Sorption and transport of aqueous salt solutions of acetates, acetic and monochloroacetic acids in polyurethane

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(Received 30 October 1989; revised 20 January 1990; accepted 6 February 1990)

Sorption, diffusion and permeation of aqueous salt solutions of acetates of sodium, calcium and nickel in addition to acetic and monochloroacetic acid solutions have been investigated in the temperature interval of 25–60°C in a commercial polyurethane. An immersion/weight-gain experiment was used to study sorption and diffusion of 0.15, 0.5 and 1.0 M solutions of acids and salts. Permeability coefficients were estimated from sorption and diffusivity coefficients. From the temperature dependence of transport coefficients, the Arrhenius activation parameters have been estimated and the results were used in the discussion of transport mechanisms. The diffusivity of monochloroacetic acid solution was smaller but its solubility was higher than all the solutions used in this research. For comparative purposes, the transport of water was also studied.

(Keywords: diffusion; permeation; sorption; polyurethane; activation parameters)

INTRODUCTION

The sorption and transport of aqueous salt and acid solutions in polymeric solids is an active area of research in view of their importance in membrane separation processes[1–4], water demineralization[5,6], chemical and food industries[7], and waste treatment[8]. Conversely, for a successful application of polymer membranes in engineering areas, an understanding of transport characteristics *versus* unfavourable liquids (referred to as penetrants) is important[9].

For the past several years, we have been actively engaged in studies related to transport of small molecules in polymer membranes of commercial interest[10–14]. In continuation of this research, we will now present some important barrier properties of polyurethane membranes for aqueous solutions of acetates of sodium, calcium and nickel in addition to acetic and monochloroacetic acid solutions. The effect of salt concentration on diffusivity D was investigated in the temperature interval of 25–60°C. From the sorption S and diffusion coefficient D, the permeability coefficients P were estimated. The temperature dependence of P, D and S has been used to estimate the activation parameters of interest. These results have been used in the discussion of penetrant transport in the polyurethane matrix.

EXPERIMENTAL

Materials

Analytical grade samples of acetates of sodium, calcium and nickel have been used directly. Solutions of acetic acid and monochloroacetic acid (Glaxo samples) were first prepared in doubly distilled water and then standardized using standard solutions of oxalic acid. The acid solutions were diluted to the desired concentrations. All salt and acid solutions were prepared in concentrations of 0.15, 0.5 and 1.0 M (moles per litre) by using doubly distilled water.

The polyurethane (PU) membrane used was obtained from PSI, Austin, Texas (USA), in sheets of thickness 0.245 cm. The base polymer used is a Vibrathane B600 (Uniroyal), which was prepared from the reaction of poly(propylene oxide) and toluene diisocyanate. The polymer was cured with 4,4′-methylene-bis(*o*-chloroaniline) (MOCA), to give the PU elastomer.

Immersion/weight-gain experiments

Circularly cut (diameter = 1.94 cm) PU samples were immersed in about 15–20 ml of the respective solutions in screw-tight capped test bottles, which were kept in a thermostatically controlled oven (Memmert, FRG) maintained within ±0.5 K of the desired temperature. The samples were periodically removed from the test bottles, surface-adhered liquid drops removed by means of smooth filter papers and samples weighed to ±0.05 mg on a Mettler balance (Switzerland). The procedure was continued until no more liquid uptake by the polymer was observed (equilibrium saturation). The percentage uptake $Q(t)$ *versus* time t was obtained for each penetrant.

RESULTS AND DISCUSSION

Sorption kinetics

The sorption curves, i.e. plots of $Q(t)$ *versus* $t^{1/2}$, for acetic acid solutions at 25°C are given in *Figure 1*. The curves are initially linear up to about 50% sorption, which at longer times tend to assume plateau regions. The maximum sorption tends to increase considerably with increase in acid concentration; however, the attainment of equilibrium sorption is found to be slower at higher concentrations. These effects also persist at higher

