Sorption and Transport of Aqueous Salt Solutions in Polyurethane Membrane at 25, 44, and 60°C

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SYNOPSIS

Sorption and transport of aqueous salt solutions in polyurethane elastomer has been investigated over the temperature interval of 25–60°C by using an immersion/weight gain method. The size of the ions has no significant effect on the penetrant transport coefficients. The sorption data have been explained in terms of the simple Fickian model. Attempts have also been made to estimate the transport parameters by applying corrections to include the spatial diffusivity of the liquids within the polymer sample. Temperature dependence of the transport coefficients has been used to estimate the activation parameters from the Arrhenius plots.

INTRODUCTION

Transport of aqueous salt solutions in solid polymer membranes has been widely studied in view of its importance in reverse osmosis,[1,2] permselective separation processes,[3,4] and undersea applications.[5-7] Numerous studies have been made to investigate the sorption and diffusion behavior of aqueous salt solutions in polymer membranes of commercial interest.[8] As a part of a broad-based research program concerning the transport characteristics of elastomer membranes, we now present some useful hydrodynamic and thermodynamic data on polyurethane and aqueous salt solutions. Thus, diffusivity (D), sorption (S), and permeability (P) of aqueous solutions of electrolyte salts over the temperature interval of 25–60°C for three different concentrations of the salts, namely, 0.15, 0.5, and 1.0 M have been calculated. The temperature-dependent transport coefficients namely, P, D, and S have been used to estimate the Arrhenius parameters for the process of diffusion and permeation. Furthermore, the transport mechanism has been explained in terms of ion sizes of the salts used.

EXPERIMENTAL

Materials

Analytical grade samples of $BaCl_2 \cdot 2H_2O$, $SrCl_2 \cdot 6H_2O$, and $MgSO_4 \cdot 7H_2O$ have been used directly. The other salts, namely, K_2CO_3, K_2CrO_4, $K_2Cr_2O_7$, KI, and potassium hydrogen phthalate (KH-phthalate) were dried for 24 h and stored in a desiccator over anhydrous $CaCl_2$ before use. All salt solutions were prepared in concentrations of 0.15, 0.5, and 1.0 M using double distilled water by weighing appropriate amounts of salts.

Polyurethane (PU) was supplied by PSI Austin, TX in sheets of thickness 0.245 cm. The base polymer used was a Vibrathane B600 (Uniroyal) cured with MOCA, 4,4′-methylene-bis(o-chloroaniline). An oven (Memmert, Germany) with a precision of ±0.5°C was used throughout the research work for maintenance of the desired temperature.

Immersion/Weight Gain Experiments

The polymer sheet to be used was cut circularly (diameter = 1.94 cm) and at least five independent measurements of thickness were made at various points on the membrane using a micrometer (Sargent-Welch Co.) with an accuracy of ±0.01 mm. Each specimen was tested in duplicate in all the liquids. After taking the dry weights of PU samples,

each one was submerged in its respective solution in air tight glass bottle. Experiments were carried out at 25, 44, and 60°C.

The liquid uptake was monitored gravimetrically by weighing the PU sample at regular intervals of time.[9] When the samples were removed from glass bottles, they were carefully blotted to remove excess liquid on the surface. The percent mass uptake of solution per unit mass of dry sample was determined until attainment of equilibrium. Removal of the specimens from the controlled environment for brief periods necessary for weighing introduced negligible errors due to low diffusivity of the test solutions in PU. Time required to make such a measurement was usually less than 30 s.

THEORY

In order to calculate liquid diffusivity in PU membrane, we consider an infinitely large polymer sample of thickness h, exposed on two sides to the same liquid so that liquid transports only in the z-direction, i.e., along the thickness. Initially (time $t \le 0$) the liquid concentration c_i inside the sample is uniform. The sample is suddenly exposed to a liquid with concentration c_∞ being constant. The liquid concentration is then described by the Fick relation[10]

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z}\left(D_z \frac{\partial c}{\partial z}\right) \qquad (1)$$

Applying the initial and boundary conditions

$$\begin{aligned} c &= c_i, & 0 < z < h, & \quad t \le 0 \\ c &= c_\infty, & z = 0, z = h, & \quad t < 0 \end{aligned} \qquad (2)$$

and for the case where the diffusivity D_z, being constant inside the sample, eq. (1) reduces to

$$\frac{\partial c}{\partial t} = D_z \frac{\partial^2 c}{\partial z^2} \qquad (3)$$

In practice, it is much easier to measure the total mass M of the penetrant which has entered the polymer up to a given time rather than determine the actual concentration profile at a given instant. Thus, the solution of eq. (3) in terms of total mass M of the PU sample is given as

$$\begin{aligned} G &= \frac{M - M_i}{M_\infty - M_i} \\ &= 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{\exp[-(2n+1)^2 \pi^2 D_z t/h^2]}{(2n+1)^2} \end{aligned} \qquad (4)$$

where M_i represents the initial weight of the liquid in the PU sample and M_∞ is the liquid after attainment of equilibrium saturation.

