

Resistivity and dimensional stability of high-performance engineering thermoplastic blend of ethylene–propylene random copolymer and isotactic polypropylene membrane in the presence of hazardous haloalkanes

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Abstract

This study addresses the solvent transport characteristics of eight haloalkanes which are considered to be hazardous liquids into the engineering copolymeric blend membrane consisting of ethylene–propylene random copolymer and isotactic polypropylene. The sorption/desorption kinetic curves obtained at different temperatures have been used to estimate the diffusion coefficients of the liquids into the matrix materials. These results have been discussed in terms of physical parameters such as size of the molecule, polarity, and the structure. The liquid concentration profiles have been obtained from the analytical solutions of the Fick's equation. These curves are compared with the model simulation results based on the finite difference method. The average values of diffusion coefficients have also been calculated to investigate their dependency on concentration. Overshoot effects, activation energies for diffusion, heats of sorption, and the values of the rates of evaporation were obtained to assess the solvent resistivity and dimensional stability of the barrier polymer in application areas involving exposure to hazardous solvents.

Keywords: Haloalkanes; Ethylene–propylene; Polypropylene; Solvent transport.

1. Introduction

Many instances of groundwater contamination by chlorinated solvents, haloalkanes, and other man-made chemicals have been reported [1–3]. Of the identified organic contaminants in subsurface drinking water supplies, halogenated organic chemicals have been detected at the highest levels of concentrations and with the

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greatest frequency [4]. Because of slow rates of subsurface transport, additional cases of groundwater contamination are likely. The transport, distribution, and fate of organic contaminants in both groundwater and surface water are known to be highly dependent on their sorptive interactions with soils, sediments, and aquifer solids. However, when the polymeric materials are used as liner materials in hazardous waste pond applications or even as containers to transport hazardous/aggressive chemicals, the solvent interactions with the barrier material needs to be evaluated before their successful field applications.

There is a growing body of literature evidence that sorption and desorption of liquids in polymeric barrier materials may not reach equilibrium within the time scales characteristics of solvent transport and that sometimes longer times are required to reach equilibrium [5]. Therefore, sorption/desorption rate limitations of organic chemicals into the polymeric materials are important [5–12]. The research described in this paper focuses on the sorption/desorption of the haloalkanes by the use of a gravimetric method, with particular emphasis on evaluating the long-term sorptive uptakes. The procedures used and the results obtained may find applications in using polymers as barrier membranes.

The barrier polymer selected for the study is a thermoplastic blend of ethylene-propylene random copolymer and isotactic polypropylene, also called Santoprene. The commercial rationale that favors the development of such materials via blending versus polymerization is well documented [13]. While not unique, these polymers are uncommon in that they form a miscible (i.e., single-phase) blend. Moreover, Santoprene is used in a wide variety of industrial and engineering areas. Its use includes hose connectors, pump-related gaskets, plugs, expansion joints, submersible cable, filter, and pump seals. The acceptability of Santoprene ultimately depends on its performance characteristics in the presence of aggressive solvent media as regards to retaining its dimensional stability and resistivity. However, a good knowledge about the transport of a liquid controlled by diffusion with subsequent changes in polymer dimension is of great interest, either from a practical or from a fundamental point of view.

In continuation of our ongoing program of research on solvent resistivity and dimensional stability of engineering polymers [6–11], we present new experimental results on sorption, desorption, and diffusion characteristics of Santoprene rubber (Grade #201-80) in the presence of carbon tetrachloride, chloroform, methylene dichloride, 1,1,2,2-tetrachloroethane, bromoform, tetrachloroethylene, 1,1,1-trichloroethane, and trichloroethylene. The liquids chosen have widespread applications in petrochemical and other industries. Experiments have been performed at 25, 40, 55, and 70 °C in order to simulate the field application conditions and, at the same time, to study the dimensional response and solvent resistivity of the barrier material under different solvent exposure conditions. Activation parameters have been evaluated for the transport processes. The concentration profiles of liquid components into the polymeric blend material have been obtained from a solution of the Fick's relation and compared with the profiles obtained from a numerical method based on the finite difference method. Diffusion results and activation parameters have been explained in terms of the concentration profiles for different liquids.

2. Experimental

Thermoplastic sheets of Santoprene (sample #201-80) were procured from Advanced Elastomer Systems, St. Louis, Missouri, in dimensions of 26 cm × 26 cm having the initial thicknesses ranging from 0.150 to 0.160 cm. The elastomer is blended with a plastic material in an extruder while simultaneously invoking free radical crosslinking reactions through addition of peroxide. There are several grades of these materials with varying proportions of the components, degree of crosslinking achieved, nature of any fillers added plus, of course, the basic composition and characteristics of the main components of the blend.

Circular disc-shaped test samples were cut with diameters ranging from 1.97 to 1.98 cm from large Santoprene sheets. The cut test samples were dried in vacuum desiccator over anhydrous calcium chloride at least for 24 h before experimentation. The reagent grade target liquids, viz., 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) were double-distilled before use.

Dried Santoprene test samples weighing (W_0) \approx 0.4600 g were immersed in screw-tight test bottles containing 20–30 ml of solvents. The samples were removed at periodic intervals, the surface adhered liquid drops were blotted off by pressing the samples in between filter paper wraps and weighed (W_t) on a digital Mettler balance, Model AE 240 (Switzerland) to an accuracy of ± 0.01 mg. Samples reached equilibrium saturation within 24 h which did not change significantly over a further period of 2 or 3 days. The weight gain during solvent sorption and weight loss during desorption were calculated in the conventional manner [9–11]. After desorption, the resorption runs were made under the same experimental conditions.

Data for each solvent–polymer pair at different temperatures and time intervals were recorded and filed in the computer for subsequent analysis. If the polymer does not show a mass loss during sorption and desorption, the initial mass of the polymer and mass after desorption should be the same. In the present investigation, some polymer mass loss occurred during sorption runs. This might have been due to loss of indigenous additives from the polymer. After complete sorption, for the subsequent resorption runs, no weight loss of the polymer occurred.

