates from the normal Fickian mode and diffusion coefficients for such systems have not been obtained.

INTRODUCTION

In recent years, there has been a tremendous increase in the use of polymers as structural engineering materials.[1-4] Therefore, it is very important to know the performance of polymers under the influence of external forces such as presence of solvents, temperature, etc. Polymer deformation is a phenomenon where the materials suffer failure under aggressive environments, such as in contact with highly reactive solvents or at elevated temperatures. Although much information is available on the deformation and failure studies of glassy polymers,[5-8] there is a need for more investigation and understanding of the transport properties of elastomer membranes under extreme service conditions.

Although much work has been done in the elucidation of the mechanism of polymer–solvent interactions with vinyl-type polymers,[9-11] comparatively little has been reported about the deformation and transport characteristics of an industrially important elastomer, namely, polyurethane. In this paper, we report the results of a systematic study on the deformation and transport behavior of polyurethane with respect to several aggressive solvents over a wide range of temperature, namely, 25–90°C. Prior to this study, very little was known[12] about the transport characteristics of polyurethane at elevated temperatures.

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TABLE I
Sorption Data for Polyurethane–Penetrant Systems at 25°C

Penetrant	bp (°C)	Temp (°C)	$Q(t)$ (max)	$D \times 10^7$ (cm²/s), eq. (1)	$D \times 10^7$ (cm²/s), eq. (5)	S (g/g)	$P \times 10^7$ (cm²/s)	n, eq. (3)	L_d (%)	Immersion time (days)
Dichloromethane	39.8	25	210	10.12	4.08	2.104	21.29	0.56	39	9
Methyl acetate	56.3	25	49	3.71	1.93	0.494	1.83	0.54	17	8
		44	51	6.43	—	0.508	3.27	0.54	17	4
Chloroform	61.2	25	421	4.09	2.86	4.206	16.13	0.74	50	7
		44	395	6.68	—	3.952	26.40	0.73	54	4
Pyridine[a]	115.3	44	1772	—	—	17.718	—	0.73	171	5
Tetrahydrofuran	66.0	25	292	2.75	1.60	2.915	8.02	0.68	62	4
Dioxane	101.3	25	227	0.28	0.37	2.267	0.64	0.61	50	10
Methyl ethyl ketone	79.6	25	126	1.48	0.85	1.261	1.87	0.61	35	8
Aniline	184.4	25	733	—	—	7.325	—	0.55	108	124
Cyclohexanol	161.1	25	520	—	—	5.199	—	0.52	91	168
Benzyl alcohol	205.5	25	422	1.22	0.22	4.221	5.1	0.56	76	6
Acetophenone	202.0	25	382	—	—	3.823	—	0.58	70	175

[a] Experiment done only at 44°C.

TABLE II
Sorption Data for Polyurethane–Penetrant Systems at Elevated Temperatures

Penetrant	Temp (°C)	$Q(t)$ (max)	Dimensional changes		$D \times 10^7$ (cm^2/s)	Immersion time (days)
			L_t (%)	L_d (%)		
n-Butanol	70	146	—	—	—	16
	80	276	67	77	—	4
	90	369	—	—	—	1
1,4-Dichlorobutane	70	96	23	25	4.01	23
	80	95	25	24	5.10	5
	90	130	30	31	—	8
Anisole	70	103	27	30	6.41	23
	80	100	28	27	7.77	5
	90	145	37	39	—	8
Toluene	70	64	22	24	8.43	20
	80	64	19	20	10.87	5
	90	76	23	26	—	8
Chlorobenzene	70	125	30	31	9.12	23
	80	123	30	29	10.22	5
	90	164	37	30	—	8
Nitrobenzene	70	152	33	34	—	23
	80	334	59	57	—	15
	90	756	98	99	—	8

The following questions are addressed. What is the effect of microphase separation of hard and soft segments of the polymer matrix? What is the effect of crosslinking? Answers to these questions are of interest both from the fundamental and practical point of view to understand the relationship between the deformation/transport behavior and microstructure of polyurethane. Also, it is useful for the application of polyurethanes as engineering plastics under extreme service conditions.[13]

EXPERIMENTAL

Materials

The solvents used were all of reagent grade and purified before use.[14] Polyurethane was supplied as a thin film of uniform thickness from PSI, Austin, TX (courtesy of Professor P. E. Cassidy). The base polymer used was a Vibrathane B600 (Uniroyal) cured with 4,4'-methylene-bis(o-chloroaniline).

Sorption Experiments

Polyurethane was 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. Their thicknesses were measured at several points using a micrometer (precision ± 0.001 cm) and the mean value was taken to be 0.250 cm. Dry weights of the cut samples were taken before immersion into the airtight metal-capped test bottles containing the liquid. After immersion into the
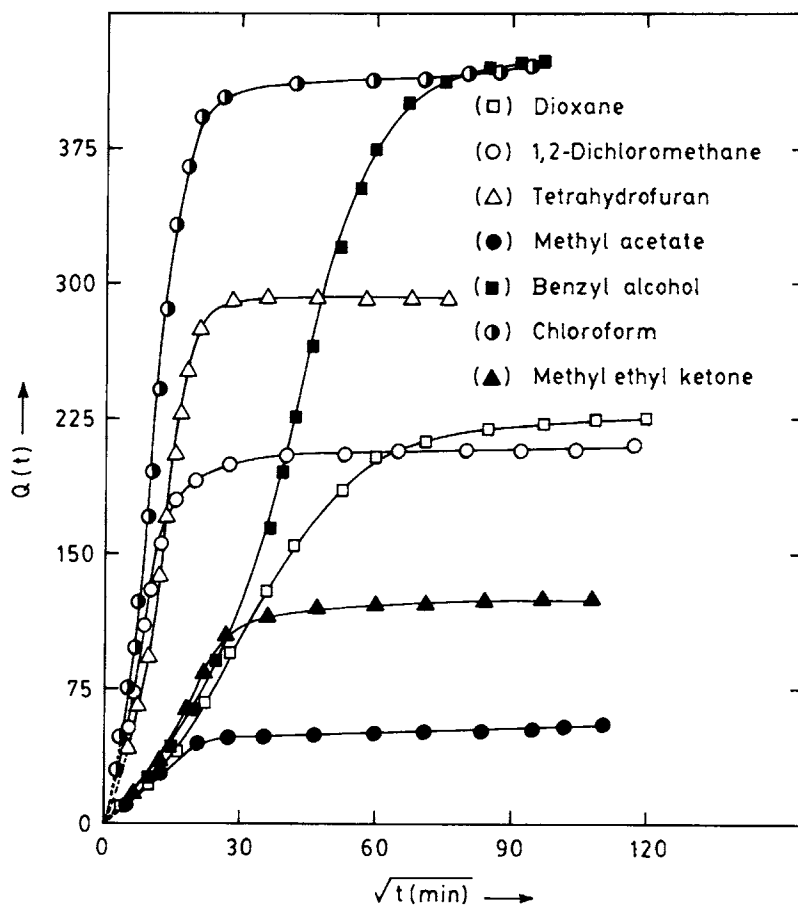
Fig. 1. Percent mass uptake of solvent $[Q(t)]$ versus square root of time $(t^{1/2})$ at 25°C: (○)
dichloromethane; (●) methyl acetate; (△) tetrahydrofuran; (□) dioxane; (▲) methyl ethyl ketone;
(■) benzyl alcohol; (◐) chloroform.

respective liquids, the bottles were placed in a thermostatically controlled oven
(±0.5°C; Memmert, Germany).

