Sorption, Desorption, Resorption, Redesorption, and Diffusion of Haloalkanes into Polymeric Blend of Ethylene–Propylene Random Copolymer and Isotactic Polypropylene

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SYNOPSIS

Molecular transport of haloalkanes into sheets of a polymeric blend of an ethylene–propylene random copolymer and isotactic polypropylene has been studied by a sorption gravimetric technique in the temperature interval of 25–70°C. For all liquids, equilibrium sorption, desorption, resorption, redesorption, and degree of penetrant overshoot have been influenced by the nature of the liquid and the temperature. Diffusion coefficients were calculated from the sorption–desorption kinetic curves using Fick's mathematical relations. The values of diffusion coefficients followed the Arrhenius-type behavior. The temperature-dependent sorption data were analyzed using the van't Hoff relation. The activation parameters for diffusion and heat of sorption data were discussed in terms of the molecular interactions between liquids and the polymer chain segments. The experimental and calculated results are discussed on the basis of the chemical nature of liquids. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Over the past two decades, there has been a great surge in the use of polymeric materials in a variety of commercial and engineering applications. Especially when such materials are used as protective barriers in chemical industries or as liners in chemical ponds, then their resistivity toward organic solvents is an important factor. Sorption and diffusion properties of polymeric membranes are therefore important to know for their end applications in hostile environments. Systematic studies on the transport characteristics of the elastomeric membranes have been pursued in our laboratories[1-8] over the past few years. The present article is an extension of these studies to evaluate the sorption, desorption, resorption, redesorption, and diffusion results for the polymeric blend of an ethylene–propylene random copolymer and isotactic polypropylene, also called Santoprene. Santoprene finds applications in a broad variety of industrial and engineering areas such as pump-related gaskets, hose connectors, plugs, windshield spacers, expansion joints, flexible cords, circuit cables, submersible cable, filters, and pump seals. However, the acceptability of Santoprene for any specific application ultimately depends on its performance requirements and, therefore, end-use performance testing is important before we can envisage its engineering applications.

Haloalkanes are widely used industrial organic solvents. In view of the nonavailability of their transport data into Santoprene, a study has been undertaken to investigate the molecular-transport characteristics of Santoprene in the presence of carbon tetrachloride, chloroform, methylene dichloride, 1,1,2,2-tetrachloroethane, bromoform, tetrachloroethylene, 1,1,1-trichloroethane, and trichloroethylene in the temperature interval of 25–70°C. Diffusion coefficients were obtained from the Fick relations. The experimental and calculated results are discussed in terms of the diffusion and sorption–desorption anomalies. The activation parameters are estimated and the polymer–solvent interactions were studied in relation to the chemical nature and structure of the solvent molecules in addition to polymer morphology.

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Table I Some Typical Mechanical Properties and Fluid Resistance Behavior of Santoprene

Mechanical				Fluid Resistivity[a]		
Properties	ASTM Test Method	Test Temp (°C)	Value	Fluid	Test Temp (°C)	Volume Swelling (%)
Hardness (5 s Shore)	D2240	25	64A	Water	100	6
Specific gravity	D297	25	0.97	15% NaCl	23	0
Tensile strength (Mpa)	D412	25	6.90	50% NaOH	23	0
Ultimate elongation (%)	D412	25	400	98% H_2SO_4	23	5
100% Modulus (MPa)	D412	25	2.3	ASTM #1 oil	100	31
Tear strength (kN/m)	D624	25	24.5	ASTM #2 oil	100	50
		100	10.2	ASTM #3 oil	100	71
Tension set (%)	D412	25	10	Brake fluid	100	−30
Compression set (%)	D395	25	23	Automatic transmission fluid	125	62
168 h		100	36			
Brittle point (°C)	D746	—	−60			

[a] Tested for 166 h.

EXPERIMENTAL

Materials

Sheets of Santoprene (sample designation #101-64) were obtained from Advanced Elastomer Systems, St. Louis, MO, in dimensions of 26 × 26 cm with the initial thicknesses ranging from 0.175 to 0.180 cm. Circular disc-shaped samples (diameter = 1.94–1.97 cm) were cut from these sheets by means of a sharp-edged carbon-tipped steel die. The samples were dried in vacuum desiccators over anhydrous calcium chloride at room temperature for about 24 h before the start of the sorption experiments. Some physical and mechanical property data of the samples are given in Table I.

