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A study of sorption/desorption profiles and diffusion anomalies of organic haloalkanes into a polymeric blend of ethylene–propylene random copolymer and isotactic polypropylene

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Experimental values for sorption, desorption, resorption and redesorption processes for a polymeric blend of ethylene–propylene random copolymer and isotactic polypropylene were obtained at 25, 40, 55 and 70°C with haloalkanes using a gravimetric method. Diffusion coefficients exhibited a dependence on the type and nature of solvent molecules. In view of an increase in diffusivity with temperature, Arrhenius relation was used to estimate the energy of activation for diffusion. These results showed a dependence on polymer–solvent interactions. A numerical method based on the finite difference method was used to calculate liquid concentration profiles into polymer membranes and these results were compared with those obtained from analytical solutions of Fick's equation. Copyright © 1996 Elsevier Science Ltd.

(Keywords: sorption; desorption; diffusion)

INTRODUCTION

Molecular transport of organic liquids into polymeric sheet membranes under the influence of a chemical potential gradient occurs primarily by the process of diffusion of permeating liquid molecules into barrier membranes. However, suitability of a particular polymeric material as a barrier under specified application conditions is determined by its sorption/desorption characteristics as well as diffusion anomalies. An important requirement of a membrane material is that it should be chemically resistant and at the same time it should retain its mechanical strength properties and dimensional stability. Synthetic polymer membranes with tailored morphology, good physical/mechanical properties with a fair degree of dimensional and chemical stability have been widely used in commercial applications. In these applications, penetrant diffusivity, an important property of the polymer–solvent system, needs to be evaluated.

An excellent summary of the earlier theoretical research on molecular transport of liquids into solid polymeric materials was covered in a volume by Crank and Park[1] and Aminabhavi *et al.*[2]. However, pioneering research efforts of Barrer[3], Mears[4], Bueche[5], Paul and DiBenedetto[7] are of special importance. More recently, Vergnaud and coworkers[8–13] have addressed different aspects of modelling and industrial applications of liquid transport processes into polymeric membrane materials. They proposed several numerical schemes to calculate diffusion coefficients and their concentration dependencies for a variety of polymer–solvent systems.

The principle objective of the present paper is to measure sorption, desorption and diffusion of haloalkanes into a miscible polymeric blend of ethylene–propylene random copolymer and isotactic polypropylene, also called Santoprene. Sorption and desorption experiments of Santoprene have been carried out gravimetrically at 25, 40, 55 and 70°C for carbon tetrachloride, chloroform, methylene dichloride, 1,1,2,2,-tetrachloroethane, bromoform, tetrachloroethylene, 1,1,1-trichloroethane and trichloroethylene. Liquid concentration profiles into a Santoprene membrane have been calculated for early stages of sorption, and these curves have been compared with the numerical method. Mathematical treatment involves solution of Fick's

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equation using various assumptions under suitable initial and boundary conditions. Experimental and calculated values have been discussed in terms of polymer–solvent interactions. From a temperature-dependence of diffusion and sorption, Arrhenius activation parameters have been estimated.

EXPERIMENTAL

Reagents and materials

Sheets of Santoprene (sample designation 103–40) were obtained from the Advanced Elastomer Systems, St. Louis, Missouri, USA in dimensions of 26 × 26 cm with initial thicknesses ranging from 0.158 to 0.161 cm. Circular disc-shaped samples (diameter = 1.97 to 1.99 cm) were cut from large sheets using a sharp edged carbon tipped steel die. Test samples were dried in vacuum desiccators over anhydrous calcium chloride at room temperature for about 24–48 h before experimentation.

The reagent grade solvents used as probe molecules are: carbon tetrachloride (Ranbaxy Laboratories Ltd., India), chloroform (Qualigens Fine Chemicals, India, HPLC grade), methylene dichloride (Ranbaxy Laboratories Ltd., India, Spectroscopic grade), 1,1,2,2-tetrachloroethane (May and Baker, India), bromoform, tetrachloroethylene, 1,1,1-trichloroethane and trichloroethylene (all from s.d. Fine Chem. Ltd, India). These solvents were double distilled before use.

X-ray diffraction (XRD) analysis

The XRD analysis was performed using a Cu K_α radiation (40 kV and 30 mA) with a scintag XDS 2000 diffractometer equipped with a graphite monochromator. Santoprene was placed in sample holder and XRD scans were run at 0.03° steps with a 7 s counting time.