At specified time intervals, the samples were removed from the bottles, and
the wet surfaces were dried between filter paper wraps and weighed immediately
to the nearest 0.05 mg by placing it on a covered watch glass within the chamber
of a Mettler balance. The samples were quickly placed back into test bottles
and then transferred to the oven. The experiments were performed from
25–90°C.

A possible source of error in this method is that the sample has to be removed
from the liquid while weighing; if this is done quickly (say within 30–50 s)
compared to the time a sample remained in the liquid between consecutive
weighings, the sample removal exerts negligible effect. For those liquids whose
density is greater than the membrane, the sample was pushed to immerse in
the liquid by a glass plunger attached to the screw cap.
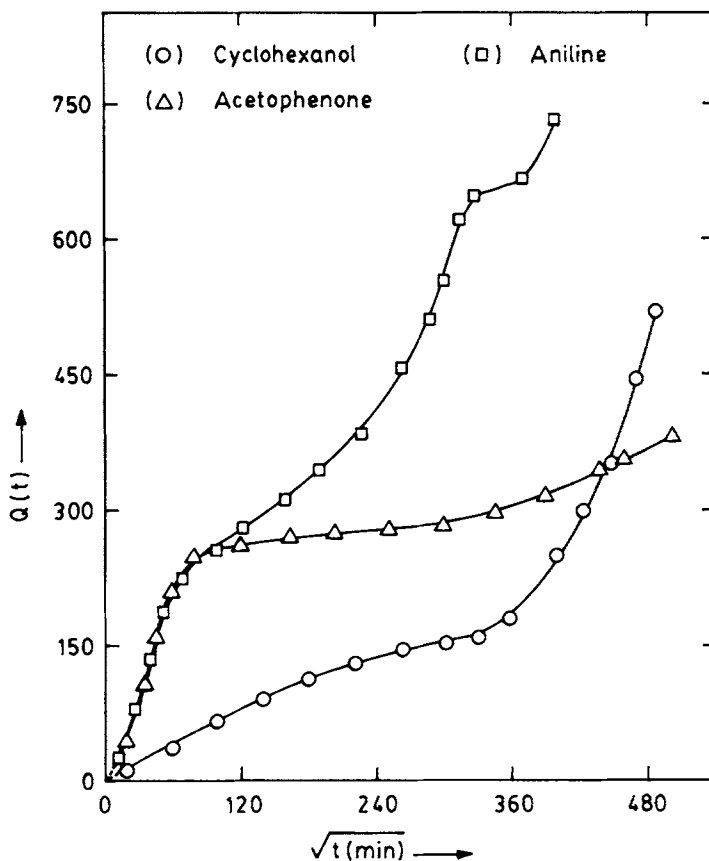
Fig. 2.   Percent mass uptake of solvent $[Q(t)]$ versus square root of time $(t^{1/2})$ at 25°C; ($\bigcirc$) cyclohexanol; ($\triangle$) acetophenone; ($\square$) aniline.

RESULTS AND DISCUSSION

Experimental results are discussed in terms of two different stresses imposed on the polyurethane: variation of solvent power and variation of temperature. Thus, the motivation of research was two-fold. In the first group of solvents, which included dichloromethane, methyl acetate, chloroform, tetrahydrofuran, dioxane, methyl ethyl ketone, aniline, cyclohexanol, benzyl alcohol, and acetophenone, we could not perform the sorption experiments above 25°C. This was because either the chosen solvent was highly interactive, as in the case of aniline, tetrahydrofuran, pyridine, benzyl alcohol, and methyl ethyl ketone, or the boiling point of the solvent was low, as in case of dichloromethane, methyl acetate, and chloroform, making it difficult to perform sorption experiments at higher temperatures. However, for methyl acetate and chloroform, experiments were also carried out at 44°C; for pyridine the only experiment tried was at 44°C.

For the second group of high boiling solvents comprising n-butanol, 1,4-dichlorobutane, anisole, toluene, chlorobenzene, and nitrobenzene, which would
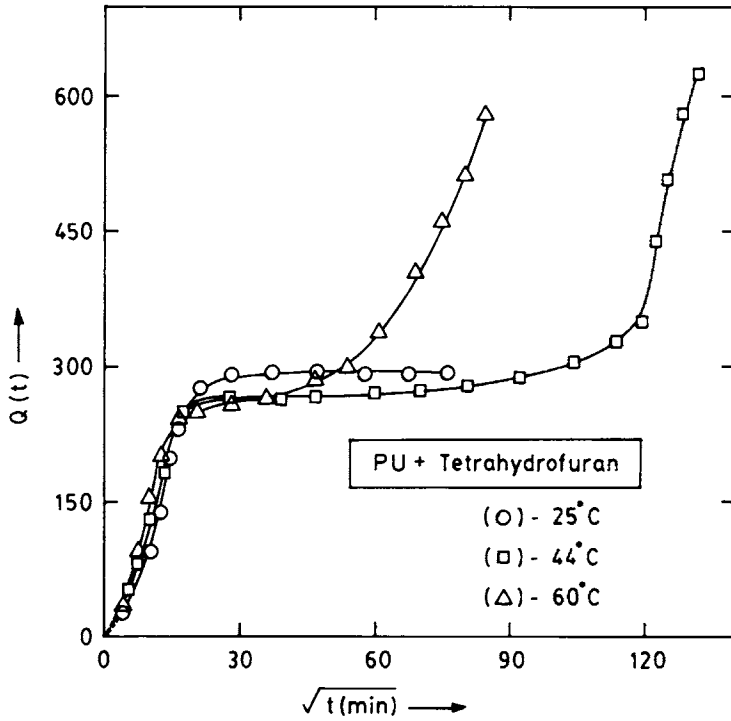
Fig. 3. Temperature dependence of sorption: $Q(t)$ versus $t^{1/2}$ for the polyurethane–tetrahydrofuran system at 25 (○), 44 (□), and 60°C (△).
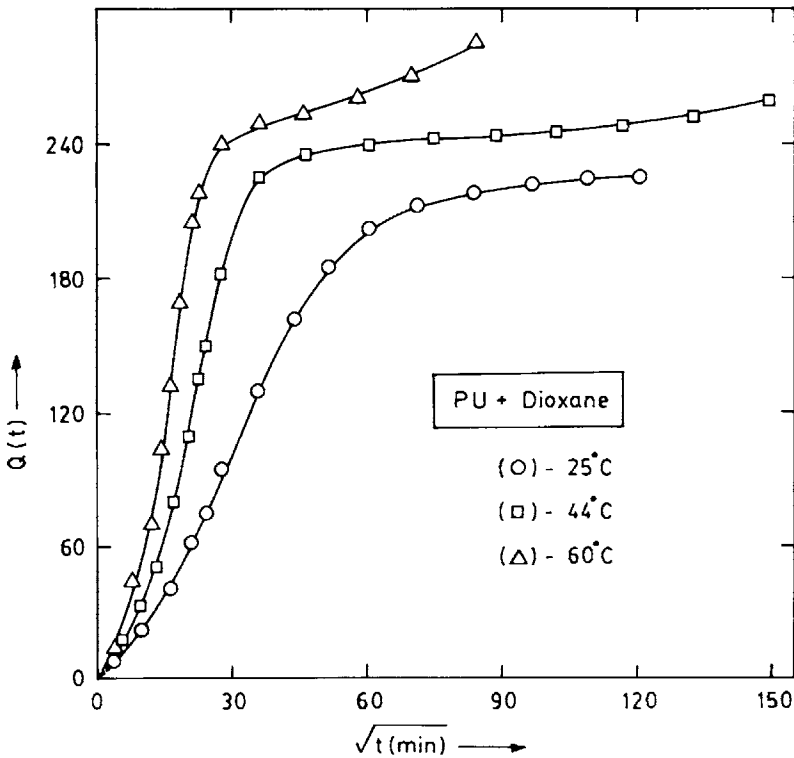

