

Migration of Substituted Aromatic Solvents into Polyurethane/Polystyrene Semi-Interpenetrating Polymer Network

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ABSTRACT: The molecular transport of substituted aromatic solvents through polyurethane/polystyrene (PU/PS, 50/50) semi interpenetrating polymer network has been investigated at 20, 40, and 60°C. Sorption–desorption–resorption–redesorption (S-D-RS-RD) experiments were performed to determine the true value of transport coefficients. Sorption results are obtained by a gravimetric method and diffusion coefficients have been calculated using Fick's equation for the linear data points of time dependent sorption/resorption curves. It was observed that most of the systems follow the Fickian mode of transport. The first order kinetic equation was used to estimate the kinetic rate constant of sorption. Activation parameters for

different transport processes were evaluated and the results were used to discuss the polymer–solvent interactions. The concentration profiles at different depths along the thickness of membranes and at different time intervals were computed using Fick's equation under appropriate boundary conditions. The rate of evaporation of liquids has been calculated for desorption and redesorption processes, and these results depend on the volatility of aromatic solvents. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 378–390, 2007

Key words: PU/PS; aromatic penetrants; Fickian; diffusion coefficient; profile

INTRODUCTION

Interpenetrating polymer network (IPN) is an entanglement of the polymer networks synthesized or crosslinked in the immediate presence of each other and consequently held together by permanent topological entanglements. Castor oil based polyurethane (PU) IPNs were extensively studied by many scientists.^{1–3} PUs are highly versatile materials that have been used in the human body for over 20 years. Properties such as durability, elasticity, fatigue resistance, compliance, and acceptance or tolerance in the body during the healing are often associated with PUs.⁴ The review article of Zdrahala et al.⁵ notice that PUs are one of the most bio- and blood-compatible materials known today. PU materials are playing major role in the development of many medical devices ranging from catheters, scaffolds, pacemakers, self-healing bandages, and total artificial heart.^{6,7} The PU materials are being modified for better medical applications.⁴ The polyethylene glycol (PEG) based PUs and its IPNs possess good physicochemical and optical properties. These IPNs are biocompatible, biostable, and some are biodegradable.^{8–10} The use of PU IPNs

as a barrier material and behavior of solvents during sorption–desorption–resorption–redesorption (S-D-RS-RD) cycle is of much relevance due to immense practical application of polymers in pervaporators,¹¹ holding tanks, packing materials, marine and biomedical applications. Though lot of attention is focused to evaluate solvent transportation into polymers, difference in sorption and desorption has not been fully established. The consistency of polymer system for repeated sorption, resorption, desorption, and redesorption is very much important for the materials to be used for aforementioned applications. The use of polymer membranes as liners in storage tanks for hazardous liquid is increasing,¹² making it very much important to understand the interaction of hazardous liquids with polymer membranes. The physical contact of polymer systems with organic liquids for long duration may lead to sorption and then desorption. But, the knowledge of desorption is very important to know whether the liquid is completely expelled or not. The contamination of PU IPNs used in biomedical applications by organic solvents may lead to degradation and thus it may become unsuitable for designed applications. The thorough literature survey revealed that there is a lack of molecular transport data on PEG based PU and its IPNs. Hence, it is essential to know the behavior of such IPNs towards different chemical environments. In this research article the systematic studies

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TABLE I
Physical Constant of Aromatic Solvents

Name	Molecular mass	Molar volume (cm ³ /mol)	Density (g/cm ³)	Viscosity (MPa s)	Solubility parameter (MPa) ^{1/2}
Benzene	78	88.7	0.879	647	18.82
Toluene	92	106.1	0.867	590	18.21
Chlorobenzene	112	101.3	1.106	830	19.84
Nitrobenzene	123	102.2	1.2033	1980	20.46

on the molecular transport of aromatic solvents into polymer of practical interest were made. The polyurethane/polystyrene (PU/PS, 50/50) IPN system was exposed to aromatic solvents to study S-D-RS-RD at different temperatures to establish structure–property relationship of polymer membrane. The S-D-RS-RD results were used to estimate the kinetic rate constant and the Arrhenius parameters for various transport phenomena. Flory–Rehner theory^{13,14} was used to obtain polymer–solvent interaction parameters. The efforts were also made to correlate sorption to solubility parameters of solvents and polymer system.