Sorption (S)–desorption (D)–resorption (RS)–redesorption (RD) experiments

Vacuum dried disc-shaped Santoprene samples weighing initially 0.4630 g were placed in screw-tight test bottles containing about 15 to 20 ml of respective solvents. Samples were removed periodically, the surface adhered liquid drops were blotted off by carefully pressing the samples in between filter paper wraps and weighed on a digital Mettler balance, Model AE 240 (Switzerland) to an accuracy of ±0.01 mg. The samples attained equilibrium saturation generally within 24 h and these did not change over a further immersion period of 2 or 3 days. The percent weight gain (%wt) during solvent sorption was calculated as

$$\%\text{wt gain}(t) = \left(\frac{W_t - W_0}{W_0}\right) \times 100 \qquad (1)$$

where W_t is weight of polymer sample after time t and W_0 is initial weight of the sample. After complete sorption, the sorbed samples were placed in a vacuum oven at constant temperature for desorption measurements. For desorption, decrease in mass was measured periodically until attainment of constant weight. The % weight loss after desorption was calculated as

$$\%\text{wt loss } (t) = \left(\frac{W_t^{\mathrm{d}} - W_0^{\mathrm{d}}}{W_t^{\mathrm{d}}}\right) \times 100 \qquad (2)$$

Here, W_t^{d} is mass of polymer during desorption at time t and W_0^{d} is mass of polymer after complete desorption. Resorption and redesorption testing was also carried out in the same manner as the sorption and desorption tests.

Data on each polymer–solvent system, including mass and time measurements were recorded and filed in a computer database for subsequent analysis. If Santoprene does not show extensive mass loss during sorption runs, then its initial mass and the mass after desorption should be the same (i.e. $W_0 = W_0^{\mathrm{d}}$). However, in the present investigation, mass loss in Santoprene occurred during sorption, suggesting the loss of indigenous additives. If during sorption cycles, Santoprene releases all additive species contributing to weight loss, then no further loss of additives should occur for resorption runs. This is indeed the case in the present experimental systems. Sorption results, S, expressed in weight % units at 25, 40, 55 and 70°C, and results of desorption, resorption and redesorption equilibrium at 25°C are given in *Table 1*. The S values for resorption are generally higher than those observed for sorption runs. However, for the desorption and redesorption runs, equilibrium sorption values are almost identical for many liquids (*Table 1*).

RESULTS AND DISCUSSION

Sorption anomaly

Sorption anomaly has been studied by fitting the weight gain (in sorption and resorption) and weight loss (in desorption and redesorption) results in the following empirical relationship[14]:

$$\frac{M_t}{M_\infty} = Kt^n \qquad (3)$$

where M_t and M_∞ refer to masses of solvent uptake or loss at time t and at equilibrium; K is an empirical parameter depending on the structural characteristics of polymer and on liquid–polymer interactions. The exponent value of n is indicative of the type of transport mechanism. For desorption, M_t and M_∞ are mass losses of the drying polymer sample at time t and the completely dried sample, respectively. Estimated values of n and K are accurate within ±0.01 units.

For all solvent–Santoprene systems, values of n for sorption runs range between 0.50 and 0.58 over the investigated temperature interval 25–70°C, suggesting diffusion to be of anomalous type[15–22]. For resorption at 25°C, values of n range from 0.51 to 0.64. For all systems, K showed an increase with increasing temperature with few exceptions, like in case of chloroform and tetrachloroethylene. However, values of K decreased with an increasing size of alkylhalides, excepting 1,1,2,2-tetrachloroethane. This further suggests that K depends on the nature of the polymer–solvent interactions.

S–D–RS–RD *phenomena*

Sorption curves of haloalkanes with Santoprene at 25°C are presented in *Figure 1*. Compared to all liquids, M_t/M_∞ values of methylene dichloride show a sudden increase followed by a decrease, and later attaining equilibrium saturation (i.e. overshoot effect). This is either due to the loss of additives from the Santoprene

Table 1 Equilibrium sorption values (wt%) for Santoprene + haloalkanes at different temperatures for sorption (*S*), desorption (*D*), resorption (*RS*) and redesorption (*RD*) experiments

	S				*D*	*RS*	*RD*
Haloalkanes	25°C	40°C	55°C	70°C	25°C	25°C	25°C
Carbon tetrachloride	103.9	113.4	128.6	150.3	61.8	155.7	61.3
Chloroform	72.9	77.2	91.5	[a]	55.7	129.4	54.8
Methylene dichloride	30.1	[a]	[a]	[a]	39.2	51.4	34.3
1,1,2,2-Tetrachloroethane	42.9	49.0	60.6	73.7	45.0	67.6	39.0
Bromoform	64.6	70.9	82.6	95.6	52.9	84.2	45.6
Tetrachloroethylene	105.5	115.1	134.2	150.2	62.7	160.1	61.8
1,1,1-Trichloroethane	60.2	67.4	75.2	(a)	50.4	96.0	49.3
Trichloroethylene	87.4	98.8	112.7	122.8	59.3	149.2	60.0

[a] Data not obtained due to their high volatility

sample during sorption, or to any possible changes in morphology of Santoprene matrix material. In order to detect the loss of additives, refractrometry was used and no changes in the refractive index values were observed between pure solvent and the solvent after completion of soaking studies. Hence, it was realized that the observed overshoot effect may probably be due to changes in complex chain morphology of Santoprene, as shown by spectral changes of the methylene dichloride soaked Santoprene as against the neat sample (*Figure 2*). Such overshoot effects have also been observed earlier by other researchers[23-26]. However, for remaining solvents (except to some extent for chloroform), the overshoot effects are not so significant. This further suggests that morphological changes of Santoprene might not have occurred in the presence of other haloalkanes.