Fig. 4. Temperature dependence of sorption: $Q(t)$ versus $t^{1/2}$ curves for the polyurethane–dioxane system. Symbols have the same meanings as in Figure 3.
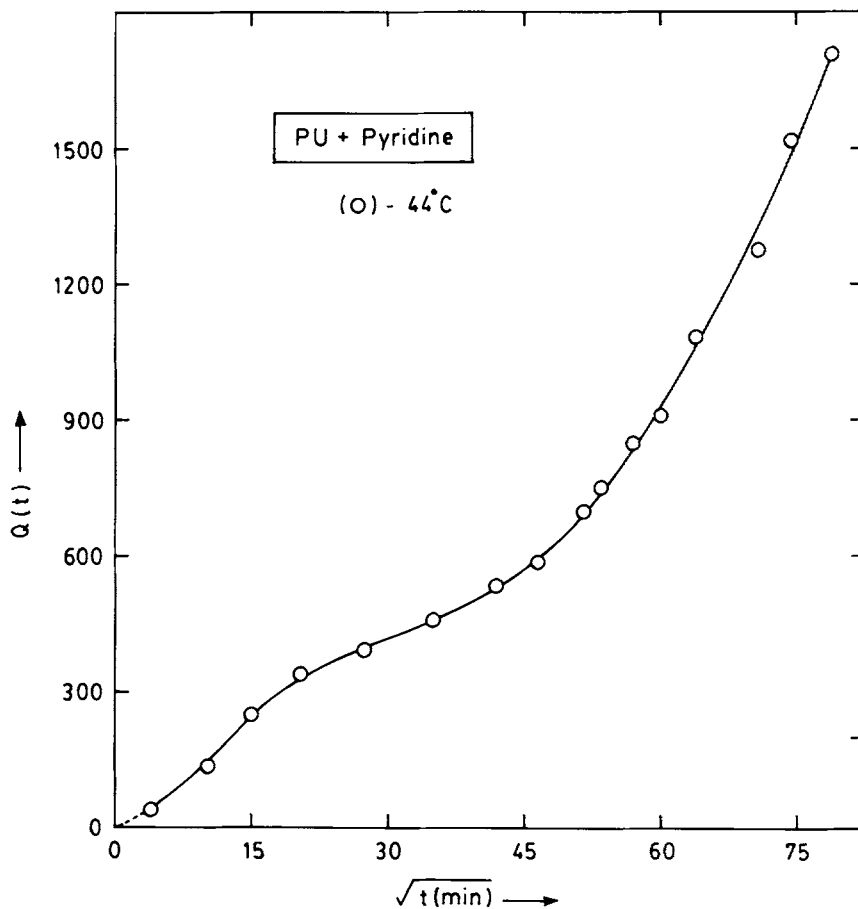
Fig. 5. Percent mass uptake of solvent $[Q(t)]$ versus square root of time $(t^{1/2})$ curve at 44°C for pyridine.
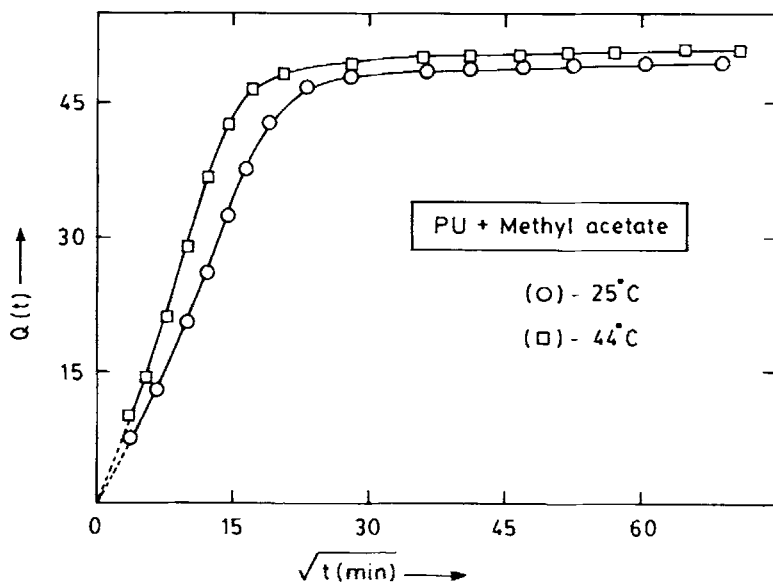

Fig. 6. Temperature dependence of sorption: $Q(t)$ versus $t^{1/2}$ for polyurethane–methyl acetate system at 25 (○) and 44°C (□).
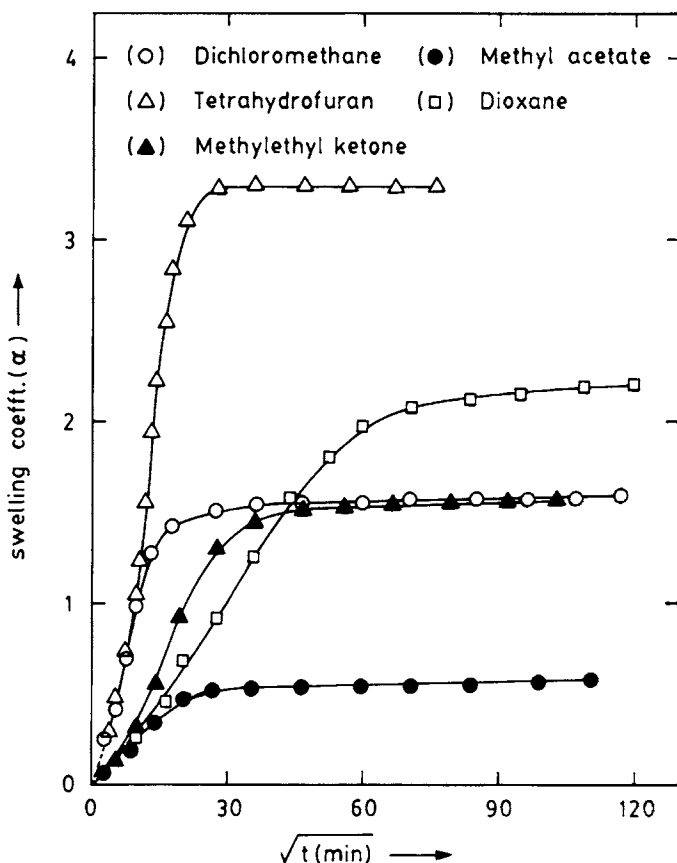
Fig. 7. Variation of swelling coefficient (α) with square root of time ($t^{1/2}$) for polyurethane-solvent systems at 25°C: (O) dichloromethane; (●) methyl acetate; (▲) methyl ethyl ketone; (△) tetrahydrofuran; (□) dioxane.

otherwise interact mildly with polyurethane, experiments have been conducted at the elevated temperatures (70–90°C). Such experiments would give us valuable information about the potential applications of the polyurethane under study when in contact with such liquids at elevated temperatures. Both of these effects will be discussed separately in this paper.