The resorbed samples were placed once again in vacuum for a second desorption. Any difference between the mass loss after redesorption indicates continued mass loss during resorption. This comparison is another way of determining the extent of continuous loss, if any, during the sorption/desorption cycles. The wt% changes in resorption experiments are generally higher than those observed in sorption. For desorption and redesorption runs, the wt% changes are the same for all liquids. However, the total percent weight losses in sorption–desorption cycles are slightly higher than resorption–redesorption cycles.

3. Results and discussion

The results of solvent migration into Santoprene matrix have been analyzed using the relation [14]

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

where M_t is the mass of solvent sorbed at time t , M_∞ represents the property at equilibrium saturation, and K is an empirical parameter which depends on the polymer structure in addition to polymer–solvent interactions. The exponent value of n is indicative of the type of transport mechanism. Eq. (1) is applicable to sorption/resorption/desorption/redesorption results initially, i.e., before the attainment of 55% of sorption or desorption equilibrium saturation. For desorption runs, M_t and M_∞ are the mass losses of the drying samples at time t and the completely dried samples, respectively. The values of n for sorption and resorption runs are accurate within ± 0.01 and varied between 0.50 and 0.64 over the temperature interval of 25–70 °C. This suggests that the diffusion follows the anomalous behavior [6–11]. However, the values of K increased with increasing temperature suggesting the increased polymer–solvent interactions. These values ranged from 0.04 to 0.18 for the systems of this study and their magnitudes did not show any dependence on the size of the solvent molecules.

The sorption breakthrough curves presented in Fig. 1 at 25 °C, exhibit the overshoot effects. The overshoot effect is more noticeable in case of methylene dichloride,

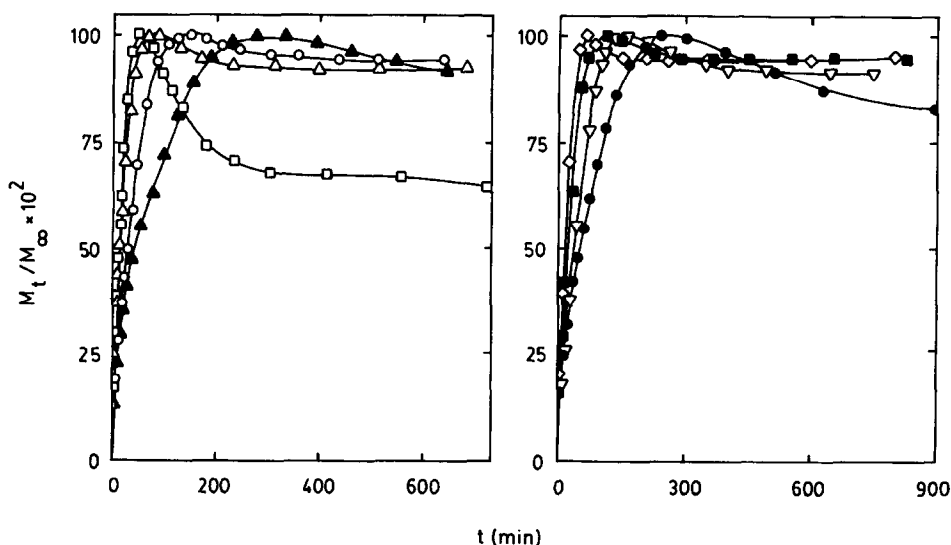


Fig. 1. Sorption curves at 25 °C for Santoprene with (○) carbon tetrachloride, (△) chloroform, (□) methylene dichloride, (▲) bromoform, (●) 1,1,2-tetrachloroethane, (■) tetrachloroethylene, (▽) 1,1,1-trichloroethane and (◇) trichloroethylene.

bromoform, chloroform, and 1,1,2,2-tetrachloroethane than other liquids. Such effects might be due to the aggressive interactions of these solvents with the Santoprene chain segments thereby affecting the equilibrium weight loss of samples [9–11, 14–16]. Among the liquids tested, bromoform and 1,1,2,2-tetrachloroethane required longer breakthrough times than others.

In order to get a comparative picture, the percent overshoot index, OI, was calculated as [14]

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

where M_m is the maximum uptake. The calculated values of OI are given in Table 1. However, overshoot effects were not observed for desorption, resorption, and re-desorption cycles as shown for chloroform and trichloroethane in Fig. 2. A smaller methylene dichloride molecule has a OI of 59 at 25 °C. On the other hand, the OI values are smaller for carbon tetrachloride, chloroform, tetrachloroethylene, 1,1,1-trichloroethane, and trichloroethylene. The values of OI for tetrachloroethylene and trichloroethylene at 25 °C are identical, but these values differ at higher temperatures. However, in case of 1,1,2,2-tetrachloroethane and 1,1,1-trichloroethane, OI values showed a decrease with increasing temperature but, no systematic effect was observed for bromoform with increasing temperature. Such effects could be attributed to changes in polymer chain conformation.

The temperature showed significant effects on the shapes as well as equilibrium values of breakthrough curves (see Fig. 3). However, the initial linear portions of breakthrough curves indicate that transport is of the Fickian nature. Sorption coefficients, S , expressed in wt% units have been calculated from the plateau regions of the breakthrough curves. The data presented in Table 2 show a dependence on the nature of the haloalkanes as well as their sizes. The sorption of chloroform at 70 °C and 1,1,1-trichloroethane, and similarly that of methylene dichloride at 40, 55, and 70 °C were not obtained due to their low boiling temperatures. Among all the liquids,

Table 1
Percent overshoot index values at different temperatures for Santoprene + haloalkanes

Haloalkanes	Temperature (°C)			
	25	40	55	70
Carbon tetrachloride	5.88	4.90	2.90	2.76
Chloroform	7.58	6.21	7.42	^a
Methylene dichloride	59.01	^a	^a	^a
1,1,2,2-tetrachloroethane	23.52	21.72	11.23	11.88
Bromoform	13.97	17.12	17.19	13.70
Tetrachloroethylene	4.61	4.43	2.96	2.74
1,1,1-trichloroethane	8.98	8.03	5.58	^a
Trichloroethylene	4.62	5.60	4.29	2.99

^a Data not obtained due to their high volatility.

