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An investigation of the long-term sorption kinetics and diffusion anomalies of chloroalkanes into tetrafluoroethylene/ propylene copolymer membranes at 30, 45 and 60°C

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An investigation of the long-term sorption kinetics and diffusion anomalies of dichloromethane, chloroform, carbon tetrachloride, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, trichloroethylene and tetrachloroethylene into the tetrafluoroethylene/propylene copolymer membranes has been carried out using gravimetric sorption technique at 30, 45 and 60°C. Coefficients of diffusion and permeation have been calculated from Fick's equation. Analytical solutions of Fick's equation have been used to compute liquid concentration profiles into polymeric sheet membranes at different times. Activation parameters for diffusion and sorption have been evaluated and these results are discussed in terms of the molecular size of the liquids and the temperature. The diffusion coefficient and activation energy for diffusion do not exhibit any systematic dependence on the size of the penetrant molecules, but these are mainly influenced by the nature of chloroalkanes. © 1997 Elsevier Science Ltd. All rights reserved.

INTRODUCTION

A fundamental understanding about the effect of chemical structure of liquid molecules on their transport characteristics into polymeric membranes is essential for the development of high performance polymer membranes that are resistant to these liquids. The transport of liquids into polymer membranes can be significantly affected by the membrane structure, its history such as the method of preparation, annealing, etc. A variety of liquid mixtures of industrial interest are separated at present by the so called selective permeation phenomenon[1]. In all such studies, sorption kinetics, permeation and diffusion anomalies of liquids into the dense membranes are important[2–7]. A comprehensive understanding of these phenomena is needed before the successful practical applications of these materials. A detailed analysis of diffusion anomalies in terms of concentration profiles is also equally important in the overall fundamental understanding of the transport of small molecules into the dense membrane materials. Several experimental techniques have been employed to measure the solvent migration into the dense polymer membranes[8–13]. However, it has been suggested that the gravimetric sorption method[14,15] also gives reliable data on polymer–solvent systems.

The tetrafluoroethylene/propylene copolymer membranes (Aflas® FA 100S and FA 150P elastomers, manufactured by 3M) exhibit a unique combination of high temperature,

chemical and electrical resistance properties. These elastomers find applications where compression set resistance and the gas (e.g., N_2, CO_2, etc.) blistering and anti-extrusion resistance are important. They also provide service life advantages in acids, bases, steam/hot water, amines, oils and hydraulic fluids. Other important applications of these elastomers include O-rings, seals used in hydraulic and brake systems, jet engines, cable clamps, electrical connectors and boots, wire and cable insulation, hose, pipeline patches, etc. Their good dimensional retention property and moderate volume swell prompted us to study the molecular transport of chloroalkanes into these membranes. Chloroalkanes are particularly chosen in view of their widespread use in a number of chemical industries.

Our recent papers[2–7], [14–18] from this laboratory addressed different aspects of diffusion anomalies for different polymer–solvent systems. In continuation of these studies and as a further contribution in this area, we report here the experimental results of sorption kinetics, diffusion and permeation of dichloromethane, chloroform, carbon tetrachloride, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, trichloroethylene and tetrachloroethylene into the polymeric sheet membranes of tetrafluoroethylene/propylene copolymer (FA 100S and FA 150P polymers) at 30, 45 and 60°C. The migration of the chosen chloroalkanes into the polymeric sheet membranes has a great practical relevance in chemical engineering areas and other related fields. From a fundamental point of view, an understanding of the molecular interactions between

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Table 1 Chemical formulae, molar volume (V_S) and dipole moment (μ) of chloroalkanes at 25°C

Liquid	Chemical formula	V_S (cm^3 mol^{-1})	μ (D)
Dichloromethane	CH_2Cl_2	64.5	1.14
1,2-Dichloroethane	CH_2Cl-CH_2Cl	79.4	1.83
Chloroform	$CHCl_3$	80.7	1.15
Trichloroethylene	$CHCl=CCl_2$	90.0	0.80
Carbon tetrachloride	CCl_4	97.1	0.00
1,1,1-Trichloroethane	CH_3CCl_3	100.0	1.70
Tetrachloroethylene	$CCl_2=CCl_2$	102.7	0.00
1,1,2,2-Tetrachloroethane	$CHCl_2-CHCl_2$	105.8	1.71

chloroalkanes and tetrafluoroethylene/propylene copolymeric sheet membranes is also important.

In the present study, molecular transport parameters viz., diffusion (D), permeation (P), sorption (S) and the kinetic rate constant (k_1), have been obtained in addition to activation parameters for sorption and diffusion. From a knowledge of these quantities and from a theoretical analysis of the data, the molecular transport phenomenon showed a slight deviation from the Fickian trend. Furthermore, the transport results have been discussed in terms of the penetrant shapes and their interactions with the polymer chain segments. The analytical solutions of Fick's equations have been used to calculate the liquid concentration profiles at different times and depths of the membrane materials[19-21]. These profiles have been discussed in terms of the diffusion parameters and the size of the solvent molecules.

EXPERIMENTAL

Materials

FA 100S and FA 150P grade Aflas® polymer sheets in dimensions of 14.7 cm × 14.7 cm with thicknesses ranging from 0.225 to 0.270 cm were obtained from 3M Industrial Chemical Products Division, St. Paul, MN, USA (courtesy of Ms. Nena McCallum).