Variation of Solvent Power

Sorption results of all the 11 liquids are given in Table I. Due to experimental difficulties (either because the penetrants are low boiling liquids, or they severely attacked the membrane), the majority of liquids were studied at room temperature. However, for liquids such as aniline, cyclohexanol, and acetophenone, diffusivities were not obtained because equilibrium was not reached even after 4 months of immersion.

Sorption data for a few typical penetrants are displayed in Figure 1. Of all the penetrants, benzyl alcohol and chloroform exhibit very high values of per cent mass increase i.e., $Q(t) = 420$, whereas methyl acetate shows lower values
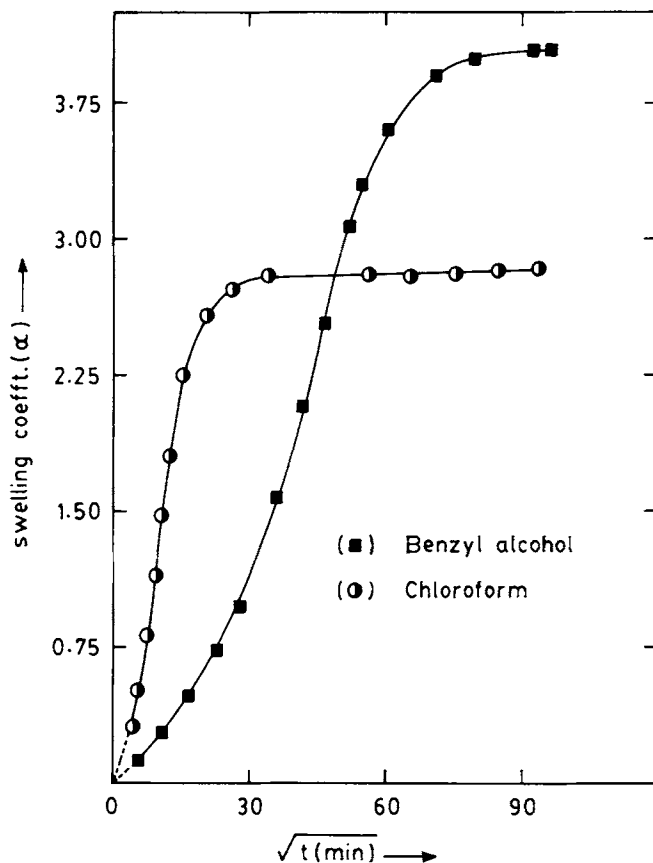
Fig. 8. Variation of swelling coefficient (α) with square root of time ($t^{1/2}$) for polyurethane-solvent systems at 25°C: (■) benzyl alcohol; (◐) chloroform.

of $Q(t)$, i.e., about 50. The intermediate values ranging from 126–290 are exhibited by dichloromethane, tetrahydrofuran, dioxane, and methyl ethyl ketone. For other penetrants like aniline, cyclohexanol, and acetophenone, equilibrium was not reached even after long exposure times up to several months.

The sigmoidal shapes of $Q(t)$ versus square root of time ($t^{1/2}$) curves for benzyl alcohol, dioxane, methyl ethyl ketone, and tetrahydrofuran suggest a departure from the normal Fickian behavior. However, the remaining penetrants shown in Figure 1 seem to exhibit the normal Fickian mode of diffusion. The penetrants like cyclohexanol, acetophenone, and aniline, whose sorption profiles are given in Figure 2, exhibit rather unusual behavior; none of these penetrants attained plateau regions and $Q(t)$ increases progressively even after long exposure times. Aniline shows a two-step sorption behavior, and thus, its transport can be classified as non-Fickian or Case II. However, acetophenone, which initially behaves (i.e., up to 7 days) almost identically to aniline, later rises continuously even after 3 months of exposure time. On the other hand, cyclohexanol shows a continuous increase in sorption after about 90 days of continuous exposure.
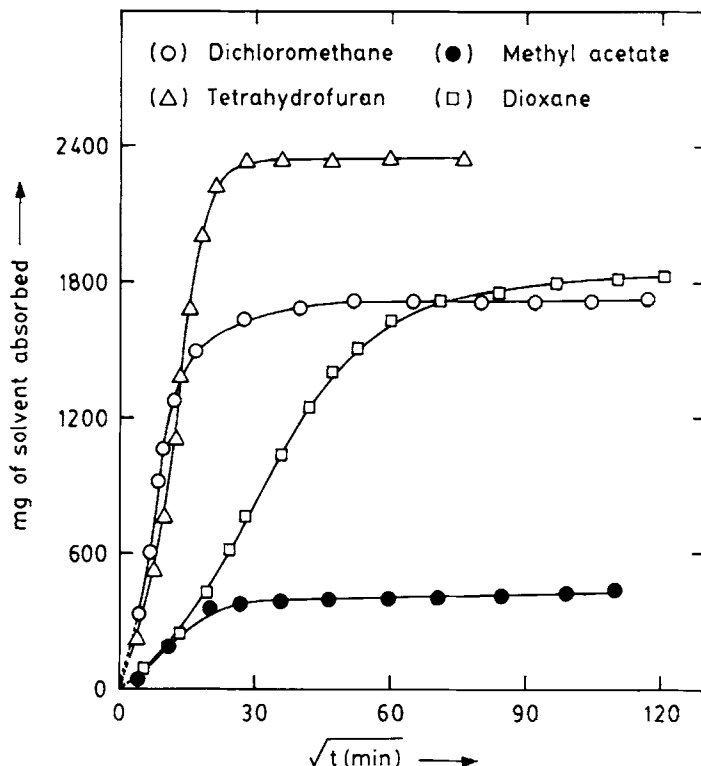
Fig. 9. Milligrams of solvent absorbed versus square root of time $(t^{1/2})$ for polyurethane-solvent systems at 25°C: (△) tetrahydrofuran; (□) dioxane; (○) dichloromethane; (●) methyl acetate.

Unusual dimensional response is shown by polyurethane in the presence of aniline, cyclohexanol, and acetophenone. The percentage increase in thickness (L_t) for these penetrants is around 90–98, whereas the percentage increase in diameter (L_d) is higher (i.e., ~108) for aniline than for cyclohexanol or acetophenone, for which L_d is 91 and 70%, respectively. For any of these penetrants, the polymer became very soft to handle; however, with aniline it became even more soft and sticky, and later started fragmenting. For these reasons, we could not further continue the sorption experiments and the experiments were stopped after about 4 months of immersion; even at this time, there were no signs of equilibrium. Similarly, with cyclohexanol and acetophenone, equilibrium was not attained even after 5–6 months of immersion. A deep dark brown color, as observed for aniline and cyclohexanol, is suggestive of chemical reactions with polyurethane segments.