Reagents

The reagent-grade solvents used as penetrants 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), and bromoform, tetrachloroethylene, 1,1,1-trichloroethane, and trichloroethylene (all from S.D. Fine Chemicals Ltd., India). All these solvents were dou-

Table II Viscosity (η), Dielectric Constant (ε), Solubility Parameter (δ), and Molar Volume (V) of Solvents Used as Penetrants at 25°C

Solvent	η (mPa-s)	ε	δ $(\text{cal cm}^{-3})^{1/2}$	V (cm^3/mol)
Carbon tetrachloride	0.90	2.2	8.6	97
Chloroform	0.54	4.8[a]	9.5	81
Methylene dichloride	0.40[b]	8.9	9.9	65
1,1,2,2-Tetrachloroethane	1.46[c]	8.2[a]	9.8	106
Bromoform	1.89	4.4[a]	10.5	88
Tetrachloroethylene	0.80[c]	2.3	9.4	103
1,1,1-Trichloroethane	0.80	7.3[a]	[d]	100
Trichloroethylene	0.53	3.4	9.3	90

[a] At 20°C.
[b] At 27.6°C.
[c] At 30°C.
[d] Value not available.

Table III Total % Weight Loss at 25°C After Sorption–Desorption (S–D) and Resorption–Redesorption (RS–RD) Cycles and Percent Overshoot Index (*OI*) Values at Different Temperatures for Santoprene + Haloalkanes

	Total % Weight Loss After		*OI* at			
Solvent	S–D Cycle	RS–RD Cycle	25°C	40°C	55°C	70°C
Carbon tetrachloride	38.5	4.2	5.55	4.98	2.81	4.90
Chloroform	39.7	3.5	8.96	6.92	4.35	[a]
Methylene dichloride	38.6	2.9	78.97	[a]	[a]	[a]
1,1,2,2-Tetrachloroethane	38.5	2.9	29.29	22.06	11.75	8.47
Bromoform	37.8	4.5	35.05	25.21	23.47	12.86
Tetrachloroethylene	38.8	4.5	5.05	4.09	4.83	3.45
1,1,1-Trichloroethane	39.4	2.2	8.20	8.19	8.36	[a]
Trichloroethylene	38.3	4.4	4.65	6.85	7.50	3.64

[a] Data not obtained due to its low boiling point.

ble-distilled before use. Some useful physical property data are given in Table II.

Sorption (S)-Desorption (D)-Resorption (RS)-Redesorption (RD) Testing

The circularly cut and dried Santoprene samples were placed in screw-tight test bottles containing about 15–20 mL of the solvents to be tested. These were removed at regular intervals, and the surface-adhered liquid drops were wiped by carefully pressing the samples in between filter paper wraps and again weighed on a digital Mettler balance, Model AE 240 (Switzerland), within the precision of ±0.01 mg. Samples generally reached equilibrium saturation within 24 h, which did not change significantly over a further period of 1 or 2 days. After sorption runs, the sorbed samples were placed in vacuum for desorption measurements. The weight percent gain in sorption and the weight percent loss after desorption were calculated in the usual manner.[1–8]

The resorption testing was carried out in the same manner as were the sorption tests. If the polymer does not exhibit any weight loss during sorption and desorption, the initial weight of the polymer and the weight after desorption should be the same. However, initially, about 38–40% weight loss of the polymer occurred in sorption–desorption runs, indicating possible leaching out of the indigenous additives from the Santoprene sample (see Table III). The resorbed samples were again placed in vacuum oven for a second desorption, i.e., redesorption and the total percent weight loss is around 2–4% (Table III). This comparison is useful to test the extent of the continuous polymer weight loss in S–D–RS–RD testing cycles.

Table IV Fitting Parameters of Eq. (1)

	n		$K \times 10^2$ (g/g min^n)	
Solvent	S 25–70°C	RS 25°C	S 25–70°C	RS 25°C
Carbon tetrachloride	0.60–0.61	(0.65)	6.45–8.80	(3.09)
Chloroform	0.59–0.61[a]	(0.63)	9.63–11.32[a]	(4.82)
Methylene dichloride	0.78–[b]	(0.55)	17.53–[b]	(8.20)
1,1,2,2-Tetrachloroethane	0.50–0.53	(0.54)	8.07–9.81	(3.28)
Bromoform	0.50–0.50	(0.52)	10.04–14.44	(3.97)
Tetrachloroethylene	0.59–0.61	(0.67)	7.35–10.29	(3.71)
1,1,1-Trichloroethane	0.59–0.61[a]	(0.62)	5.86–8.62[a]	(3.00)
Trichloroethylene	0.60–0.62	(0.66)	9.63–13.35	(5.20)

[a] 25–55°C.