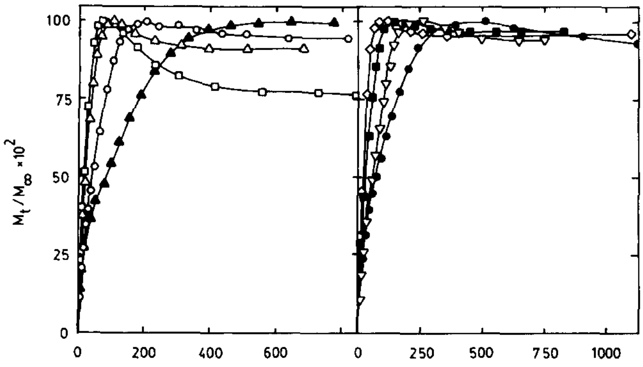

Figure 1 Sorption curves at 25°C for Santoprene with (○) carbon tetrachloride, (△) chloroform, (□) methylene dichloride, (▲) bromoform, (●) 1,1,2,2-tetrachloroethane, (■) tetrachloroethylene, (▽) 1,1,1-trichloroethane and (◇) trichloroethylene

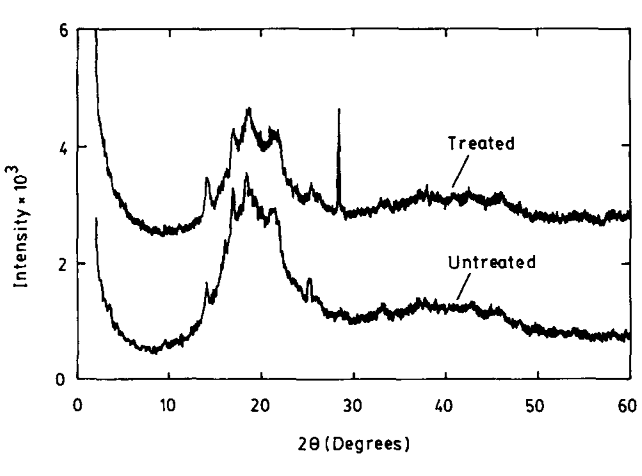

Figure 2 XRD tracings of untreated and methylene dichloride treated Santoprene samples

Results of equilibrium sorption, *S* presented in *Table 1* are dependent on the nature and type of solvent molecules. Sorption values for chloroform and 1,1,1-trichloroethane at 70°C and that for methylene dichloride at higher temperatures (viz. 40, 55 and 70°C) were not obtained due to their low boiling points. However, for carbon tetrachloride, trichloroethylene and tetrachloroethylene, higher sorption values are observed at all temperatures when compared to other liquids. On the other hand, sorption of methylene dichloride at 25°C is quite small, i.e. 30% only. The *S* values of 1,1,1-trichloroethane and bromoform are somewhat similar, though the molecular structures of these liquids are not the same. For the remaining liquids viz. 1,1,2,2-tetrachloroethane, chloroform and 1,1,1-trichloroethane, sorption values fall within the range of 43–92%. However, trichloroethylene shows sorption values from 87 to 123% for the rise in temperature from 25 to 70°C. Though 1,1,1-trichloroethane and trichloroethylene are not very different structurally (except of course for the presence of ethylenic double bond in the latter), their sorption values are quite different. Similar effect is seen with 1,1,2,2-tetrachloroethane and tetrachloroethylene. Higher sorption values of trichloroethylene and tetrachloroethylene than their ethane homologues are probably due to the presence of ethylene moiety in Santoprene polymer, following the principle of 'like sorbs the like'.

Sorption coefficients follow a systematic increase with increasing temperature in all cases, suggesting increased molecular interactions at higher temperatures. However, no regular trend with size of haloalkanes is observed. On the other hand, for description runs, equilibrium values are lower than those observed in sorption cycles for all liquids except methylene dichloride and 1,1,2,2-tetrachloroethane. Also, the resorption equilibrium values of all liquids at 25°C are higher than those observed for sorption runs. This further suggests that during resorption cycles, more of the solvent molecules get sorbed within the available free volume of the Santoprene matrix created during sorption/desorption cycles. On the other hand, desorption and redesorption equilibrium values are somewhat identical for all solvents. Typical *S–D–RS–RD* tracings for carbon tetrachloride and trichloroethane at 25°C are shown in *Figure 3*.

Computation of diffusion coefficient

In order to calculate diffusion coefficients, D of polymer–solvent systems, we need to solve Fick's equation under suitable initial and boundary conditions using the following assumptions:

(i) sorption and desorption processes occur under transient conditions with a constant diffusivity;
(ii) diffusion into a thin Santoprene sheet is considered uni-directional;
(iii) during the immersion test, the liquid concentration on the polymer surface reaches equilibrium immediately upon exposure;
(iv) desorption is controlled both by diffusion and evaporation phenomena, and rate of evaporation is either very high (with a zero concentration of liquid on the surface) or proportional to the difference in liquid concentration;
(v) dimensional changes of the Santoprene samples are considered to be negligible during sorption/desorption cycles;
(vi) the time required for Santoprene to attain thermal equilibrium is negligible when compared to times for sorption and desorption runs.