For most practical purposes, we are interested in the percent liquid uptake $Q(t)$, calculated as[9]

$$Q(t) = \left(\frac{W - W_i}{W_i}\right) \times 100 \qquad (5)$$

Since $W = W_i + M$, eq. (4) may be rearranged to give

$$Q(t) = G(M_\infty - M_i) + M_i \qquad (6)$$

For the case when the initial polymer material is completely dry, then $M_i = 0$ so that eq. (6) becomes

$$Q(t) = GM_\infty \qquad (7)$$

The above development considers diffusion in one dimension only, i.e., along the z-axis. If absorption takes place in all the three directions of the sample, then following the procedure given by Shen and Springer[11] for rectangular geometry, we propose to write a relation [eq. (8)] for a circular disc of radius r:

$$D = D_z\left[1 + \frac{h}{r}\left(\frac{D_r}{D_z}\right)^{1/2} + \frac{h}{2\pi r}\left(\frac{D_\theta}{D_z}\right)^{1/2}\right]^2 \qquad (8)$$

where D_z can be extracted from sorption data up to 50% uptake of the liquid from the relation

$$Q(t) = \left(\frac{4M_\infty}{h}\right)\left(\frac{D_z t}{\pi}\right)^{1/2} \qquad (9)$$

The quantities D_r and D_θ represent diffusion coefficient in the radial and angular directions of the sample. For homogeneous materials, $D_z = D_r = D_\theta$, eq. (8) becomes

$$D = D_z\left(1 + \frac{h}{r} + \frac{h}{2\pi r}\right)^2 \qquad (10)$$

Clearly, eq. (9) gives $Q(t)$ as a linear function of

$t^{1/2}$. Therefore, the slope Y, of the plot of $Q(t)$ versus $t^{1/2}$, leads to the calculation of D_z. Thus,

$$D_z = \pi \left(\frac{hY}{4M_\infty} \right)^2 \qquad (11)$$

Since significant swelling did not occur with any of the salt solutions, we prefer to use the original h and r values of PU sample in the calculation of D from eq. (10).

RESULTS AND DISCUSSION

During initial sorption stages, i.e., up to 50% of the completion of sorption, penetrant uptake increased linearly with $t^{1/2}$ values. At later stages of sorption experiments, due to the saturation equilibrium, the sorption curves for all the penetrants at all the temperatures attained plateau regions. Initial linear part of the sorption curves were used to compute the penetrant diffusivity in polyurethane by using eqs. (10) and (11). An increase in liquid uptake (up to 50% saturation) was observed with an increase in temperature. However, at later stages of sorption, i.e., beyond 50%, the solubility as manifested in sorption equilibrium decreased considerably even as compared to room temperature data (see Fig. 1 for 0.15 M MgSO$_4$). However, at higher concentrations of the salt, e.g., for 0.5 and 1.0 M MgSO$_4$ solutions, the sorption equilibrium curves seem to have the
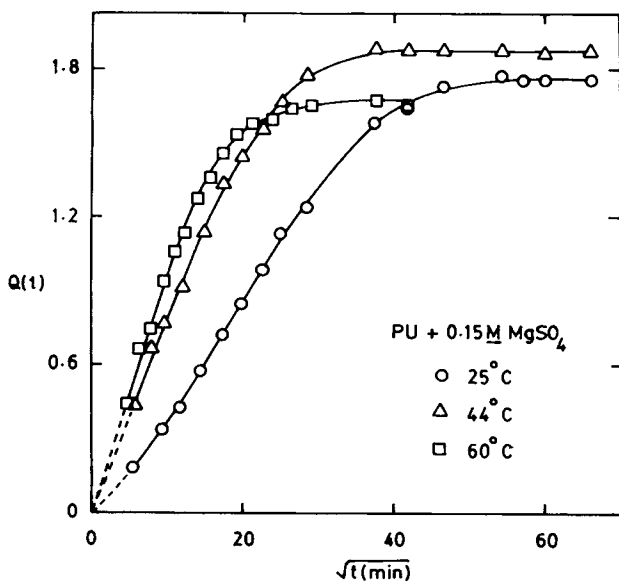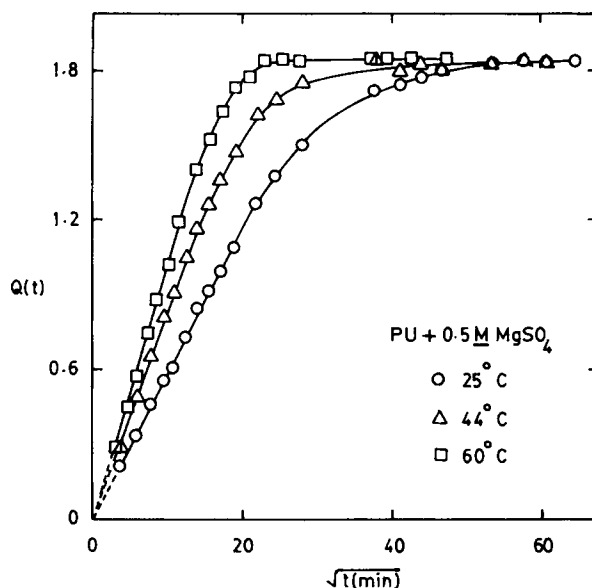
Figure 2   Sorption curves for 0.5 M MgSO$_4$.