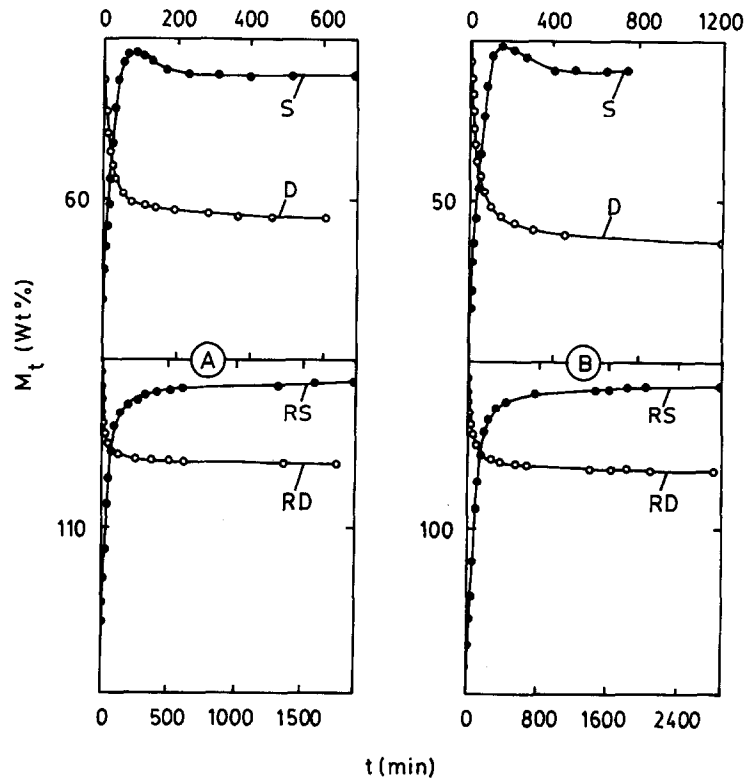


Fig. 2. Sorption (S), desorption (D), resorption (RS) and redesorption (RD) curves at 25 °C for (A) chloroform and (B) 1,1,1-trichloroethane.

methylene dichloride showed the highest S , whereas 1,1,2,2-tetrachloroethane has the lowest S value varying in the range 66–110 wt%. In all cases, S increases with increasing temperature. The S values for desorption, resorption, and redesorption runs at 25 °C are given in Table 3. The S values for desorption runs are generally lower than sorption results (see Table 2). For instance, carbon tetrachloride and tetrachloroethylene showed almost identical values for sorption and desorption runs. Methylene dichloride having the highest sorption value of 436 exhibited the lowest desorption values of 49. The intermediary values are observed for the remaining haloalkanes in the sorption/desorption cycles. The resorption uptake values are also generally higher than the sorption, desorption, and redesorption data for all the systems. However, the results of desorption and redesorption are almost identical, exhibiting the identical desorption mechanisms for the Santoprene–haloalkanes systems.

Diffusion coefficients, D , of the polymer–solvent systems are important in order to know the resistivity of the barrier material to the presence of aggressive liquids. Several procedures are available to calculate D of the solvent–polymer systems. The

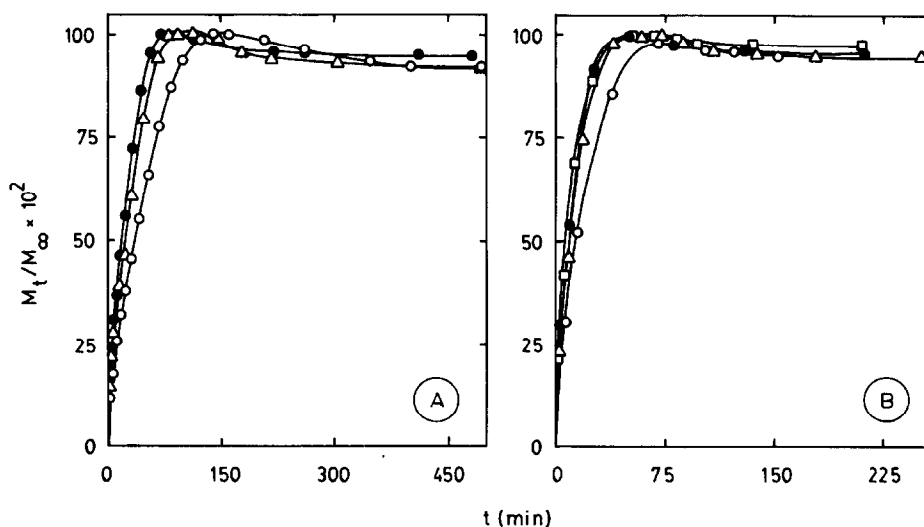


Fig. 3. Sorption curves for (A) 1,1,1-trichloroethane and (B) trichloroethylene at (○) 25 °C, (△) 40 °C, (●) 55 °C and (□) 70 °C.

Table 2
Solubility (*S*) and diffusivity (*D*) for sorption

Haloalkanes	Temperature (°C)			
	25	40	55	70
	<i>S</i> (wt%)			
Carbon tetrachloride	166.93	171.92	186.87	201.97
Chloroform	114.21	119.66	136.51	^a
Methylene dichloride	436.22	^a	^a	^a
1,1,2,2-tetrachloroethane	66.04	76.57	86.09	109.98
Bromoform	86.20	96.84	115.10	133.45
Tetrachloroethylene	166.44	181.64	194.45	205.75
1,1,1-trichloroethane	98.31	109.07	114.55	^a
Trichloroethylene	142.62	154.52	164.66	171.29
	$10^6 D$ (cm ² /s)			
Carbon tetrachloride	0.798	1.022	1.281	1.718
Chloroform	1.769	2.113	2.217	^a
Methylene dichloride	2.922	^a	^a	^a
1,1,2,2-tetrachloroethane	0.435	0.579	0.712	0.940
Bromoform	0.460	0.590	0.721	0.875
Tetrachloroethylene	1.211	1.544	1.717	2.190
1,1,1-trichloroethane	0.623	0.955	1.302	^a
Trichloroethylene	2.066	2.572	3.079	3.387

^a Data not obtained due to their high volatility.