During processing, these elastomers are mixed with curatives, fillers and other compounding ingredients by the conventional mill or internal mixing methods. In typical formulations, the peroxide curing agent and the co-agent are preblended with dry powders prior to adding to the base gum on the mill. For internally mixed compounds, a two pass procedure is recommended with peroxide being added in the second pass. Care should be taken to avoid mixing temperatures above 121°C. After mixing, the stock solution should be cooled rapidly either by an air or water cooling technique. The mixed catalysed compound should be stored in a cool, dry place prior to use. Elastomer compositions and some of their representative physical/mechanical properties have been summarised in our earlier paper[7].

Chemicals

The reagent grade chemicals used are dichloromethane (Sisco Chem. Industries, Mumbai, India), chloroform, carbon tetrachloride, 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, trichloroethylene and tetrachloroethylene (all from s.d. Fine Chem. Pvt. Ltd., Mumbai, India). These were used directly as supplied. The chemical formulae along with some of their important properties are listed in *Table 1*.

Sorption experiments

Circular shaped sheet membrane samples of diameter 1.966 cm were cut from the large polymer sheets using a sharp-edged carbon-tipped steel die. The cut polymer samples were dried by storing them in a vacuum oven at 30°C for 48 h before use. These samples were then soaked into screw-tight test bottles containing 15–20 ml of the respective solvent maintained at the desired temperature (±0.5°C) in an electronically controlled hot air incubator (WTB Binder, Germany). The samples were removed periodically from the solvent containers, the surface adhered solvent drops were wiped off using the filter paper wraps and then weighed immediately on a digital Mettler balance (Model AE 240, Switzerland) within the precision of ±0.01 mg. Extreme care was taken to reduce the loss of solvent molecules from the polymer samples by covering the samples using a steel plated cover. This step was performed very quickly i.e., within a 20 sec. to minimise any possible evaporation losses. In each case, three independent readings were taken and the average value was considered for the calculation. Other experimental details remain the same as given in our earlier papers[2-7, 14-18].

When the polymer samples attained equilibrium sorption, no more weight gain was observed and this did not change significantly by further keeping the samples in solvents over an extended period of 1 or 2 days. Instead of computing the weight % gain of the polymer samples by the solvent molecules (which gives a misleading picture of the solvents' relative rates of diffusion), a more useful and meaningful alternative quantity to consider would be the number of moles of solvent absorbed per unit mass of the polymer. This quantity, referred to as mol % sorption, M_t, is defined as the fractional weight increase of the polymer divided by the molar mass of the solvent in question. Thus, M_t is calculated as:

$$M_t = \left(\frac{W_t - W_0}{W_0}\right) \times \frac{100}{M} \tag{1}$$

where W_0 is the initial weight of the polymer sample, W_t is its weight at time t, for the immersion lapse period and M is molecular weight of the solvent under question.

RESULTS AND DISCUSSION

Sorption behaviour

The mol % sorption results of all the liquids with FA 100S and FA 150P polymers at 30 and 60°C are displayed graphically in *Figure 1*. Of all the liquids, chloroform exhibits the highest sorption for both the polymers and
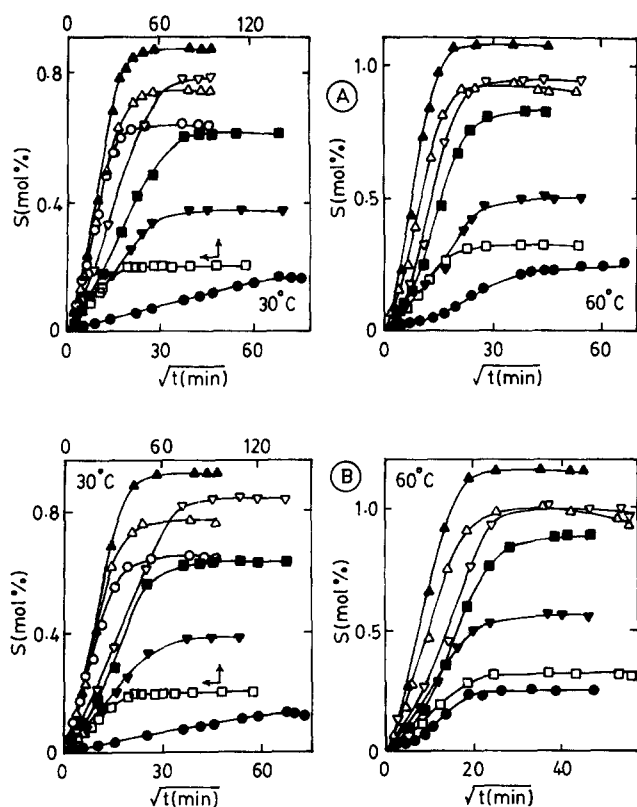
Figure 1 Sorption curves of (A) FA 100S and (B) FA 150P for (O) dichloromethane, (▲) chloroform, (■) carbon tetrachloride, (□) 1,2-dichloroethane, (▽) 1,1,1-trichloroethane, (●) 1,1,2,2-tetrachloroethane, (△) trichloroethylene and (▼) tetrachloroethylene at 30 and 60°C