With tetrahydrofuran, a normal Fickian behavior is observed at 25°C. This prompted us to carry out experiments at 44 and 60°C; unfortunately, these experiments could not be continued because the membrane became soft, sticky, and unmanageable at higher temperatures. This can be seen in Figure 3, wherein the equilibrium was not attained even after 14 days of continuous immersion. Additionally, the membrane became highly swollen with about 960% increase
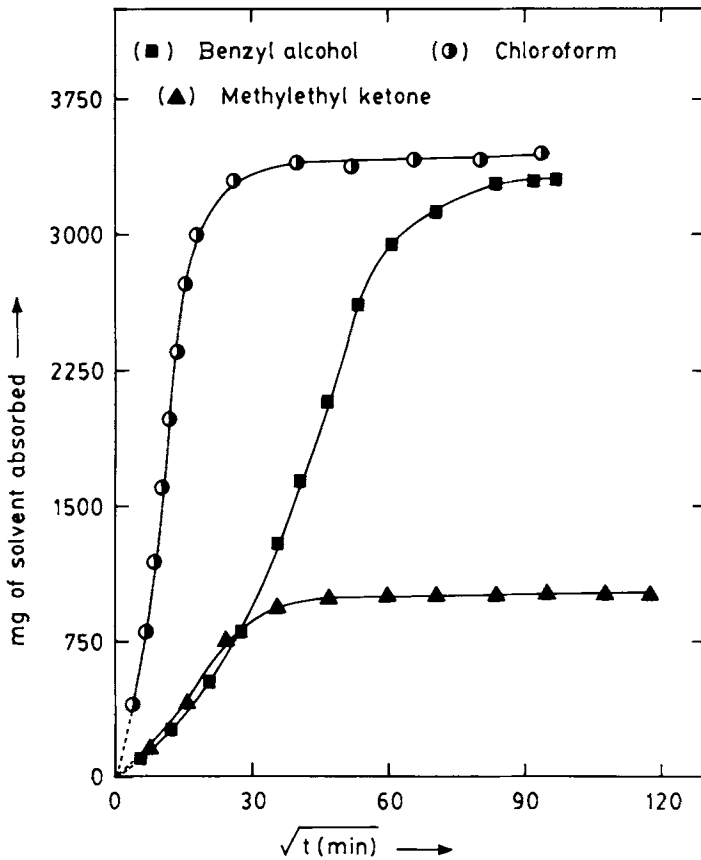
Fig. 10.   Milligrams of solvent absorbed versus square root of time ($t^{1/2}$) for polyurethane-solvent systems at 25°C: (■) benzyl alcohol; (▲) methyl ethyl ketone; (◑) chloroform.

in mass, 140% increase in thickness, and about 140% increase in diameter. It thus appears that tetrahydrofuran, which shows a normal Fickian behavior at 25°C, appears to exhibit non-Fickian diffusion at higher temperatures; moreover, the solvent seems to attack the polymer. A similar observation could be made with dioxane, which follows Fickian pattern at 25 and 44°C (see Fig. 4), but not at 60°C. At 60°C, the polymer became soft and started rupturing after a week of immersion. In addition, the swelling was very high with a mass gain of about 720%. The L_t was about 115%, whereas the L_d was about 110%. This can be explained in terms of non-Fickian diffusion mechanism.

   The sorption curve for pyridine at 44°C is presented in Figure 5. In the presence of pyridine, the polymer acquired a curdy and pasty appearance, even before the attainment of equilibrium. After about 5 days of immersion, swelling was high with a maximum $Q(t)$ of about 1772, the highest among the liquids chosen for study. Similarly, L_t and L_d values are about 210 and 170%, respectively. The sorption curves at 25 and 44°C for the low swelling liquid, namely, methyl acetate, are quite systematic, and these are shown in Figure 6. Due to its low boiling point, experiments at 60°C were not conducted.
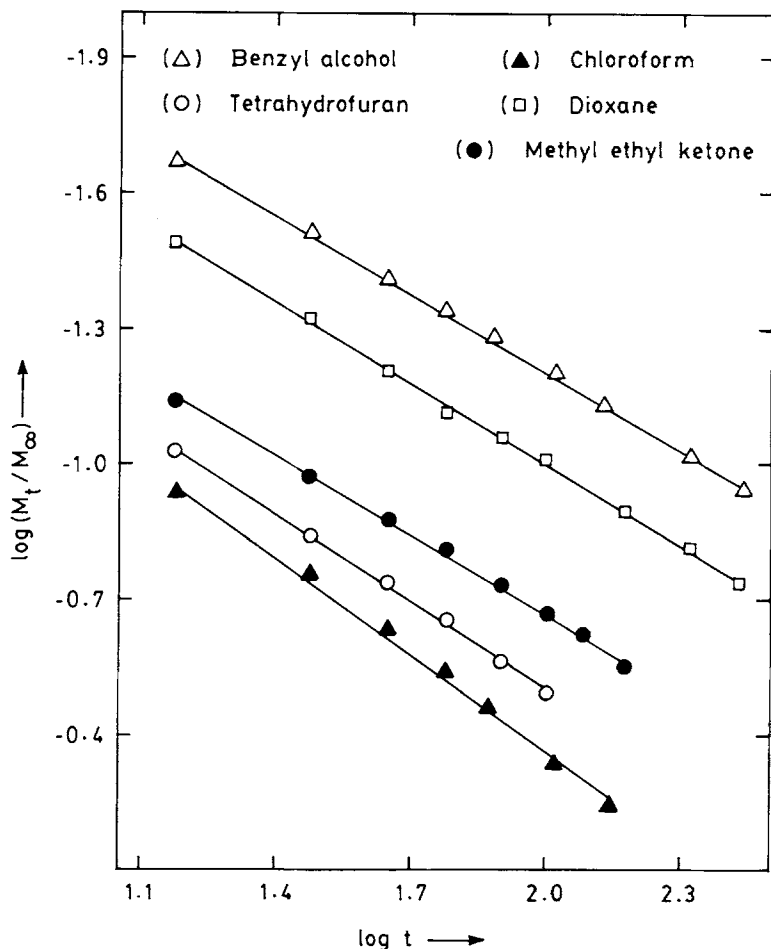
Fig. 11. $\log(M_t/M_\infty)$ versus $\log t$ for polyurethane–solvent systems at 25°C. Symbols: ($\triangle$) benzyl alcohol; ($\square$) dioxane; ($\blacktriangle$) chloroform; ($\bigcirc$) tetrahydrofuran; ($\bullet$) methyl ethyl ketone.

Figures 7 and 8 show the dependence of swelling coefficient [$\alpha = Q(t)/$ solvent density] on $t^{1/2}$; Figures 9 and 10 present the dependence of milligrams of solvent sorbed versus $t^{1/2}$. The general behavior of the dependence of either α or milligrams of solvent on $t^{1/2}$ is quite analogous to the dependence of $Q(t)$ on $t^{1/2}$ shown earlier in Figure 1. It is interesting to note that polyurethane absorbs about 3500 mg benzyl alcohol, whereas with methyl acetate the sorption is about 400 mg. This suggests that benzyl alcohol creates more free volume in polyurethane than methyl acetate.