EXPERIMENTAL

Materials

Polyethylene glycol-400 (PEG) and 4,4'-diphenyl methane diisocyanate (MDI) based PU/PS (50/50, wt/wt ratio) semi interpenetrating polymer network (SIPN) was prepared as reported elsewhere.¹⁵ The tensile strength and percentage elongation at break for tough and transparent IPN sheets are 21.45 MPa and 22, respectively. The free volume measured by positron annihilation life time studies indicates 17.53% of hole with the size of 60.25 Å in the polymer network. The solubility parameter of the PU/PS IPN is calculated by Small's group additive method and it is found to be 23.51 (MPa)^{1/2}.

The analytical grade benzene, toluene, chlorobenzene, and nitrobenzene were procured from SD fine chem. (Mumbai, India). These solvents were distilled before being used and some of the properties of penetrants are given in Table I.

Sorption–desorption–resorption–redesorption experiments

Circular disc shaped samples of diameter ranging from 1.609 to 1.618 cm and thickness ranging from 0.042 to 0.122 cm were cut from these sheets using sharp-edged carbon-tipped steel die. The samples were initially dried in vacuum desiccators over anhydrous calcium chloride at room temperature for 24 h before the experiments. The previously weighed dry and disc shaped PU/PS (50/50) samples were soaked in screw-tight bottles containing about 15–20 cm³ of the liquids maintained at the desired temperature

(±0.5°C) in thermostatically controlled oven (M/s Tempo Laboratories, Mumbai). Polymer samples were removed periodically, the solvent drops adhering to the surface were wiped off using filter paper wraps, and samples were weighed immediately on a digital analytical balance (Mettler Toledo, Switzerland) with in the accuracy of 0.01 mg. Samples reached equilibrium saturation such that no more mass gain occurred and this did not change significantly by keeping the samples inside the container for a further period of one or two days. The weight gain during sorption is expressed as moles of solvent uptake by 100 g of polymer sample (C_t , mol %):

$$C_t \text{ mol \%} = \frac{\text{Mass of solvent sorbed/Molar mass of solvent}}{\text{Mass of polymer}} \times 100 \quad (1)$$

After sorption experiments, the sorbed IPN specimens were taken out of solvent and placed at same temperature for desorption of solvent. The decrease in weight was monitored periodically until constant weight is achieved. The weight loss after desorption were expressed as moles of solvent lost by 100 g of polymer sample (C_d mol %):

$$C_d \text{ mol \%} = \frac{\text{Mass of solvent desorbed/Molar mass of solvent}}{\text{Mass of polymer}} \times 100 \quad (2)$$

Mass of polymer

The resorption experiment was carried out in the same manner as sorption. The resorbed samples were subjected to redesorption as explained earlier. The comparisons of S-D-RS-RD results help us to know the consistency and suitability of membrane for pervaporation, geotextile, and other engineering applications.

RESULTS AND DISCUSSION

Sorption kinetics

The dynamic aromatic penetrant sorption results were analyzed using the empirical equation¹⁶:

TABLE II
System Parameters n and K for PU/PS IPN Membranes at Different Temperatures

Penetrants	Temp (°C)	$n \pm 0.01$		$K \pm 0.05$ (g/g, min ^{n})	
		Sorption	Resorption	Sorption	Resorption
Benzene	20	0.55	0.53	117.78	45.16
	40	0.52	0.54	78.37	16.45
	60	0.50	0.54	35.35	32.85
Toluene	20	0.49	0.51	31.87	41.18
	40	0.51	0.51	37.67	29.39
	60	0.54	0.51	46.49	26.38
Chlorobenzene	20	0.51	0.56	28.11	24.49
	40	0.56	0.53	15.71	12.31
	60	0.52	0.51	29.53	18.65
Nitrobenzene	20	0.59	0.54	37.65	24.85
	40	0.49	0.50	7.94	9.13
	60	0.55	0.47	17.5	10.73