Figure 2 Sorption curves of (A) FA 100S with chloroform and tetrachloroethylene and (B) FA 150P with the same liquids at different temperatures

over the entire range of temperature. In the specific case of 1,1,2,2-tetrachloroethane (molar volume of 105.8 cm³ mol⁻¹) and 1,2-dichloroethane (molar volume of 79.4 cm³ mol⁻¹), the resultant uptake curves for the latter molecule show higher uptake values than 1,1,2,2-tetrachloroethane at all the temperatures. This would clearly indicate the greater rate of solvent uptake and the greater ultimate level of uptake of 1,2-dichloroethane over 1,1,2,2-tetrachloroethane. Among the uptake values of 1,1,1-trichloroethane (molar volume of 100 cm³ mol⁻¹) and trichloroethylene (molar volume of 90 cm³ mol⁻¹), the equilibrium sorption of 1,1,1-trichloroethane is slightly higher than that observed for trichloroethylene for both FA 100S and FA 150P polymers at all the temperatures. However, while comparing the uptake values of carbon tetrachloride and dichloromethane at 30°C, it is observed that the equilibrium sorption for carbon tetrachloride is slightly lower than that observed for dichloromethane for both FA 100S and FA 150P samples. The sorption results of dichloromethane at 60°C are not obtained due to its lower boiling temperature (b.p. = 39.64°C). It is observed in general that for FA 100S, the sorption uptake values are slightly lower than observed for FA 150P at all the temperatures and for all the solvents. At 60°C, the sorption curves for almost all the solvents exhibit sigmoidal trends suggesting slight departures from the Fickian sorption kinetics. Also, sorption is quicker at 60°C when compared to 30°C.

The sorption results presented in *Figure 1* indicate that the shapes of the curves, the equilibrium uptake values and the time to attain equilibrium sorption are dependent upon the size and chemical characteristics of the solvent molecules. For instance, the larger size molecule such as
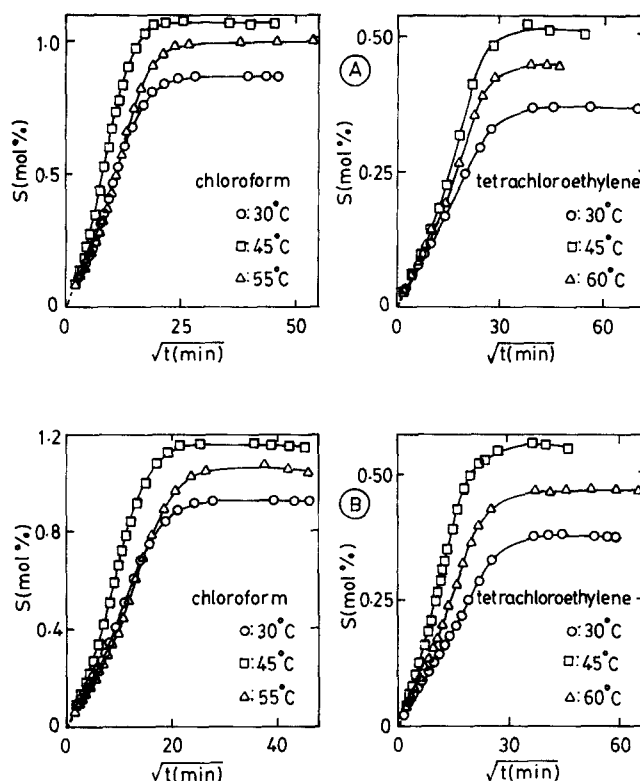
1,1,2,2-tetrachloroethane takes longer time to attain equilibrium saturation when compared to other chloroalkanes. Due to the increased uptake values with increase in temperature, we observe a systematic increase of S with temperature in all the cases. This indicates increased molecular mobility of the polymer chain segments with respect to solvent molecules. The temperature dependent uptake curves for chloroform and tetrachloroethylene with FA 100S and FA 150P samples are presented in *Figure 2*. The results of sorption coefficients, S (which are calculated in mol % units from the plateau regions of the sorption curves) are given in *Table 2*.

The initial sorption kinetic curves have been used to estimate the first order kinetic rate constants, k_1, by using[15,16]:

$$k_1 t = \ln\left[\frac{M_\infty}{(M_\infty - M_t)}\right] \quad (2)$$

These results are also included in *Table 2*. For chloroform, trichloroethylene and tetrachloroethylene with FA 100S polymer, the kinetic rate constants do not vary systematically with temperature. For the remaining liquids, the results of k_1 increase with increasing temperature. Similarly, for the FA 150P, the rate constants for chloroform, carbon tetrachloride and trichloroethylene do not show any systematic increase with temperature. However, for the remaining liquids, k_1 values increase with temperature.