same plateau regions (see Fig. 2) or they may be slightly higher as shown in Figure 3 for 1.0 M MgSO$_4$. A similar behavior is also shown by 0.15, 0.5, and 1.0 M solutions of BaCl$_2$, SrCl$_2$, and KI salts (results not shown graphically). This anomaly is attributed to the fact that, at higher temperatures and in dilute solutions, the solutions of the salts of MgSO$_4$, BaCl$_2$, SrCl$_2$, and KI are partly dissociated and the ions thus formed may get themselves immobilized within the polymer matrix. At room temperature or in some cases, at 44°C, the solutions of
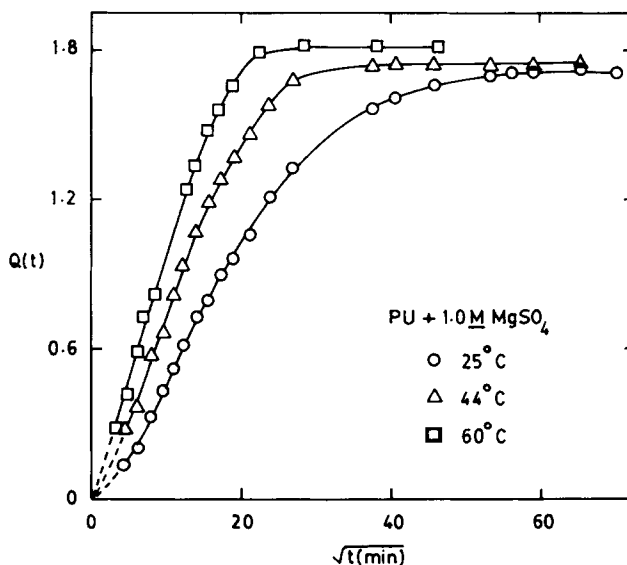
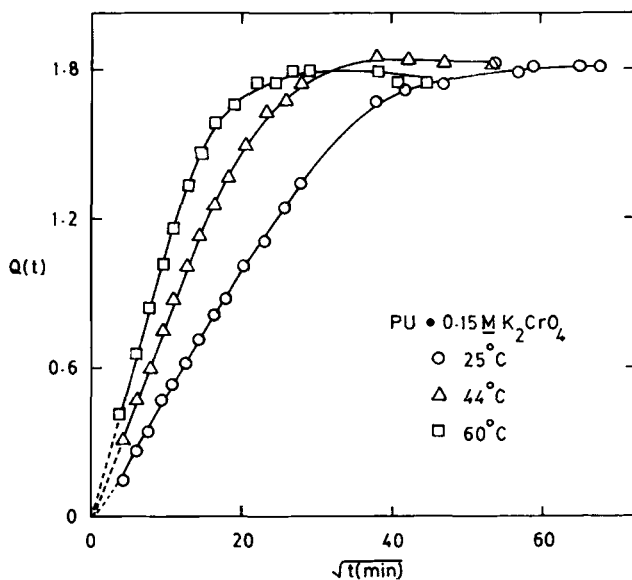**Figure 1**   Sorption curves for 0.15 M MgSO$_4$.

Figure 3   Sorption curves for 1.0 M MgSO$_4$.

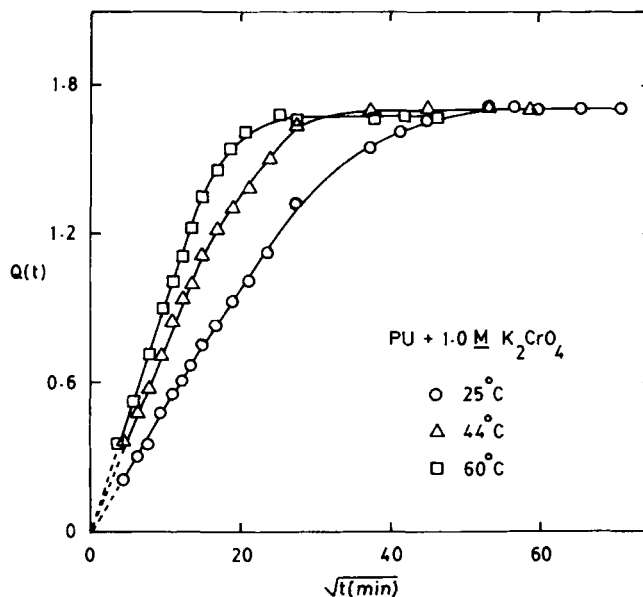**Figure 4** Sorption curves for 0.15 M K_2CrO_4.

Figure 6 Sorption curves for 1 M K_2CrO_4.

the salt may be transported as a whole, thereby increasing the sorption. This is also true of the other salts, namely, K_2CO_3, K_2CrO_4, $K_2Cr_2O_7$, and KH-phthalate. Due to the limited solubility of $K_2Cr_2O_7$ and KH-phthalate, the sorption experiments for these salts are conducted only at 0.15 M concentration. Moreover, the sorption curves for these salts (at 0.15 M) increase systematically with a rise in temperature. The sorption behavior of K_2CrO_4 as shown in Figures 4–6 is almost identical to that of $MgSO_4$ solution.
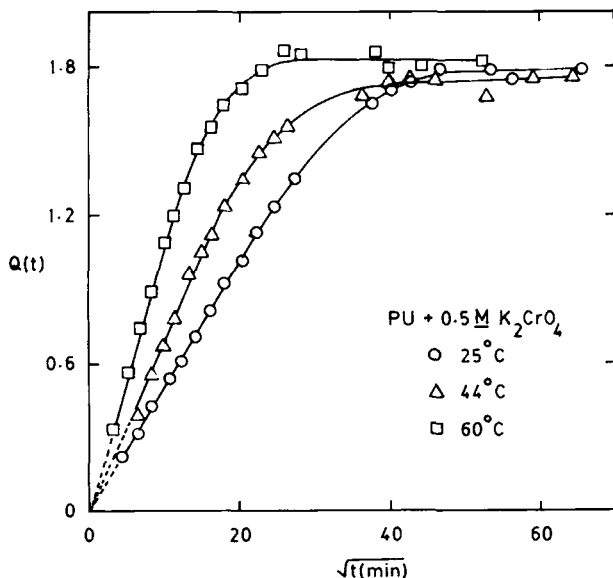