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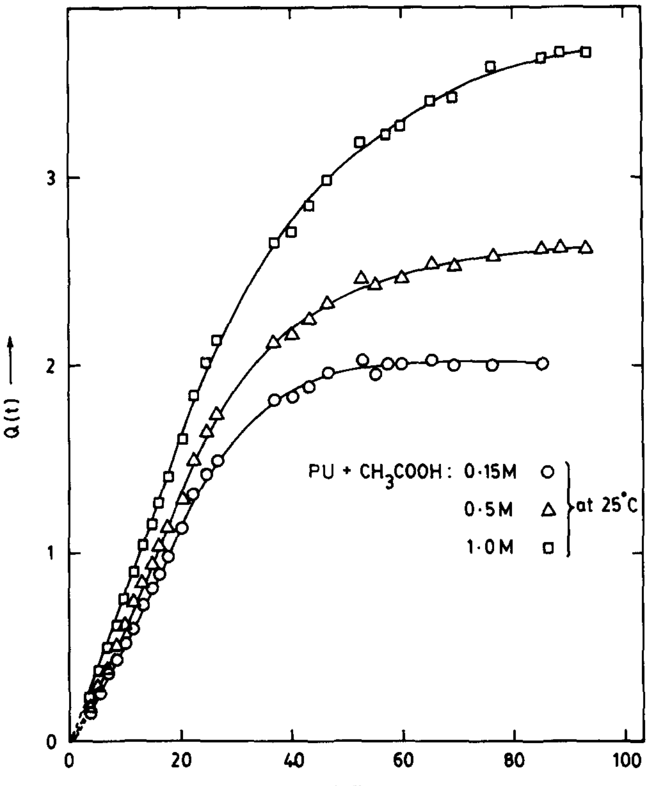

Figure 1 Sorption curves for 0.15 M, 0.5 M and 1 M acetic acid in polyurethane at 25°C

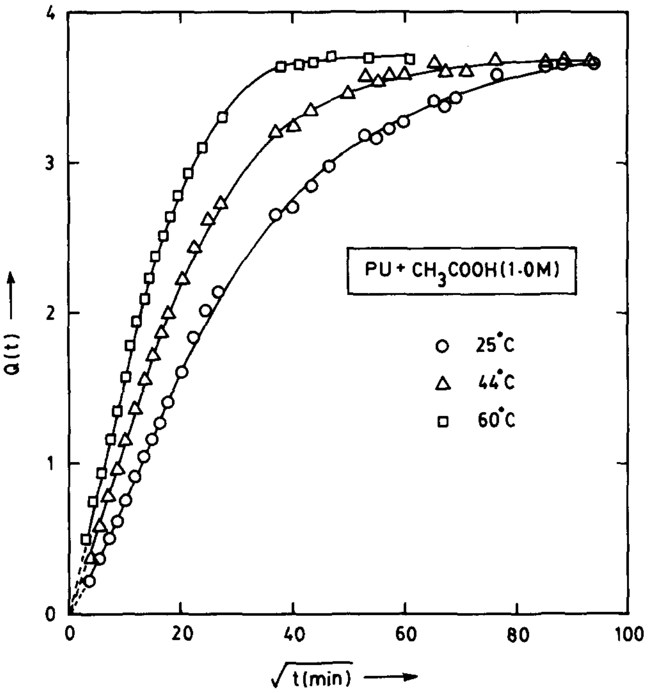

Figure 2 Sorption curves for 1 M acetic acid in polyurethane

temperatures (44 or 60°C) as shown in *Figure 2* for 1 M acetic acid solutions.

The sorption behaviour of monochloroacetic acid is very different from those of acetic acid solutions. For all the concentrations (0.15, 0.5 and 1.0 M), the $Q(t)$ *versus* $t^{1/2}$ curves as given in *Figure 3* at 25°C seem to follow the normal Fickian behaviour. However, at higher temperatures (40 or 60°C), the maximum sorption (see e.g. *Figure 4*) tends to decrease even though there is attainment of equilibrium saturation. Such a decrease in maximum sorption is more rapid for 0.15 and 0.5 M solutions of monochloroacetic acid than for 1.0 M solution. This type of effect at higher temperature and lower concentration of the acid solutions may be attributed to the ionization of monochloroacetic acid

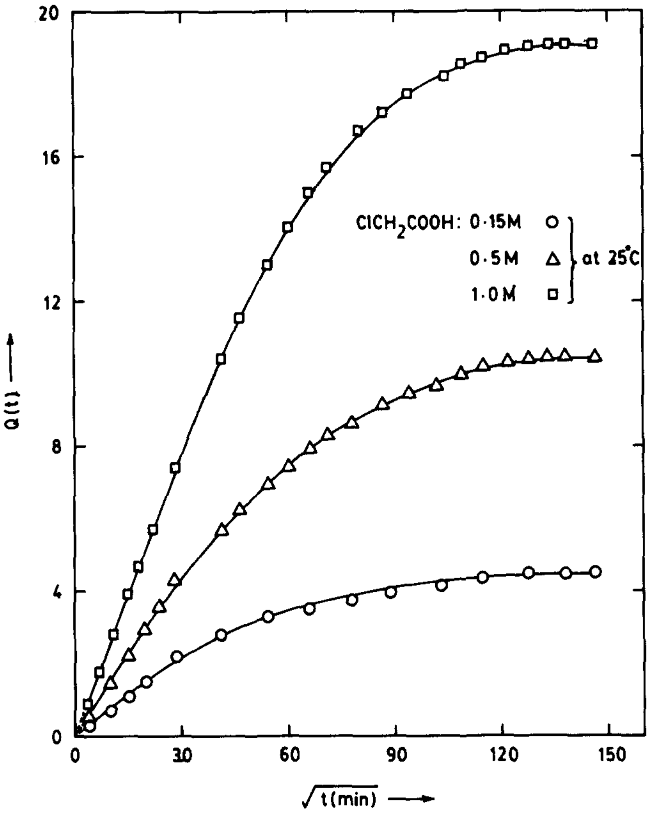

Figure 3 Sorption curves for 0.15 M, 0.5 M and 1 M monochloroacetic acid in polyurethane at 25°C