The initial sorption results i.e., before completion of 55% of equilibrium sorption, vary linearly with $t^{1/2}$ and these results have been fitted to the empirical equation[22,23]:

$$\frac{M_t}{M_\infty} = K t^n \quad (3)$$

Table 2 Sorption coefficients and kinetic rate constants of Aflas® membranes with chloroalkanes at different temperatures

Liquid	S (mol%) $\times 10^2$			$k_1 \times 10^3$ (min^{-1})		
	30°C	45°C	60°C	30°C	45°C	60°C
Aflas® FA 100S						
Dichloromethane	63.93	$-^a$	$-^a$	8.06	$-^a$	$-^a$
1,2-Dichloroethane	20.01	24.93	32.30	2.14	3.72	5.28
Chloroform	87.14	100.36	107.00^b	6.37	5.09	8.84^b
Trichloroethylene	74.58	85.71	93.85	6.14	5.57	6.20
Carbon tetrachloride	61.03	72.20	82.55	2.12	2.44	2.89
1,1,1-Trichloroethane	86.31	87.06	94.24	2.35	2.71	3.65
Tetrachloroethylene	37.26	45.08	51.00	2.53	2.38	2.42
1,1,2,2-Tetrachloroethane	16.81	20.30	25.35	0.64	0.96	1.13
Aflas® FA 150P						
Dichloromethane	65.04	$-^a$	$-^a$	7.32	$-^a$	$-^a$
1,2-Dichloroethane	19.92	25.01	32.51	1.74	3.92	5.12
Chloroform	92.60	108.19	115.99^b	5.85	3.98	7.63^b
Trichloroethylene	77.23	92.66	101.32	6.68	4.61	5.64
Carbon tetrachloride	63.34	76.60	88.57	2.31	2.04	2.62
1,1,1-Trichloroethane	84.30	95.36	101.66	2.11	2.13	2.50
Tetrachloroethylene	38.20	47.16	56.45	2.66	3.30	4.71
1,1,2,2-Tetrachloroethane	13.54	20.52	25.57	0.60	0.84	0.96

^{a}Data not obtained due to its low boiling point
^{b}Experiments were done at 55°C due to its low boiling point

Table 3 Estimated parameters of equation (3)

Liquid	n			$K \times 10^2$ (g g^{-1} min^n)		
	30°C	45°C	60°C	30°C	45°C	60°C
Aflas® FA 100S						
Dichloromethane	0.55	$-^a$	$-^a$	4.51	$-^a$	$-^a$
1,2-Dichloroethane	0.52	0.51	0.52	2.75	3.45	4.00
Chloroform	0.57	0.59	0.58^b	3.39	2.73	3.98^b
Trichloroethylene	0.56	0.55	0.57	3.63	3.52	3.45
Carbon tetrachloride	0.56	0.59	0.56	1.96	1.67	2.00
1,1,1-Trichloroethane	0.59	0.55	0.59	1.78	2.35	2.04
Tetrachloroethylene	0.52	0.51	0.51	2.84	3.27	2.67
1,1,2,2-Tetrachloroethane	0.50	0.54	0.51	1.94	1.24	1.71
Aflas® FA 150P						
Dichloromethane	0.55	$-^a$	$-^a$	4.32	$-^a$	$-^a$
1,2-Dichloroethane	0.51	0.51	0.52	2.49	3.63	3.93
Chloroform	0.57	0.58	0.59^b	3.28	2.50	3.50^b
Trichloroethylene	0.57	0.56	0.57	3.60	3.08	3.13
Carbon tetrachloride	0.56	0.58	0.56	1.99	1.54	1.84
1,1,1-Trichloroethane	0.58	0.56	0.54	1.71	1.91	2.22
Tetrachloroethylene	0.52	0.55	0.57	3.00	2.65	3.05
1,1,2,2-Tetrachloroethane	0.51	0.53	0.50	1.42	1.20	1.54

^{a}Data not obtained due to its low boiling point
^{b}Experiments were done at 55°C due to its low boiling point

Here, the parameters, K and n have been obtained by the method of least-squares. The values of n indicate the type of diffusion mechanism. For a Fickian diffusion, the value of n is around 0.50, while for the non-Fickian diffusion, n approaches unity. For most of the rubbery polymers with organic solvents, the values of n vary between 0.50 and 1.00, and this is classified as the anomalous diffusion behaviour. The estimated values of K and n are presented in *Table 3*. The estimated errors in n and K values are within 1–1.5%. For both FA 100S and FA 150P, the values of n range between 0.50 and 0.59 signifying a slight deviation from Fickian diffusion and following the so called anomalous behaviour. However, these results do not show any systematic variation with temperature. This is further supported by almost initial linear variation of M_t versus $t^{1/2}$ (*Figures 1 and 2*).

The results of K which represent the solvent interaction with the polymer chain segments at 30°C are higher for smaller molecules like dichloromethane, trichloroethylene and chloroform. These results at 30°C

Table 4 Diffusion and permeability coefficients of Aflas® membranes with chloroalkanes at different temperatures

Liquid	$D \times 10^7$ (cm^2 s^{-1})			$P \times 10^7$ (cm^2 s^{-1})		
	30°C	45°C	60°C	30°C	45°C	60°C
Alfas® FA 100S						
Dichloromethane	9.74	–[a]	–[a]	5.29	–[a]	–[a]
1,2-Dichloroethane	2.34	4.56	7.33	0.46	1.12	2.34
Chloroform	5.60	6.66	9.29[b]	5.82	7.97	11.87[b]
Trichloroethylene	6.19	6.97	8.11	6.07	7.85	10.01
Carbon tetrachloride	2.32	2.49	3.09	2.18	2.77	3.92
1,1,1-Trichloroethane	2.42	2.61	4.27	2.79	3.03	5.37
Tetrachloroethylene	2.55	2.82	3.10	1.57	2.11	2.62
1,1,2,2-Tetrachloroethane	0.71	0.95	1.02	0.16	0.32	0.43
Alfas® FA 150P						
Dichloromethane	9.43	–[a]	–[a]	5.21	–[a]	–[a]
1,2-Dichloroethane	1.72	4.37	6.66	0.34	1.08	2.14
Chloroform	5.03	6.08	8.94[b]	5.58	7.85	8.94[b]
Trichloroethylene	6.86	7.81	8.74	6.96	9.51	11.64
Carbon tetrachloride	2.29	2.52	3.74	2.23	3.11	5.10
1,1,1-Trichloroethane	2.82	2.93	3.14	3.18	3.73	4.26
Tetrachloroethylene	2.99	5.33	6.56	1.90	4.17	6.14
1,1,2,2-Tetrachloroethane	0.64	1.02	1.08	0.15	0.35	0.46

