

# Molecular migration of hazardous liquids into thermoplastic ethylene–propylene random copolymer and isotactic polypropylene membranes

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## Abstract

The molecular migration of hazardous organic halocarbons into thermoplastic polymer blend membranes has been studied using a gravimetric technique. From the sorption results, the diffusion and permeation of liquids have been calculated. Molecular migration depends on the nature of the halocarbons, membrane–solvent interactions, temperature, and availability of free volume within the membrane matrix. The size and the polarity of liquids do not show any systematic effect on sorption and desorption phenomena. The liquid migration results have been analyzed using a Fickian mechanism of sorption and diffusion. A numerical method based on the finite difference approach has been used to compute the liquid concentration profiles in the membrane materials. The estimated Arrhenius activation energy for diffusion and the heat of sorption are indicative of the nature of the liquids and their interactions with the membrane. The rate of evaporation of liquids has been calculated for sorption and desorption runs, and these results depend on the volatility of the halocarbons.

*Keywords:* Diffusion Coefficient; Fickian; Hazardous liquid; Profile; Santoprene

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## 1. Introduction

Increasing scientific concern over the problem of hazardous waste disposal has promoted the study of such fundamental processes as sorption, desorption, permeation

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and diffusion of hazardous chemicals into polymeric barriers. Several experimental methods and theoretical models have been used to assess the resistivity of barrier materials upon exposure to liquids. In most of these, the primary goal has been to estimate the sorption, diffusion and permeation parameters for the membrane–solvent systems. Low molecular weight organic halocarbons released in waste landfills are known to contaminate ground water, soil and air, posing an immediate threat to human health and hygiene [1]. However, the molecular migration of chemicals in the environment is a complex hydrodynamic phenomenon which involves the sorption/desorption and diffusion of liquids into the soil [2].

The use of polymer membranes as liners and storage tanks for hazardous liquids is increasing [3]. In the applications of such membranes as barrier materials, it is important to understand their interactions with organic liquids of environmental concern. This in turn contributes greatly to an understanding of liquid transport phenomena. It is therefore important to study the characteristics of membrane materials in the presence of hazardous liquids before they are used in the field.

In earlier papers from our laboratories [4–7], molecular migration into different types of Santoprene, grades 101-64, 101-80, 103-40 and 201-80, has been studied. In continuation of this program, we now report useful experimental data on the sorption/desorption, diffusion and permeation of Santoprene (sample 201-64) in the presence of carbon tetrachloride, chloroform, methylene dichloride, 1,1,2,2-tetrachloroethane, bromoform, tetrachloroethylene, 1,1,1-trichloroethane and trichloroethylene. A gravimetric method is used to obtain data at 25°C, 40°C, 55°C and 70°C. These results are discussed in terms of the nature of the permeating liquids. Fick's equation has been solved using appropriate boundary conditions to compute the concentration profiles of liquids. Such profiles have also been calculated from a numerical method based on the finite difference approach [8–13]. This approach is useful to predict the liquid concentration profiles within the dense polymer barrier at different times. The present study is thus useful in studying solvent migration into polymers of practical interest and in understanding the resistivity of polymers in field applications involving exposure to hazardous liquids. It is observed that the sorption (S), desorption (D), resorption (RS) and redesorption (RD), i.e., S–D–RS–RD testing of a polymer is important to predict its suitability as a barrier in the chosen chemical environment.

## 2. Experimental

### 2.1. Reagents and materials

Santoprene (sample 201-64) sheet membranes of dimensions 26 cm × 26 cm with initial thicknesses ranging from 0.164 to 0.174 cm were obtained from Advanced Elastomer Systems, St. Louis, MO. Circular polymer samples with diameters ranging from 1.94 to 1.97 cm were cut from large sheets using a sharp-edged carbon tipped steel die. The samples were dried in a vacuum desiccator over anhydrous calcium chloride for about 24 h before experimentation.

The solvents, carbon tetrachloride (Ranbaxy Laboratories Ltd., India), chloroform

Table 1  
Viscosity  $\eta$  (mPa s), dielectric constant  $\epsilon$  and molar volume  $V$  ( $\text{cm}^3 \text{mol}^{-1}$ ) of the solvents at 25°C

Solvent	$\eta$	$\epsilon$	$V$
Carbon tetrachloride	0.90	2.23	97.1
Chloroform	0.54	4.81 <sup>a</sup>	80.7
Methylene dichloride	0.40 <sup>b</sup>	8.93	64.5
1,1,2,2-Tetrachloroethane	1.46 <sup>c</sup>	8.20 <sup>c</sup>	105.8
Bromoform	1.89	4.39 <sup>a</sup>	87.8
Tetrachloroethylene	0.80 <sup>c</sup>	2.28	102.7
1,1,1-Trichloroethane	0.80	7.25 <sup>a</sup>	100.3
Trichloroethylene	0.53	3.42	90.0

<sup>a</sup> At 20°C.

<sup>b</sup> At 27.6°C.

<sup>c</sup> At 30°C.

(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 Chemicals Ltd., India) were doubly distilled before use. Some useful properties of these solvents are given in Table 1.