[b] Data not obtained due to its low boiling point.

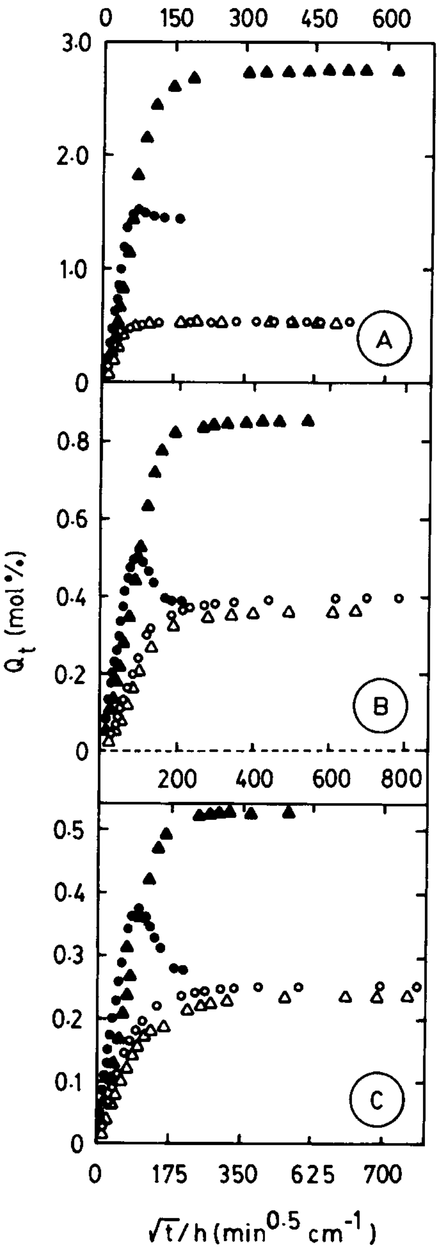

Figure 1 Reduced plots of mol % sorption, desorption, resorption, and redesorption (S-D-RS-RD) at 25°C for (A) carbon tetrachloride, (B) tetrachloroethylene, and (C) bromoform. Symbols: (●) sorption; (○) desorption; (▲) resorption; (△) redesorption.

RESULTS AND DISCUSSION

Sorption Anomaly

To analyze the type of solvent transport into the Santoprene matrix, the dynamic sorption data were analyzed using[9]

$$\frac{Q_t}{Q_\infty} = Kt^n \qquad (1)$$

where Q_t and Q_∞ are the masses of solvent sorbed at time t and at equilibrium time, and K is an empirical parameter which depends on the nature of polymer and on the penetrant–polymer interactions. The exponent value of n is indicative of the type of transport mechanism. In desorption experiments, Q_t and Q_∞ represent the mass losses of the drying polymer sample at time t and the completely dried sample, respectively. The estimated values of n and K for sorption and resorption runs given in Table IV are accurate within ±0.01. In the majority of cases, the values of n for sorption experiments fall between 0.50 and 0.78 over the temperature interval 25–70°C, suggesting the observed diffusion to be of an anomalous type.[1-8] For resorption at 25°C, n range from 0.52 to 0.67. However, in all cases, K increases with temperature, suggesting increased polymer–solvent interactions.

S–D–RS–RD Phenomena

In the present work, the sorption results are presented using the normalized parameter, $t^{1/2}/h$, to avoid any differences in the thickness of the samples. Such plots are called reduced plots and this way of presentation is useful because it shows any deviations of the penetrant transport from the Fickian behavior. Reduced plots of S-D-RS-RD runs for carbon tetrachloride, tetrachloroethylene, and bromoform at 25°C presented in Figure 1 indicate an overshoot, i.e., an increase in sorption followed by an immediate decrease in uptake for the sorption process. The overshoot effect is more for bromoform and tetrachloroethylene than for carbon tetrachloride. Such an effect might be due to the loss of additives from the Santoprene sample or due to its two-phase complex morphology. This phenomenon was also observed by others[10-13] in the literature.

