

Liquid transport into polymeric blend of ethylene-propylene random copolymer and isotactic polypropylene in the temperature interval of 25-70°C[†]

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Sorption, desorption and diffusion coefficients have been obtained for benzene, toluene, ethyl benzene, *p*-xylene, chlorobenzene, bromobenzene, 1,2-dichlorobenzene and mesitylene into thermoplastic blend of ethylene-propylene random copolymer and isotactic polypropylene in the temperature range of 25-70°C. Diffusion coefficients have been correlated with liquid viscosity and follow the expected trend of decrease in diffusivity with increase in liquid viscosity. The concentration dependency of diffusion coefficients has also been studied.

Liquid transport in terms of solvent sorption, desorption and diffusion into polymeric membranes has been investigated extensively over the past decades. Several types of diffusion anomalies such as case-I, case-II or super case-II and anomalous diffusion (non-Fickian) have been described¹. For an understanding of the molecular transport of liquids into polymeric membranes, it is important to estimate the sorption, desorption and diffusion parameters. Thus, an accurate knowledge on solvent sorption, desorption and diffusion profiles into network polymers is needed before we envisage the diverse applications of polymers in hostile solvent media.

This paper presents the sorption, desorption and diffusion results on thermoplastic blend of ethylene-propylene random copolymer and isotactic polypropylene, also known as Santoprene, upon exposure to benzene, toluene, ethyl benzene, *p*-xylene, chlorobenzene, bromobenzene, 1,2-dichlorobenzene and mesitylene over the temperature interval of 25-70°C. These liquids are chosen in view of their industrial importance. On the other hand, Santoprene finds a number of engineering applications such as in the manufacturing of hose connectors, plugs and o-rings. Hence, interaction of aromatic liquids with Santoprene is of some importance before the intended applications

of the polymer in the presence of solvents. The experimental results of diffusion, sorption and desorption parameters have been discussed in terms of temperature, solvent size, shape and polymer morphology. The concentration-dependency of diffusion coefficients has also been analyzed. Arrhenius parameters for different transport processes have been estimated.

Experimental Procedure

Santoprene rubber samples (sample designation # 103-40) and preparation of test samples are the same as reported earlier². The reagent grade benzene (Sisco Chem, India), toluene (Fischer Inorganics and Aromatics, India), ethyl benzene (Riedel, Germany), *p*-xylene (sd Fine Chem, India), chlorobenzene (sd Fine Chem, India), bromobenzene (Ranbaxy, India), 1,2-dichlorobenzene (Sisco Chem, India) and mesitylene (Merck-Schuchardt, Germany) were double distilled before use.

Sorption (S)—Desorption (D)—Resorption (RS)—Redesorption (RD) Testing—Circularly cut and vacuum dried Santoprene samples weighing initially ≈ 0.4630 g were placed in screw-tight test bottles containing about 15 to 20 mL of the solvents. The samples were removed from the bottles at regular intervals, the surface adhered liquid drops were wiped by pressing the samples in-between filter paper wraps and again weighed on a digital Mettler balance, Model AE 240 (Switzerland) within a precision of ± 0.01 mg. Equilibrium sorption was attained within 24 h which did not change over a continuing period of one or

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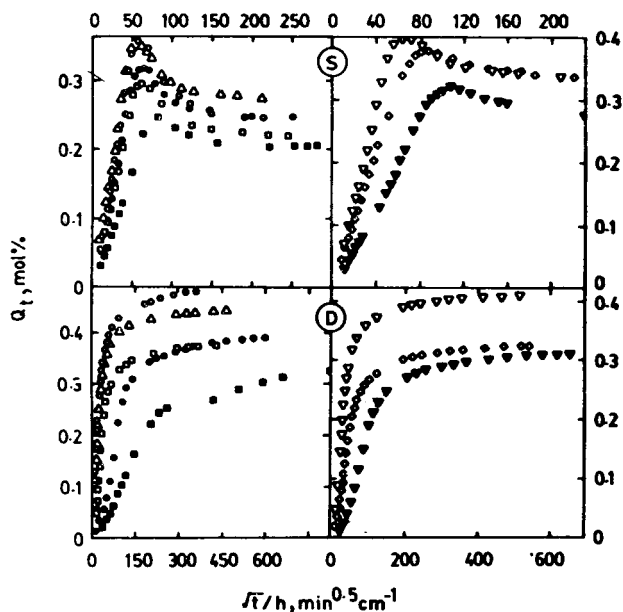