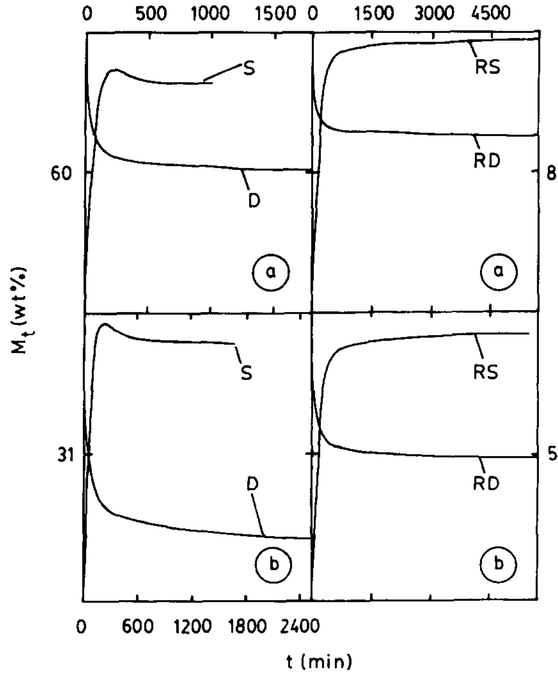

Figure 3 Sorption (S), desorption (D), resorption (RS) and redesorption (RD) curves at 25°C for (a) carbon tetrachloride and (b) trichloroethane

The uni-directional diffusion is described by Fick's second law for a constant diffusivity as[27]

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

where C is liquid concentration within a Santoprene material at time, t and distance x, under the following initial and boundary conditions:

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

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

The analytical solution of equation (4) for finding the liquid concentration during sorption through a Santoprene sheet of thickness h, at time t, and distance x, is given by[27]

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

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

The amount of liquid sorbed by Santoprene is given by

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

where M_t is mass sorbed at time t and M_∞ is mass sorbed at equilibrium time. Diffusivity at short times, i.e. $M_t/M_\infty < 0.55$ is then calculated by using

$$\frac{M_t}{M_\infty} = \frac{4}{h}\left(\frac{Dt}{\pi}\right)^{1/2} \tag{9}$$

The initial concentration of solvent within Santoprene is uniform due to the attainment of sorption equilibrium. On the other hand, for desorption, the rate of loss in Santoprene weight due to evaporation is given by [8]

$$-D\left(\frac{\partial C}{\partial x}\right)_{x=h} = F_0(C_0 - C_{\text{ext}}) \tag{10}$$

where F_0 is rate of evaporation of liquid, C_0 is concentration of liquid on the surface and C_{ext} is the concentration that is in equilibrium with the surrounding atmosphere.

The solution of equation (10) is given as [8]

$$\frac{C_\infty - C_{\text{ext}}}{C_\infty - C_0} = \sum_{n=1}^{\infty}\frac{2M\cos(\beta_n x/h)}{(\beta_n^2 + M^2 + M)\cos\beta_n}\exp\left(-\frac{\beta_n^2}{h^2}Dt\right) \tag{11}$$

where the β_ns are the positive roots of

$$\beta\tan\beta = M \tag{12}$$

with the dimensionless parameter M, given by

$$M = \frac{hF_0}{D} \tag{13}$$

The total amount of liquid M_t, leaving the Santoprene membrane after a lapse of time t, is expressed as a fraction of the corresponding quantity after an infinite time M_∞, by

$$\frac{M_\infty - M_t}{M_\infty} = \sum_{n=1}^{\infty} \frac{2M^2}{\beta_n^2(\beta_n^2 + M^2 + M)} \exp\left(-\frac{\beta_n^2}{h^2} Dt\right) \tag{14}$$

The values of β_n were taken from the literature[8].

A comparison of D values between 25 and 70°C for sorption and at 25°C for D–RS–RD runs is made in *Table* 2. The results of D are different in all these processes, and the values are not dependent on the size of the penetrant molecules. Among the haloalkanes considered, methylene dichloride, trichloroethylene and chloroform exhibit higher D values than the remaining liquids for all processes. The least diffusivity is observed by 1,1,2,2-tetrachloroethane and bromoform. The intermediate values of D are exhibited by other haloalkanes presented in *Table* 2. For sorption, values of D increase systematically from 25 to 70°C. This is supportive of the fact that at higher temperatures, due to the increased segmental movements of Santoprene chains, solvent diffusivity also increases. Values of D for desorption and redesorption at 25°C are higher than those observed in sorption cycles for all liquids except 1,1,2,2-tetrachloroethane and bromoform. On the other hand, diffusivities for resorption cycles at 25°C are quite smaller than those observed for S–D–RD runs.