[a]Data not obtained due to its low boiling point
[b]Experiments were done at 55°C due to its low boiling point

vary according to the sequence: dichloromethane > trichloroethylene > chloroform > tetrachloroethylene > 1,2-dichloroethane > carbon tetrachloride > 1,1,2,2-tetrachloroethane > 1,1,1-trichloroethane. However, at 45 and 60°C, the trends in the variation of K are slightly different. This sequence also does not show any relation with the size of the chloroalkanes. The values of K increase with increasing temperature except in a few cases. This further suggests that the solvent diffusion into the polymer is an activated process and at higher temperatures the solvent molecules have higher thermal energies. However, a simple consideration of a random walk would also give an increased rate of uptake at higher temperature. Also, the values of K are generally higher for FA 100S polymer than FA 150P, suggesting the increased solvent interactions with the FA 100S polymer than FA 150P.

Diffusion coefficients

Concentration-independent diffusion coefficient, D of the solvent–polymer systems for the uni-directional flow of liquids has been calculated using Fick's equation[24]:

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2}\right) \tag{4}$$

where C is liquid concentration in the polymer at time t and distance x. To solve the above equation, it was assumed that:

(1) when the membrane is soaked into the solvent medium, its concentration on the membrane surface reaches equilibrium immediately;
(2) the time to attain thermal equilibrium for the polymer is negligible when compared to the sorption time;
(3) changes in the membrane dimensions are negligible during the full solvent exposure time.

Using the following boundary conditions,

$$t = 0 \qquad 0 < x < h \qquad C = 0 \tag{5}$$

$$t > 0 \qquad x = 0, \qquad x = h \qquad C = C_\infty \tag{6}$$

equation (4) was solved to obtain the liquid concentration profiles into the membrane of thickness h, at time t and distance x, to give[19–21]

$$\frac{C_{(t,x)}}{C_\infty} = 1 - \frac{4}{\pi} \sum_{m=0}^{\infty} \frac{1}{(2m+1)} \exp\left[-\frac{D(2m+1)^2 \pi^2 t}{h^2}\right]$$
$$\sin\left[\frac{(2m+1)\pi x}{h}\right] \tag{7}$$

where $C_{(t,x)}$ and C_∞ are the solvent concentrations at time t, distance x and at equilibrium, respectively; and n is an integer.

The values of concentration-independent diffusion coefficients D have been calculated from the relation[24]

$$D = \pi\left(\frac{h\theta}{4M_\infty}\right)^2 \tag{8}$$

where θ is the slope of the initial linear portion of the sorption curves. Here, D is the unidirectional (axial) diffusivity and h is the sample thickness. In reality, diffusion occurs in all the directions of the disc-shaped samples and hence, it is important to consider the correction for diffusivity as done earlier[25,26] in order to calculate the effective diffusion coefficient, D_{eff} using:

$$D_{\mathrm{eff}} = D\left(1 + \frac{\bar{h}}{\bar{r}} + \frac{\bar{h}}{2\pi\bar{r}}\right)^2 \tag{9}$$

where $\bar{h}$ and $\bar{r}$ are respectively, the average values of the sample thickness and radius before and after swelling.