Figure 5 Sorption curves for 0.5 M K_2CrO_4.

The room temperature (25°C) sorption curves for 0.15 M solutions of $BaCl_2$, $SrCl_2$, and $MgSO_4$ are given in Figure 7, whereas such data for potassium salts are given in Figure 8. The maximum values of sorption solubilities of salts of Mg, Sr, and Ba lie within a narrow range and these vary in the sequence: $MgSO_4$ < $SrCl_2$ < $BaCl_2$. However, the potassium salts at 25°C, vary according to the sequence: $K_2Cr_2O_7$ < KH-phthalate < K_2CrO_4 < K_2CO_3 < KI. The data for water lie between $K_2Cr_2O_7$ and KH-phthalate. This sequence of maximum sorption of salt solutions will be changed slightly if we express the sorption in terms of moles per gram of the polyurethane.[‡] This quantity will have much more basic meaning than the weight percent gain. Excepting $MgSO_4$ and K_2CO_3 solutions, there is a systematic trend in mole percent sorptivity of salts with concentration. For instance, S decreases at all the temperatures from 0.15 to 1 M solutions. However, in case of less soluble salts like $K_2Cr_2O_7$ and KH-phthalate S of 0.15 M solutions increase systematically with a rise in temperature. This trend also exists for pure water.

The temperature dependence of sorption behavior of water is presented in Figure 9. Here, the sorption

[‡] To calculate sorption in mol/100 g of polyurethane, effective molecular weight of the salt solution is used: $\bar{M} = x_1 M_1 + x_2 M_2$, where x_1, M_1 and x_2, M_2 are the mole fractions and molecular weights of water and salt, respectively, in the aqueous phase. Furthermore, an assumption is made that the concentration of salt solution will not change drastically even after complete sorption.
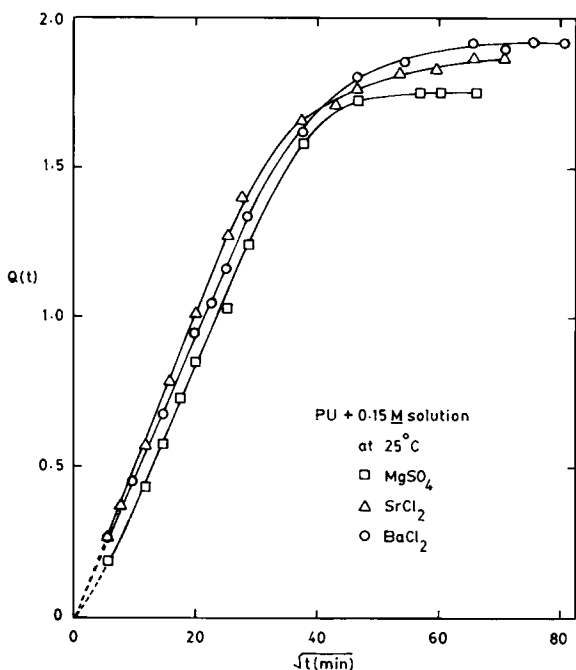
Figure 7 Sorption curves for 0.15 M solutions of $BaCl_2$, $MgSO_4$, and $SrCl_2$ at 25°C.
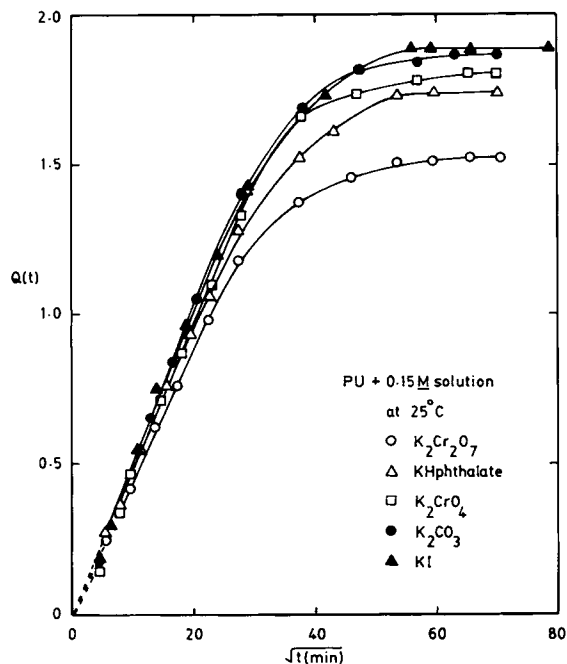

Figure 8 Sorption curves for 0.15 M solutions of $K_2Cr_2O_7$ KH-phthalate, K_2CrO_4, K_2CO_3, and KI at 25°C.

curves increase systematically with a rise in temperature. The sorption equilibrium is higher at higher temperatures. A close comparison of the sorption results of the salt solutions with that of water suggests that the transport mechanisms for salt solutions are different than that for water.