Fig. 1—Reduced plots of mol % sorption (S) and desorption (D) at 25°C for (○) benzene, (Δ) toluene, (□) ethyl benzene, (●) *p*-xylene, (▽) chlorobenzene, (◇) bromobenzene, (▼) 1,2-dichlorobenzene and (■) mesitylene.

two days. After sorption, the sorbed samples were placed in vacuum for desorption.

Resorption testing was carried out in the same manner as sorption. If Santoprene does not exhibit any weight loss during sorption and desorption, the initial weight of the polymer and weight after desorption should be the same. Initially, a weight loss of about 24–27% of Santoprene was observed during sorption and desorption runs. This is attributed to the complicated morphology of Santoprene samples. The resorbed samples were again placed in vacuum oven for a second desorption, i.e., redesorption cycle. At this time, the total percent weight loss was within 1% indicating no change in the morphological set up of the polymer.

The following relations were used to calculate the *Wt % gain* and *Wt % loss*, respectively.

$$Wt \% \text{ gain} = \frac{W_t - W_0}{W_0} \times 100 \quad \dots (1)$$

$$Wt \% \text{ loss} = \frac{W_0 - W_d}{W_0} \times 100 \quad \dots (2)$$

where W_0 and W_t are, respectively, the polymer initial weight and weight at different times of sorption experiments. W_d is the weight of the polymer after desorption.

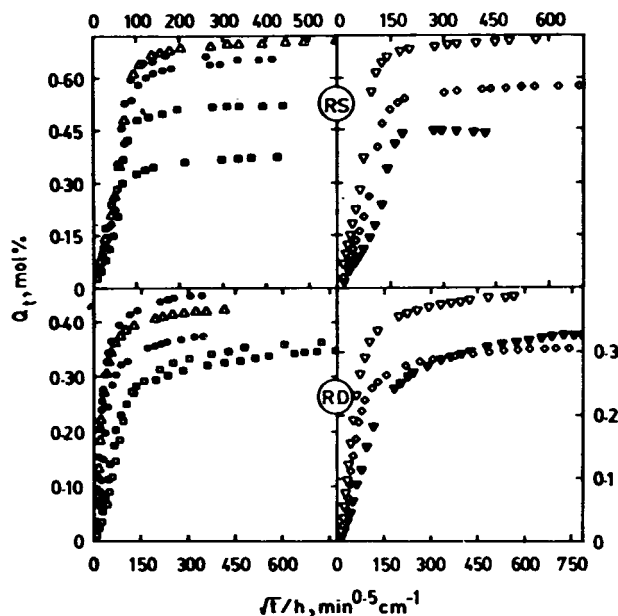


Fig. 2—Reduced plots of mol % resorption (RS) and redesorption (RD) at 25°C for Santoprene + aromatics. Symbols are the same as in Fig. 1

Results and Discussion

S–D–RS–RD phenomena—The dynamic sorption results have been fitted to the relation³:

$$\frac{Q_t}{Q_\infty} = Kt^n \quad \dots (3)$$

where Q_t is mass of solvent sorbed at time t , Q_∞ is equilibrium value and K is an empirical parameter which depends on the structural characteristics of the polymer and its interaction with solvent molecules. In desorption, Q_t and Q_∞ are the mass loss of the drying sample at time t and the completely dried sample, respectively. The value of the exponent, n indicates the type of transport mechanism. For all transport processes under consideration, the values of n vary between 0.51 to 0.68 in the temperature interval of 25–70°C suggesting the observed diffusion to be of anomalous type⁴. The values of K increase with temperature but decrease with increasing size of the liquid molecules in case of methyl-substituted benzenes suggesting the increased polymer-solvent interactions.