## 2.2. Sorption / desorption runs

Santoprene samples with initial mass  $W_0 \approx 0.4980$  g were immersed in screw-tight test bottles containing about 15 to 20 ml of the solvents. These samples were then periodically removed, the surface-adhering liquid drops were blotted off by carefully pressing the samples between a filter paper wrap and the samples were again weighed ( $W_t$ ) on a digital Mettler balance, Model AE 240 (Switzerland), within an accuracy of  $\pm 0.01$  mg. For all liquids, equilibrium was reached within 24 h, and this did not change over an extended immersion period of one or two days. After sorption runs, the samples were placed in a vacuum oven maintained at a constant temperature of 25°C and desorption profiles were obtained by a periodic measurement of the decrease in polymer mass until constant mass was attained. The percentage mass gain during solvent sorption and mass loss during desorption runs, in mass% units, have been calculated as described earlier [4–7]. After desorption, the Santoprene samples were immersed again in solvent containers to study resorption in the same manner as for sorption.

## 3. Results and discussion

### 3.1. Sorption / desorption anomaly

During sorption, a mass loss in the polymer occurred. An obvious possibility is that additives in the polymer leached out from the network structure or that there were changes in the polymer morphology. If, after the first sorption and desorption runs, the

polymer releases some of the indigenous additives contributing to polymer mass loss, then no further loss in polymer mass will occur during subsequent resorption and redesorption cycles.

The resorbed samples were placed once again in a vacuum oven for a second desorption. This comparison is useful in testing any loss of additives from the polymer samples. Thus, S–D–RS–RD testing of a polymer in the presence of hazardous liquids is important to judge its suitability in field applications. It is observed that the mass% change in resorption runs is generally higher than the changes observed for absorption runs in all cases. For desorption cycles, the mass% losses are within 3–6% for all liquids. However, the total percentage mass losses in sorption/desorption cycles are higher than those in resorption/redesorption cycles and these data vary within 39–40 mass%. This further suggests that the extraction of additive(s) from the polymer for different liquids (before 55% equilibrium) remains almost the same.

### 3.2. Kinetics of sorption

The initial sorption and desorption results of solvent migration into Santoprene have been analyzed using the empirical relationship [14,15]

$$\frac{M_t}{M_\infty} = Kt^n \quad (1)$$

where  $M_t$  and  $M_\infty$  are the mass uptake values of Santoprene at time  $t$  and at equilibrium. For desorption runs,  $M_t$  and  $M_\infty$  are the mass losses of the drying sample at time  $t$  and the completely dried sample respectively.  $K$  is an empirical parameter signifying the extent of polymer–solvent interactions. The value of exponent  $n$  indicates the type of transport mechanism. Eq. (1) is applicable to all the S–D–RS–RD cycles. The calculated values of  $n$  for sorption and resorption runs (accurate to  $\pm 0.01$  unit) vary between 0.50 and 0.64 unit in the temperature interval 25–70°C, suggesting a slight deviation from Fickian diffusion. The values of  $K$  increase with increasing temperature, which supports the premise of increased polymer–solvent interactions. These values increase from 0.04 to 0.18 over the investigated temperature range. However, no correlation is observed between the magnitude of  $K$  and the nature of the halocarbons employed.

The sorption curves at 25°C, presented in Fig. 1, exhibit overshoot effects. These effects are greater for methylene dichloride, bromoform, chloroform and 1,1,2,2-tetrachloroethane than for other halocarbons. For bromoform and 1,1,2,2-tetrachloroethane, equilibrium sorption was not reached even after 1000 min of continuous immersion, showing the slower transport of these liquids by the polymer when compared with other liquids. This effect is attributed to their high viscosity values. Overshoot effects have also been observed earlier in the literature for other polymer–solvent systems [4–6],[15–18]. Using these results, the percent overshoot index OI is calculated as [15]

$$OI = \frac{M_m - M_\infty}{M_\infty} \times 100 \quad (2)$$

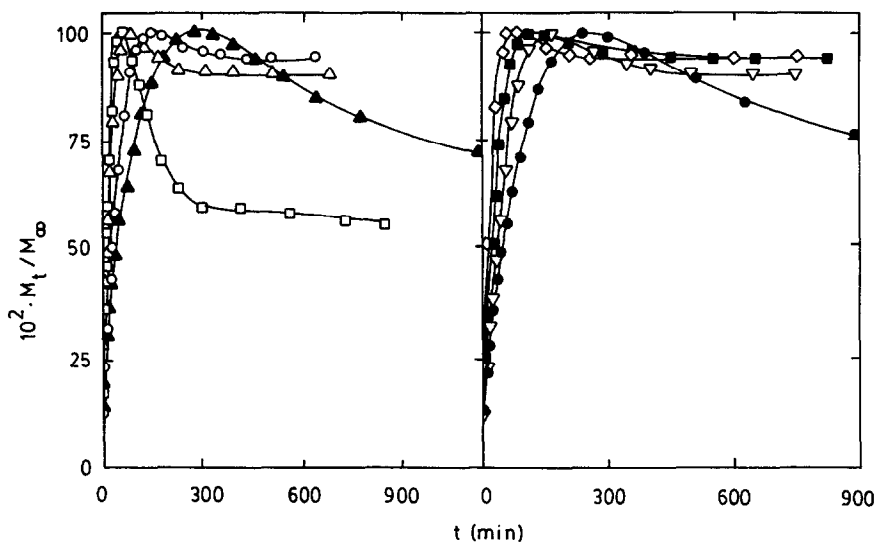


Fig. 1. Sorption curves at 25°C for Santoprene with (O) carbon tetrachloride, ( $\Delta$ ) chloroform, ( $\square$ ) methylene dichloride, ( $\blacktriangle$ ) bromoform, ( $\bullet$ ) 1,1,2,2-tetrachloroethane, ( $\blacksquare$ ) tetrachloroethylene, ( $\nabla$ ) 1,1,1-trichloroethane and ( $\diamond$ ) trichloroethylene.

where  $M_m$  is the maximum uptake for each polymer–liquid system at the specified temperature. The overshoot effects are not observed for desorption, resorption and redesorption cycles with bromoform and tetrachloroethylene (see Fig. 2). The calculated values of OI are given in Table 2.