Table 3
Comparison of solubility (*S*) and diffusivity (*D*) for desorption (D)–resorption (RS)–redesorption (RD) runs at 25 °C

Solvent	D	RS	RD
	<i>S</i> (wt%)		
Carbon tetrachloride	75.00	431.74	75.32
Chloroform	68.90	209.55	68.60
Methylene dichloride	48.74	80.23	44.89
1,1,2,2-tetrachloroethane	57.28	114.11	52.18
Bromoform	62.15	119.91	56.83
Tetrachloroethylene	75.21	298.14	75.52
1,1,1-trichloroethane	65.60	188.00	65.88
Trichloroethylene	72.42	^a	^a
	$10^6 D$ (cm ² /s)		
Carbon tetrachloride	2.083	0.285	1.936
Chloroform	2.995	0.397	2.455
Methylene dichloride	2.232	0.429	1.834
1,1,2,2-tetrachloroethane	0.107	0.068	0.040
Bromoform	0.262	0.082	0.144
Tetrachloroethylene	1.227	0.418	0.238
1,1,1-trichloroethane	1.671	0.158	1.558
Trichloroethylene	1.419	^a	^a

^a Data not obtained.

mathematical treatment in such studies involves the solution of the Fick's equation under suitable boundary conditions. In the present experimental systems, considering the unidirectional diffusion transport and that during immersion tests, the liquid concentration on the polymer surface reaches equilibrium immediately upon exposure; Fick's second-order differential equation was used [17]:

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2} \right). \quad (3)$$

Further, it was assumed that sorption and desorption take place under the transient conditions with a constant diffusivity (without much changes in the sample dimension) and that desorption is controlled both by diffusion and evaporation phenomena and the rate of evaporation is either very high (with a zero concentration of the liquid on the surface). Using these assumptions and under the following initial and boundary conditions,

$$t = 0, \quad 0 < x < h, \quad C = 0, \quad (4)$$

$$t > 0, \quad x = 0, x = h, \quad C = C_{\infty}, \quad (5)$$

Eq. (3) was solved for liquid concentration C_t in the polymer at time t and distance x for a polymer thickness h to give

$$\frac{C_{(t,x)}}{C_{\infty}} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{1}{(2n+1)} \exp \left[-\frac{D(2n+1)^2 \pi^2}{h^2} t \right] \sin \left[\frac{(2n+1)\pi}{h} x \right], \quad (6)$$

where $C_{(t,x)}$ and C_∞ are sorbed liquid concentrations at time t , distance x , and at equilibrium, respectively; n is an integer. The amount of liquid sorbed by the polymer is given by [17]

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-\frac{D(2n+1)^2\pi^2}{h^2} t\right]. \quad (7)$$

Solvent diffusivity at short times, i.e., before 0.55% equilibrium was calculated as [17]

$$\frac{M_t}{M_\infty} = \frac{4}{h} \left(\frac{Dt}{\pi}\right)^{1/2}. \quad (8)$$

For sorption, the initial liquid concentration within the polymer is assumed to be uniform. On the other hand, for desorption, the rate of weight loss is Santoprene membrane due to evaporation is important and this is calculated as [18]

$$-D \left(\frac{\partial C}{\partial x}\right)_{x=h} = F_0(C_0 - C_{\text{ext}}), \quad (9)$$

where F_0 is the rate of evaporation of liquid, C_0 is the concentration of liquid on the surface and C_{ext} is the concentration in equilibrium with the surrounding atmosphere. The solution of Eq. (9) gives [18]

$$\frac{C_\infty - C_{\text{ext}}}{C_\infty - C_0} = \sum_{n=1}^{\infty} \frac{2M \cos(\beta_n x/h)}{(\beta_n^2 + M^2 + M) \cos \beta_n} \exp\left(-\frac{\beta_n^2}{h^2} Dt\right), \quad (10)$$

where the β_n 's are the positive roots of

$$\beta \tan \beta = M \quad (11)$$

with the dimensionless parameter M , given by

$$M = \frac{hF_0}{D}. \quad (12)$$

The amount of liquid M_t , evaporating from the polymer after time t , is then calculated as

$$\frac{M_\infty - M_t}{M_\infty} = \sum_{n=1}^{\infty} \frac{2M^2}{\beta_n^2(\beta_n^2 + M^2 + M)} \exp\left(-\frac{\beta_n^2}{h^2} Dt\right). \quad (13)$$

The values of β_n have been taken from Ref. [18].

The results of diffusion coefficients at 25 °C for sorption, S, desorption, D, resorption, RS, and redesorption, RD, i.e., S–D–RS–RD cycles presented in Tables 2 and 3 are different. However, due to the overshoot effects observed in sorption cycles, some uncertainty exists to estimate the accurate equilibrium sorption values and, thus, the values of D obtained for sorption may be considered to be approximate. At any rate, these values give us an indication of the extent of leaching out phenomenon. The results of D for sorption cycles increased with increasing temperature for all the liquids. The diffusion values are not dependent on the size of haloalkanes for the S–D–RS–RD runs. For instance, 1,1,2,2-tetrachloroethane and bromoform exhibited

lower D values when compared to other liquids. On the other hand, methylene dichloride and trichloroethylene showed higher values of D than the rest. However, for the D–RD runs, the diffusion coefficients were higher than those observed for the S–RS runs. Especially, for the RS runs, the diffusion coefficients of 1,1,2,2-tetrachloroethane and bromoform were smaller by an order of magnitude when compared to haloalkanes.