Calculation of concentration profiles

Concentration profiles, i.e. $C_{(t,x)}/C_\infty$ of liquids at different thicknesses (i.e. depths) of Santoprene have been calculated[8] using equation (7). Here, the values of D used are the ones calculated from equation (9). Calculated profiles for different liquids after a lapse of 2 min during the sorption experiment are presented in *Figure 4* at 25 and 70°C. A noticeable effect of the temperature on the shapes of these profiles is observed. For instance, at 70°C, due to higher diffusivity, concentration profiles attain higher values than those observed at 25°C. Concentration profiles for chloroform, methylene dichloride and 1,1,1-trichloroethane at 70°C are not included in *Figure 4* due to their low boiling points. Similar plots for resorption runs at 25°C displayed in *Figure 5*, show lower values of concentration profiles when compared to sorption runs at 25°C. Profiles of liquid concentration as a function of polymer sample thickness (i.e. up to the middle of the sample, $h/2$) in case of bromoform (having low values of D) and trichloroethylene (having high values of D) at 25 and 70°C are compared in *Figure 6*. It is observed that in case of bromoform, whose D value being smaller than trichloroethylene, the concentration profiles are also lower than those observed for trichloroethylene at both

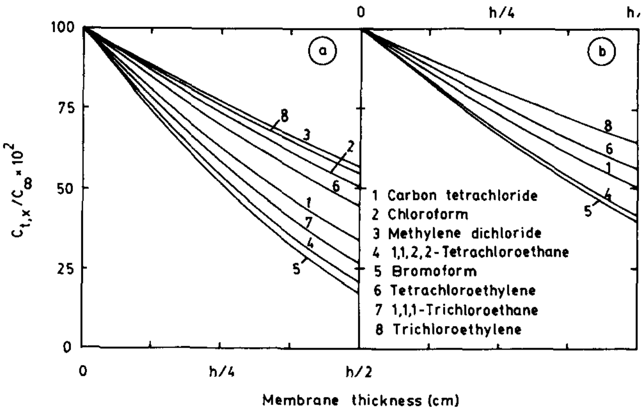

Figure 4 Profiles of the liquid concentration for sorption of haloalkanes calculated from equation (7) for different thicknesses within Santoprene at (a) 25°C and (b) 70°C for 2 min

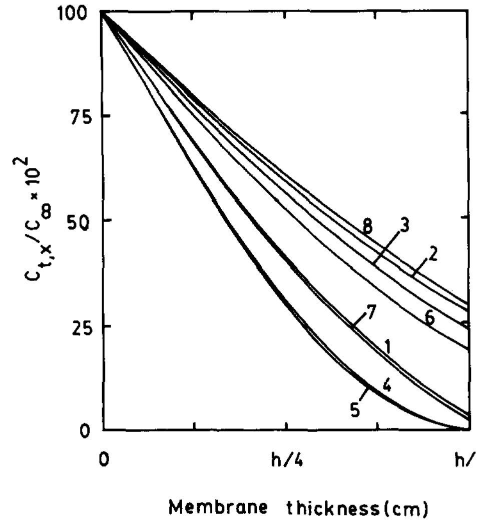

Figure 5 Profiles of the concentration for resorption calculated from equation (7) for Santoprene thicknesses at 25°C for 2 min. The numbers on the curves refer to the same liquids given in *Figure 4*

Table 2 Diffusion coefficients $\times 10^7$ (cm^2 s^{-1}) of Santoprene + haloalkanes from sorption (S), desorption (D), resorption (RS) and redesorption (RD) experiments

	S				*D*	*RS*	*RD*
Haloalkanes	25°C	40°C	55°C	70°C	25°C	25°C	25°C
Carbon tetrachloride	5.3	6.9	8.6	11.2	13.2	1.2	13.1
Chloroform	11.3	14.3	17.1	^{a}	22.3	1.9	19.2
Methylene dichloride	14.7	^{a}	^{a}	^{a}	20.1	2.6	13.3
1,1,2,2-Tetrachloroethane	2.9	4.0	5.0	7.1	1.3	0.4	0.5
Bromoform	2.4	3.9	5.6	5.9	1.7	0.4	1.1
Tetrachloroethylene	8.3	11.7	12.4	14.3	13.5	2.1	3.6
1,1,1-Trichloroethane	4.0	6.3	9.1	^{a}	10.4	1.0	8.4
Trichloroethylene	13.9	18.4	18.9	24.5	19.3	3.2	12.8