The concentration-independent diffusion coefficients for penetrant–polyurethane matrix have been calculated[15,16] from the sorption data by using

$$D \ (\text{cm}^2/\text{s}) = \pi\left(\frac{h\theta}{4Q(t)_m}\right)^2 \Big/ 60 \tag{1}$$
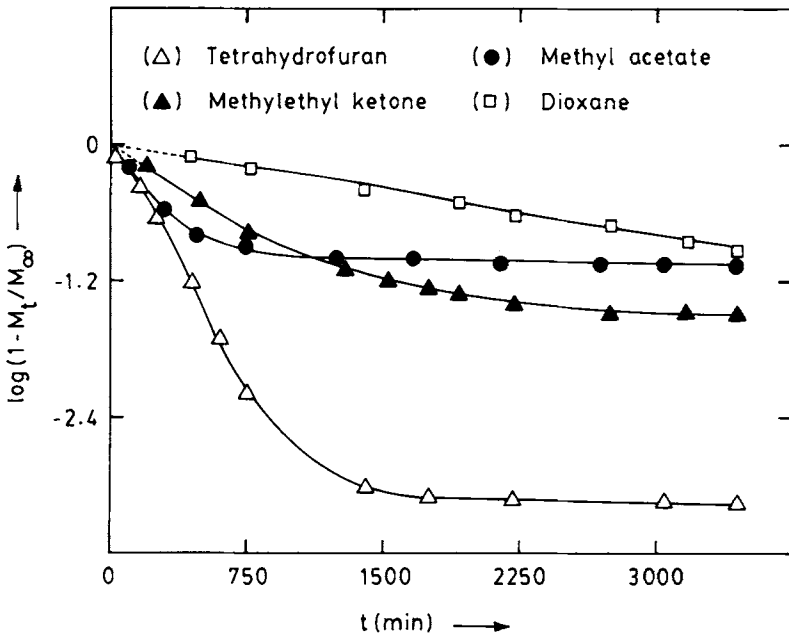
Fig. 12. $\log(1 - M_t/M_\infty)$ versus time (t) curves for polyurethane–solvent systems 25°C: ($\triangle$) tetrahydrofuran; ($\blacktriangle$) methyl ethyl ketone; ($\square$) dioxane; ($\bullet$) methyl acetate.
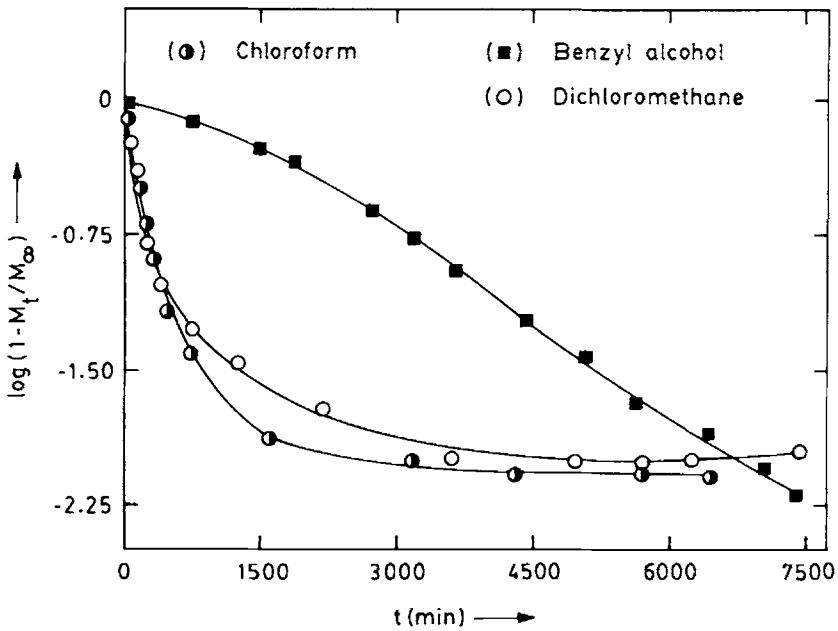

Fig. 13. $\log(1 - M_t/M_\infty)$ versus time (t) curves for polyurethane–solvent systems at 25°C. Symbols: ($\blacksquare$) Benzyl alcohol; ($\bullet$) Chloroform; ($\bigcirc$) Dichloromethane.
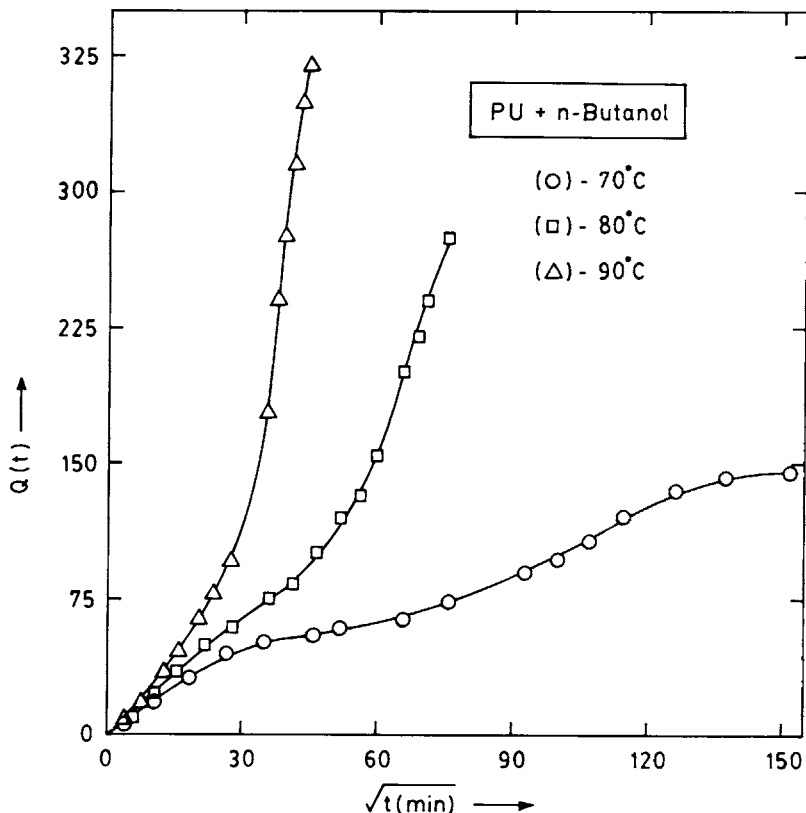
Fig. 14.   Temperature dependence of sorption: $Q(t)$ versus $t^{1/2}$ curves for the polyurethane-n-butanol system at 70 ($\bigcirc$), 80 ($\square$), and 90°C ($\triangle$).

where θ is the slope of the linear portions of the plot of $Q(t)$ versus $t^{1/2}$ as obtained from the least-squares analysis, $Q(t)_m$ represents the maximum per cent increase in mass (equilibrium value) and h is membrane thickness. The permeability coefficient (P) can be computed from a knowledge of solubility coefficient (S) and D by using

$$P \ (\mathrm{cm}^2/\mathrm{s}) = \mathrm{D.S.} \qquad (2)$$

The solubility coefficient S (g/g) is obtained from the plateau regions of sorption curves. All these parameters together with other relevant data are presented in Table I. The values of D were not obtained for those penetrants for which no equilibrium sorption was observed.