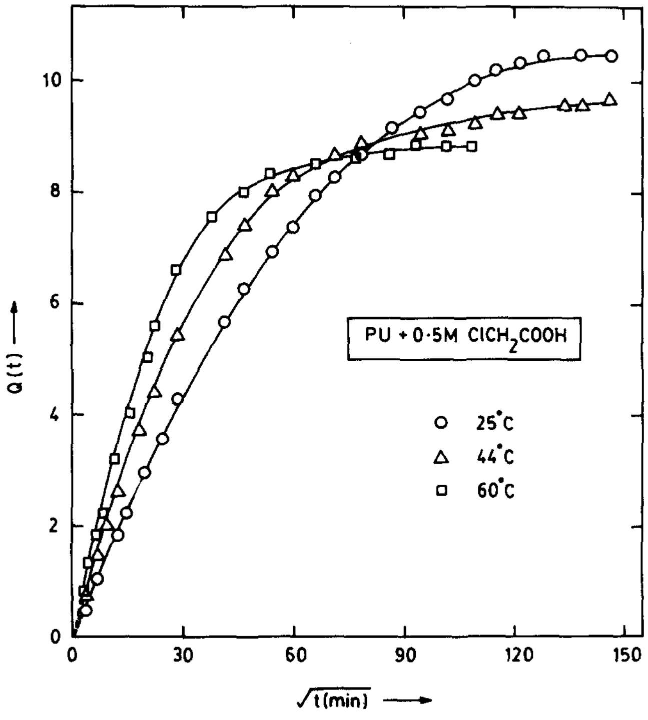

Figure 4 Sorption curves for 0.5 M monochloroacetic acid in polyurethane

($k_d = 1.4 \times 10^{-3}$ at 25°C) into its constituent ions, facilitating higher transport. This effect was not seen in the case of acetic acid solutions and this may be due to the fact that acetic acid remains in the undissociated form because of its lower value of dissociation constant ($k_d = 1.76 \times 10^{-5}$ at 25°C) than for monochloroacetic acid. Thus, acetic acid moves as a whole molecular unit in the aqueous phase through polyurethane. From a comparison of data given in *Figures 1* and *3*, it is observed that the sorption capacity of monochloroacetic acid solutions is about 10 times greater than that of acetic acid solutions.

In order to see the effect of cations from acetate salt solutions, we have chosen to study the sorption and transport of acetates of sodium, calcium and nickel. We found that there are no significant differences between the sorption behaviours of these salts in the investigated intervals of temperature and concentration. Sorption curves for all the acetate salt solutions seem to follow the normal Fickian trend. For instance, some representative plots of $Q(t)$ *versus* $t^{1/2}$ for 1 M sodium acetate solutions, as given in *Figure 5*, indicate Fickian transport mode. With 0.15 M sodium acetate solution (figure not displayed), the equilibrium sorption was lower at higher temperatures (i.e. at 40 and 60°C) than at room temperature (25°C). However, this effect is found to be diminishing for 1.0 M sodium acetate solution (see *Figure 5*), wherein the equilibrium sorption at 60°C is higher than at either 25 or 40°C. The sorption curves at 25 and 40°C merge into a single curve, suggesting that the transport mechanism after attainment of equilibrium saturation remains the same irrespective of the temperature. Such a behaviour has also been observed for acetates of calcium and nickel; however, in order to avoid duplication, these plots are not shown.

On the whole, it may be noted that acetates of sodium, calcium and nickel behave differently at lower concentrations and at higher temperatures. This is attributed to the different transport mechanisms that are operative with different cations of the acetate salts. Thus, the transport of the ions may be greatly influenced by the ionic spheres of the cations and this sphere can be easily perturbed at lower concentrations and at higher temperatures. For comparative purposes, the sorption curves of water are displayed in *Figure 6*. Water is a stable molecule up to 60°C and thus the sorption behaviour of water is quite systematic in that it increases with temperature. The sorption curves at all the temperatures seem to follow the normal Fickian behaviour.