To estimate the overshoot effect, the percent overshoot index, OI, was calculated as[10]

$$OI = \frac{Q_m - Q_\infty}{Q_\infty} \times 100 \qquad (2)$$

where Q_m refers to maximum uptake. Overshoot effects are not observed for desorption, resorption, and redesorption runs (see Figs. 1–3). The calculated values of OI are included in Table III. Extremely high values of OI are observed for methylene dichloride. For the remaining liquids, the values of OI

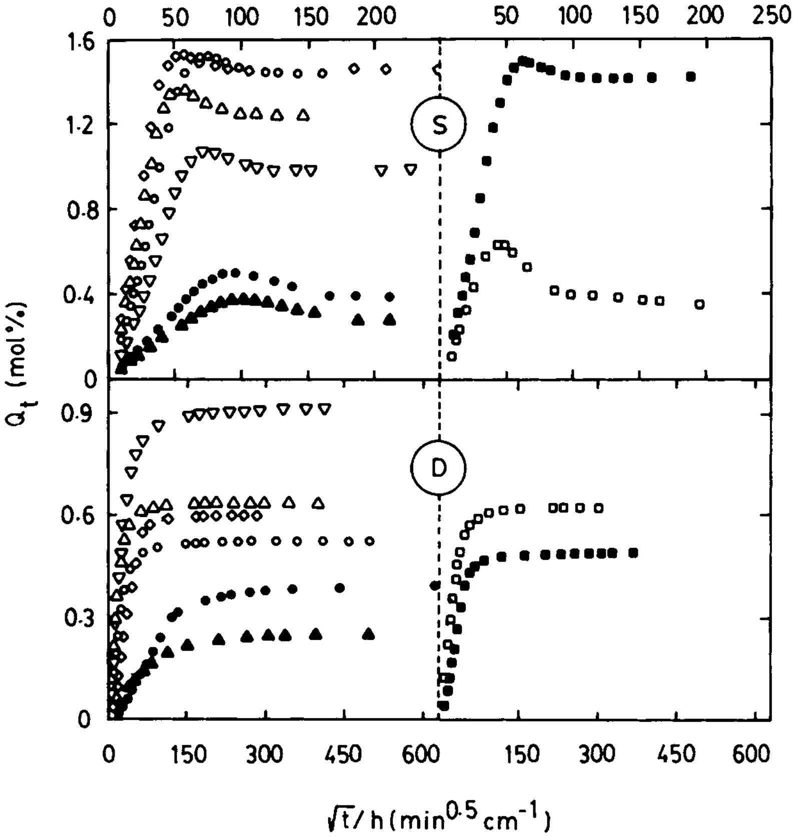

Figure 2 Reduced plots of mol % sorption (S) and desorption (D) at 25°C for (○) carbon tetrachloride, (△) chloroform, (□) methylene dichloride, (●) tetrachloroethane, (▲) bromoform, (■) tetrachloroethylene, (▽) trichloroethane, and (◇) trichloroethylene.

depend on their solubility parameter: δ values. For instance, bromoform with a high δ value of 10.5 exhibits a higher value of *OI* than does carbon tetrachloride, which has a lower δ, i.e., 8.6, and shows a lower value of *OI* than that of all other liquids. In the present research, no systematic dependence of *OI* on temperature was observed. However, the values of *OI* for the remaining liquids also vary according to their δ values. It is found that the desorption and redesorption curves for carbon tetrachloride are quite identical, whereas such curves for tetrachloroethylene and bromoform are slightly different, but the pattern of the curves remained almost identical for the latter (Fig. 1).

Sorption coefficients, *S*, have been calculated in mol % units, i.e., moles of solvent sorbed per 100 g of the polymer as obtained from the plateau regions of the sorption and desorption curves. The results of equilibrium sorption presented in Table V vary depending on the nature of the liquid. Sorption data for chloroform and 1,1,1-trichloroethane at 70°C and that of methylene dichloride at 40, 50, and 70°C were not obtained due to their high volatilities. The results of sorption, desorption, and redesorption at 25°C are given in Figures 2 and 3. It was found that the *S* values for carbon tetrachloride, chloroform, trichloroethylene, and tetrachloroethylene at all the temperatures are higher than those of the other liquids.