In order to investigate the type of diffusion mechanism, attempts were made to estimate the values of n from the following empirical relation:[12,13]

$$\log(M_t/M_\infty) = \log k + n \log t \qquad (12)$$

The value of $n = 1$ represents non-Fickian diffusion whereas $n = \frac{1}{2}$ describes the Fickian diffusion mode. The estimated values of n and $\log k$ are given in Table I. It may be noted that for almost all the penetrants the estimated value of n is close to 0.5, but occasionally goes up to 0.6 or 0.7; thus, the transport mechanism may be classified as the Fickian mode. However, $\log k$ values seem to increase systematically with a rise in temperature, but this effect is not seen with the values of n. No significant swelling took place for any of the penetrants giving further evidence of the Fickian type transport mode.

The results of diffusivity, sorption coefficient, and permeability of penetrants in polyurethane as presented in Tables II–IV throw additional light towards the understanding of transport mechanism.

Diffusivity and permeability coefficients showed a systematic increase with a rise in temperature, suggesting increased movement of the ions or salt solutions with an increase in temperature. Also, at higher temperatures, the intersegmental movements of polyurethane chains will possibly create more free volume, accommodating increased amounts of the penetrant molecules and thereby increasing their transport in the polymer matrix. At room temperature, the diffusivity of water was higher than all the 0.15 M salt solutions. However, this is not true
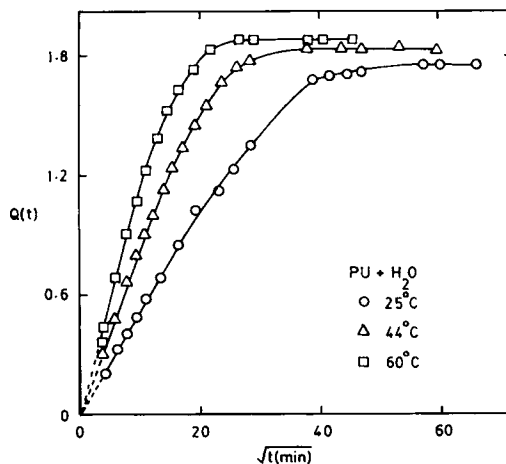

Figure 9 Sorption curves for distilled water.

Table I   Analysis of Sorption Data for Polyurethane + Penetrant Systems

Salt	Mol/L (M)	n at °C 25	n at °C 44	n at °C 60	log k at °C 25	log k at °C 44	log k at °C 60
BaCl$_2$	0.15	0.50	0.50	0.50	0.465	0.665	0.867
	0.5	0.52	0.50	0.51	0.458	0.656	0.738
	1.0	0.51	0.50	0.51	0.455	0.608	0.740
SrCl$_2$	0.15	0.53	0.53	0.50	0.363	0.568	0.788
	0.5	0.50	0.51	0.54	0.523	0.625	0.690
	1.0	0.50	0.51	0.50	0.470	0.623	0.752
MgSO$_4$	0.15	0.59	0.50	0.50	0.150	0.667	0.814
	0.5	0.52	0.53	0.55	0.456	0.608	0.645
	1.0	0.69	0.61	0.56	0.020	0.393	0.629
K$_2$CO$_3$	0.15	0.50	0.55	0.53	0.459	0.535	0.724
	0.5	0.50	0.56	0.52	0.481	0.491	0.716
	1.0	0.53	0.50	0.52	0.407	0.705	0.772
KI	0.15	0.58	0.50	0.50	0.263	0.673	0.742
	0.5	0.55	0.61	0.51	0.363	0.361	0.740
	1.0	0.50	0.50	0.51	0.473	0.667	0.768
K$_2$CrO$_4$	0.15	0.60	0.55	0.50	0.180	0.528	0.778
	0.5	0.51	0.59	0.52	0.437	0.403	0.743
	1.0	0.52	0.50	0.52	0.420	0.693	0.695
K$_2$Cr$_2$O$_7$	0.15	0.50	0.54	0.53	0.459	0.567	0.704
KH-phthalate	0.15	0.50	0.53	0.52	0.440	0.553	0.706
H$_2$O		0.52	0.51	0.50	0.424	0.635	0.810

at higher temperatures and concentrations. Salts of Ba, Sr, and Mg exhibit almost identical diffusion coefficients over the whole composition range and at all the temperatures. In general, diffusion coef-ficients of potassium salts are somewhat higher than those of alkaline earth metal salts (i.e., salts of Ba, Sr, and Mg). Since permeability coefficient P is obtained from the product of D and S and because the

Table II   Diffusivity ($D \times 10^7$ cm^2/s) Data for Polyurethane + Penetrant Systems at Different Concentrations and Temperatures