$$M_t/M_\infty = Kt^n \quad (3)$$

where, M_t and M_∞ are mass of solvent sorbed at time t and equilibrium, respectively, and K is system parameter which depends on the structural characteristics of the polymer material and on the penetrant-polymer interactions. The exponent n tells about the type of transport mechanism. If the value of n is around 0.5 then the transport phenomenon is said to be Fickian. If the value is 1, then the transport of solvents is found to be non-Fickian. But when the value of n lies closer to 0.5 for almost all polymer-solvent system, it is said to be near Fickian. The estimated values of n and K by least square analysis method at 95% confidence level for the sorption and resorption processes are compiled in Table II. The estimated values of n and K are accurate to ± 0.01 and ± 0.05 units, respectively.

The values of n for sorption varied 0.49–0.59 in the temperature intervals of 20–60°C, whereas for resorption it was 0.47–0.56 in the same temperature range. In majority of the cases n value lie in the range 0.5–0.6, suggesting that the diffusion mechanism to be of anomalous type, but still closer to Fickian trend.¹⁷ No systematic dependence of n with temperature is observed for all IPN-solvent systems. The values of K for resorption are smaller than those observed for sorption, indicating milder IPN-aromatic penetrant interactions. The value of K did not show any systematic variation.

The S-D-RS-RD of nitrobenzene, chlorobenzene, toluene, and benzene for PU/PS membrane at 20°C are given in Figure 1(a–d). From the figure it is observed that the mass uptake is highest for nitrobenzene and lowest for toluene during sorption. The time required to attain equilibrium is different for different penetrants and it depends on molar volume,¹⁸ nature, size, and solubility parameter of probe molecules. Nitrobenzene reached equilibrium in short duration,

whereas toluene took more time. This is due to lower molar volume of nitrobenzene as compared to toluene. Desorption curves indicate that the mass of solvent desorbed at 20°C is more for nitrobenzene and low for toluene. The sorption and desorption is following almost same trend for all solvent-polymer systems. During resorption the mass uptake is in the order nitrobenzene > chlorobenzene > benzene > toluene. Same trend continued during redesorption.

The mol % sorption coefficient S for sorption and resorption processes is calculated from the following equation¹⁸:

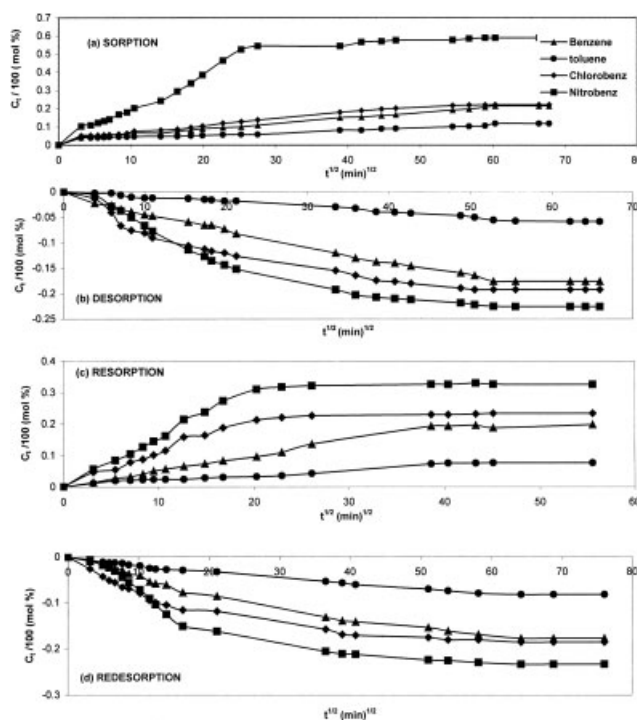


Figure 1 (a–d): The sorption (S), desorption (D), resorption (RS), and redesorption (RD) of nitrobenzene, chlorobenzene, toluene, and benzene at 20°C with PU/PS IPN.