In this study, diffusion coefficients are not dependent on the size of the solvent molecules. However, the type and nature of these molecules exhibited some effect on diffusivity. Methylene dichloride has a higher D than other liquids, while D for bromoform is quite smaller than chloroform. The lower D for bromoform than chloroform is attributed to the fact that bromoform is less polar and less viscous than chloroform; also, bromoform is a larger molecule than chloroform. Similarly, with two almost identical molecules, viz., 1,1,1-trichloroethane and trichloroethylene, the latter has a higher D than the former for sorption at all temperatures and a reverse effect was observed for the desorption runs. A similar dependency is seen for 1,1,2,2-tetrachloroethane and tetrachloroethylene.

In several application areas, it is important to know about the rate of solvent evaporation F_0 from the polymeric materials and it was calculated for desorption and redesorption cycles using [12, 18]

$$F_0 = \left(\frac{dM_t}{dt} \right) \text{ for } t \rightarrow 0. \quad (14)$$

The calculated values of F_0 are given in Table 4. It is noticed that the rate of evaporation is fast in case of chloroform for both desorption and redesorption cycles. However, for bromoform, it is very slow and these results for 1,1,2,2-tetrachloroethane were not obtained within the reasonable time period of the experimentation.

When the hazardous liquids are in contact with the container vessels, it is very important to know about the penetration concentrations of the liquids into the walls of the barrier containers. In order to study this effect, the concentration profiles of liquids at different depths of Santoprene were calculated [18] from the analytical

Table 4
Rate of evaporation (F_0) for desorption (D) and redesorption (RD) runs

Haloalkanes	F_0 (cm/s)	
	D	RD
Carbon tetrachloride	1.620	1.168
Chloroform	2.167	1.727
Methylene dichloride	1.564	1.359
1,1,2,2-tetrachloroethane	^a	^a
Bromoform	0.278	0.180
Tetrachloroethylene	0.890	0.251
1,1,1-trichloroethane	1.190	1.081

^aData not obtained.

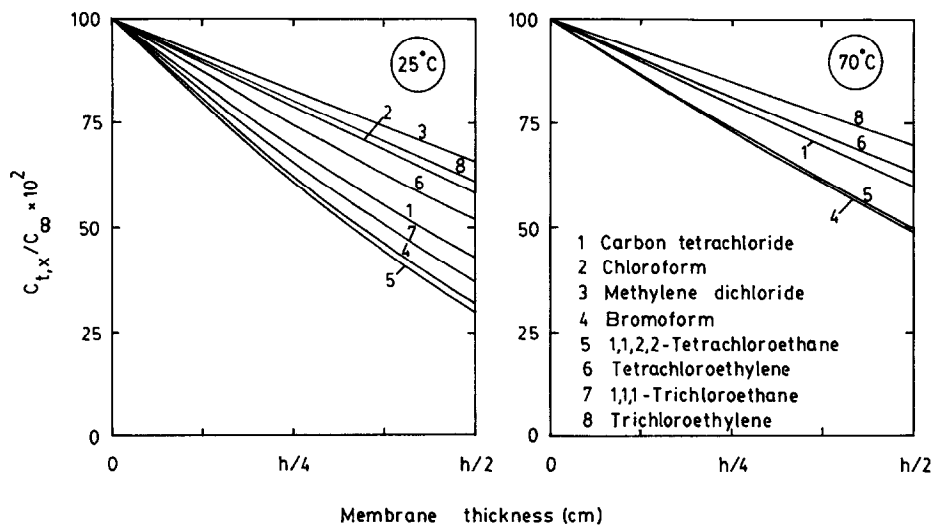


Fig. 4. Profiles of liquid concentration at 2 min of sorption of haloalkanes calculated from Eq. (6) for different thickness intervals within Santoprene at 25 and 70 °C.

solutions of Eq. (6). These profiles for 2 min of immersion are presented in Fig. 4 at 25 and 70 °C. It is found that temperature had an effect on the shapes of these profiles. For instance, at 70 °C, due to higher values of D , the profiles are more narrowly spaced when compared to those observed at 25 °C.

The profiles of concentrations for chloroform, methylene dichloride, and 1,1,1-trichloroethane at 70 °C are not included in Fig. 4 due to their low boiling points. The shapes of liquid profile concentrations at 25 and 70 °C for 1,1,2,2-tetrachloroethane (having low D) and trichloroethylene (having higher D) shown in Fig. 5 are different and these depend upon the diffusivities of the liquid molecules as well as the times of immersion experiments. Similarly, the concentration profiles for 1,1,2,2-tetrachloroethane (having low D) and tetrachloroethylene (having high D) for resorption runs at 25 °C are compared in Fig. 6. It may be noted that for resorption runs, the curves are more widely spaced than the sorption runs due to the lower D values for resorption than sorption.

Realizing the fact that sorption curves show only slight sigmoidal trends initially, we felt it essential to obtain the liquid concentration profiles by using the model simulation technique [18]. This method also takes into account the concentration dependency of diffusivity. Moreover, the analytical solutions to Fick's diffusion equations are not possible for those polymer–solvent systems that exhibit concentration dependency. In such cases, the model simulation techniques using finite difference method are useful [18] in predicting the liquid concentration profiles at various time intervals for different membrane thicknesses. The following relation was used [18]:

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

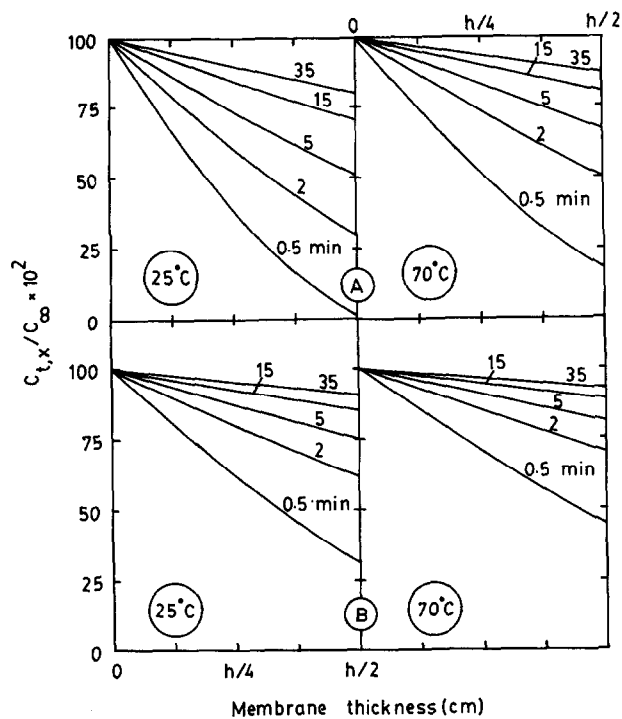


Fig. 5. Profiles of concentration of (A) 1,1,2,2-tetrachloroethane and (B) trichloroethylene for sorption calculated from Eq. (6) at different penetration depths within Santoprene at 25 and 70°C.