Salt	0.15 M at °C 25	0.15 M at °C 44	0.15 M at °C 60	0.5 M at °C 25	0.5 M at °C 44	0.5 M at °C 60	1.0 M at °C 25	1.0 M at °C 44	1.0 M at °C 60
BaCl$_2$	1.955	5.599	11.348	3.660	6.946	11.642	2.825	5.961	11.067
SrCl$_2$	2.624	5.883	10.563	2.718	6.831	12.700	2.915	5.922	10.993
MgSO$_4$	2.290	5.365	10.379	3.442	7.359	10.950	4.295	7.955	11.331
K$_2$CO$_3$	2.720	6.602	12.150	2.793	6.225	10.636	3.176	7.554	14.006
K$_2$CrO$_4$	2.741	6.903	11.799	2.759	6.451	12.535	2.891	6.351	11.733
KI	2.858	6.468	10.579	3.081	6.326	11.730	3.125	7.237	12.769
K$_2$Cr$_2$O$_7$	2.758	6.836	11.850						
KH-phthalate	2.540	5.766	11.231						
H$_2$O	2.875	6.786	13.450						

Table III   Sorption ($S \times 10^2$) Data for Polyurethane + Penetrant Systems at Different Concentrations and Temperatures[a]

Salt	0.15 M at °C			0.5 M at °C			1.0 M at °C		
	25	44	60	25	44	60	25	44	60
BaCl$_2$	1.919 (10.37)	1.889 (10.20)	1.727 (9.33)	1.806 (9.17)	1.805 (9.16)	1.812 (9.20)	1.749 (8.19)	1.675 (7.84)	1.728 (8.09)
SrCl$_2$	1.870 (10.18)	1.836 (9.99)	1.842 (10.25)	1.826 (9.48)	1.758 (9.13)	1.760 (9.14)	1.610 (7.86)	1.669 (8.15)	1.652 (8.05)
MgSO$_4$	1.756 (9.61)	1.877 (10.27)	1.652 (9.04)	1.836 (9.71)	1.833 (9.69)	1.844 (9.75)	1.712 (8.64)	1.751 (8.84)	1.814 (9.16)
K$_2$CO$_3$	1.870 (10.78)	1.895 (10.40)	1.660 (9.12)	1.804 (9.63)	1.781 (9.51)	1.744 (9.32)	1.889 (9.72)	1.659 (8.54)	1.756 (9.04)
K$_2$CrO$_4$	1.813 (9.81)	1.827 (9.89)	1.790 (9.69)	1.782 (9.11)	1.754 (8.96)	1.824 (9.32)	1.706 (8.08)	1.714 (8.12)	1.663 (7.87)
KI	1.888 (10.26)	1.938 (10.53)	1.687 (9.17)	1.640 (8.49)	1.677 (8.68)	1.768 (9.15)	1.668 (8.09)	1.632 (7.92)	1.794 (8.70)
K$_2$Cr$_2$O$_7$	1.524 (8.13)	1.802 (9.61)	1.824 (9.73)						
KH-phthalate	1.749 (9.45)	2.038 (11.02)	2.041 (11.03)						
H$_2$O	1.757 (9.76)	1.839 (10.22)	1.883 (10.46)						

[a] The values in the parenthesis are expressed in terms of mole percent of the penetrant.

sorption coefficient of salt solution is different; thus, the permeability data do not follow the same trend as those of diffusivity results.

The diffusion coefficients are dependent on salt concentration. This effect is shown in Figure 10. There is a systematic trend for the dependence of D on concentration with respect to temperature in case of BaCl$_2$ solution, i.e., a sharp convex shape

Table IV   Permeability ($P \times 10^9$, cm^2/s) Data for Polyurethane + Penetrant Systems at Different Concentrations and Temperatures

| Salt	0.15 M at °C			0.5 M at °C			1.0 M at °C		
	25	44	60	25	44	60	25	44	60
BaCl$_2$	3.752	10.577	19.598	6.610	12.538	21.095	4.941	9.985	19.124
SrCl$_2$	4.907	10.801	19.457	4.963	12.009	22.352	4.693	9.884	18.160
MgSO$_4$	4.021	10.070	17.146	6.320	13.489	20.192	7.353	13.929	20.554
K$_2$CO$_3$	5.470	12.511	20.169	5.039	11.087	18.549	5.999	12.532	24.595
K$_2$CrO$_4$	4.969	12.612	21.120	4.917	11.315	22.535	4.932	10.886	19.512
KI	5.396	12.535	17.847	5.053	10.609	20.739	5.213	11.811	22.908
K$_2$Cr$_2$O$_7$	4.203	12.319	21.614						
KH-phthalate	4.443	11.751	22.923						
H$_2$O	5.051	12.479	25.420						
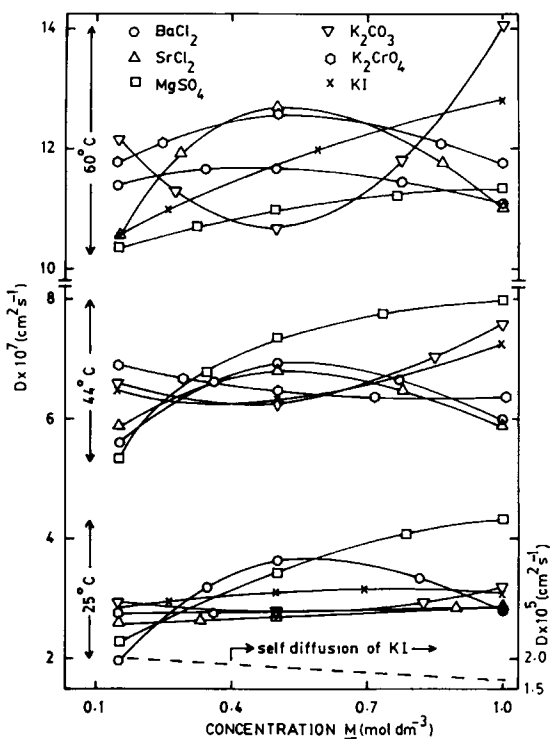
Figure 10 Concentration dependence of diffusion coefficient for solutions of $BaCl_2$, $SrCl_2$, $MgSO_4$, K_2CO_3, K_2CrO_4, and KI.