Methylene dichloride shows the highest value of OI compared with other solvents. The values of OI for carbon tetrachloride, chloroform, tetrachloroethylene, 1,1,1-trichloroethane and trichloroethylene are smaller. For chloroform and 1,1,1-trichloroethane at 25°C, OI values are almost identical. Similarly, carbon tetrachloride and tetrachloroethylene (molecules having almost identical dielectric constants) exhibit identical values of OI. For 1,1,2,2-tetrachloroethane, bromoform and 1,1,1-trichloroethane, the values of OI decrease with increasing temperature. However, the overshoot effects are not observed for desorption, resorption and redesorption runs (Fig. 2). The temperature also affects sorption, as shown in Fig. 3. The initial linear portion of the sorption curves before 55% equilibrium sorption/desorption runs are indicative of Fickian transport (Figs. 1–3).

From the sorption/desorption results, the values of the first order kinetic rate constants  $k_1$  have been calculated as [19]

$$k_1 t = \ln \left[ M_\infty / (M_\infty - M_t) \right] \quad (3)$$

These results are included in Tables 2 and 3. For all liquids, the values of  $k_1$  increase with increasing temperature and decrease with increasing size of halocarbon (Table 2). For 1,1,2,2-tetrachloroethane  $k_1$  is lowest, and for methylene dichloride it is highest. Because of their low boiling points, sorption experiments for methylene dichloride at 40°C, 55°C and 70°C and also for chloroform and 1,1,1-trichloroethane at 70°C have not been performed.

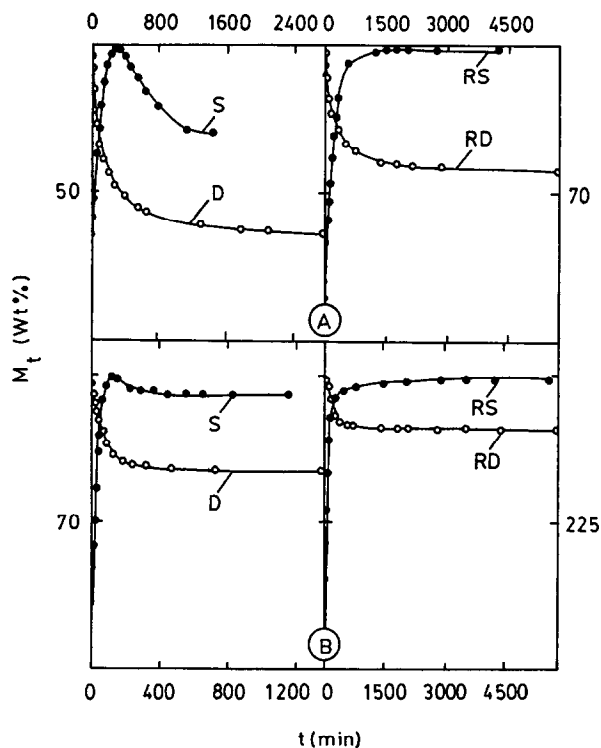


Fig. 2. Sorption (S), desorption (D), resorption (RS) and redesorption (RD) curves at 25°C for (A) bromoform and (B) tetrachloroethylene.

Sorption coefficients  $S$ , calculated in mass% units from the plateau regions of the sorption curves presented in Table 2, depend on the chemical nature of the halocarbons rather than their size. Comparing all the liquids, tetrachloroethylene, trichloroethylene and carbon tetrachloride show higher  $S$ , ranging from 204 for trichloroethylene at 25°C to 283 for tetrachloroethylene at 70°C. However, methylene dichloride shows the lowest sorption of 56% at 25°C. For all halocarbons, sorption increases with increasing temperature. However, the  $S$  values for desorption, resorption and redesorption runs at 25°C included in Table 3 are different compared with those in sorption runs. The general trend in the variation of these results is almost identical to that observed for sorption, except for a few liquids. Also, for all liquids, the resorption uptake values are higher than those observed in sorption, desorption and redesorption runs. The  $S$  values of desorption and redesorption cycles are somewhat similar.

### 3.3. Mathematical treatment of diffusion

Various approaches are available for studying the sorption and desorption curves of polymer–solvent systems [8–13]. These are basically derived from Fick's relationship.

Table 2

Percent overshoot index values OI, kinetic rate constants  $k_1$  ( $\text{min}^{-1}$ ), solubility  $S$  (wt%) and diffusivity  $D$  ( $\text{cm}^2 \text{s}^{-1}$ ) for sorption