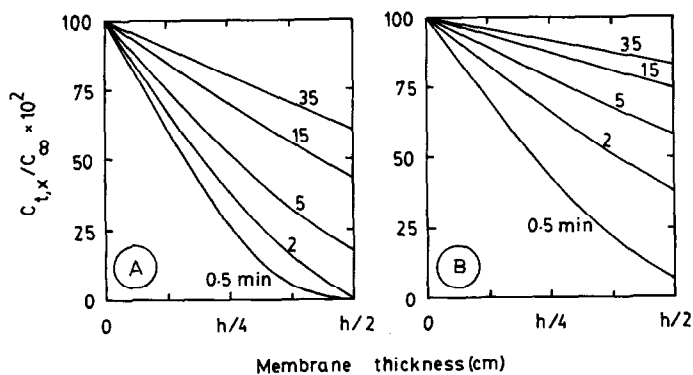


Fig. 6. Profiles of concentration of (A) tetrachloroethylene and (B) 1,1,2,2-tetrachloroethane for resorption using Eq. (6) at different penetration depths of Santoprene at 25°C.

with the dimensionless parameter M_n ,

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

While solving Eqs. (15) and (16), the membrane thickness was divided into 10 slices of equal size, Δx , and each slice was characterized by the integer n . The C_n and CN_n are the concentrations at position n , at time t , and after elapse of time Δt , respectively. For each slice, the liquid concentration curves were simulated for different time intervals. The model is built for unidirectional diffusion only. The concentration profiles of haloalkanes calculated by this method at 10 min of immersion presented in Fig. 7 at 25 and 70 °C exhibit slightly different patterns to those obtained at 2 min of immersion (see Figs. 4 and 7). This again proves the fact that the shapes of the sorption breakthrough curves are dependent on the immersion times. The effect of temperature on the shapes of the curves were also observed for the numerical method. The numerically calculated profiles for 1,1,2,2-tetrachloroethane (low D) and trichloroethylene (high D) at 25 and 70 °C presented in Fig. 8 also exhibit similar effects when compared to those curves given in Fig. 5. Similarly, the resorption profiles for 1,1,2,2-tetrachloroethane and tetrachloroethylene presented in Fig. 9 exhibited similar tendencies as given in Fig. 6. In Fig. 10, the profiles calculated by Eq. (6) for 2 min of immersion and Eq. (15) for 10 min of immersion are compared for the systems, Santoprene–haloalkanes at 25 °C.

As a further test of the model simulation technique, we have used the diffusion results obtained from Eq. (8) to generate the theoretical sorption breakthrough curves using Eq. (7). The theoretical curves are compared well with the initial experimental

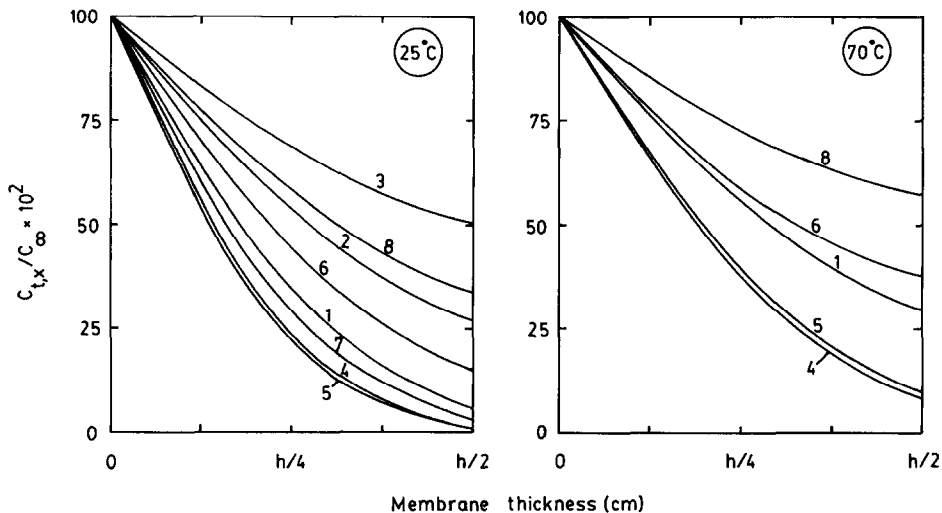


Fig. 7. Profiles of liquid concentration at 10 min of sorption of haloalkanes calculated from Eq. (15) for different thickness intervals within Santoprene at 25 and 70 °C.