The reduced plots of *S–D* runs at 25°C are presented in Fig. 1, while those for *RS–RD* runs are given in Fig. 2. In all cases, the reduced curves for sorption show the overshoot effects. This effect is more for benzene and toluene than other liquids suggesting higher interactions with benzene than toluene. The overshoot effect is a

Table 1—Percent overshoot index values, solubility and diffusivity for sorption at different temperatures

Solvent	Temperature, °C			
	25	40	55	70
<i>OI</i>				
Benzene	44.91	30.92	24.31	14.99
Toluene	28.63	24.06	22.29	12.07
Ethyl benzene	34.04	26.63	22.22	13.95
<i>p</i> -Xylene	27.99	23.37	17.63	13.33
Chlorobenzene	17.23	17.11	13.90	7.69
Bromobenzene	12.25	12.68	9.85	10.35
1,2-Dichlorobenzene	16.02	9.69	16.35	1.75
Mesitylene	19.06	20.29	14.33	3.87
<i>S</i> , mol %				
Benzene	0.246	0.309	0.381	0.460
Toluene	0.275	0.315	0.363	0.455
Ethyl benzene	0.221	0.256	0.298	0.369
<i>p</i> -Xylene	0.248	0.296	0.343	0.398
Chlorobenzene	0.337	0.375	0.438	0.524
Bromobenzene	0.337	0.368	0.434	0.512
1,2-Dichlorobenzene	0.277	0.349	0.368	0.458
Mesitylene	0.207	0.240	0.290	0.393
$10^6 D$, cm ² /s				
Benzene	2.32	2.49	3.11	3.22
Toluene	2.10	2.36	2.53	3.15
Ethyl benzene	1.94	2.23	2.47	2.89
<i>p</i> -Xylene	1.55	2.30	2.42	3.30
Chlorobenzene	1.40	1.70	1.99	2.65
Bromobenzene	0.90	1.18	1.53	1.98
1,2-Dichlorobenzene	0.43	0.60	1.06	1.06
Mesitylene	0.79	1.13	1.34	1.22

further proof of the changes in morphology of Santoprene sample. Such overshoot effects have also been observed earlier^{3,5-7}.

The extent of overshoot effect has been calculated as percent overshoot index, *OI*, using³

$$OI = \frac{Q_m - Q_\infty}{Q_\infty} \times 100 \quad \dots (4)$$

where Q_m is the maximum overshoot uptake value. However, overshoot effects are not observed for desorption, resorption and redesorption runs (Figs 1 and 2). The calculated values of *OI* are given in Table 1. Of all the liquids, benzene exhibits a maximum value of *OI*. Furthermore, the values of *OI* decrease from benzene to mesitylene. Also, *OI* values show a decrease with increasing temperature. This type of dependency is not ob-

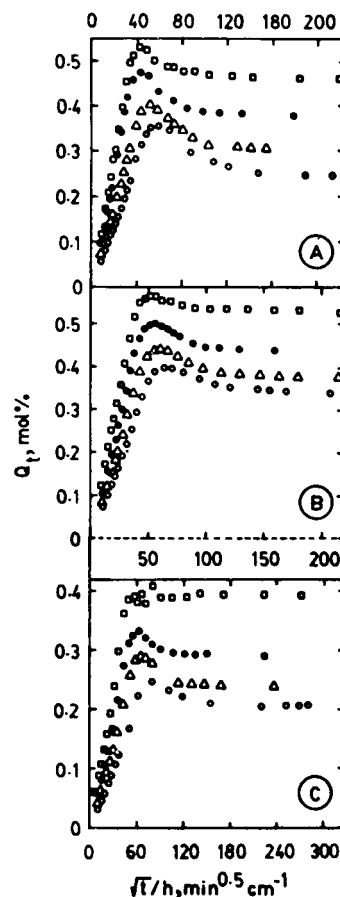


Fig. 3—Effect of temperature on sorption curves for (A) benzene, (B) chlorobenzene and (C) mesitylene. Symbols: (○) 25°C, (Δ) 40°C, (●) 55°C, (□) 70°C.

served with the *halo*-substituted benzenes. The observed lower values of *OI* for a bigger mesitylene molecule is attributed to the slow relaxation of Santoprene chain segments in the presence of a smaller benzene molecule.