The corrected values of D (i.e., D_{eff}) calculated from equation (9) are presented in *Table 4*. The D_{eff} values are accurate to 1% or even less in some cases. For dichloromethane at 30°C, the largest value of $D_{\mathrm{eff}} = 9.74 \times 10^{-7}$ cm^2 s^{-1} is observed whereas, the lowest values of $D_{\mathrm{eff}} = 0.71 \times 10^{-7}$ cm^2 s^{-1} is found at all the temperatures
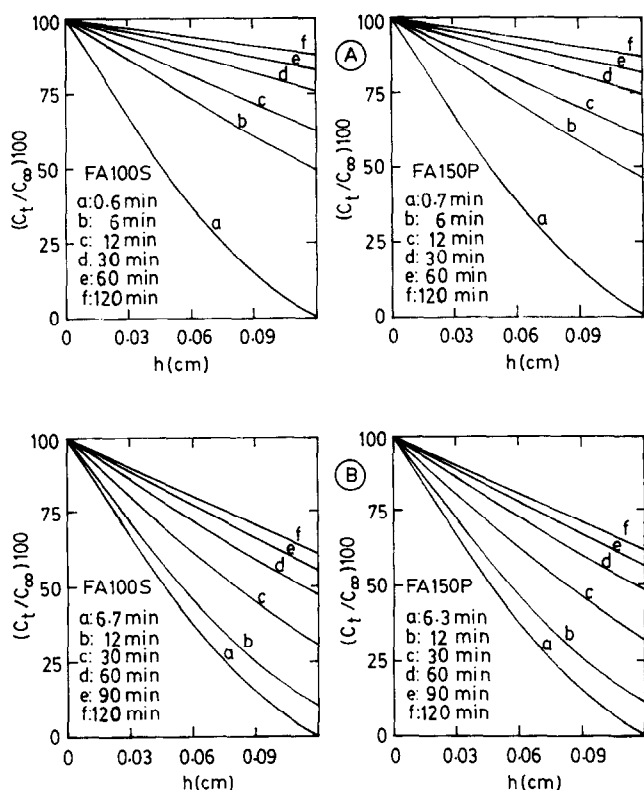
Figure 3 Concentration profiles calculated from equation (7) for FA 100S and FA 150P with (A) chloroform and (B) 1,1,2,2-tetrachloroethane at 30°C
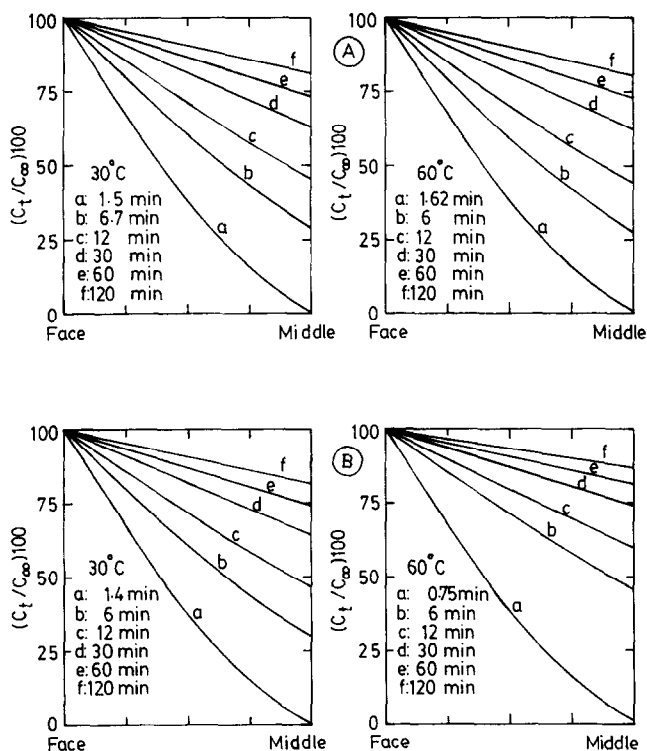

Figure 5 Comparison of theoretical (solid curves) and experimental sorption points for (A) FA 100S and FA 150P with dichloromethane and (B) FA 100S and FA 150P with tetrachloroethylene at 30°C

Figure 4 Concentration profiles calculated from equation (7) for (A) FA 100S and (B) FA 150P with tetrachloroethylene at 30 and 60°C

for 1,1,2,2-tetrachloroethane with both FA 100S and FA 150P membranes. This trend in the variation of D_{eff} is in accordance with the size of these molecules, i.e., 1,1,2,2-tetrachloroethane is a larger molecule than dichloromethane. However, for other molecules, the variation in
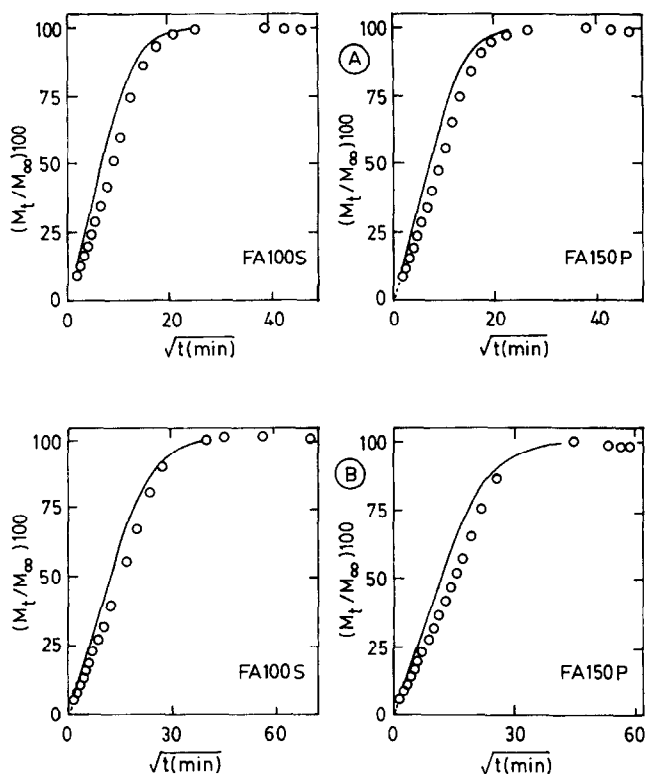
D_{eff} values is not in proportion to their sizes. For instance, the molecular sizes of 1,2-dichloroethane and chloroform are almost the same, but their D_{eff} values are quite different. Chloroform exhibits higher D_{eff} values than 1,2-dichloroethane. Similarly, carbon tetrachloride having a lower molar volume than 1,1,1-trichloroethane and tetrachloroethylene exhibit lower D_{eff} values at all the temperatures and for both polymers. At 30°C, the D_{eff} values vary according to the sequence: dichloromethane > trichloroethylene > chloroform > tetrachloroethylene > 1,2-dichloroethane > 1,1,1-trichloroethane > carbon tetrachloride > 1,1,2,2-tetrachloroethane. This trend also proves the fact that there is no systematic dependence of D_{eff} on the size of the solvent molecules. The results of permeability coefficients, P calculated from the relation: $P = S \times D_{eff}$ are also included in *Table 4*. These results in the temperature range investigated follow the same sequence as those of D_{eff} and k_1 discussed before.