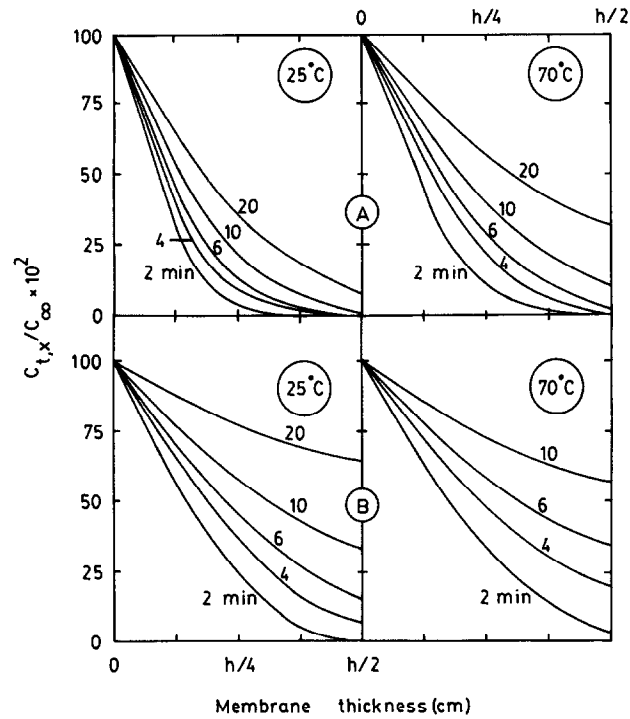


Fig. 8. Profiles of concentration of (A) trichloroethylene and (B) 1,1,2,2-tetrachloroethane for sorption calculated from Eq. (15) at different penetration depths of Santoprene at 25 and 70 °C.

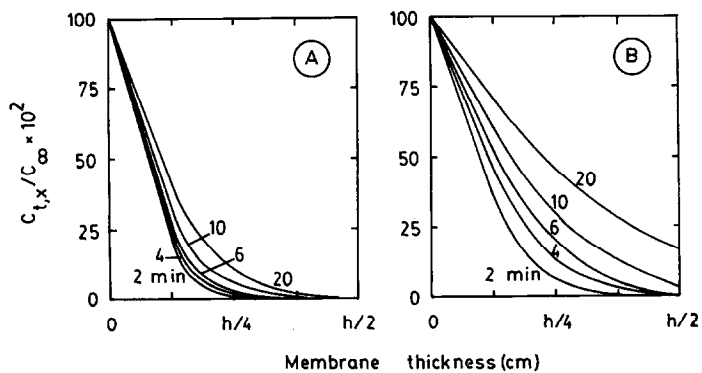


Fig. 9. Profiles of concentration of (A) trichloroethylene and (B) 1,1,2,2-tetrachloroethane for resorption calculated using Eq. (15) at different penetration depths within Santoprene at 25 °C.

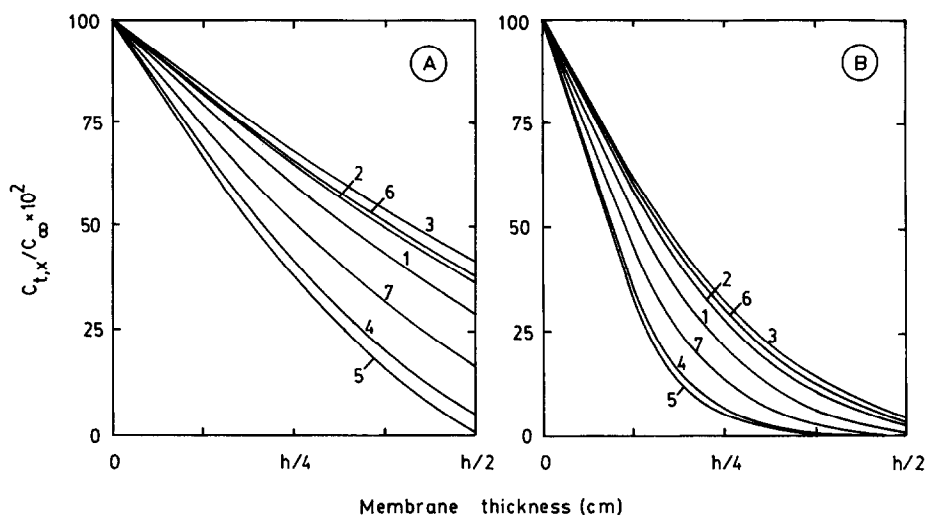


Fig. 10. Profiles of liquid concentration for resorption of haloalkanes calculated from (A) Eq. (6) at 2 min and (B) Eq. (15) at 10 min at different penetration depths within Santoprene at 25 °C.

breakthrough curves for carbon tetrachloride and chloroform at 25 and 70 °C in Fig. 11. A good agreement is observed before the completion of 55% of equilibrium sorption. However, the deviations at longer sorption times may be due to the concentration dependence of diffusivity. In view of this anomaly, we have calculated the average values of diffusion coefficients \bar{D} over the concentration intervals C_1 to C_2 using the relation [17]

$$\bar{D} = \frac{1}{C_1 - C_2} \int_{C_2}^{C_1} D \, dc. \quad (17)$$

The curves displaying the dependence of average diffusivity on concentration at 25 °C are given in Fig. 12 for both sorption and resorption runs.

The temperature-dependent sorption and diffusion results were analyzed by using the following Arrhenius relationship:

$$X = X_0 \exp(-E_X/RT), \quad (18)$$

where E_X is the activation energy term; for diffusion, it is E_D and X_0 becomes D_0 which is a preexponential factor. The term RT has the usual energy meaning. For sorption however, $X = S$, $X_0 = S_0$ and $E_X = \Delta H_S$, i.e., heat of sorption. The results of E_D , given in Table 5, range from 6.2 kJ/mol for chloroform to 20.0 kJ/mol for 1,1,1-trichloroethane. This suggests that the activation parameters depend on the nature and type of solvents. However, the E_D of bromoform is almost twice higher than chloroform. The E_D values of carbon tetrachloride and 1,1,2,2-tetrachloroethane are identical though these molecules have different structural identities, but their heats of sorption are different. An unsymmetrical molecule like 1,1,1-trichloroethane exhibits higher E_D than a symmetric carbon tetrachloride molecule.