^{a} Data not obtained due to their high volatility

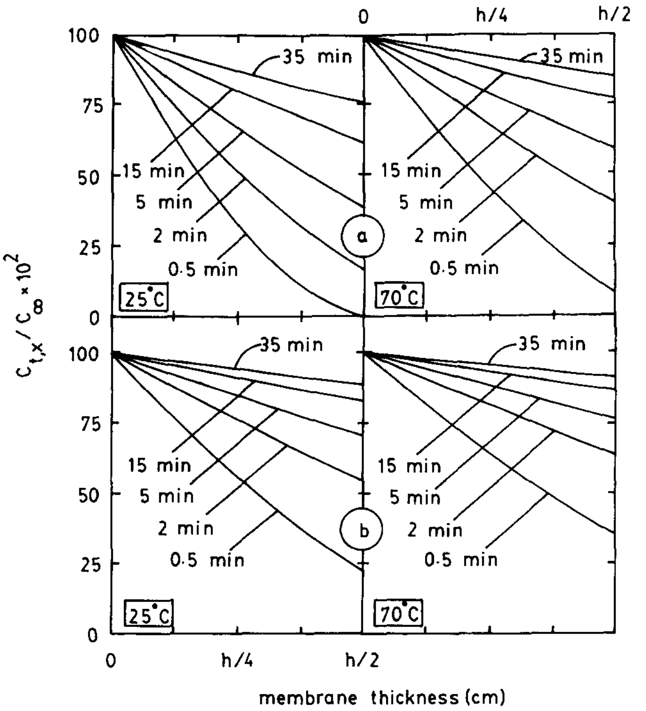

Figure 6 Profiles of the concentration of (a) bromoform and (b) trichloroethylene for sorption calculated from equation (7) within Santoprene for different thicknesses

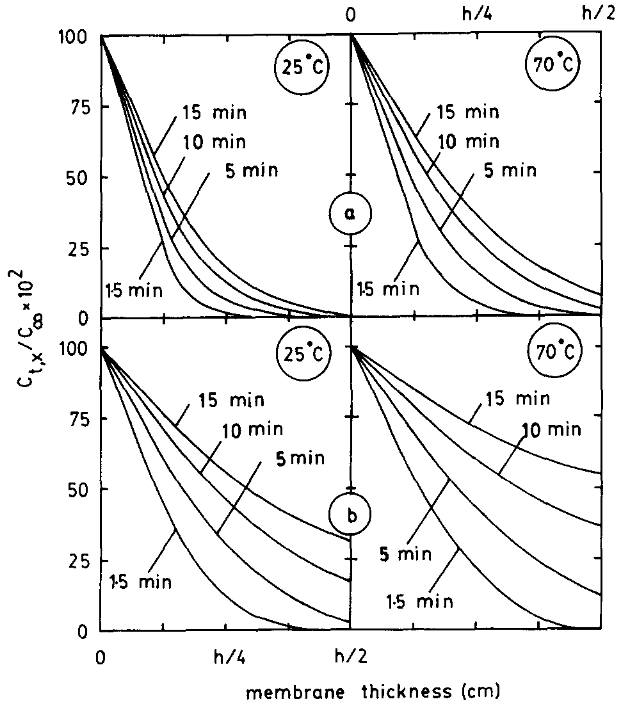

Figure 7 Profiles of the concentration of (a) bromoform and (b) trichloroethylene for sorption calculated from numerical equation (15) for different Santoprene thicknesses at 25 and 70°C

25 and 70°C. Additionally, the effect of temperature shows a significant influence on the shapes of these curves.

Numerical method to calculate concentration profiles

Vergnaud *et al.*$^{8-13}$ developed several numerical schemes using the finite difference method to calculate concentration profiles of liquids developed within membrane materials. Following their procedures, we have computed liquid concentration profiles at various time intervals for different membrane thicknesses (up to the middle of the polymer sample) using the relation^{8}

$$CN_n = \frac{1}{M_n}[C_{n-1} + (M_n - 2)C_n + C_{n+1}] \qquad (15)$$

with the dimensionless parameter, M_n, given as

$$M_n = \frac{(\Delta x)^2}{\Delta t}\frac{1}{D} \qquad (16)$$

In equation (16), for computational purposes, we have divided the polymer membrane thickness into 10 slices of equal size, Δx. Higher number of slices (i.e. up to 100 or even more) can also be used, but, the final results will not be affected. Therefore, we restricted our calculations up to 10 slices only. Each slice is characterized by the integer n. The terms C_n and CN_n are concentrations at position n, at time t and after a lapse of time Δt, respectively. For each slice, liquid concentration curves were obtained at different times. The numerical scheme is also used under conditions of uni-directional diffusion.

Calculated concentration profiles for bromoform and trichloroethylene at 25 and 70°C presented in *Figure 7* show distinct differences depending upon the diffusion values of these liquids. Thus, the concentration profiles exhibit lower values for bromoform than observed for trichloroethylene, a similar trend as observed with the analytical solution discussed before. However, a more distinct behaviour is seen with these liquids for resorption cycles at 25°C, shown in *Figure 8* for different time intervals. Concentration profiles at 25°C for sorption and resorption cycles are displayed in *Figure 9*. These profiles being different, further support the morphological changes in the Santoprene sample as discussed before from the XRD tracings of the methylene dichloride soaked sample (*Figure 2*). It may be noted that in *Figure 9b*, a common curve is shown for 1,1,2,2-tetrachloroethane and bromoform as the calculated concentration profiles for these liquids are quite identical. As the size of haloalkane increases, the concentration profile values are lower, suggesting the slow transport of bigger molecules into the Santoprene network. The same observation is