Haloalkanes	Temperature ( $^{\circ}\text{C}$ )			
	25	40	55	70
	OI			
Carbon tetrachloride	6.25	6.79	5.98	5.82
Chloroform	10.90	7.41	8.45	– <sup>a</sup>
Methylene dichloride	83.04	– <sup>a</sup>	– <sup>a</sup>	– <sup>a</sup>
1,1,2,2-Tetrachloroethane	33.39	25.01	11.77	8.75
Bromoform	38.98	34.00	25.65	16.94
Tetrachloroethylene	6.19	4.81	5.07	4.74
1,1,1-Trichloroethane	10.43	9.91	6.05	– <sup>a</sup>
Trichloroethylene	5.83	7.56	4.74	4.29
	$k_1 \times 10^2$			
Carbon tetrachloride	2.038	2.685	3.044	3.445
Chloroform	3.817	4.516	5.453	– <sup>a</sup>
Methylene dichloride	5.632	– <sup>a</sup>	– <sup>a</sup>	– <sup>a</sup>
1,1,2,2-Tetrachloroethane	1.273	1.613	1.675	2.290
Bromoform	1.403	1.829	1.963	2.377
Tetrachloroethylene	2.869	3.661	3.992	4.601
1,1,1-Trichloroethane	1.795	2.506	3.320	– <sup>a</sup>
Trichloroethylene	4.552	5.357	5.744	7.120
	$S$			
Carbon tetrachloride	236.56	241.85	258.43	269.07
Chloroform	165.24	169.93	181.75	– <sup>a</sup>
Methylene dichloride	55.56	– <sup>a</sup>	– <sup>a</sup>	– <sup>a</sup>
1,1,2,2-Tetrachloroethane	84.90	101.35	127.35	141.91
Bromoform	98.03	113.66	134.83	161.36
Tetrachloroethylene	247.96	254.37	271.37	283.17
1,1,1-Trichloroethane	144.92	155.28	158.20	– <sup>a</sup>
Trichloroethylene	203.91	215.08	224.47	234.93
	$D \times 10^6$			
Carbon tetrachloride	0.971	1.169	1.389	1.658
Chloroform	1.912	2.417	2.572	– <sup>a</sup>
Methylene dichloride	2.878	– <sup>a</sup>	– <sup>a</sup>	– <sup>a</sup>
1,1,2,2-Tetrachloroethane	0.536	0.682	0.840	0.977
Bromoform	0.571	0.739	0.794	0.871
Tetrachloroethylene	1.357	1.647	1.874	2.088
1,1,1-Trichloroethane	0.800	1.171	1.473	– <sup>a</sup>
Trichloroethylene	2.211	2.483	2.855	3.322

<sup>a</sup> Data not obtained owing to low boiling point of solvents.

### 3.3.1. Sorption:

The uni-directional diffusion coefficient  $D$  of the liquid into a membrane of thickness  $2h$  is calculated from Fick's law with constant diffusivity [20]

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

where  $C$  is the concentration of liquid in the polymer at time  $t$  and position  $x$ . Eq. (4) can be solved by setting the initial and boundary conditions

$$t = 0 \quad -h < x < h \quad C = 0 \quad (5)$$

$$t > 0 \quad x = \pm h \quad C = C_\infty \quad (6)$$

The following assumptions are made.

(1) The thickness of the membrane remains constant during sorption/desorption cycles.

(2) Sorption is controlled by transient diffusion through the membrane thickness with a constant diffusivity.

(3) Desorption is controlled by transient diffusion of liquid through the membrane and evaporation from the surface.

(4) The rate of evaporation is proportional to the difference between the actual concentration of liquid on the membrane surface and the concentration of the liquid on the surface which is at equilibrium with the vapor pressure of the liquid in the surrounding atmosphere, the coefficient of proportionality being the rate of evaporation of the liquid under the same conditions.

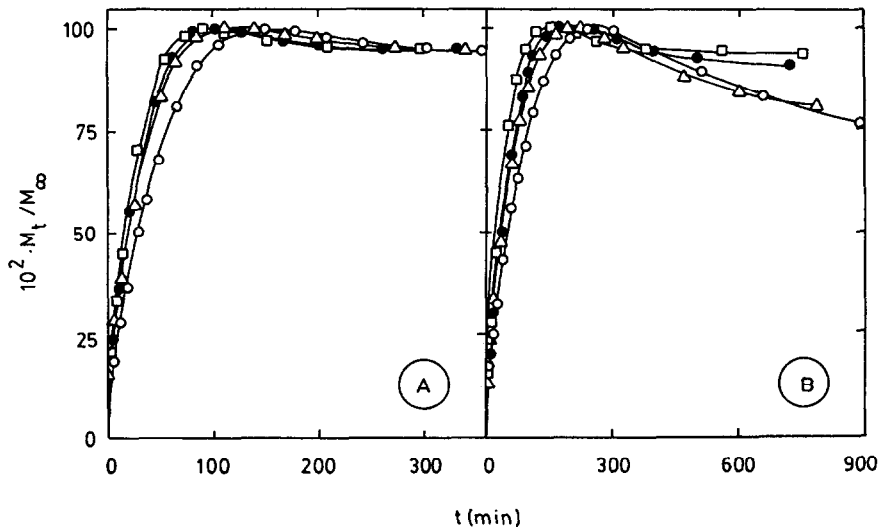


Fig. 3. Sorption curves for (A) carbon tetrachloride and (B) tetrachloroethane at (○) 25°C, (△) 40°C, (●) 55°C and (□) 70°C.



Table 3

Comparison of kinetic rate constants  $k_1$  ( $\text{min}^{-1}$ ), solubility  $S$  (wt%) and diffusivity  $D$  ( $\text{cm}^2 \text{s}^{-1}$ ) for desorption (D)–resorption (RS)–redesorption (RD) runs at 25°C