The desorption, resorption and redesorption curves at 25°C are different when compared to sorption curves. Generally, the resorption uptake values are higher than the desorption or redesorption uptake values. The uptake values for desorption and redesorption runs are not very much different indicating the identical drying mechanisms in Santoprene samples. The redesorption curves follow an identical pattern to those observed for desorption runs. The time required to reach equilibrium desorption are higher in redesorption than desorption runs. Of all the liquids, mesitylene in desorption runs shows a more sigmoidal behaviour than other liquids. However, equilibrium desorption values for *p*-xylene and ethyl benzene are almost identical for desorption runs (Fig. 1). In all cases, the desorption and redesorption curves show Fickian trends. On the

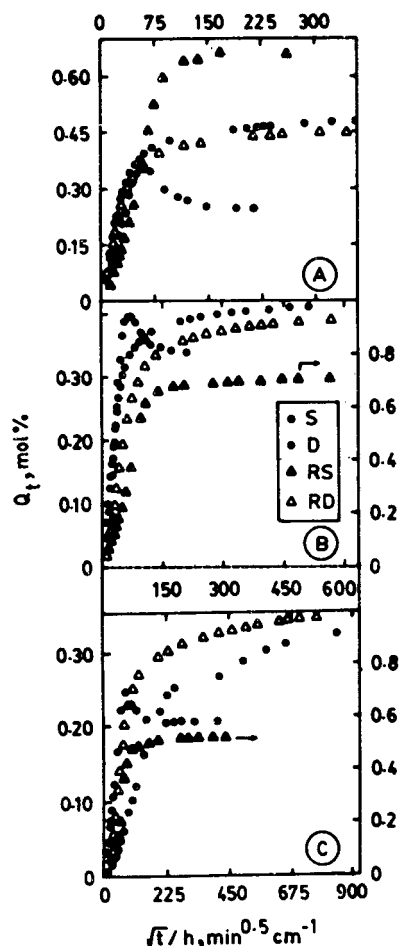


Fig. 4—Reduced plots of mol % sorption, desorption and resorption and redesorption (S—D—RS—RD) at 25°C for (A) benzene, (B) chlorobenzene and (C) mesitylene. Symbols: (●) sorption, (○) desorption, (▲) resorption, (△) redesorption.

other hand, for resorption, slight sigmoidal tendencies are observed for almost all solvents.

Typical temperature dependent sorption plots presented in Fig. 3 for benzene, chlorobenzene and mesitylene exhibit overshoot effects even at higher temperatures, but the effect is smaller at higher temperatures than at ambient conditions. This, however, depends on the type of liquid used. Typical S—D—RS—RD plots at 25°C are presented in Fig. 4, wherein, it is seen that the shapes of the curves are different for the S—D—RS—RD runs suggesting different types of transport mechanisms operating in these processes. For instance, with benzene, the desorption and redesorption curves are somewhat identical whereas, with chlorobenzene and mesitylene, the shapes of such curves in desorption and redesorption experiments are different. For chlorobenzene, all the S—D—RS—RD curves are more sigmoidal when compared to benzene or mesitylene.