TABLE III
Sorption (*S*), Diffusion (*D*), and Permeation Coefficients of PU/PS IPN Membranes
During Sorption and Resorption Processes

Penetrants	Temp (°C)	$S \times 10^2$ ($\pm 0.3\%$) (mol %)		$D \times 10^8$ ($\pm 0.4\%$) (cm ² /s)		$P \times 10^8$ ($\pm 0.35\%$) (cm ² /s)	
		Sorption	Resorption	Sorption	Resorption	Sorption	Resorption
Benzene	20	30.15	19.78	0.3	0.74	0.09	0.15
	40	40.4	35.5	1.06	2.3	0.43	0.82
	60	55.76	46.22	3.49	5.41	1.95	2.5
Toluene	20	18.13	7.68	0.24	0.69	0.04	0.05
	40	21.09	18.49	0.42	0.85	0.09	0.16
	60	36.43	33.68	1.32	2.64	0.48	0.9
Chlorobenzene	20	37.52	28.3	1.35	0.87	0.5	0.25
	40	40.41	36.9	3.98	4.9	1.6	1.81
	60	52.74	52.12	5.52	13.42	2.91	7
Nitrobenzene	20	56.16	32.53	4.06	2.06	2.28	0.67
	40	58.57	50.94	4.73	5.15	2.77	2.62
	60	66.51	63.15	9.78	16	6.5	10.11

$$S = M_{\infty}/M_p \quad (4)$$

where, M_{∞} is the mass of solvent uptake at equilibrium and M_p is the initial polymer mass. The measured S values are given in Table III and it depends on the chemical nature of solvent rather than their size.¹⁹ Comparing all the liquids, nitrobenzene shows higher S value, ranging from 56.2 to 66.5 during sorption and from 32.5 to 63.1 for resorption process. However, toluene shows the lowest S value of 18.1–36.4 during sorption whereas 7.7–33.7 during resorption process.

The temperature-dependent sorption curves are given in Figure 2 for all substituted aromatic solvents. From these figure it was noticed that the sorption increases with temperature.²⁰ The equilibrium sorption for toluene was smaller than other solvents during both sorption and resorption processes. The order of solubility parameter of solvent is nitrobenzene > chlorobenzene > benzene > toluene. The S value for nitrobenzene is higher than other penetrants. This can be attributed to less difference in solubility parameter between PU/PS [23.51 (MPa)^{1/2}] and nitrobenzene [20.46 (MPa)^{1/2}]. As the difference between solubility parameter of polymer and solvent decreases the S value increases. We have noticed similar trend for the sorption of substituted aromatic solvents into PU/PMMA IPNs.²¹ Karst and Yang also made similar observation for the sorption of dyes on polylactides.²² From Figure 3 it was observed that sorption increases as solubility parameter of the solvent approaches the solubility parameter of IPN. However, it was observed that the mass uptake values are higher for sorption than the corresponding resorption process. This may be due to change in morphology of polymer membrane.

The first-order kinetic model has been used to follow the kinetics of sorption and diffusion of solvents through PU/PS IPN. To apply this kinetic model it is

assumed that during sorption of solvents, structural changes may occur in polymer chains, which require a rearrangement of the polymer segments that can dominate the kinetic behavior.²³ According to the first-order kinetic equation

$$dc/dt = k(C_{\infty} - C_t) \quad (5)$$

where, k is the first-order rate constant, and C_t and C_{∞} represent the concentrations at time t and at equilibrium, respectively. Integration of the above equation gives

$$kt = 2.303 \log[C_{\infty}/(C_{\infty} - C_t)] \quad (6)$$

From the plots of $\log[C_{\infty}/(C_{\infty} - C_t)]$ versus t for different solvents, rate constant were calculated by regression analysis and the results are given in Table IV. The rate constant for sorption and resorption process increases with increase in temperature. The calculated values of k are in expected lines. The values tabulated in Table IV reveals that k value increases with increase in solubility parameter of the penetrant molecule. However, higher k value was noticed for resorption process. This may be probably due to free path created by the relaxation of polymer chains during sorption and desorption.