Haloalkane	D	RS	RD
	$k_1 \times 10^2$		
Carbon tetrachloride	3.211	1.025	1.744
Chloroform	4.785	1.810	3.435
Methylene dichloride	4.808	2.471	4.403
1,1,2,2-Tetrachloroethane	0.207	0.437	0.061
Bromoform	0.671	0.514	0.467
Tetrachloroethylene	1.387	1.113	0.330
1,1,1-Trichloroethane	2.246	0.879	1.979
Trichloroethylene	1.484	2.503	4.694
	$S$		
Carbon tetrachloride	81.49	431.74	82.11
Chloroform	76.14	303.07	76.66
Methylene dichloride	53.87	97.63	50.75
1,1,2,2-Tetrachloroethane	63.53	151.18	59.29
Bromoform	64.57	137.72	60.15
Tetrachloroethylene	81.78	443.79	82.48
1,1,1-Trichloroethane	74.38	286.56	74.82
Trichloroethylene	79.56	392.83	80.57
	$D \cdot 10^6$		
Carbon tetrachloride	2.916	0.285	1.790
Chloroform	3.778	0.536	2.948
Methylene dichloride	2.587	0.598	2.018
1,1,2,2-Tetrachloroethane	0.101	0.100	0.189
Bromoform	0.304	0.126	0.175
Tetrachloroethylene	1.159	0.252	0.217
1,1,1-Trichloroethane	1.832	0.224	1.703
Trichloroethylene	1.269	0.655	0.866

(5) During sorption, the concentration of liquid on the membrane surface reaches equilibrium as soon as it comes into contact with the liquid, and diffusion is considered to be uni-directional.

The solution of Eq. (4) is then

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

where  $C_{x,t}$  is the liquid concentration in the polymer at time  $t$  and position  $x$  and  $C_\infty$  is the concentration within the membrane after infinite time.

The kinetics of sorption are obtained by integrating the concentration with respect to space within the membrane to give

$$\frac{M_{\infty} - M_t}{M_{\infty}} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-\frac{(2n+1)^2 \pi^2}{4h^2} Dt\right] \quad (8)$$

where  $M_t$  and  $M_{\infty}$  have the same meanings as discussed before and  $n$  is an integer.

For short times, i.e., when  $M_t/M_{\infty} < 0.55$ , the following equation is used

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

Thus, by plotting liquid uptake vs. (time)<sup>1/2</sup>, a straight line is obtained initially in the majority of cases and the diffusivity can be calculated from Eq. (9). These results are presented in Table 2.

### 3.3.2. Desorption

For desorption, it is important to calculate the rate of mass loss of the membrane due to solvent evaporation [8]

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

where  $F_0$  is rate of evaporation of pure solvent under the same conditions,  $C_0$  is the actual concentration of the liquid on the membrane surface, and  $C_{\text{ext}}$  is the concentration on the surface which is at equilibrium with the surrounding environment. The gradient of concentration on the surface is calculated by solving Eq. (10) to give [8]

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

where the  $\beta_n$  values are the positive roots of

$$\beta \tan \beta = M \quad (12)$$

with the dimensionless parameter  $M$  given by

$$M = \frac{hF_0}{D} \quad (13)$$

The total amount of liquid  $M_t$  leaving the polymer after time  $t$  is expressed as a fraction of the corresponding quantity after infinite time using

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

In order to solve Eq. (14), the values of  $\beta_n$  were taken from the literature [8]. The diffusivity was then calculated for long times, when only the first term of the series is considered to give

$$\ln\left(\frac{M_{\infty} - M_t}{M_{\infty}}\right) = \left(\frac{\beta^2}{h^2}\right) Dt + \ln\left[\frac{2h^2}{\beta^2 (\beta^2 + M^2 + M)}\right] \quad (15)$$

However, it is possible to calculate the value of the diffusion coefficient from Eq. (15) by an iterative procedure if the rate of evaporation is known.

The rate of evaporation is determined from the kinetics of evaporation of the liquid at the beginning of the process when the initial concentration is uniform. The boundary condition is that the rate of evaporation of the vapor out of the membrane surface is equal to the rate of transport of the liquid by diffusion through the membrane near the surface per unit area

$$-D \left( \frac{\partial C}{\partial x} \right)_{\text{surface}} = F_0 (C_0 - C_{\text{ext}}) \quad (16)$$

Thus, at the beginning of the process, for  $t \rightarrow 0$ , the initial rate of evaporation is

$$\left( \frac{dM_t}{dt} \right)_{t=0} = F_0 (C_0 - C_{\text{ext}}) \quad (17)$$

so that

$$F_0 = \frac{(dM_t/dt)}{C_0 - C_{\text{ext}}} \quad (18)$$

This equation is useful to determine the rate of evaporation of the liquid when the concentration  $C_0$  on the surface is known.

The results for  $D$  at 25°C, 40°C, 55°C and 70°C for sorption and for D–RS–RD cycles at 25°C are given in Tables 2 and 3 respectively. The values of  $D$  are different for the sorption/desorption cycles. The values of  $D$  for the process of sorption increase with increasing temperature for all liquids and do not show any dependence on the size of the liquids. For instance, 1,1,2,2-tetrachloroethane and bromoform exhibit considerably smaller values of  $D$  than the other liquids for the S–D–RS–RD runs. For carbon tetrachloride, chloroform and methylene dichloride, the desorption and redesorption values are higher than for the other liquids. However, in the case of RS runs, higher values of  $D$  are observed for chloroform, methylene dichloride and trichloroethylene. Molecular diffusion of organic solvents into the membranes is dependent upon several factors [21–23] such as: (i) porosity or the area available for free diffusion, (ii) the constriction resulting from alternately small and large pores in the transport path, (iii) the constriction resulting from the very close approach of the boundaries of the limiting pore within the transport path, and (iv) the tortuosity imparted by the membrane material. The diffusion of solvent molecules into the dense polymer expands the network matrix and thereby weakens the molecular interaction between the neighboring polymer segments. A highly crosslinked polymer inhibits diffusion of liquid molecules more than a linear uncrosslinked polymer.