curve at 25°C seem to be diminishing at higher temperatures. Similarly, for K_2CO_3 the concave behavior at increased temperature appears to be more pronounced. However, for all the salts (except KI at 25°C) D varies nonlinearly with the concentration, and this, to a great extent, appears to be different at different temperatures.

The temperature dependence of transport coefficients (P, D, and S) have been used to compute the energy of activation for the processes of diffusion and permeation from a consideration of the Arrhenius relationship:

$$X = X_0 \exp[-E_x/RT] \qquad (13)$$

Here, X is P, D, or S and X_0 represents the constant term. E_x is activation energy, R is the universal gas constant, and T is the temperature in absolute. The heat of solution ΔH_s, as computed from the difference, ($E_P - E_D$), together with E_D and E_P are given in Table V. The Arrhenius plots namely, log D (or log P) versus $1/T$ are shown in Figures 11 and 12. The activation energies (E_D or E_P) do not show any systematic trend with the salt concentration and vary generally from 23 to 41 kJ/mol. However, water exhibits an E_D or E_P value of around 36–38 kJ/mol.

It should be noted that the diffusivities of the salt solutions measured by the immersion/weight gain method are to be regarded as mutual diffusion coefficients. A value of D at 25°C 2.875×10^{-7} cm^2/s for 1.0 M KI solution agrees reasonably well for 0.86 M KI solution for the same polyurethane[14] employed in this work ($D = 3.025 \times 10^{-7}$ cm^2/s at 23°C). If we attempt to calculate theoretically the self-diffusion coefficients of these salts, then these values should be higher than the present results. In order to check this we have used Onsager–Fuoss theory[15,16] to calculate self-diffusion coefficients of salt solutions. According to this theory, D is given as

$$D = (\nu_1 + \nu_2) 10^3 RT \left(1 + c\frac{\partial \ln y_\pm}{\partial c}\right)$$

$$\times \left[1.07 \times 10^{-20}\left(\frac{\lambda_1^0 \lambda_2^0}{\nu_1 |z_1| \Lambda^0}\right) + \frac{\Delta M'}{c} + \frac{\Delta M''}{c}\right] \qquad (14)$$

Table V   Activation Parameters for Polyurethane + Penetrant Systems

| Salt	Concentration (M)	E_D (kJ/mol)	E_P (kJ/mol)	ΔH_s (kJ/mol)
$BaCl_2$	0.15	41.652	39.254	−2.397
	0.50	27.288	27.363	0.075
	1.00	32.163	31.819	−0.364
$SrCl_2$	0.15	32.924	32.547	−0.377
	0.50	36.522	35.978	−0.536
	1.00	31.250	31.924	0.674
$MgSO_4$	0.15	35.677	34.464	−1.213
	0.50	27.560	27.652	0.092
	1.00	23.054	24.380	1.326
K_2CO_3	0.15	35.349	32.797	−2.552
	0.50	31.669	30.886	−0.782
	1.00	35.095	33.175	−1.920
K_2CrO_4	0.15	34.681	33.459	−1.222
	0.50	35.719	35.886	0.167
	1.00	33.062	32.505	−0.556
KI	0.15	31.066	28.610	−2.456
	0.50	31.485	33.217	1.732
	1.00	33.338	34.907	1.569
$K_2Cr_2O_7$	0.15	34.602	38.991	4.389
KH-phthalate	0.15	35.054	38.840	3.787
H_2O	—	36.480	38.130	1.650
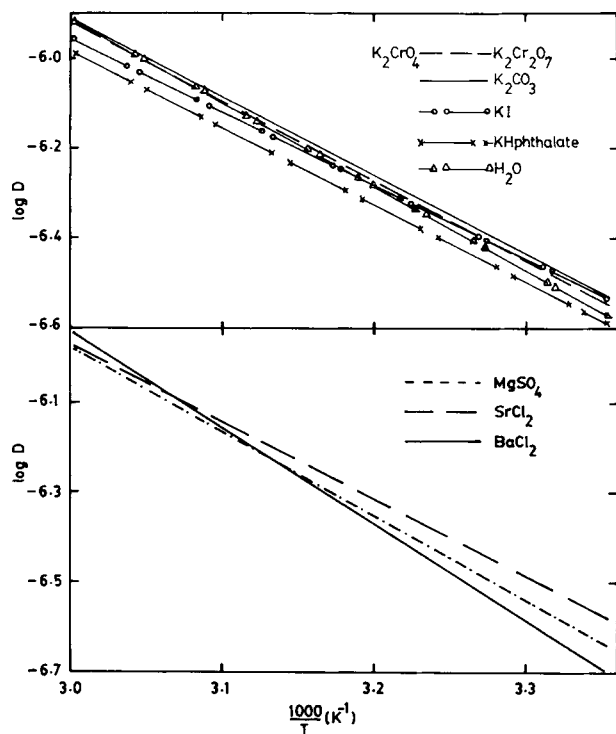
Figure 11   Arrhenius plots ($\log D$ vs. $1/T$) for various salt solutions in polyurethane.
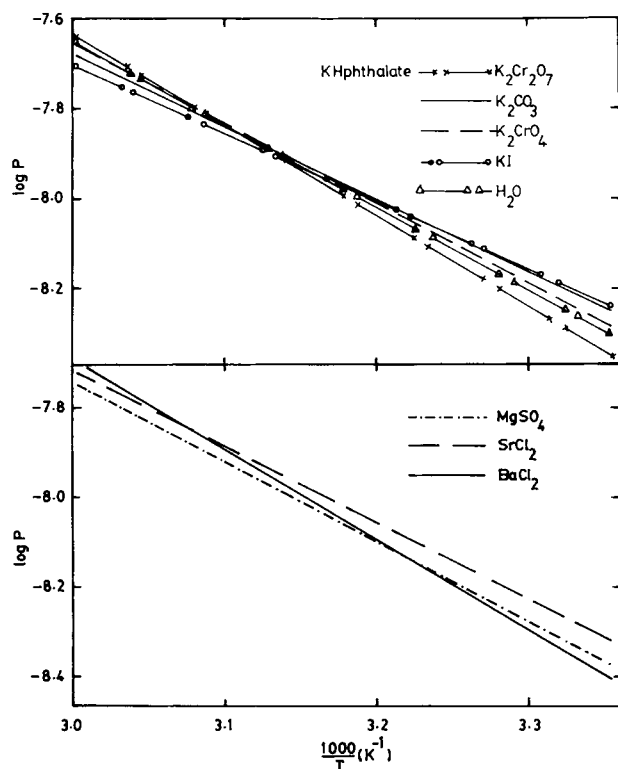