Table 2—Comparison of solubility and diffusivity for desorption (D)—resorption (RS)—redesorption (RD) runs at 25°C

Solvent	D	RS	RD
		<i>S</i> , mol %	
Benzene	0.480	0.661	0.448
Toluene	0.443	0.707	0.422
Ethyl benzene	0.374	0.591	0.363
<i>p</i> -Xylene	0.389	0.654	0.373
Chlorobenzene	0.410	0.709	0.389
Bromobenzene	0.325	0.578	0.306
1,2-Dichlorobenzene	0.311	0.445	0.329
Mesitylene	0.326	0.521	0.346

	$10^6 D$, cm ² /s		
	D	RS	RD
Benzene	1.29	0.23	0.98
Toluene	0.97	0.22	0.84
Ethyl benzene	0.42	0.15	0.05
<i>p</i> -Xylene	0.03	0.19	0.33
Chlorobenzene	0.48	0.17	0.14
Bromobenzene	0.19	0.08	0.13
1,2-Dichlorobenzene	0.02	0.05	0.03
Mesitylene	0.01	0.13	0.07

In desorption experiments, a major portion of the total polymer void region is lost initially due to volume collapse of the material as observed by a decrease in the size of Santoprene samples. This is probably due to a mismatch of the time scale for liquid diffusion and polymer chain relaxation phenomenon. However, during resorption, the large scale molecular rearrangement may not take place and diffusion may be more of a void-filling process. Thus, sorption results are dependent on solvent size, its polarity, void volume and polymer morphology. It is, therefore, difficult to attribute the transport results to any one particular phenomenon and at best, it may be regarded as a combination of many transport processes occurring simultaneously.

Within the investigated temperature range, the *mol %* sorption coefficients, *S* obtained from the true equilibrium sorption values increase with temperature showing the net effect of polymer segmental movements and creation of extra free volume within the polymer matrix. These values are given in Table 1. The *S* values of benzene at 25 and 40°C are smaller than toluene, whereas at higher temperatures, these decrease with increasing size of liquids in a related series of *methyl*-substituted benzenes. However, a symmetric molecule like *p*-xylene shows lower *S* than the relatively unsymmetrical toluene at all temperatures.

On the other hand, a more polar molecule like 1,2-dichlorobenzene exhibits lower sorption than *chloro-* or *bromo-*benzenes. This suggests that the sorption results are not merely influenced by the size of the solvent molecules, but by their shapes and the interacting groups.

The *mol %* uptake values (i.e., moles of solvent sorbed per 100 g of the polymer) for D-RS-RD experiments obtained at 25°C are compiled in Table 2. The resorption uptake values follow the same trend as those observed for sorption (Table 1), but the *S* values for resorption are higher than sorption. On the other hand, desorption and redesorption values decrease from benzene to mesitylene, thus showing a dependence on the size of the liquid molecule in a related series of liquids. However, ethyl benzene shows lower values for desorption and redesorption than toluene or *p*-xylene. With *halo*-substituted benzenes, the sorption and resorption data show a decreasing trend with an increase in the size of the penetrant molecules but, for redesorption, bromobenzene exhibits the intermediary values between those of chlorobenzene and 1,2-dichlorobenzene.

Computation of diffusion coefficients—The concentration average diffusion coefficients, *D* have been calculated from the relation⁸:

$$\frac{Q_t}{Q_\infty} = 1 - \left(\frac{8}{\pi^2} \right) \sum_{n=0}^{\infty} \left\{ \left[\frac{1}{(2n+1)^2} \right] \exp \left[\frac{-D(2n+1)^2 \pi^2 t}{h^2} \right] \right\} \quad \dots (5)$$

Several numerical solutions to Eq. (5) have been suggested⁹. In the present approach, an algorithm was used to compute *D* over a range of concentration points up to about 50-55% of equilibrium sorption by the iterative procedure by fitting up to 11 points (i.e., *n* ≤ 10). Thus, the *D* values calculated by Eq. (5) and compiled in Tables 1 and 2 are regarded as the average values taken over a range of concentrations. The symbol *h* in Eq. (5) indicates thickness of the polymer sample.