Diffusion coefficients

The diffusion coefficient D can be calculated using the following equation²⁴:

$$C_t/C_{\infty} = [1 - [8/\pi^2] \sum_{n=0}^{\infty} \left\{ [1/(2n+1)]^2 \times \exp[-D(2n+1)^2 \pi^2 t/h^2] \right\}] \quad (7)$$

where, t is the time and h is the initial thickness of the polymer membrane. During early stages of sorption,

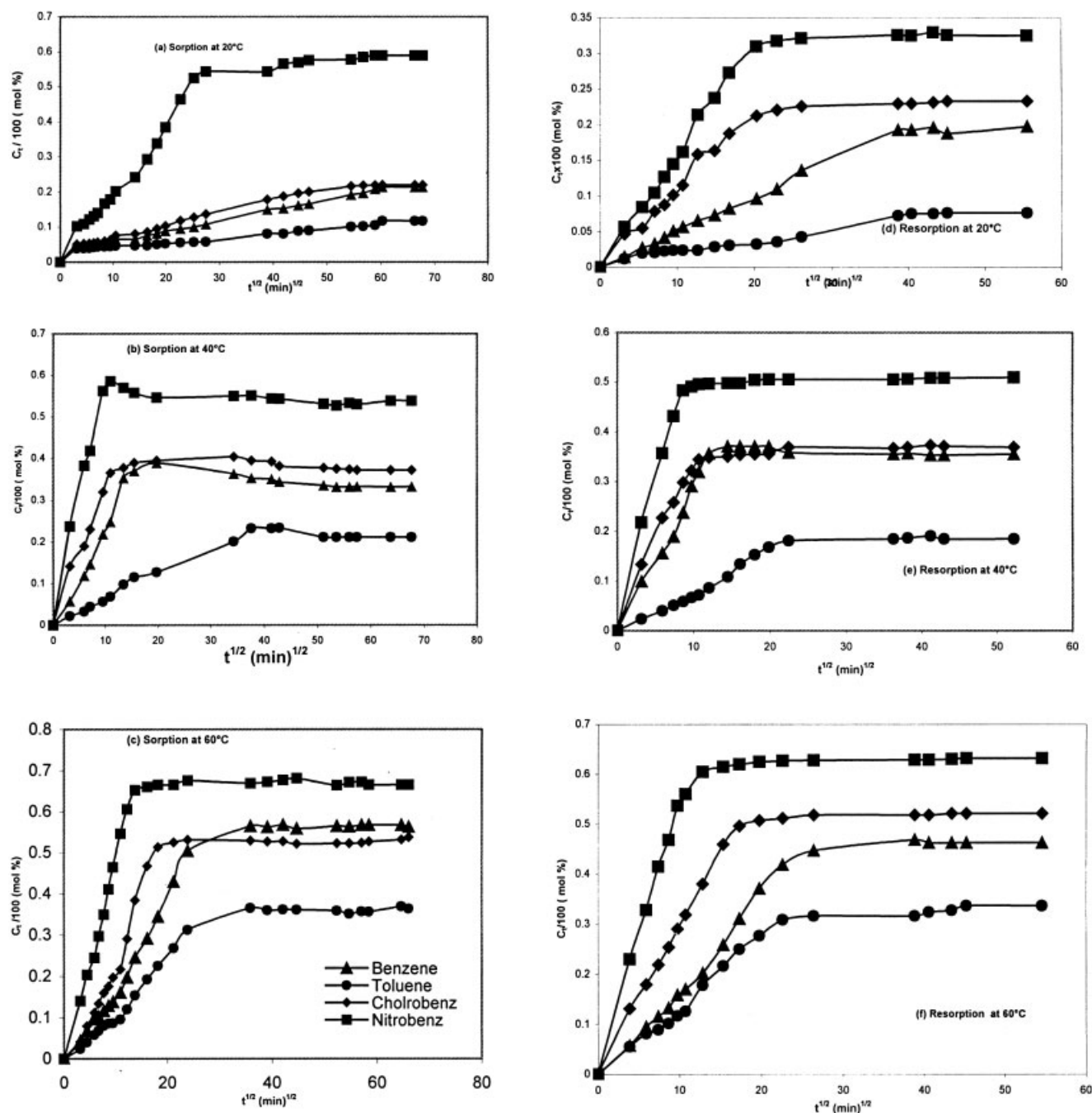


Figure 2 The mol % uptake of nitrobenzene, chlorobenzene, toluene, and benzene during (a–c) sorption and (d–f) desorption processes at different temperatures.