In addition to the above mentioned factors, liquid viscosity  $\eta$  and dielectric constant  $\epsilon$  show an effect on the transport coefficient. For instance, molecules like bromoform and 1,1,2,2-tetrachloroethane with high viscosities exhibit lower diffusivities. However, the dependence between molecular size and diffusivity is noted. For larger molecules such as 1,1,2,2-tetrachloroethane, the values of  $D$  are lowest in all the S–D–RS–RD runs, and the  $D$  for this molecule is slightly higher than that observed for bromoform in

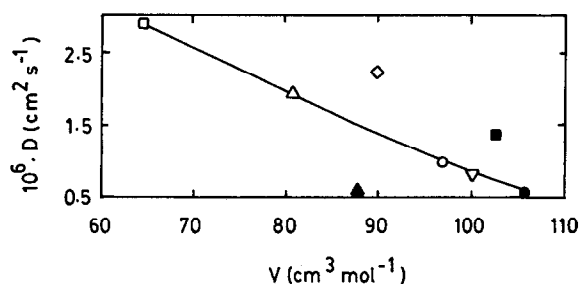


Fig. 4. Dependence of molar volume  $V$  on diffusivity  $D$  for Santoprene + halocarbons. Symbols have the same meaning as in Fig. 1.

the RD cycle. A trend of molar volume on diffusivity does exist as shown in Fig. 4. This trend is also documented in the literature for molecular diffusion in water [24] and is expected from physical chemistry concepts. Larger molecules have shorter mean free paths and lower mean velocities for Brownian motion to take place.

### 3.4. Numerical analysis

In application areas, especially when storing liquids in polymer containers, it is very important to know the depth of penetration of the liquid into the container's polymeric material. The liquid concentration profiles at different penetration depths from the surface of the polymer samples have been calculated [8–12] from the analytical solution

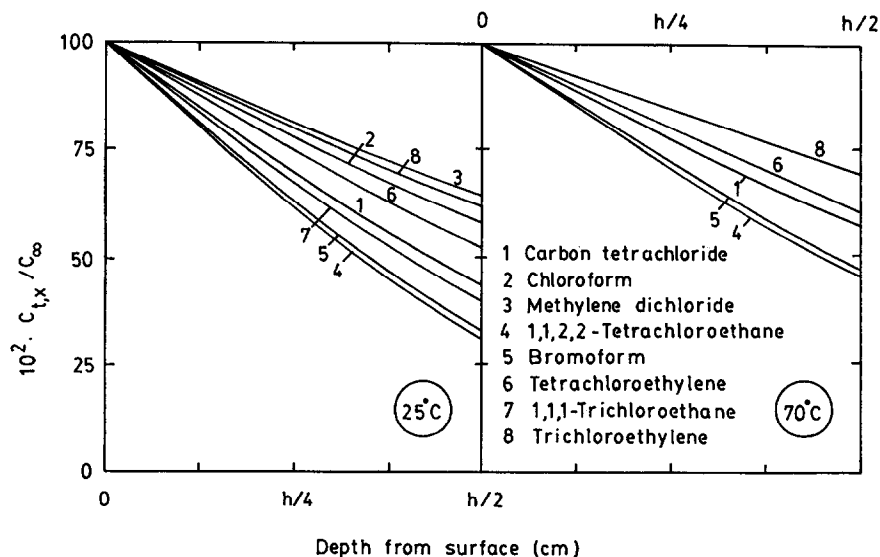


Fig. 5. Liquid concentration profiles at different penetration depths from the surface of Santoprene calculated from Eq. (7) for sorption of halocarbons at 25°C and 70°C for 2 min.

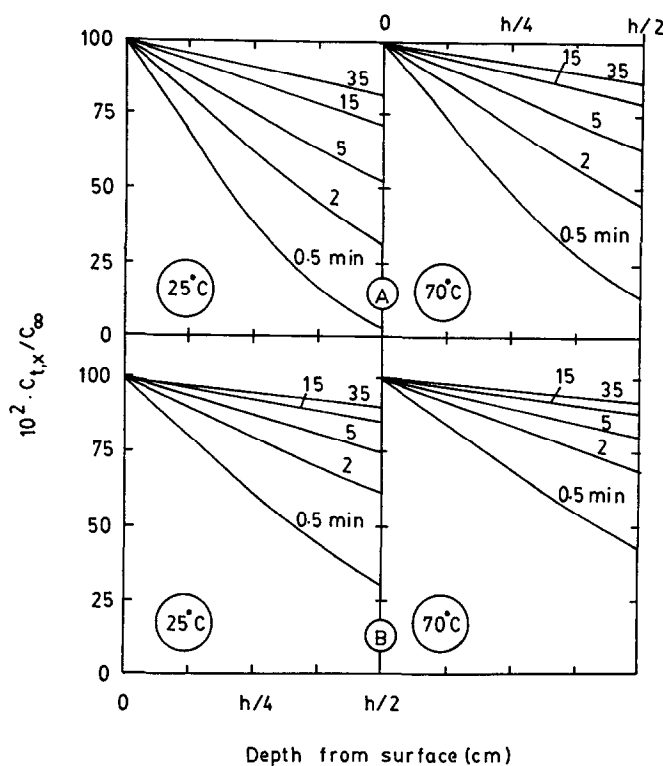


Fig. 6. Liquid concentration profiles of (A) 1,1,2,2-tetrachloroethane and (B) trichloroethylene at different penetration depths from the surface of Santoprene calculated from Eq. (7) at 25°C and 70°C.

of Eq. (7). These profiles for the earliest 2 min of sorption at 25°C and 70°C are presented in Fig. 5. The curves exhibit different shapes depending on the nature of the liquid, the diffusion coefficient and the temperature. For instance, at 70°C, owing to higher diffusivity, the concentration profiles are higher and more narrowly spaced than those observed at 25°C. This is due to a slower transport rate at lower temperatures. The concentration profiles of chloroform, methylene dichloride and 1,1,1-trichloroethane at 70°C are not included in Fig. 5, as these liquids are more volatile at high temperature.