Both diffusivity and permeability are highest for dichloromethane and lowest for dioxane. The D of methyl acetate and chloroform are somewhat identical but their permeabilities are quite different. This is due to the difference in their solubilities. For tetrahydrofuran and methyl ethyl ketone, D values are respectively, 2.75×10^{-7} and 1.867×10^{-7} cm^2/s. However, the observed D and P values for benzyl alcohol are to be treated as approximate because, for this penetrant, a true equilibrium was never reached, thus prohibiting the prediction of accurate $Q(t)_m$ values to be used in eq. (1).
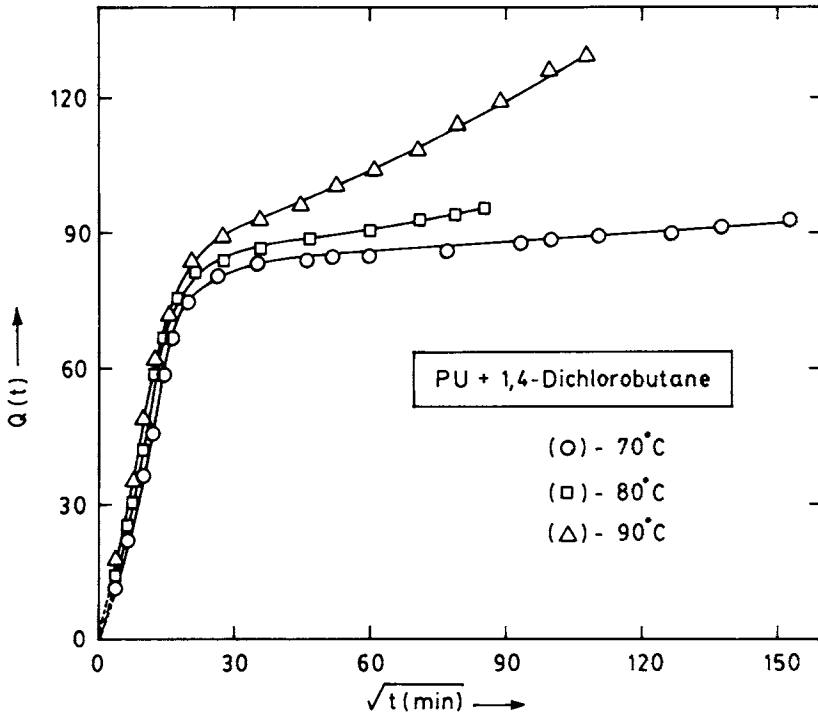
Fig. 15. Temperature dependence of sorption: $Q(t)$ versus $t^{1/2}$ curves for the polyurethane–1,4-dichlorobutane system at 70, 80, and 90°C. Symbols have the same meaning as in Figure 14.
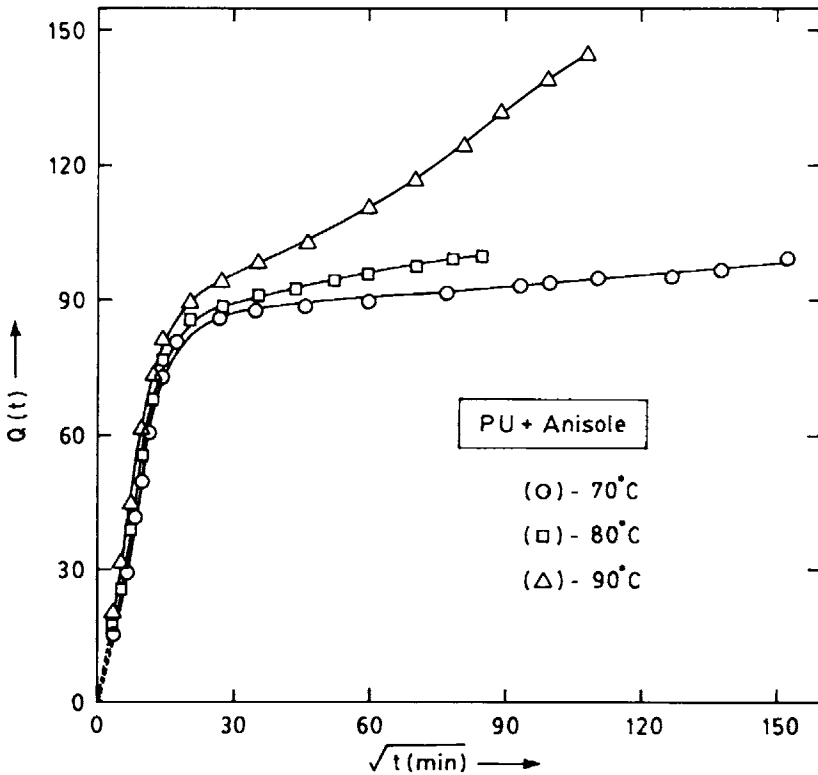

Fig. 16. Temperature dependence of sorption: $Q(t)$ versus $t^{1/2}$ curves for the polyurethane–anisole system at 70, 80, and 90°C. Symbols have the same meaning as in Figure 14.
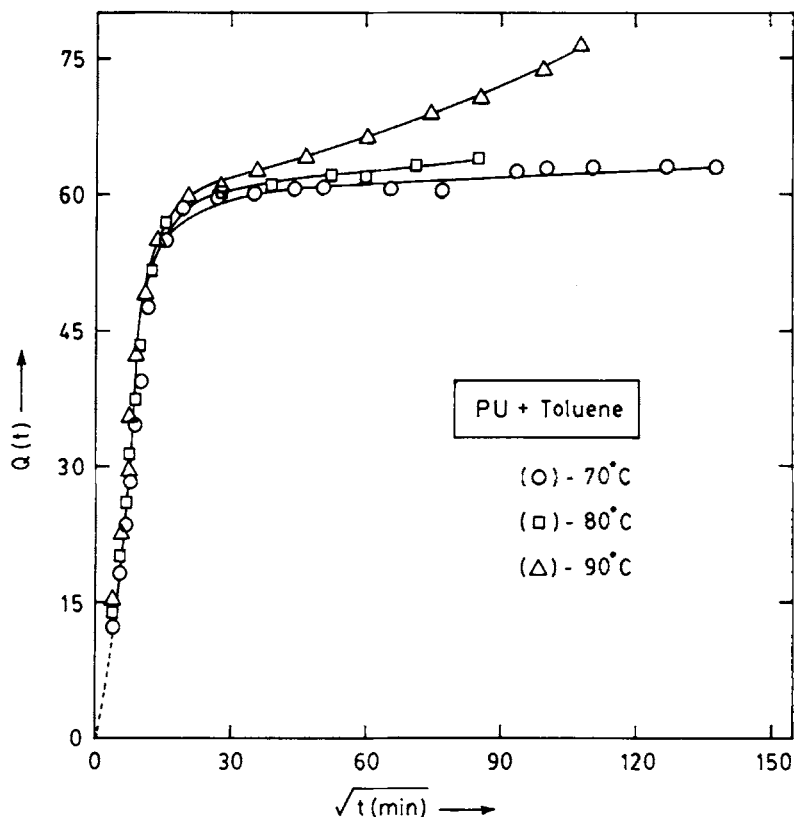
Fig. 17. Temperature dependence of sorption: $Q(t)$ versus $t^{1/2}$ curves for the polyurethane-toluene system at 70, 80, and 90°C. Symbols have the same meaning as in Figure 14.

Sorption data have been further analyzed from the empirical relation.[17,18]

$$\log(M_t/M_\infty) = \log k + n \log t \qquad (3)$$

where M_t and M_∞ are, respectively, mass uptakes at time t and at equilibrium time, k is a constant, and n decides the type of diffusion mechanism. The values of n as estimated from the least-squares analysis of the slope of the plots of $\log(M_t/M_\infty)$ versus $\log t$ are also included in Table I. A representative plot is given in Figure 11. The magnitude of $n = 0.52$–0.74 suggests that diffusion mechanism is not strictly Fickian and may therefore be classified as non-Fickian.