The concentration profiles calculated from equation (7) at different exposure times and membrane thicknesses for chloroform and 1,1,2,2-tetrachloroethane with FA 100S and FA 150P samples at 30°C are shown in *Figure 3*. The diffusivity values of these liquids are very different, so their concentration profiles are also different. For instance, D_{eff} of chloroform is higher than that observed for 1,1,2,2-tetrachloroethane and thus, its concentration profiles i.e., $C_{(t,x)}/C_\infty$ values, are higher than those for the latter molecule at the same time. Furthermore, the concentration profiles at 30 and 60°C for the FA 100S and FA 150P samples with tetrachloroethylene are displayed in *Figure 4*. It is observed that for FA 100S, the variations in concentration profiles are not very significant whereas, with FA 150P, the increased concentration profiles are observed at higher temperature (i.e., at 60°C rather than at 30°C).
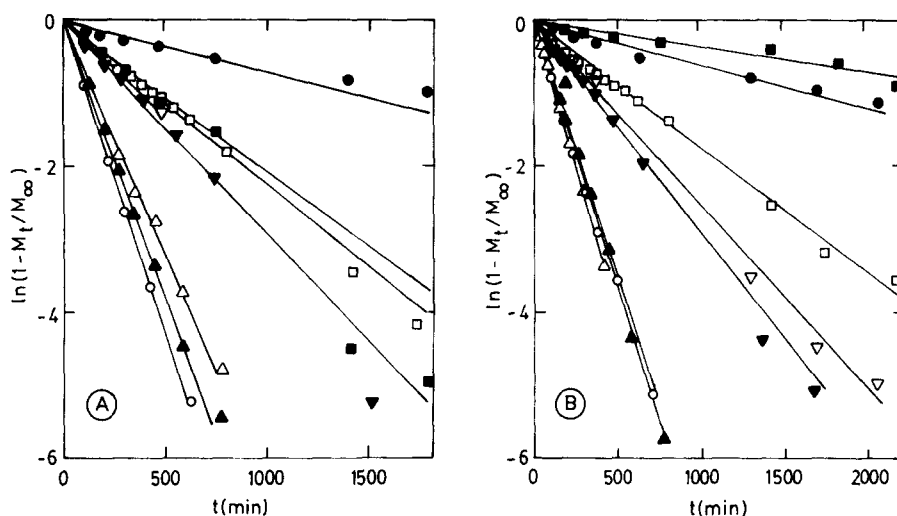
Figure 6 $\ln(1-M_t/M_\infty)$ *versus* t plots for polymer-solvent systems with the same symbols for liquids as given in *Figure 1*
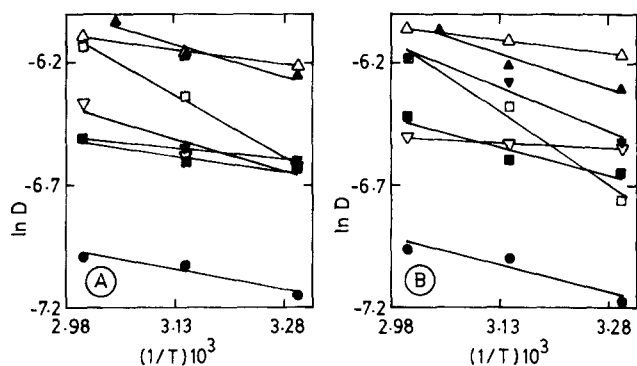

Figure 7 Arrhenius plots of $\ln D$ *versus* $1/T$ for (A) FA 100S and (B) FA 150P samples. Symbols for liquids are as given in *Figure 1*

Inserting the values of D_{eff} as calculated from equation (9), the theoretical sorption curves have been generated from equation (10):

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-D\frac{(2n+1)^2\pi^2 t}{h^2}\right] \quad (10)$$

These curves are compared with the experimental sorption kinetic curves in *Figure 5* for dichloromethane and tetrachloroethylene with FA 100S and FA 150P polymers at 30°C. The agreement between the theoretical solid curves and the experimental points is good initially, but at longer times, these curves deviate slightly, suggesting the concentration dependency of diffusivity; a problem that needs to be investigated in detail. At longer diffusion times, equation (10) can be simplified to give[27]

$$\ln\left(1 - \frac{M_t}{M_\infty}\right) = \ln\left(\frac{8}{\pi^2}\right) - \frac{D\pi^2 t}{h^2} \quad (11)$$

so that the plot of $\ln(1 - M_t/M_\infty)$ *versus* t should be linear and the slope of these lines is proportional to D. Some of our data have been plotted in this format, which are in conformity with equation (11) (see *Figure 6*). The calculated values of D from equation (11) are about 10% lower than those calculated from equation (9). However, these values are not presented in *Table 4*. At longer sorption times, the term $n \geq 1$ as well as $\ln(8/\pi^2)$ may be ignored so that

equation (11) becomes:

$$\ln\left(\frac{M_\infty}{M_\infty - M_t}\right) \cong \frac{\pi^2 D t}{h^2} \quad (12)$$

where

$$k_1 = \frac{\pi^2 D}{h^2} \quad (13)$$

This further proves that sorption results of this study can be analysed by using the first order kinetics and that diffusivity is proportional to k_1, as discussed before.