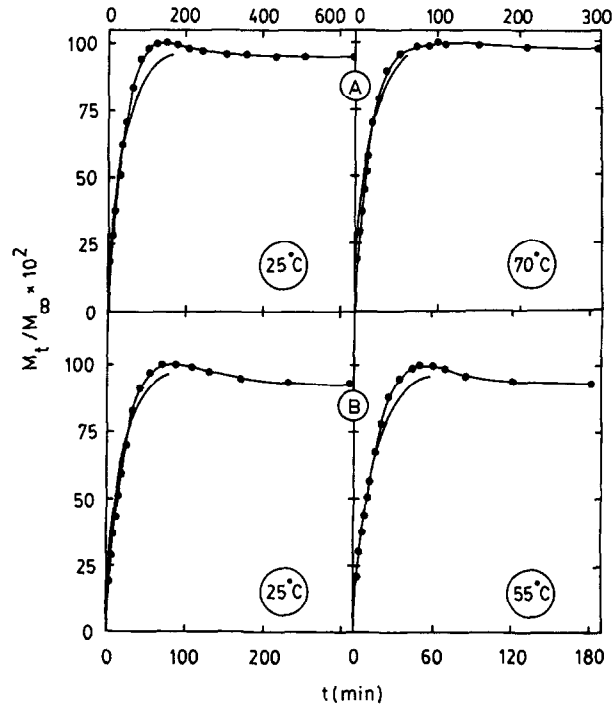


Fig. 11. Comparison of experimental sorption curves (points) for (A) carbon tetrachloride and (B) chloroform with theoretical curves (solid lines) calculated from Eq. (8).

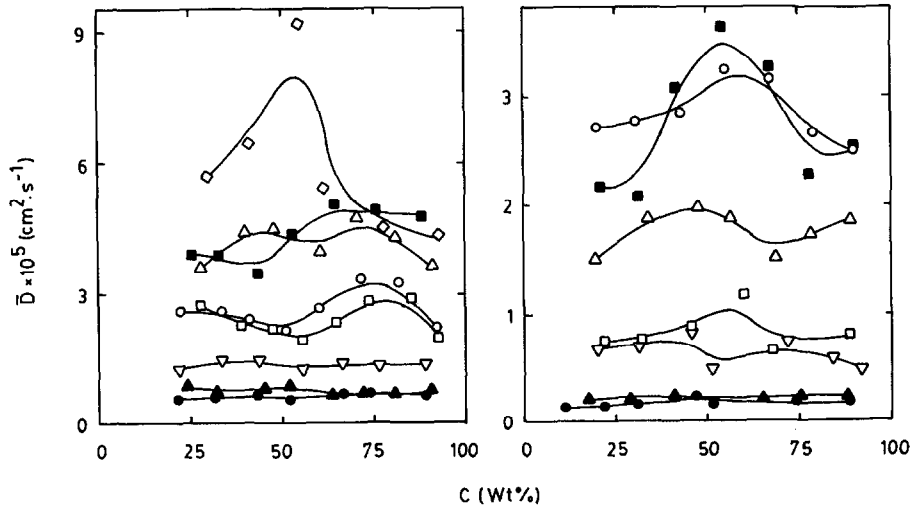


Fig. 12. Average diffusion coefficient versus concentration (in wt%) for (A) sorption and (B) resorption cycles. Symbols have the same meanings as in Fig. 1.

Table 5
Activation parameters (E_D and ΔH_S) for Santoprene + haloalkanes

Alkanes	$E_D \pm \sigma$ (kJ/mol)	$\Delta H_S \pm \sigma$ (kJ/mol)
Carbon tetrachloride	14.3 ± 0.9	3.7 ± 0.6
Chloroform	6.2 ± 1.8	4.8 ± 1.5
1,1,2,2-tetrachloroethane	14.3 ± 0.7	9.3 ± 1.3
Bromoform	12.1 ± 0.2	8.4 ± 0.6
Tetrachloroethylene	10.7 ± 1.1	4.0 ± 0.2
1,1,1-trichloroethane	20.0 ± 1.3	4.2 ± 0.7
Trichloroethylene	9.5 ± 0.9	3.5 ± 0.3

The results of ΔH_S for tetrachloroethylene and 1,1,1-trichloroethane are almost identical probably because of their almost similar sizes and similar viscosities. Similarly, carbon tetrachloride and trichloroethylene exhibit almost identical ΔH_S values, but these values are smaller than those observed for other haloalkanes. The observed higher values of ΔH_S for bromoform and 1,1,2,2-tetrachloroethane may be the result of slow transport of these molecules within the membrane material. At any rate, for all the systems, the values of ΔH_S are positive suggesting the mild endothermic interactions between the systems of this study.

4. Conclusions

Careful long-term sorption/desorption measurements of the kind reported here are required to obtain an accurate estimate of sorption equilibrium, and such estimates provide a sound foundation for subsequent analysis of sorption rate behavior. It is becoming increasingly apparent that sorption/desorption rates may be sufficiently slow to impact solvent transport in groundwater environments. Good understanding of both equilibrium and rate behavior is required for an accurate description of the fate of the contaminant transport in the subsurface. The ability of small molecules to diffuse into a solid polymeric phase (described by a diffusion coefficient) is of interest when considering polymers as barrier materials for industrial applications in the presence of hazardous liquid pollutants. A large value of D indicates that the process takes place quickly. The ingress of chemicals into storage tanks and pipes in the chemical and petroleum industries are examples of applications where knowledge of sorption and diffusion coefficients are needed.

In conclusion, for the study of solvent resistivity and dimensional stability of Santoprene in the presence of aggressive solvents, it becomes necessary to perform the repeated sorption/desorption testing which provides a better picture as to its suitability in field applications. It was shown that the gravimetric method used here will be a good screening test method for the polymer barrier/solvent systems. Diffusion and kinetic parameters may be derived from the gravimetric data on polymer–liquid systems. At higher temperatures, an increase in solvent diffusion due to the increase in

polymer free volume might have resulted in high equilibrium liquid uptake. The overshoot effects are associated with the complicated two-phase morphology of the polymer and also due to slight indigenous additive loss from the polymer. Such effects are not observed for the subsequent desorption/sorption cycles. In the present experimental systems, the transport phenomenon is found to follow the anomalous behavior. The models proposed and the experimental procedures may be helpful for a study of other polymeric membranes and solvent systems.

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