The values of *D* are different in all the S-D-RS-RD processes suggesting different drying and sorption mechanisms of Santoprene in the presence of solvent media. In the present experimental systems, at all temperatures, the values of *D* for benzene are higher than the other substituted benzenes. The presence of pendant methyl groups in benzene increases the molecular size and thereby show a decrease in *D*. Mesitylene has the smallest *D* than other *methyl*-substituted ben-

zenes. The presence of a still larger ethyl group as in ethyl benzene renders the molecule more sluggish showing a decrease in *D* as compared to toluene. Similarly, diffusivity decreases systematically with increasing size of *halo*-substituted benzenes. However, in all cases, the values of *D* increase with increasing temperature. The *D* values for D-RS-RD processes at 25°C also decrease with increasing size of *methyl*-substituted benzenes as well as *halo*-substituted benzenes. Ethyl benzene shows lower *D* values than a somewhat similar size liquid such as *p*-xylene for the RS-RD runs. Similar observations also hold good for toluene and bromobenzene which have almost identical size, but *D* is higher than bromobenzene for the D-RS-RD processes. This suggests that the diffusion results are affected not only by the type of substitution on benzene, but also the nature of the transport processes.

Diffusion of homologous paraffin hydrocarbons into rubbery polymers has been studied¹⁰. It was observed that the presence of side methyl groups in a molecule lowers diffusivities more than in the absence of such groups. Conversely, when liquid molecules are of comparable diameter, but having different substitutions, then the effect of change in polarity of the molecule governs the diffusion mode. This appears to be the case for 1,2-dichlorobenzene whose *D* values are smaller than other *halo*-substituted benzenes, because of its high polarity.

Solvent diffusion into solid polymer matrices also depends on the availability of appropriate molecular size, free voids and the attractive forces between the liquids and the polymer. The presence of voids is a function of both polymer structure and its morphology. Santoprene is a lightly crosslinked polymer with dense regions distributed randomly within the entire matrix. When in contact with the liquid media, due to solvent migration, Santoprene chains expand so that the chain-links become somewhat weaker. This implies that polymer chains between crosslinks move more freely and the molecular mobility of the network is enhanced through diffusion of solvent molecules. Diffusion in rubbery polymers is thus influenced by solvent viscosity, *η*, as shown in Fig. 5. Such a correlation was also observed earlier by Vahdat¹¹. The trend in the variation of *D* with liquid viscosity is also in accordance with the well-known Stokes-Einstein relation¹²:

$$D = \frac{kT}{6\pi\eta r} \quad \dots (6)$$

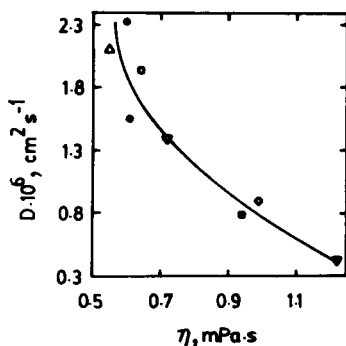


Fig. 5—Relationship between viscosity and diffusivity for Santoprene + aromatics at 25°C. Symbols are the same as in Fig. 1.

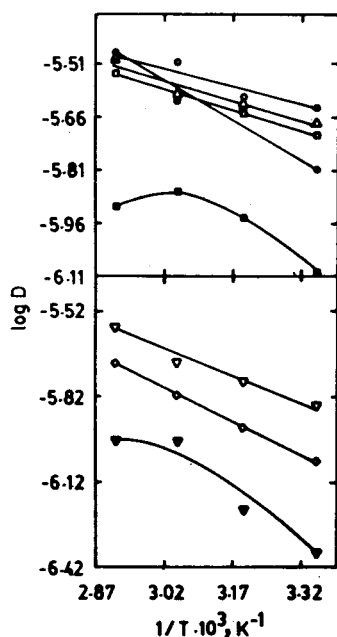


Fig. 6—Arrhenius plots for the dependence of $\log D$ vs $1/T$ for Santoprene + aromatics. Symbols are the same as in Fig. 1.

where k is Boltzmann constant, T is temperature in absolute and r is hydrodynamic radius of the transporting molecule into the polymer matrix.