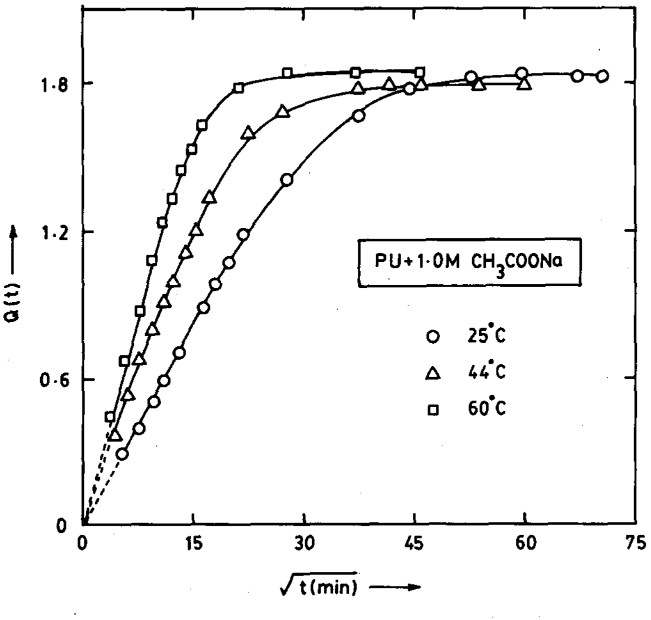

Figure 5 Sorption curves for 1 M sodium acetate solution in polyurethane

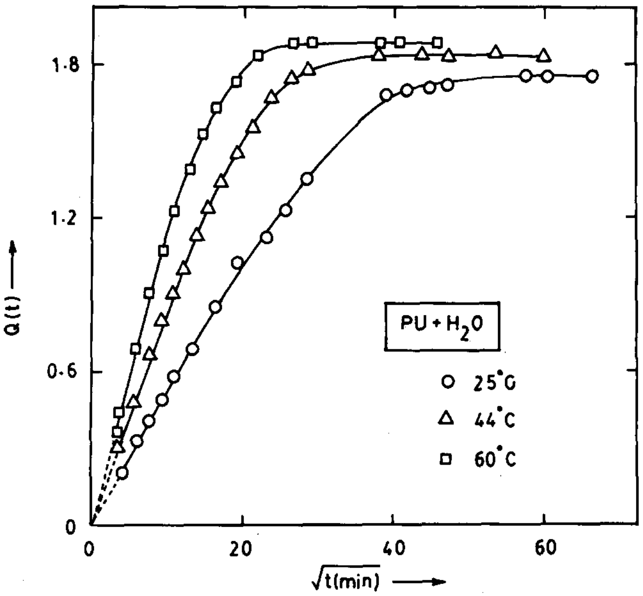

Figure 6 Sorption curves for water in polyurethane

In order to confirm the Fickian mode of transport, we have analysed the sorption data in terms of an empirical relation[15] of the type:

$$\log(M_t/M_\infty) = \log k + n \log t \qquad (1)$$

where M_t is the mass uptake at time t and M_∞ represents the corresponding equilibrium value. The value of the constant k gives an idea about the extent of polymer–solvent interaction. The numerical value of n decides the mode of transport mechanism. If the estimated value of n comes out to be close to $\frac{1}{2}$, then the process is indicative of the Fickian mode of transport. For values of $n = 1$, we get a non-Fickian mode of transport. For all the polymer–penetrant pairs, the values of n were found to vary between 0.5 up to a maximum of 0.60, suggesting thereby that the transport of salt or acid solutions may be classified to be of Fickian type. These results are presented in *Table 1*. In general, the values of n tend to decrease with a rise in temperature, but they do not exhibit any systematic trend with salt concentrations. Similarly, log k values are increasing with temperature, but decrease with increased concentrations of acetic and monochloroacetic acid solutions. However, no systematic trend could be seen with other salt solutions.

Diffusion coefficients

For the case of constant diffusion coefficient, $D(c) = D_0$, there are three methods to determine D_0, two using initial-time data and the third using long-time data. From the initial rates of sorption, for one-dimensional transport the diffusion coefficient D_0 is given as[14]:

$$D_0 = \pi(hG/4M_\infty)^2 \qquad (2)$$

where G is the slope of the linear portion of the plot of

Table 1 Analysis of sorption data using equation (1)