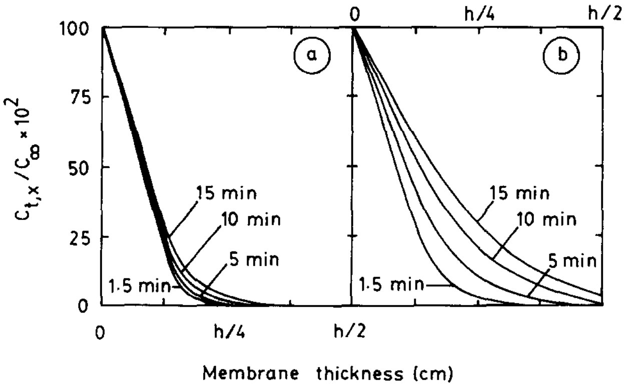

Figure 8 Profiles of the concentration of (a) bromoform and (b) trichloroethylene for resorption using numerical equation (15) for different Santoprene thicknesses at 25°C

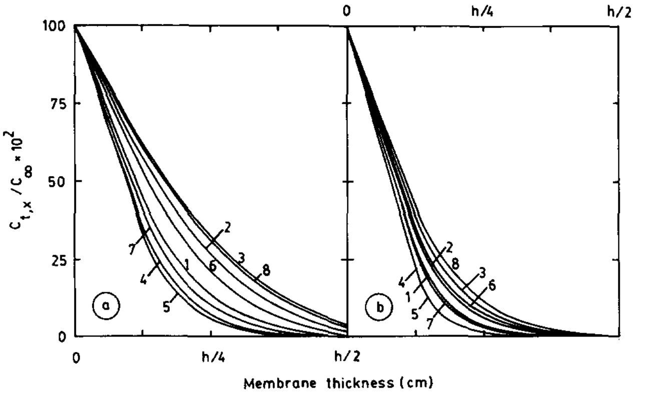

Figure 9 Profiles of the concentration for (a) sorption and (b) resorption at 25°C calculated from numerical equation (15) for different Santoprene thicknesses. The numbers on the curves refer to the same liquids given in *Figure 4*. (A common curve is shown for liquids 4 and 5)

true for resorption (see *Figure 9*), desorption and redesorption cycles, but the curves for the latter two processes are not presented to avoid overcrowding.

Typical experimental sorption curves for carbon tetrachloride, bromoform, 1,1,2,2-tetrachloroethane and tetrachloroethylene at 25 and 70°C are compared in *Figure 10* with the theoretically simulated curves using equation (8). It is observed that in all cases, the agreement is good up to about 55% completion of equilibrium sorption. The deviations at longer sorption times might be attributed to the concentration-dependency of diffusivity. However, this anomaly is not so significant, as noticed by the non-sigmoidal shapes of the sorption curves and the values of n of equation (3) fall in the range 0.50–0.58 (nearer to the expected values observed for Fickian mechanism).

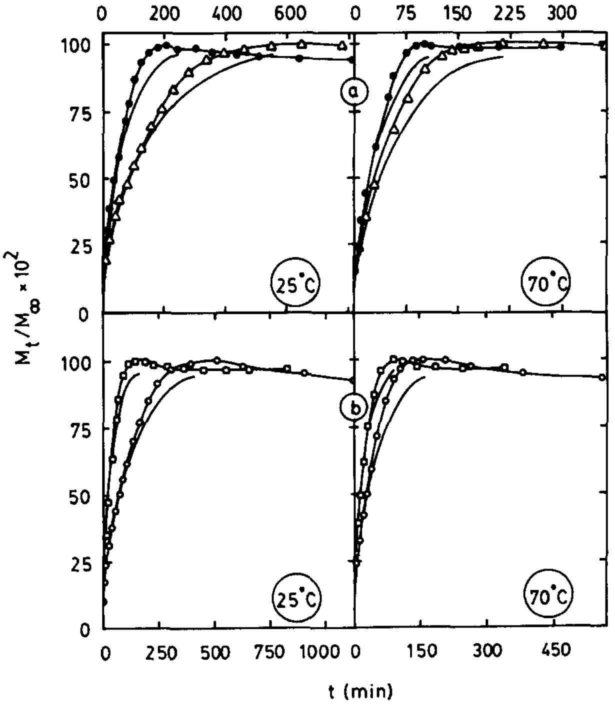

Figure 10 Comparison of experimental sorption curves (points) for (a) (●) carbon tetrachloride and (△) bromoform and (b) (○) 1,1,2,2-tetrachloroethane and (□) tetrachloroethylene with theoretically simulated curves (solid lines) calculated from equation (8)

The rate of evaporation for the desorption and redesorption cycles has been calculated using the initial rate of desorption/redesorption[8]:

$$F_0 = \left(\frac{\mathrm{d}M_t}{\mathrm{d}t}\right) \text{ for } t \longrightarrow 0 \tag{17}$$

These values for the desorption and redesorption runs are given in *Table 3*. It is observed that the rate of evaporation is fast in the case of chloroform, methylene dichloride and trichloroethylene for both desorption/redesorption cycles. For bromoform, it is very slow.