D becomes concentration dependent so that it can be calculated by using

$$C_t/C_\infty = (4/h) (Dt/\pi)^{1/2} \quad (8)$$

From the plots of C_t versus $t^{1/2}$, a straight line is obtained initially in the majority of cases. Thus D can be calculated from a rearrangement of eq. (8) as

$$D = \pi [h \theta/4 C_\infty]^2 \quad (9)$$

where, h is the sample thickness, and θ is the slope of the initial linear portion of sorption curves, i.e., before the attainment of 50% of equilibrium uptake. The diffusion coefficients obtained from eq. (9) for sorption and desorption processes are presented in Table III. The D value for sorption is high for nitrobenzene and low for toluene at all temperatures. This is probably due to higher affinity of nitrobenzene to polar PU/PS IPN system. Aithal et al.²⁵ noticed similar trend for diffusion of aromatic compounds through PU membranes. Even during desorption the D value is highest

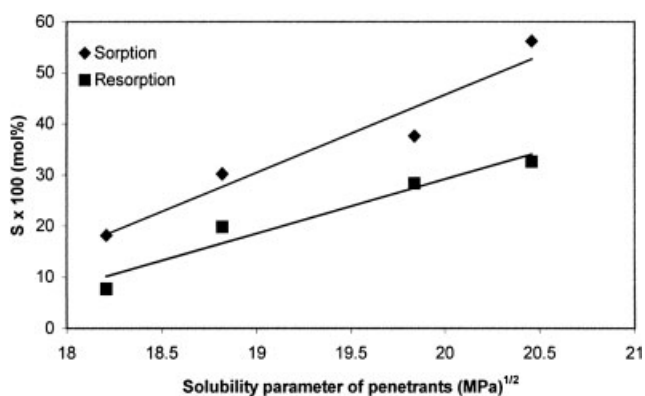


Figure 3 Sorption coefficient versus solubility parameter of penetrants.

for nitrobenzene and lowest for toluene. In majority of cases the D value during resorption process is found to be more than the corresponding value in sorption. This indicates that there may be structural and morphological changes that take place in SIPN and thus, there is an increase in diffusion of solvent into membranes. The values of D for the process of sorption increase with increase in temperature for all liquids and do not show any dependence on the size of the liquids. For instance bulkier nitrobenzene and chlorobenzene exhibit higher values of D .¹⁹ The effect of solubility parameter of penetrants (Table I) on D values at 20°C is shown in Figure 4. The solubility parameters of penetrants are lower than the solubility parameter of PU/PS IPN. As the solubility parameter of solvents approaches the solubility parameter of IPN, the value of D is found to increase. This clearly indicates that there is more interaction between polymer and solvents.

The permeability coefficient P is calculated^{24–26} using $P = DxS$. The penetrant molecules are first sorbed by polymer followed by diffusion through the polymer membrane. The net diffusion through polymer depends on the concentration gradient of penetrant molecules between the two surfaces.²⁷ It was generally observed that the results of P followed the same pattern as those of D in the investigated temperature range. The sorption, diffusion, and permeation coefficients at 20, 40, and 60°C for sorption–resorption processes are given in Table III. The values of these

coefficients were different for these processes, suggesting the possible morphological changes of PU/PS in the presence of penetrant during the cyclic S-D-RS-RD experiments.