To continue our analysis further, the sorption data have been treated[19] by means of eq. (4) under the conditions when $(M_t/M_\infty) > 0.4$,

$$\log(1 - M_t/M_\infty) = \log(8/\pi^2) - D\pi^2 t/h^2 \qquad (4)$$

Such plots for a few representative penetrants are given in Figures 12 and 13. By estimating the slopes (θ) of the initial linear portions we have estimated the diffusivity values as

$$D \ (\text{cm}^2/\text{s}) = \frac{\theta h^2}{\pi^2} \bigg/ 60 \qquad (5)$$
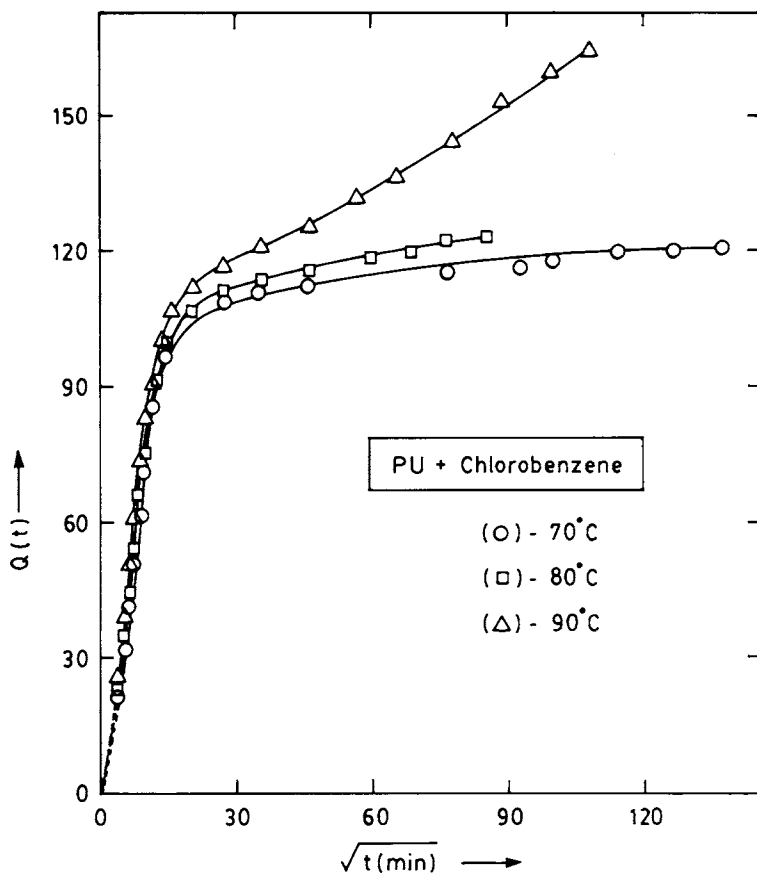
Fig. 18.   Temperature dependence of sorption: $Q(t)$ versus $t^{1/2}$ curves for the polyurethane–chlorobenzene system at 70, 80, and 90°C. Symbols have the same meaning as in Figure 14.

The estimated values of D as presented in Table I agree somewhat with those obtained by the use of eq. (1).

Sorption at Elevated Temperatures

As one would expect from the two-phase morphology of polyurethane, it shows two different glass transition temperatures (T_g): one at −43°C (for the soft domain) and the other around 100°C (for the hard phase). Above the T_g of the soft phase, polyurethane exhibits an elastomeric behavior. In an earlier study,[20] the sorption experiments were carried out in the temperature range of 25–60°C for a variety of penetrants. In order to see the transport characteristics of polyurethane at elevated temperatures, we decided to raise the temperature from 70° to 90°C for n-butanol, 1,4-dichlorbutane, anisole, toluene, chlorbenzene, and nitrobenzene (see Table II). The sorption curves for all these penetrants are presented in Figures 14–19. In all the cases, raising the temperature seems to increase the sorption process. For almost all the penetrants selected in this group, 70°C seems to be the upper limit to study the sorption behavior within a reasonable amount of time without destroying the membrane. Raising
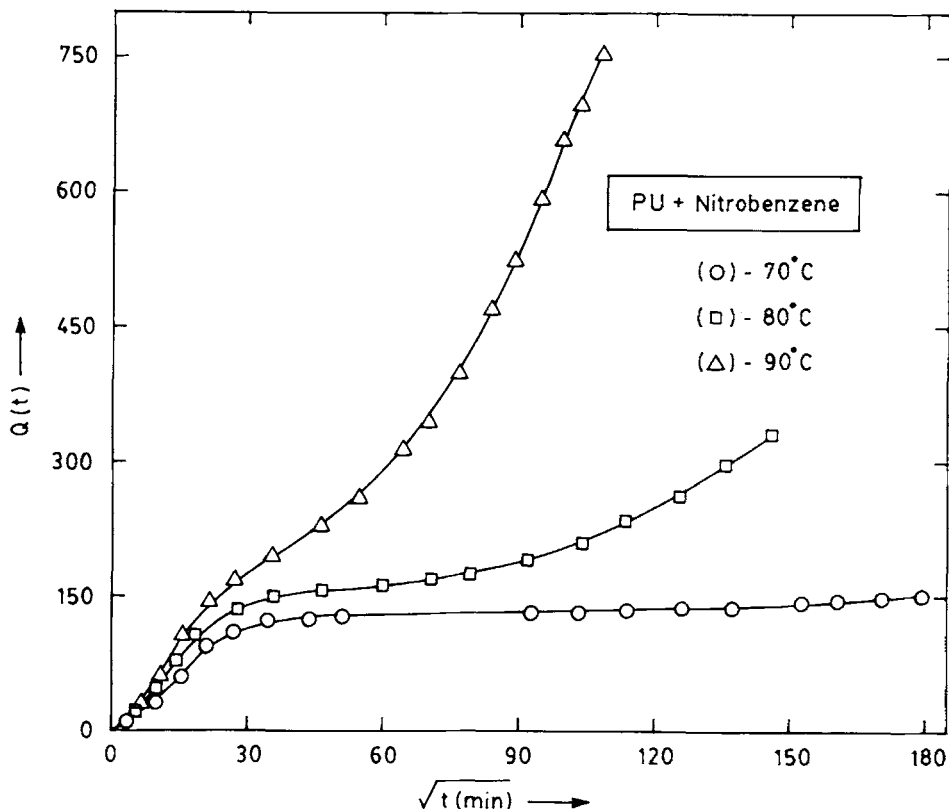
Fig. 19.   Temperature dependence of sorption: $Q(t)$ versus $t^{1/2}$ curves for the polyurethane-nitrobenzene system at 70, 80, and 90°C. Symbols have the same meaning as in Figure 14.

the temperature higher than 70°C, i.e., up to 80 or 90°C, is not a favorable situation for the attainment of equilibrium, as the hard part of the polyurethane might also contribute towards the overall transport process at elevated temperatures.

CONCLUSIONS

The increasing use of polymers in aggressive technological environments is a cause of concern to the polymer engineers and presents a challenge to research chemists. The contact of polymers with a liquid aggressive media is accompanied by a complex range of physical and chemical processes such as absorption and diffusion of the medium. The problem of the chemical resistance of polymers confronts research workers, engineers, and designers in various fields of industry. If, in service or storage, polyurethane comes in contact with aggressive media, under the action of these media at elevated temperatures the following fundamental processes may occur:

1. Chemical degradation of polyurethane leading to a change in its shape and physical appearance. In order to establish the mechanism of chemical degradation in aggressive media it is necessary to know how the diffusion

of each of the aggressive media proceeds. Thus, diffusion of aggressive media in polymers is not merely of theoretical interest but also of considerable practical interest.

2. Sorption of the components of the aggressive media by the polymer.
3. Desorption of various additives such as stabilizers, plasticizers, pigments, fillers, crosslinking units, etc.

The occurrence of these processes usually leads to overall changes in the major service properties: sorption, diffusion, and outward appearance of the polymer. It is of practical importance to be able to predict the service properties of a polymer in an aggressive media over a wide range of temperatures in order to forecast the durability of the polymer under the stated conditions.

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