		n			$\log k$		
Penetrant	Concentration (mol l^{-1})	25°C	44°C	60°C	25°C	44°C	60°C
CH_3COOH	0.15	0.60	0.58	0.50	0.196	0.422	0.748
	0.5	0.59	0.57	0.51	0.160	0.378	0.684
	1.0	0.57	0.56	0.50	0.147	0.364	0.630
$CH_2ClCOOH$	0.15	0.51	0.53	0.50	0.194	0.390	0.616
	0.5	0.53	0.53	0.52	0.087	0.282	0.448
	1.0	0.52	0.51	0.51	0.074	0.295	0.410
CH_3COONa	0.15	0.52	0.50	0.50	0.383	0.736	0.850
	0.5	0.52	0.50	0.50	0.430	0.598	0.796
	1.0	0.51	0.50	0.50	0.450	0.679	0.803
$(CH_3COO)_2Ca$	0.15	0.54	0.51	0.50	0.091	0.607	0.786
	0.5	0.51	0.50	0.50	0.425	0.640	0.827
	1.0	0.57	0.52	0.51	0.310	0.621	0.762
$(CH_3COO)_2Ni$	0.15	0.56	0.53	0.50	0.306	0.571	0.810
	0.5	0.51	0.50	0.50	0.450	0.670	0.754
	1.0	0.55	0.54	0.51	0.337	0.565	0.739
H_2O	–	0.52	0.51	0.50	0.424	0.635	0.810

$Q(t)$ *versus* $t^{1/2}$. Here, D_0 represents the unidirectional (axial) diffusivity; h is sample thickness.

If absorption takes place in all directions of the sample, then following the procedure developed by Shen and Springer[16] for rectangular geometry, we propose to correct for diffusivity as:

$$\bar{D}(c)=D_0\left[1+\frac{\bar{h}}{\bar{r}}\left(\frac{D_r}{D_0}\right)^{1/2}+\frac{\bar{h}}{2\pi\bar{r}}\left(\frac{D_\theta}{D_0}\right)^{1/2}\right]^2 \qquad (3)$$

Here, D_r and D_θ are, respectively, the diffusion coefficients along the radial and angular directions of the disc-shaped polymer sample. Under isotropic conditions, we may assume that $D_0=D_r=D_\theta$, so that equation (3) can be solved for average diffusivity as:

$$\bar{D}(c)=D_0\left(1+\frac{\bar{h}}{\bar{r}}+\frac{\bar{h}}{2\pi\bar{r}}\right)^2 \qquad (4)$$

in equations (3) and (4), the quantities $\bar{h}$ and $\bar{r}$ represent the average values of sample dimensions before and after swelling. The value of D_0 for the pre-swollen polymer can be computed from equation (2).

The foundation for interpreting sorption data for concentration-dependent diffusivity was laid by the pioneering work of Crank and Park[17] in addition to several others[18,19]. The subject has also been reviewed by Crank[20], who showed that equation (4) also provides the same average of the concentration-dependent $\bar{D}$, given in the first approximation by:

$$\bar{D}(c_0)=\frac{1}{c_0}\int_0^{c_0} D(c)\,\mathrm{d}c \qquad (5)$$

where c_0 is penetrant concentration at membrane surface and $\bar{D}(c)$ gives the average diffusivity of the penetrant over the concentration interval studied.

The diffusion coefficients as computed from equation (4) are summarized in *Table 2*. Included in the same table are the sorption coefficients (as obtained from maximum sorption, i.e. M_∞) and permeability coefficients $\bar{P}(\equiv\bar{D}S)$.

Sorption results have also been calculated in terms of moles per gram of the polyurethane. In such calculations, the effective molecular weight of the salt solution is used, $\bar{M}=x_1M_1+x_2M_2$, 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 solutions will not change drastically even after complete sorption. These results are also included in *Table 2* and represent the sorbed equilibrium concentrations of various penetrants in polyurethane. These results also follow the same general trend as those of sorptivities calculated on the basis of gram of solvent per gram of polymer. However, the mole per cent values have more basic meaning than percentage weight uptake data.

As shown in *Table 2*, the diffusion coefficients of acetic acid solutions are higher than those of monochloroacetic acid solutions. With a rise in temperature, $\bar{D}$ also increases continuously. This dependence is also true for all salts at all concentrations. However, in the case of acetates of sodium, calcium and nickel, the transport coefficients do not vary drastically among themselves and thus these data are not too different compared with water.

The concentration dependence of diffusion coefficients of acetic and monochloroacetic acid solutions is noteworthy. For instance, $\bar{D}$ *versus* concentration plots as shown in *Figure 7* for acid solutions show linear variations at 25°C, but at higher temperatures (i.e. at 40 or 60°C) such dependences are slightly curved. The diffusion coefficients of both the acid solutions tend to decrease with an increase in concentration and this decrease is steeper at higher temperatures. In *Figure 8*, the dependence of $\bar{D}$ on concentration of acetate salt solutions is presented at 25, 44 and 60°C. At 25°C, $\bar{D}$ does not seem to depend greatly on concentration; however, at higher temperatures, $\bar{D}$ tends to increase with an increase in salt concentrations. Thus, it appears that the concentration dependence of $\bar{D}$ for acetate salt solutions is quite different from those of acid solutions.