Using the D values calculated from eq. (8), the theoretical sorption curves have been generated using eq. (7) and these are compared with the experimental curves in Figure 5 for toluene, chlorobenzene, and nitrobenzene at 20°C for sorption. The coexistence of curves indicates the agreement between theoretical and experimental value. The comparison of experimental and theoretical curves for resorption at 20°C in Figure 6 shows a good agreement. Verification of these theoretical and experimental data for nitrobenzene at 40°C for sorption and resorption processes are shown in Figure 7. From the figure it is found that the agreement between calculated and experimental curves is not very good at longer sorption times, suggesting the possible concentration dependence of D .

Concentration profiles

Diffusion coefficient has been calculated from Fickian equation. Liquid ingress into the polymeric sheet materials is a phenomenon of great technological importance. Hence, the concentration profiles of liquids through PU/PS IPN membranes have been evaluated by computer-simulated method. To calculate concentration profiles Fick's second order differential equation is used in its most general form:

$$\partial c / \partial t = D(\partial^2 c / \partial x^2) \quad (10)$$

where, D is the concentration-independent diffusion coefficient, t is the sorption time, c is the liquid concentration within the membrane materials, and $\partial c / \partial x$ is the concentration gradient along the x direction. Equation (10) is solved using the following assumptions: (i) liquid diffusion into the membrane takes place in one direction only; (ii) sorption takes place under transient conditions with a constant diffusivity; (iii) during sorption, when the membrane is exposed to solvent, its concentration on the membrane surface reaches equilibrium immediately; (iv) the time required for the membrane to establish thermal equilibrium is negligible when compared to the time of

TABLE IV
Rate Constant (k) for Diffusion of Penetrant During Sorption and Resorption Processes

Temp (°C)	$k \times 10^3 (\pm 2\%) (\text{min}^{-1})$							
	Benzene		Toluene		Chlorobenzene		Nitrobenzene	
	Sorption	Resorption	Sorption	Resorption	Sorption	Resorption	Sorption	Resorption
20	0.5	1.1	0.04	0.8	0.08	2.0	1.7	2.1
40	1.5	1.4	0.6	1.3	1.7	3.5	3.5	7.5
60	2.3	3.8	1.7	1.7	4.1	7.5	5.1	7.7

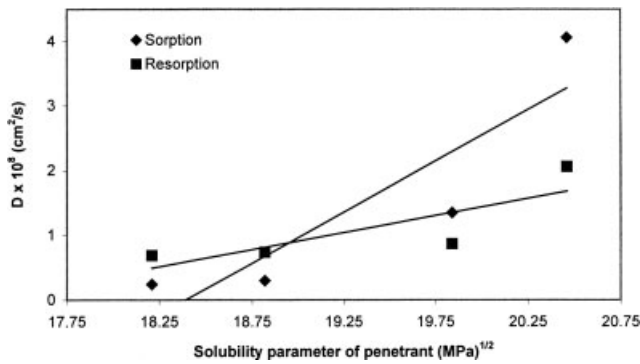


Figure 4 Diffusion coefficient versus solubility parameter of penetrants.

sorption; and (v) changes in the membrane dimensions are negligible during the liquid exposure at the initial and boundary conditions, that is,

$$t = 0 \quad 0 \leq x < h \quad c = 0 \quad (11)$$

$$t \geq 0 \quad x = 0, \quad x = h \quad c = c_{\infty} \quad (12)$$

$$\partial c / \partial x = 0, \quad x = 0, \quad t > 0 \quad (13)$$

In many instances, it would be necessary to know the penetration depths of the liquids into polymers. However, their accurate experimental calculations require the use of sophisticated experiments. In the absence of these tools, we can predict the probable concentration profiles by solving eq. (10) under the