Arrhenius activation parameters

For all liquids, sorption and diffusion results have shown an increase with increasing temperature, but no systematic dependence of these parameters on penetrant size was observed. Diffusion results have been analysed using the Arrhenius relationship,

$$\ln D = \ln D_0 - E_D/RT \tag{18}$$

to estimate the activation energy, E_D, for diffusion. Here, D is a pre-exponential factor and RT has the usual meaning.

A typical plot of log D *versus* $1/T$ is shown in *Figure 11*. Linearity is observed in the investigated range of temperature for all liquids except bromoform. The results of E_D presented in *Table 4* range from 9.3 kJ mol^{-1} for tetrachloroethylene to 21.9 kJ mol^{-1}

Table 3 Rate of evaporation F_0 (cm s^{-1}) for desorption (D) and redesorption (RD) runs

Haloalkanes	*D*	*RD*
Carbon tetrachloride	0.95	0.80
Chloroform	1.53	1.23
Methylene dichloride	1.14	0.74
Bromoform	0.16	0.10
Tetrachloroethylene	0.89	0.26
1,1,1-Trichloroethane	0.64	0.50
Trichloroethylene	0.99	0.82

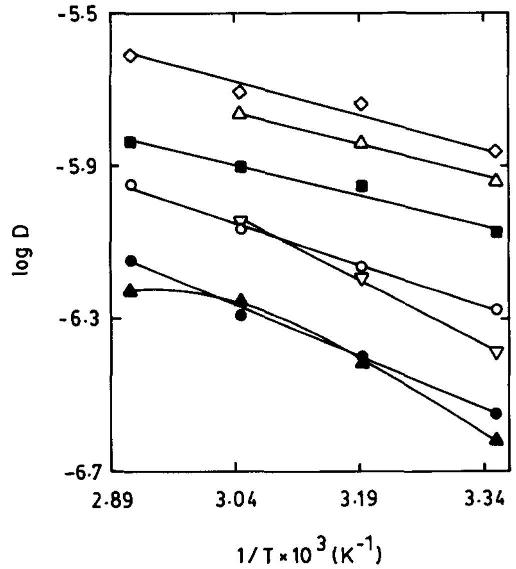

Figure 11 Arrhenius plots of log D *versus* $1/T$ for sorption cycles. The symbols have the same meaning as given in *Figure 1*

Table 4 Activation parameters E_D and ΔH_S (kJ mol^{-1}) for Santoprene + haloalkanes

Haloalkenes	$E_D \pm \sigma$	$\Delta H_S + \sigma$
Carbon tetrachloride	14.0 ± 0.5	7.0 ± 0.8
Chloroform	11.1 ± 0.6	6.1 ± 1.9
1,1,2,2-Tetrachloroethane	16.9 ± 1.2	10.4 ± 1.0
Bromoform	17.5 ± 3.3	7.1 ± 1.3
Tetrachloroethylene	9.3 ± 1.9	6.9 ± 0.6
1,1,1-Trichloroethane	21.9 ± 0.9	6.0 ± 0.1
Trichloroethylene	9.8 ± 2.0	6.5 ± 0.3

σ represents the standard error

for 1,1,1-trichloroethane. The E_D values for bromoform and 1,1,2,2-tetrachloroethane are somewhat comparable. Similarly, results of E_D for tetrachloroethylene and trichloroethylene are comparable. An unsymmetrical molecule like 1,1,1-trichloroethane exhibits a higher value of E_D (21.9 kJ mol^{-1}) than a symmetric carbon tetrachloride, which has an E_D of 14.0 kJ mol^{-1}.

The results of S have been analysed using van't Hoff relationship with a pre-exponential factor, S_0 as

$$S = S_0 \exp(-\Delta H_S/RT) \qquad (19)$$

where ΔH_S is heat of sorption and is a composite parameter depending upon both Henry's law and Langmuir's type sorption. The ΔH_S values for 1,1,2,2-tetrachloroethane are higher (10.4 kJ mol^{-1}) than those observed for other liquids, for which the ΔH_s values range from 6.0 to 7.0 kJ mol^{-1} (*Table 4*). For all systems, the values of ΔH_S are positive, suggesting the sorption process to be dominated by Henry's law sorption mode giving an endothermic contribution.

CONCLUSIONS

This paper presents an analysis of sorption, desorption, resorption, redesorption and diffusion anomalies of haloalkanes into a Santoprene membrane material by the sorption gravimetric method in the temperature interval of 25–70°C. At higher temperatures, an increase in solvent diffusion and the concurrent polymer chain relaxation might have resulted in a higher equilibrium penetrant uptake. Activation energy for diffusion and heat of sorption data have been obtained from a temperature dependence of diffusion and sorption coefficients. Solvent overshoot effects have been associated with the complicated morphology of Santoprene. In the present experimental systems, molecular transport was found to follow the anomalous-type behavior. Diffusion results have been obtained from Fick's equation and the profiles of liquid concentration have been calculated. A numerical method was also used to obtain the concentration profiles and compared with the analytical solutions. These profiles follow the trends exhibited by the diffusion/sorption behaviour of penetrant molecules into polymeric sheet membranes.

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