Table 2 Transport data for polyurethanes plus penetrant systems at different temperatures and concentrations of salt solutions

	0.15 M			0.5 M			1 M		
Penetrant	25°C	44°C	60°C	25°C	44°C	60°C	25°C	44°C	60°C
				Diffusivity, $\bar{D}\times10^7$ (cm^2 s^{-1})					
CH_3COOH	2.83	6.04	10.56	2.23	4.70	7.99	1.75	3.46	6.09
$CH_2ClCOOH$	0.95	2.75	4.82	0.70	1.59	3.02	0.63	1.32	2.65
CH_3COONa	2.54	5.82	9.71	3.04	6.30	11.58	3.01	7.27	12.32
$(CH_3COO)_2Ca$	2.89	6.28	9.76	2.94	6.28	10.66	2.91	7.15	12.37
$(CH_3COO)_2Ni$	2.67	6.17	10.80	3.14	6.00	11.30	3.23	6.92	10.88
H_2O	2.88	6.79	13.45						
				Solubility, $S\times10^{2\,a}$					
CH_3COOH	2.01	2.04	2.15	2.63	2.66	2.75	3.66	3.68	3.69
	(11.14)	(11.31)	(11.92)	(14.31)	(14.48)	(14.97)	(19.53)	(19.63)	(19.69)
CH_2ClOOH	4.50	4.01	3.87	10.48	9.59	8.84	19.08	17.59	15.68
	(24.72)	(22.03)	(21.26)	(56.10)	(51.33)	(47.32)	(98.60)	(90.90)	(81.03)
CH_3COONa	1.80	1.79	1.75	1.98	1.95	1.80	1.83	1.79	1.84
	(9.91)	(9.86)	(9.63)	(10.66)	(10.50)	(9.69)	(9.57)	(9.36)	(9.62)
$(CH_3COO)_2Ca$	1.81	1.78	1.75	1.95	1.89	1.78	1.69	1.70	1.78
	(9.85)	(9.69)	(9.52)	(10.13)	(9.82)	(9.25)	(8.25)	(8.30)	(8.69)
$(CH_3COO)_2Ni$	1.88	1.84	1.70	1.98	1.95	1.83	1.87	1.82	1.81
	(10.20)	(9.99)	(9.23)	(10.20)	(10.04)	(9.43)	(8.99)	(8.75)	(8.70)
H_2O	1.76	1.84	1.88						
				Permeability, $\bar{P}\times10^9$ (cm^2 s^{-1})					
CH_3COOH	5.66	12.30	22.73	5.86	12.48	21.94	6.42	12.72	22.47
$CH_2ClCOOH$	4.27	11.02	18.66	7.34	15.28	26.74	12.08	23.15	41.60
CH_3COONa	4.56	10.39	17.03	6.02	12.28	20.88	5.49	13.04	22.64
$(CH_3COO)_2Ca$	5.24	11.18	17.08	5.75	11.89	19.00	4.93	12.12	21.97
$(CH_3COO)_2Ni$	5.02	11.34	18.34	6.23	11.68	20.70	6.03	12.59	19.60
H_2O	5.05	12.48	25.42						

[a] Values in parentheses are computed on the basis of moles/mass of polymer, i.e. per 100 g of polymer

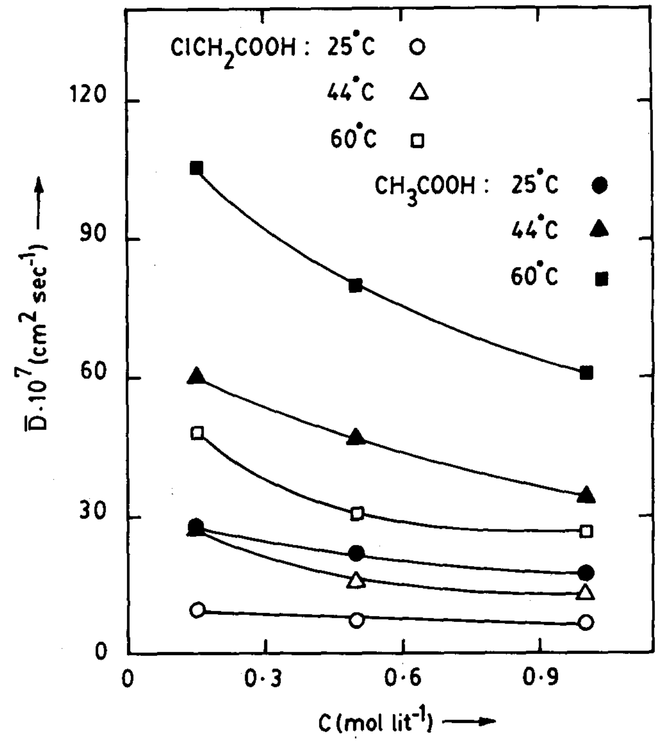

Figure 7 Diffusivity *versus* concentration of acetic acid at (●) 25°C, (▲) 44°C, (■) 60°C and of monochloroacetic acid at (○) 25°C, (△) 44°C, (□) 60°C