Figure 12   Arrhenius plots ($\log P$ vs. $1/T$) for various salt solutions in polyurethane.

where

$$\left(1 + c\,\frac{\partial \ln y_{\pm}}{\partial c}\right)$$

$$= 1 - \frac{1.1514 S_f \sqrt{c}}{(1 + A'\sqrt{c})^2} + 2.303 Bc - c\psi(d) \quad (15)$$

the last term, $c\psi(d)$, has been neglected for the values of concentrations used in this work. The electrophoretic terms $\Delta M'$ and $\Delta M''$ are computed as

$$\frac{\Delta M'}{c} = -\frac{(|Z_2|\lambda_1^0 - |Z_1|\lambda_2^0)^2}{(\Lambda^0)^2 |Z_1 Z_2|(\nu_1 + \nu_2)}$$

$$\times \frac{3.132 \times 10^{-19}}{\eta_0(\epsilon T)^{1/2}}\frac{\sqrt{\tau}}{(1 + \kappa a)} \quad (16)$$

and

$$\frac{\Delta M''}{c} = \frac{(Z_2^2 \lambda_1^0 + Z_1^2 \lambda_2^0)^2}{(\Lambda^0)^2}$$

$$\times \frac{9.304 \times 10^{-13}}{\eta_0(\epsilon T)^2} \cdot c\phi(\kappa a) \quad (17)$$

Here, the equivalent conductance of an electrolyte at infinite dilution is $\Lambda^0 = \lambda_1^0 + \lambda_2^0$, where λ_1^0 and λ_2^0 are limiting ionic conductivities of cations and anions, respectively; ν_1, ν_2 and Z_1, Z_2 are, respectively, the number and charges of cations and anions; ϵ is the dielectric constant; and η_0 is the viscosity of the medium. The symbol a represents the mean distance of the closest approach of ions, c is the electrolyte concentration, and $y_{\pm}$ is the mean molar activity coefficient. The function $\phi(\kappa a)$ is given elsewhere[16] in which κ is the Debye–Huckel reciprocal radius. S_f is the limiting slope of the Debye–Huckel theory and B is the salting constant. The relevant data at 25°C to compute D are taken from Harned and Owen.[16] These results at 25°C for various con-

Table VI   Self-Diffusion Coefficients ($D \times 10^5$, cm²/s) of Salt Solutions at 25°C Computed on the Basis of Eq. (14)

Salt	0.15 M	0.5 M	1.0 M
BaCl$_2$	1.375	1.138	0.790
SrCl$_2$	1.273	0.973	0.564
KI	2.002	1.844	1.655
MgSO$_4$[a]	3.086	11.555	25.028

[a] Based on the equation $(1 + c(\partial \ln y_{\pm}/\partial c)) = 1 + 28.48c - 6.187c^{1/2}$.

centrations of the salt solutions are presented in Table VI. The D values are decreasing systematically with an increase in concentration of the salt except that the $MgSO_4$ solution gives a reverse trend. This is because of the use of the empirical relation in view of the nonavailability of the pertinent data for $MgSO_4$ salt. A theoretical curve at 25°C for self-diffusion of KI is also included in Figure 10. However, the order of magnitude of theoretically calculated self-diffusivities for the salt solutions are 100 times higher than those found in the present work (see Table I). This further confirms that the transport of salt solutions is much slower when polyurethane is acting as a barrier. More research on the investigation of transport of acid electrolyte solutions is in progress and will be published in the future.

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