Arrhenius activation parameters—It was realized that the temperature dependence of both sorption and diffusion follow Arrhenius behaviour. The activation energy for diffusion, E_D has been estimated from a least-squares analysis of the $\log D$ versus $1/T$ results, presented in Fig. 6, according to the following relation.

$$\ln D = \ln D_0 - E_D/RT \quad \dots (7)$$

Here, D_0 is a pre-exponential factor and RT has the usual meaning of energy. The E_D values presented in Table 3, increase with increasing size of

Table 3—Arrhenius values and molar volume for Santoprene + liquids

Solvent	E_D , kJ/mol	ΔH_s^* , kJ/mol	V^* , cm ³ /mol
Benzene	6.88	11.82	89.4
Toluene	7.20	9.29	106.9
Ethyl benzene	7.37	9.52	123.1
<i>p</i> -Xylene	13.19	8.86	123.9
Chlorobenzene	11.72	8.33	102.2
Bromobenzene	14.92	8.00	105.5
1,2-Dichlorobenzene	18.83	8.85	113.1
Mesitylene	8.61	11.85	135.6

*Calculated at 25°C using $V = \frac{\text{mol wt}}{\text{density}}$

the *methyl*-substituted benzenes except mesitylene. For *halo*-substituted benzenes, E_D increases from chlorobenzene to 1,2-dichlorobenzene showing a dependence on the molar volume of the liquid.

The results of S have been analyzed using van't Hoff equation:

$$\ln S = \ln S_0 - \frac{\Delta H_s}{RT} \quad \dots (8)$$

where ΔH_s is heat of sorption and is a composite parameter which depends on both Henry's law and Langmuir's type sorption, S_0 is a pre-exponential factor, R is universal gas constant and T is temperature in absolute. In the present systems, the values of ΔH_s are positive indicating the presence of Henry's law sorption mode. The values of ΔH_s decrease from benzene to *p*-xylene except mesitylene. However, the ΔH_s values for benzene and mesitylene are almost identical signifying no side group substitution effect on the parent benzene moiety.

Conclusions

This paper presents an analysis of sorption, desorption, resorption, redesorption and diffusion of *methyl*- and *halo*-substituted benzenes into Santoprene by a gravimetric method in the temperature interval of 25–70°C. Analysis of the results leads to the understanding that solvent transport depends on the size as well as their chemical interactions. At higher temperatures, the increase in diffusion and relaxation rates of the polymer, accompanied by an increase in Santoprene void volume resulted in a higher equilibrium penetrant uptake. The overshoot effects have been associated with the

complicated morphology of Santoprene matrix. The Santoprene-solvent systems of the present study are classified to follow the anomalous type transport mechanism.

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Nomenclature

S - D - RS - RD = Sorption-Desorption-Resorption-Redesorption

W_0	= Initial weight of the polymer, g
W_t	= Weight of the wet polymer sample at time t , g
W_d	= Weight of polymer after desorption, g
Q_t	= Mass of solvent sorbed at time t , mol%
Q_∞	= Mass of solvent at equilibrium, mol%
K	= Empirical parameter in Eq. (3)
n	= Exponent of t in Eq. (3)
OI	= Percent overshoot index
Q_m	= Maximum overshoot uptake value, mol%
S	= Sorption coefficient, mol%
n	= Number of terms used for calculation in Eq. (5)
D	= Diffusion coefficient, cm^2/s
t	= time, min
h	= Initial thickness of the polymer sample, cm
η	= Viscosity of liquid, mPa s
T	= Temperature in absolute scale, K
E_D	= Energy of activation for diffusion, kJ/mol

D_0	= Pre-exponential factor in Eq. (7)
R	= Gas constant, J/mol K
S_0	= Pre-exponential factor in Eq. (8)
ΔH_s	= Heat of sorption, kJ/mol
k	= Boltzmann constant
r	= Hydrodynamic radius of the transporting molecule
V	= Molar volume of liquid, cm^3/mol

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