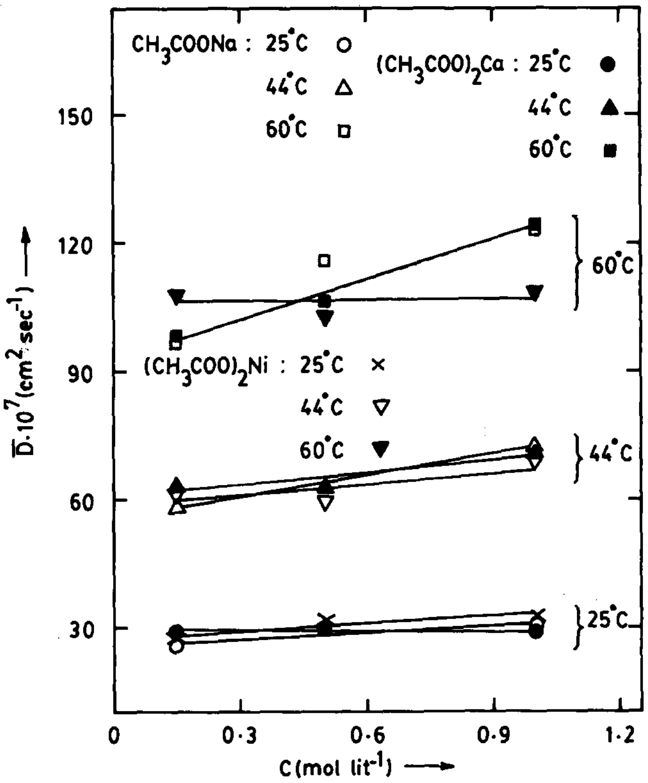

Figure 8 Diffusivity *versus* concentration of sodium acetate solution at (○) 25°C, (△) 44°C, (□) 60°C, of calcium acetate solution at (●) 25°C, (▲) 44°C, (■) 60°C and of nickel acetate solution at (×) 25°C, (▽) 44°C, (▼) 60°C

Table 3 Activation parameters for polyurethane plus penetrant systems

Penetrant	Concentration (mol l^{-1})	Activation parameters E_D (kJ mol^{-1})	 E_P (kJ mol^{-1})	 ΔH_s (kJ mol^{-1})
CH_3COOH	0.15	31.2	32.8	1.6
	0.5	30.2	31.2	1.0
	1.0	28.1	29.5	1.4
$CH_2ClCOOH$	0.15	38.7	35.1	−3.6
	0.5	34.5	30.6	−4.0
	1.0	33.7	29.1	−4.6
CH_3COONa	0.15	31.8	31.3	−0.5
	0.5	31.5	29.4	−2.1
	1.0	33.5	33.6	0.1
$(CH_3COO)_2Ca$	0.15	28.9	28.1	−0.8
	0.5	30.5	28.4	−2.1
	1.0	35.4	35.4	1.0
$(CH_3COO)_2Ni$	0.15	33.1	30.8	−2.3
	0.5	30.1	28.2	−1.8
	1.0	28.9	28.0	−0.9
H_2O	–	36.5	38.1	1.7

Arrhenius parameters

From the temperature dependence of transport coefficients we have estimated the activation parameters E_D and E_P, for the processes of diffusion and permeation respectively, from the Arrhenius relationship. The estimated values of E_D and E_P together with the computed heat of sorption ΔH_s ($\equiv E_P - E_D$) for all the penetrants are given in *Table 3*.

There were no significant trends observed for the effect of ion size on the values of E_D or E_P, which ranged from 29 to 38 kJ mol^{-1}. This can be explained on the basis of the results of Barker and Thomas[21] who measured the ionic conductivities of cellulose acetate membranes soaked in 0.1 M aqueous chloride solutions of Li, Na, K, Rb and Cs. The values of activation energies for diffusion observed below the T_g of the polymer showed an increase with ionic volume. However, the activation energies above the T_g of cellulose acetate were not greatly affected by ionic size. This lack of dependence of E_D on ionic volume above T_g may be understood in terms of free-volume theory, if the average local free volumes at those temperatures are large compared with the sizes of the ions. The T_g of the PU sample used in this work is around −43°C and thus there is no trend for the dependence of E_D or E_P on ion size. Once the ions enter into the membrane matrix, they get immobilized, and any increase in temperature will result in the same transport mechanism for all the ions. However, as expected, for all the penetrants, diffusivity and permeability increase with increasing concentration of the solution, while the activation parameters (E_D or E_P) decrease. The heat of sorption ΔH_s is negative for some penetrants but acetic acid solutions exhibit positive values of ΔH_s.