To display the effects of diffusivity and temperature, two liquids are chosen: one is 1,1,2,2-tetrachloroethane, which has lower diffusivity, and the other is trichloroethylene, having higher diffusivity. The plots at 25°C and 70°C are compared in Fig. 6. It is observed that for 1,1,2,2-tetrachloroethane, the concentration profiles are more widely spaced (owing to lower transport rates) than for trichloroethylene, which is the smaller molecule. Similar effects are observed with temperature. For instance, the concentration profiles at 25°C are more widely spaced than those at 70°C, suggesting higher diffusivity with increasing temperature.

The computed values of liquid concentration profiles for various time intervals and for different penetration depths from the surface of the polymer along the direction of its

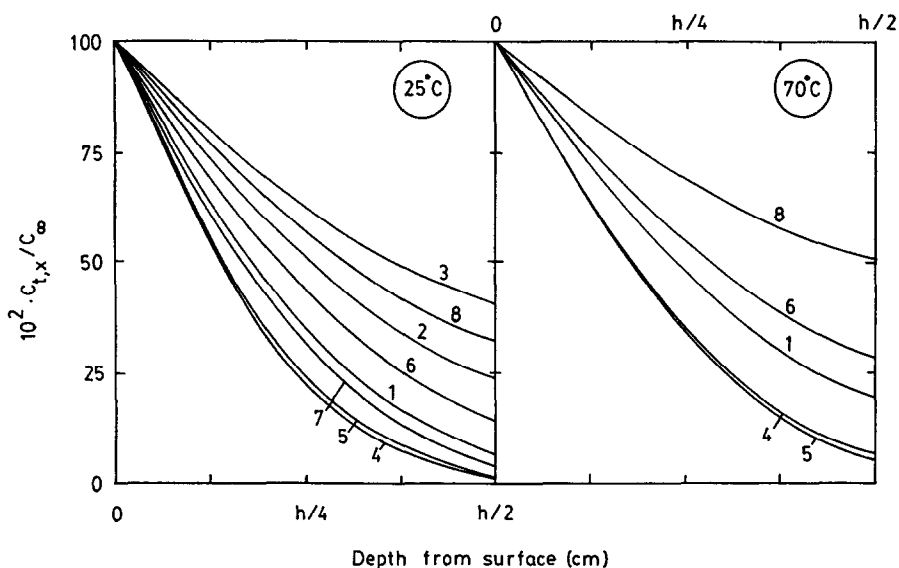


Fig. 7. Liquid concentration profiles at different penetration depths from the surface of Santoprene calculated from Eq. (19) for sorption of halocarbons at 25°C and 70°C for 10 min.

thickness have been calculated from the following relationship, which is based on the finite difference method [8–12]

$$CN_m = \frac{1}{M_m} [C_{m-1} + (M_m - 2)C_m + C_{m+1}] \quad (19)$$

with the dimensionless parameter  $M_m$  given by

$$M_m = \frac{(\Delta x)^2}{\Delta t} \frac{1}{D} \quad (20)$$

In Eq. (20), the polymer thickness is divided into 10 slices of equal size  $\Delta x$ , each slice being characterized by the integer  $m$ . The parameters  $C_m$  and  $CN_m$  are the concentrations at position  $m$  at time  $t$  and after a lapse of time  $\Delta t$ , respectively. For each slice, the liquid concentration profiles are generated for different time intervals. The simulated concentration profiles for trichloroethylene and 1,1,2,2-tetrachloroethane at 25°C and 70°C presented in Fig. 7 for different time intervals exhibit distinct differences depending upon the  $D$  values of the liquids, and this trend is similar to the one observed using Eq. (7) (Fig. 6).

To test the validity of the diffusion data, the experimental uptake curves with the calculated profiles for sorption and desorption cycles calculated from Eq. (8) at 25°C for sorption of 1,1,1-trichloroethane and trichloroethylene are compared in Fig. 8. For the initial sorption uptake, a good agreement is observed between the theoretical curves and the experimental data points, suggesting the validity of the method used to calculate  $D$  from Eq. (9).

### 3.5. Temperature effects

Diffusion and sorption results exhibit a systematic increase with increasing temperature. This is attributable to the increased segmental movements of the polymer. Diffusion results are analyzed using the Arrhenius relationship

$$\ln D = \ln D_0 - E_D/RT \quad (21)$$

where  $E_D$  is the activation energy for diffusion,  $D_0$  is a pre-exponential factor and  $RT$  has the conventional meaning of energy. The values of  $E_D$  and  $D_0$  have been calculated from the linear least-squares fit of the plot of  $\log D$  vs.  $1/T$  (not presented graphically). Linearity is observed for all the liquids in the investigated temperature interval. The values of  $E_D$  range from 7.7 to 16.6 kJ mol<sup>-1</sup>, and depend upon the nature of the halocarbons (see Table 4). For instance, the values of  $E_D$  for bromoform and trichloroethylene are the same. However, the calculated values of  $E_D$  do not show any dependence on the size of the halocarbons. Identical values of  $E_D$  are also found for tetrachloroethylene and chloroform. An asymmetrical molecule like 1,1,1-trichloro-