For desorption experiments, the uptake values are different from those observed for sorption (Fig. 2). For instance, trichloroethane exhibits the highest desorption equilibrium value and bromoform has the lowest. The intermediary values are observed for the remaining liquids. During redesorption, a very slight departure from the regular Fickian trend (sigmoidal) is observed only in case of tetrachloroethylene (Fig. 3) and this difference might be due to the possible morphological changes of the polymer during S–D–RS–RD testing. In desorption and redesorption runs, the equilibrium sorption values are lower for 1,1,2,2-tetrachloroethane, bromoform, and tetrachloroethylene than for the other liquids. The initial redesorption curves for chloroform and trichloroethylene and, similarly, the curves for trichlo-

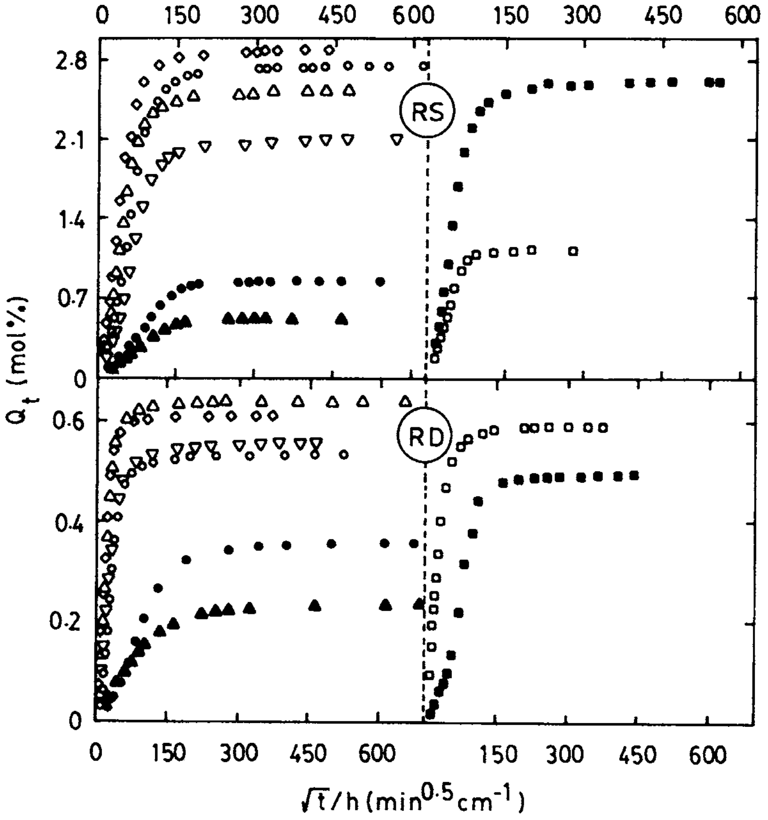

Figure 3 Reduced plots of mol % resorption (RS) and redesorption (RD) at 25°C for Santoprene + haloalkanes. Symbols are the same as in Figure 2.

roethane and carbon tetrachloride are almost identical, indicating identical desorption patterns (Fig. 3).

A typical temperature-dependence sorption plot for carbon tetrachloride, tetrachloroethylene, and bromoform are displayed in Figure 4. The overshoot effects are present even at higher temperatures. However, the equilibrium values for carbon tetrachloride are within a narrow range, while for tetrachloroethylene and bromoform, these values varied over a wider range. A plausible explanation for this effect is that at high penetrant concentration, i.e., in the later stages of the sorption process, the distribution of solvent molecules into the dense region of the polymer becomes quite significant. This probably produces a mismatch of the time scale for diffusion and molecular rearrangement of the polymer chains, facilitating diffusion of solvent molecules and thereby attaining equilibrium.

Calculation of Diffusion Coefficients

Diffusion coefficients, D, have been obtained from the Fick's second law of diffusion[14]:

$$\frac{\partial C}{\partial t} = \text{div}\,(D\ \text{grad}\ C) \tag{3}$$

where C is the local concentration of the diffusant molecule and t is the time. For a slab geometry of the polymer sample immersed in an infinite bath of the liquid, the diffusion coefficient, being independent of concentration, is assumed to be constant. A solution to eq. (3) in terms of Q_t given by Crank[14] reads

$$\frac{Q_t}{Q_\infty} = 1 - \left(\frac{8}{\pi^2}\right) \times \sum_{n=0}^{\infty} \left\{ \left[\frac{1}{(2n+1)^2}\right] \exp\left[\frac{-D(2n+1)^2\,\pi^2 t}{h^2}\right] \right\} \tag{4}$$

Equation (4) suggests that a plot of fractional equilibrium uptake vs. $t^{1/2}/h$ is linear at small times (i.e., up to 55% attainment of equilibrium sorption). Thus, the values of D can be calculated from the initial slopes of the reduced plots.