Arrhenius effects

The sorption and diffusion results increase with increasing temperature so that the Arrhenius activation energy, E_D, for diffusion has been calculated using:

$$D = D_0 \exp\left(\frac{-E_D}{RT}\right) \quad (14)$$

where D_0 is a pre-exponential factor and RT is the energy term. As the size of the penetrant molecule increases, activation energy increases, polymer cohesive energy becomes greater and polymer chain segments become more rigid. In a similar way, S can be expressed by van't Hoff's equation with a pre-exponential factor, S_0 as:

$$S = S_0 \exp\left(\frac{-\Delta H_S}{RT}\right) \quad (15)$$

where ΔH_S is heat of sorption and is a composite parameter. This involves contributions from Henry's law which requires positive heats of sorption for the formation of a site and the dissolution of the chemical species into that site. This gives the endothermic contribution. Secondly, the Langmuir's (hole filling) type sorption mechanism requires the pre-existence of the site and sorption by the hole filling mechanism gives an exothermic heat of sorption.

The Arrhenius plots of $\ln D$ *versus* $1/T$ for both FA 100S and FA 150P samples are shown in *Figure 7*. From these plots, the results of E_D have been obtained using the slopes of the lines as calculated from the least-squares procedures. Similarly, the results of ΔH_S have been obtained by the least-squares fitting of the $\ln S$ *versus* $1/T$ results. These data are compiled in *Table 5* along with the percent errors. The results of E_D and ΔH_S do not show any systematic

Table 5 Activation energy for diffusion (E_D) and enthalpy of sorption (ΔH_S) for Aflas® membranes with chloroalkanes

Liquid	E_D (kJ mol^{-1})	ΔH (kJ mol^{-1})
Alfas® FA 100S		
1,2-Dichloroethane	32.00 ± 2.25	13.38 ± 1.00
Chloroform	14.08 ± 2.97	6.87 ± 0.53
Trichloroethylene	7.54 ± 0.72	6.45 ± 0.61
Carbon tetrachloride	7.90 ± 2.58	8.46 ± 0.33
1,1,1-Trichloroethane	15.66 ± 7.15	2.43 ± 1.20
Tetrachloroethylene	5.53 ± 0.30	8.81 ± 0.85
1,1,2,2-Tetrachloroethane	10.32 ± 3.23	11.47 ± 0.86
Alfas® FA 150P		
1,2-Dichloroethane	38.03 ± 7.22	13.69 ± 0.94
Chloroform	16.00 ± 3.59	7.54 ± 0.61
Trichloroethylene	6.80 ± 0.27	7.63 ± 1.29
Carbon tetrachloride	14.28 ± 5.66	9.40 ± 0.47
1,1,1-Trichloroethane	2.95 ± 0.48	5.26 ± 0.82
Tetrachloroethylene	22.12 ± 5.40	10.93 ± 0.21
1,1,2,2-Tetrachloroethane	13.68 ± 5.72	17.86 ± 2.68

relationship with the size of the chloroalkanes. The 1,2-dichloroethane exhibits higher E_D values than other chloroalkanes for both polymers. The values of ΔH_S are positive, suggesting Henry's type of endothermic sorption. In all cases, the ΔH_S values are positive, suggesting that sorption is mainly dominated by Henry's sorption mode giving an endothermic contribution.

CONCLUSIONS

The results of this study on two important engineering elastomers (FA 100S and FA 150P) in the presence of chloroalkanes indicate that the transport processes are mainly governed by the Fickian mechanism and that diffusion coefficients for the polymer–solvent systems can be obtained for both the short-time and long-time sorption experiments. The values of diffusion coefficients calculated by these two methods are comparable within the experimental precision of the technique used. Sorption, diffusion and permeation results are dependent primarily on the nature of chloroalkanes than their sizes. Increase in these parameters with increasing temperature has been analysed in terms of the activation parameters and these showed a dependence on the chemical nature of the liquids.

The kinetic rate constants as estimated from the first order kinetic equation have shown a direct dependence on the values of diffusion coefficients. The liquid concentration profiles calculated from the analytical solution of Fick's equation are dependent on the size of the liquid molecules and their effective diffusivity values. In many respects, both FA 100S and FA 150P polymers behave almost identically to the presence of chloroalkanes used. Thus, for field applications, it becomes difficult to make a selective choice between the two elastomers in the presence of liquids. This is because both the polymers exhibit identical resistivity to the presence of liquids investigated.

Furthermore, both the polymers remain intact and no loss of additives or change in dimensional stability was observed. It is to be realised that for the successful field applications of these polymers, a fundamental investigation into the molecular transport phenomenon in terms of sorption, diffusion and permeation is important.

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