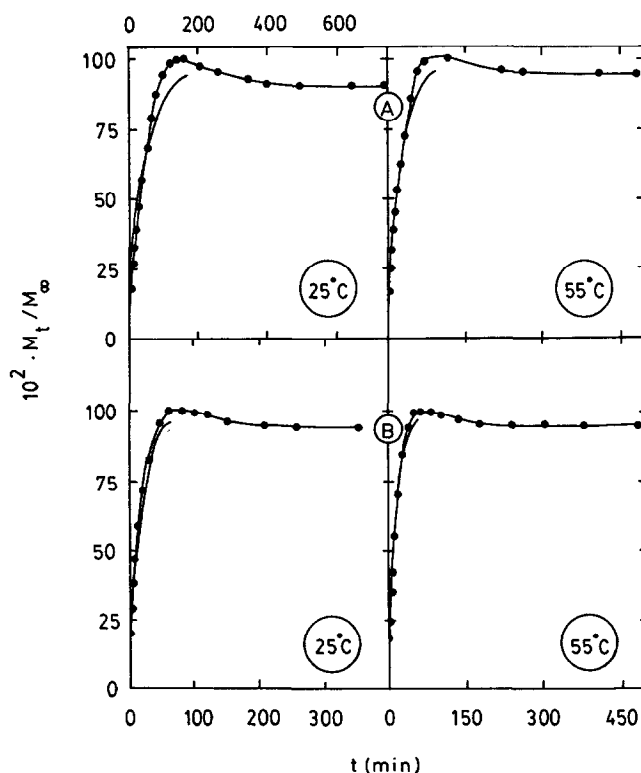


Fig. 8. Comparison of experimental sorption curves (points) for (A) 1,1,1-trichloroethane and (B) trichloroethylene with theoretically simulated curves (solid lines) calculated from Eq. (8).

Table 4

Rate of evaporation  $F_0$  ( $\text{g cm}^{-2} \text{s}^{-1}$ ) for desorption (D) and redesorption (RD) runs and activation energy for diffusion  $E_D$  ( $\text{kJ mol}^{-1}$ ) and sorption  $\Delta H_S$  ( $\text{kJ mol}^{-1}$ ) for Santoprene + haloalkane systems

Haloalkane	$F_0$		$E_D \pm \sigma$	$\Delta H_S \pm \sigma$
	D	RD		
Carbon tetrachloride	1.767	0.931	$10.1 \pm 0.3$	$2.6 \pm 0.4$
Chloroform	2.318	1.815	$8.1 \pm 1.5$	$2.6 \pm 0.7$
Methylene dichloride	1.669	1.338	$11.4 \pm 0.5$	$10.1 \pm 0.8$
Bromoform	0.290	0.191	$7.7 \pm 1.5$	$9.4 \pm 0.6$
Tetrachloroethylene	0.832	0.206	$8.1 \pm 0.6$	$2.6 \pm 0.3$
1,1,1-Trichloroethane	1.083	0.944	$16.6 \pm 1.0$	$2.4 \pm 0.7$
Trichloroethylene	0.816	0.554	$7.7 \pm 0.5$	$2.7 \pm 0.1$

ethane exhibits a higher  $E_D$  than the symmetrical carbon tetrachloride. The  $E_D$  results for carbon tetrachloride and 1,1,2,2-tetrachloroethane are virtually identical.

The results of  $S$  have been analyzed using a van't Hoff equation with a pre-exponential factor  $S_0$

$$\ln S = \ln S_0 - \Delta H_S/RT \quad (22)$$

where  $\Delta H_S$  is the heat of sorption which a composite parameter depending on both Henry's law and a Langmuir-type sorption. In the present systems, the  $\Delta H_S$  values are positive, suggesting the dominance of Henry's law with an endothermic contribution. The  $\Delta H_S$  values for carbon tetrachloride, chloroform, trichloroethylene, tetrachloroethylene and 1,1,1-trichloroethane are almost identical (see Table 4). However, higher  $\Delta H_S$  values of 9.4 and 10.1  $\text{kJ mol}^{-1}$  are observed for bromoform and 1,1,2,2-tetrachloroethane respectively.

#### 4. Conclusions

In the present study, sorption/desorption experiments have been performed to study the interactions of halocarbons with a Santoprene membrane in view of the importance of the membrane in a variety of engineering applications. The results suggest that effective diffusion coefficients of halocarbons in Santoprene when used as a barrier are dependent on several factors, such as the nature of the material, its compatibility with the penetrants, and also their chemical characteristics. The contact times used to generate the sorption curves typically ranged from 1 to 3 days. The influence of solvent structure on sorption/desorption kinetics may impact on the modeling of the transport phenomena and the fate of organic contaminants in the subsurface. The present results also have implications concerning the rate-limiting mechanisms responsible for non-equilibrium sorption of organic solvents. A method describing the penetration of liquids on the sorption/desorption kinetics has been presented. The measured sorption data compare well with those predicted from Fick's relationship. The mechanism responsible for the impact of the solvent on sorption kinetics is postulated to involve changes in polymer conformation, which might be induced by changes in solvent polarity.



Diffusive mass transport of halocarbons within Santoprene, the apparent cause of the observed overshoot effects in some cases, are affected by changes in the morphology of the polymer. This interpretation is based on indirect experimental data and on the inferred similarity to other polymer–solvent systems. However, substantiation of these postulates awaits direct molecular-scale investigation. Because contamination and remediation in the natural environment occur over very long periods, such long-term equilibrium and rate phenomena are important. The experimental results reported in this paper may have implications for modeling the fate of organic pollutants and their transport in the subsurface, and also for the proper design of the associated laboratory experiments in hazardous waste application areas.

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