Diffusion coefficients, calculated from eq. (4) as per the procedures explained earlier,[5] are compiled

Table V Solubility (S) and Diffusivity (D) Values for Sorption Runs at Different Temperatures

	Temperature (°C)			
	25	40	55	70
Solvent	S (Mol %)			
Carbon tetrachloride	1.438	1.487	1.561	1.650
Chloroform	1.247	1.329	1.457	[a]
Methylene dichloride	0.353	[a]	[a]	[a]
1,1,2,2-Tetrachloroethane	0.386	0.483	0.627	0.760
Bromoform	0.276	0.351	0.427	0.555
Tetrachloroethylene	1.421	1.441	1.522	1.625
1,1,1-Trichloroethane	0.988	1.057	1.123	[a]
Trichloroethylene	1.459	1.530	1.570	1.651
	$D \times 10^6$ (cm^2/s)			
Carbontetrachloride	0.924	1.232	1.436	1.707
Chloroform	1.879	2.153	2.446	[a]
Methylene dichloride	5.856	[a]	[a]	[a]
1,1,2,2-Tetrachloroethane	0.860	0.967	0.987	1.218
Bromoform	1.037	1.200	1.319	1.579
Tetrachloroethylene	1.258	1.687	1.781	2.130
1,1,1-Trichloroethane	0.769	1.136	1.378	[a]
Trichloroethylene	1.990	2.785	2.987	3.241

[a] Data not obtained due to its low boiling point.

in Tables V and VI. The diffusion of the solvent into the polymer matrix expands the system and thus weakens the molecular interaction between neighboring polymer chains. This implies that the polymer chains between crosslinks move freely and the molecular mobility of the network is enhanced through diffusion of solvent molecules. However, the fraction of the constrained regions of the network chains may decrease through an interaction between the network chains of the polymer and the solvent molecules. A highly crosslinked polymer structure will inhibit the diffusion process more than will a linear polymer because such chains are more tightly bound together and resist the separation necessary to form a void capable of accommodating a diffusing molecule. The energy to create such voids will therefore be large.

A comparison of diffusion coefficients at 25°C for the S–D–RS–RD experiments is made in Table VI. The values of D are different in all these processes, suggesting the possible morphological changes in the polymer. Diffusion coefficient values do not show any dependence on the size of the solvent molecules. However, in the case of methylene dichloride, the smallest among the series of liquids considered, a diffusivity of 5.856×10^{-6} cm^2/s is observed. On the other hand, the bigger 1,1,2,2-tetrachloroethane exhibits the smallest D. With other penetrants, the molecular size dependency of D is not observed. The chemical interactions of the liquid molecules seem to influence their transport characteristics. Between chloroform and bromoform, the latter exhibits a smaller D than does the former, probably because bromoform is more polar and viscous than is chloroform (see Table II) and, also, the size of the bromine atom is bigger than that of chlorine. Similarly, with two almost identical-size molecules, viz., 1,1,1-trichloroethane and trichloroethylene, the values of D are higher. A similar dependency is shown for 1,1,2,2-tetrachloroethane and tetrachloroethylene.

A plot showing the dependence of liquid viscosity, η on D, displays this effect (see Fig. 5). Such a correlation was also attempted earlier by Vahdat[15] for rubbery polymer–solvent systems. Additionally, the solubility parameter values of the liquids also exert some effect on diffusivity results. For instance, the δ of 1,1,2,2-tetrachloroethane, being higher than that of tetrachloroethylene, exhibits lower D than does the less polar tetrachloroethylene. Similar effects can be seen in the