Barrie and coworkers[22] have measured the diffusion coefficient of water/PU systems. For Adiprene CM, Elastothane ZR625 and Genthane S polyurethanes, D was found to be $(5–26) \times 10^{-7}$ cm^2 s^{-1} in the temperature interval of 35–60°C and E_D was 42–48 kJ mol^{-1}. In our study, $\bar{D}$ for water varied in the range $(2.9–13.5) \times 10^{-7}$ cm^2 s^{-1} and E_D is about 37 kJ mol^{-1}. Thus, it appears that the transport properties of the PU elastomers reflect more strongly the differences in structure.

Self-diffusion coefficients

Attempts have been made to compute theoretically the self-diffusion coefficients of the penetrants by using Onsager–Fuoss theory[23]. Thus:

$$D = (v_1 + v_2)10^3 RT\left(1 + c\frac{\partial \ln y_\pm}{\partial c}\right) \times \left[1.074 \times 10^{-20}\left(\frac{\lambda_1^0 \lambda_2^0}{v_1 |Z_1| \Lambda_0^0}\right) + \frac{\Delta M'}{c} + \frac{\Delta M''}{c}\right] \quad (6)$$

where

$$\left(1 + c\frac{\partial \ln y_\pm}{\partial c}\right) = 1 - \frac{1.1514 S_f c}{(1 + A'c)^2} + 2.303Bc - c\psi(d) \quad (7)$$

The last term, $c\psi(d)$, can be neglected for lower concentrations. The electrophoretic terms $\Delta M'$ and $\Delta M''$ are given as:

$$\frac{\Delta M'}{c} = -\frac{(|Z_2|\lambda_1^0 - |Z_1|\lambda_2^0)^2}{\Lambda_0^2 |Z_1 Z_2| (v_1 + v_2)} \frac{3.132 \times 10^{-19}}{\eta_0 (\varepsilon T)^{1/2}} \frac{\Gamma}{1 + \kappa a} \quad (8)$$

$$\frac{\Delta M''}{c} = \frac{(|Z_2^2|\lambda_1^0 - |Z_1^2|\lambda_2^0)^2}{\Lambda_0^2} \frac{9.304 \times 10^{-13}}{\eta_0 (\varepsilon T)^2} c\phi(\kappa a) \quad (9)$$

In the above equations, the equivalent conductance of the electrolyte at infinite dilution is $\Lambda_0 = \lambda_1^0 + \lambda_2^0$ where λ_1^0 and λ_2^0 are respectively the limiting ionic conductivities of cations and anions. The other symbols, namely v_1, v_2 and Z_1, Z_2, are respectively the number and charges of cations and anions of the electrolyte; $y_\pm$ is the mean activity coefficient, a is the mean distance of closest approach of ions, c is concentration of the electrolyte, ε is dielectric constant and η_0 is the viscosity of the medium. The function $\phi(\kappa a)$ is given elsewhere[24], T is absolute

Table 4 Theoretical calculations of self-diffusion coefficients at 25°C

	Diffusion coefficient ($10^5\,cm^2\,s^{-1}$)		
Salt	0.15 M	0.5 M	1.0 M
CH_3COONa	1.18	1.12	1.03
CH_3COOH	1.84 (1.18)[a]	1.76 (1.14)[a]	1.68 (1.08)[a]

[a] Ref. 25

temperature, S_f is limiting slope of the Debye–Hückel theory and B is salting constant.

The available data from various sources for sodium acetate[24] and acetic acid solutions[25] have been used in equations (6) to (9) to compute self-diffusion coefficients at 25°C. For both the salt solutions, the D values tend to decrease with increase in concentration of the salt solution (see data given in *Table 4*). However, the orders of magnitude of theoretical diffusivities are higher than those found in the present work (see *Table 2*). This further suggests the slow diffusion rates of salt solutions in polyurethane.

CONCLUSIONS

The effect of ion size on water transport through a polyurethane membrane has been studied as a function of temperature and salt concentration. The diffusion results have been corrected for sorption in three dimensions. Solute size showed no observable effects on water transport through polyurethane. This information may be useful in the development of efficient permselective membranes for biomedical purposes and in the elucidation of transport phenomena.

ACKNOWLEDGEMENT

The authors are extremely grateful to the University Grants Commission, New Delhi, India for the award of a teacher fellowship under F.I.P. Scheme for Mr S. B. Harogoppad to study at Karnatak University. We also thank Professor P. Cassidy of Southwest Texas State University, USA, for the supply of PU membranes used in this research.

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