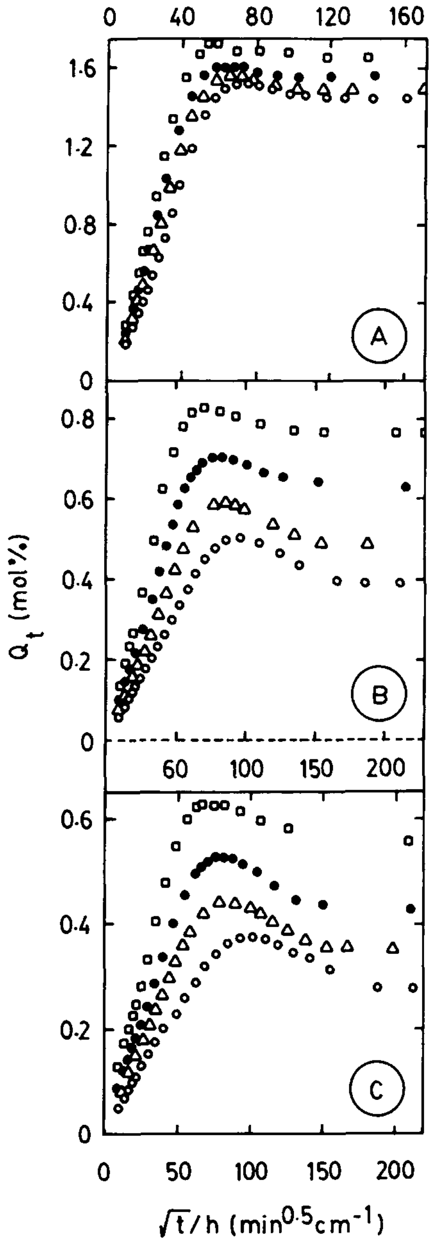

Figure 4 Effect of temperature on sorption curves for (A) carbon tetrachloride, (B) tetrachloroethylene, and (C) bromoform. Symbols: (O) 25°C; (△) 40°C; (●) 55°C; (□) 70°C.

case of chloroform and bromoform and of 1,1,1-trichloroethane and trichloroethylene.

Table VI Comparison of Solubility (*S*) and Diffusivity (*D*) Values for Desorption (D)–Resorption (RS)–Redesorption (RD) Runs at 25°C

	D	RS	RD
Solvent	*S* (Mol %)		
Carbon tetrachloride	0.526	2.752	0.532
Chloroform	0.636	2.535	0.640
Methylene dichloride	0.621	1.116	0.592
1,1,2,2-Tetrachloroethane	0.395	0.850	0.357
Bromoform	0.252	0.524	0.234
Tetrachloroethylene	0.490	2.614	0.495
1,1,1-Trichloroethane	0.915	2.105	0.557
Trichloroethylene	0.600	2.903	0.610
	$D \times 10^6$ (cm^2/s)		
Carbontetrachloride	1.127	0.277	0.275
Chloroform	1.614	0.493	0.666
Methylene dichloride	1.320	0.644	1.293
1,1,2,2-Tetrachloroethane	0.038	0.121	0.024
Bromoform	0.141	0.136	0.099
Tetrachloroethylene	0.277	0.430	0.031
1,1,1-Trichloroethane	0.733	0.201	0.477
Trichloroethylene	0.257	0.695	1.066

Arrhenius Activation Parameters

In all cases, the sorption and diffusion results increased with increasing temperature, showing an enhanced rate of molecular transport due to increased polymer chain segmental movements. However, no systematic dependence of these parameters on penetrant size is observed. Diffusion results have been analyzed using the Arrhenius relation

$$D = D_0 \exp(-E_D/RT) \tag{5}$$

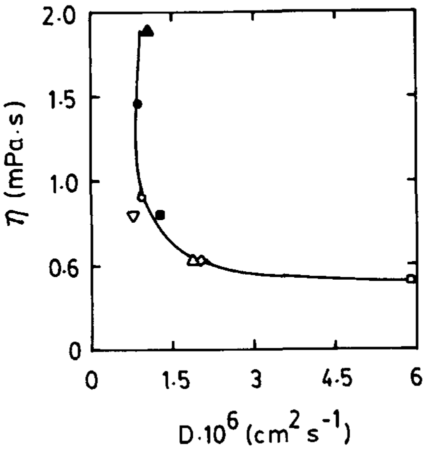

Figure 5 Dependence of diffusivity on solvent viscosity for Santoprene + haloalkanes at 25°C. Symbols are the same as in Figure 2.

where E_D is activation energy for diffusion and is a function of the intra- and interchain forces that must be overcome in order to create the space for a unit diffusional jump of the penetrant molecule, D_0 is a preexponential factor, and RT has the usual meaning. A typical plot of log D vs. $1/T$ is given in Figure 6 and linearity is observed in the investigated range of temperature. The results of E_D vary from 5.98 to 15.89 kJ/mol depending on the nature of the solvent molecules (Table VII). These values for carbon tetrachloride and chloroform are quite different, whereas the values for chloroform and bromoform are somewhat comparable. The results of E_D do not show any dependence on the size of the penetrant molecules. The E_D values for carbon tetrachloride and 1,1,1-trichloroethane are higher than those for other liquids. An unsymmetrical molecule like 1,1,1-trichloroethane shows higher E_D than does a symmetric carbon tetrachloride. The smaller values of E_D for the liquid–polymer systems of the present study are indicative of the fact that the barrier structure is somewhat less rigid.

The results of S have been analyzed using the van't Hoff relation with a preexponential factor, S_0, as

$$S = S_0 \exp(-\Delta H_S/RT) \qquad (6)$$

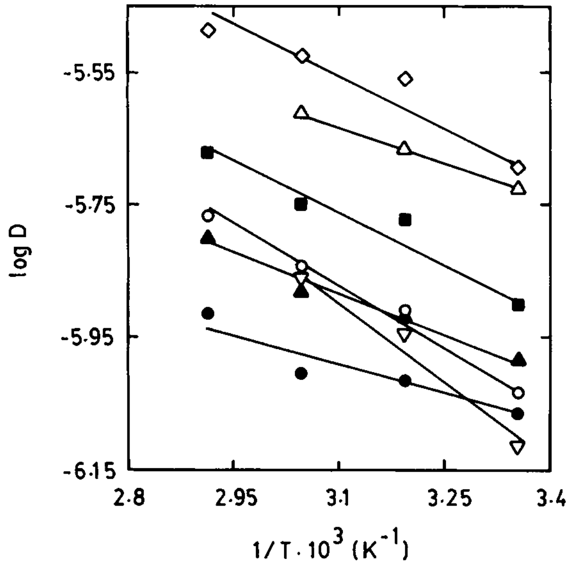

Figure 6 Arrhenius plots for the dependence of log D vs. $1/T$ for Santoprene + haloalkanes. Symbols are the same as in Figure 2.

Table VII Activation Energy of Diffusion, E_D, from Arrhenius Relation [Eq. (5)] and Heat of Sorption, ΔH_S, from van't Hoff Relation [(Eq. (6)] for Santoprene + Haloalkanes

Solvent	E_D (kJ/mol)	ΔH_S (kJ/mol)
Carbon tetrachloride	11.36	2.60
Chloroform	7.15	4.21
1,1,2,2-Tetrachloroethane	5.98	13.01
Bromoform	7.66	12.98
Tetrachloroethylene	9.31	2.56
1,1,1-Trichloroethane	15.89	3.47
Trichloroethylene	8.82	2.25

where ΔH_S is the heat of sorption and is a composite parameter depending upon both Henry's law and Langmuir's type sorption. The ΔH_S values for chloroform, trichloroethylene, and 1,1,1-trichloroethane are different, but for carbon tetrachloride, tetrachloroethane, and trichloroethane, these values are identical (Table VII). For all systems, the values of ΔH_S are positive, suggesting that the sorption is dominated by Henry's law sorption with the endothermic contribution.

CONCLUSIONS

This article has presented an analysis of sorption, desorption, resorption, redesorption, and diffusion of halogenated alkanes into Santoprene by a sorption gravimetric method in the temperature interval 25–70°C. At higher temperature, an increase in solvent diffusion and relaxation rate of the polymer accompanied by an increase in the polymer free volume resulted in a higher equilibrium penetrant uptake. The overshoot effect might have been associated with the complicated two-phase morphology of the polymer and also due to indigenous additive loss from the polymer. For the present experimental systems, the transport phenomenon was characterized by the anomalous-type behavior. For the present systems, even though the n values vary between 0.50 and 0.67, they are close to 0.50, suggesting the transport to be close to the simple Fickian type. However, the deviation observed for methylene dichloride ($n = 0.78$) at 25°C attributed to the polymer chain relaxation effects. Moreover, the initial near-linearity in the reduced plots of sorption results suggests that the transport may be a Fickian-type process.

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