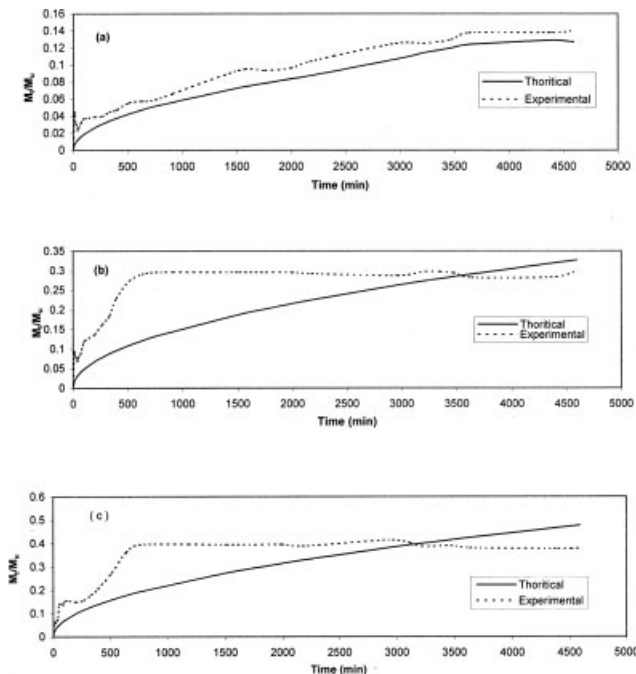


Figure 5 Comparison of theoretical M_t/M_{∞} with experimental of (a) toluene, (b) chlorobenzene, and (c) nitrobenzene with PU/PS at 20°C during sorption.

suitable boundary conditions to give the concentration profile $c_{(t,x)}/c_{\infty}$ of the liquids within the polymer membrane as a function of the penetration depth (i.e., distance x), the thickness of the membrane, and time t :

$$C_{(t,x)}/C_{\infty} = 1 - \frac{4}{\pi} \sum \frac{1}{(2n+1)} \times \exp[-d(2n+1)^2\pi^2t/h^2] \sin[(2n+1)\pi x/h] \quad (14)$$

where, $C_{(t,x)}$ and C_{∞} are concentration of liquid sorbed at time t and distance x and at equilibrium, respectively, n is an integer. Solving eq. (14), we get concentration profiles of the migrating liquids developed within the membrane. These data are useful to study the liquid migration as a function of time and penetration of the liquid from face to the middle of the membranes along the thickness direction.

The concentration profiles generated for PU/PS based IPN with chlorobenzene during sorption at 20 and 40°C with different time intervals are given in Figure 8. From this it was observed that the higher values of $C_{(t,x)}/C_{\infty}$ at 40°C for PU/PS-chlorobenzene system. From these figures it is noticed that with increase in temperature the values of $C_{(t,x)}/C_{\infty}$ increases.

The concentration profiles of PU/PS IPN at 20°C with benzene, toluene, chlorobenzene, and nitrobenzene for resorption process are shown in Figure 9. From Figure 9 higher $C_{(t,x)}/C_{\infty}$ value was noticed for nitrobenzene. This is due to higher interaction of PU/PS IPN with more polar nitrobenzene. Thus the simulation method appears to be a sensitive test protocol

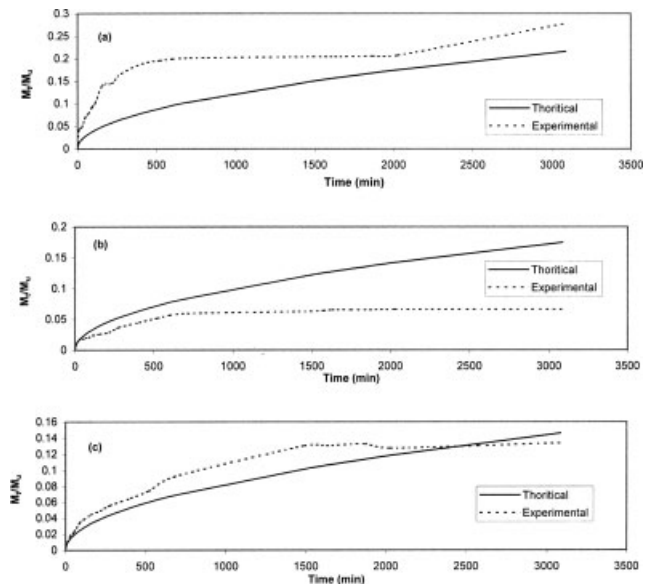


Figure 6 Comparison of theoretical M_t/M_{∞} with experimental for (a) chlorobenzene, (b) toluene, and (c) benzene with PU/PS during resorption at 20°C.

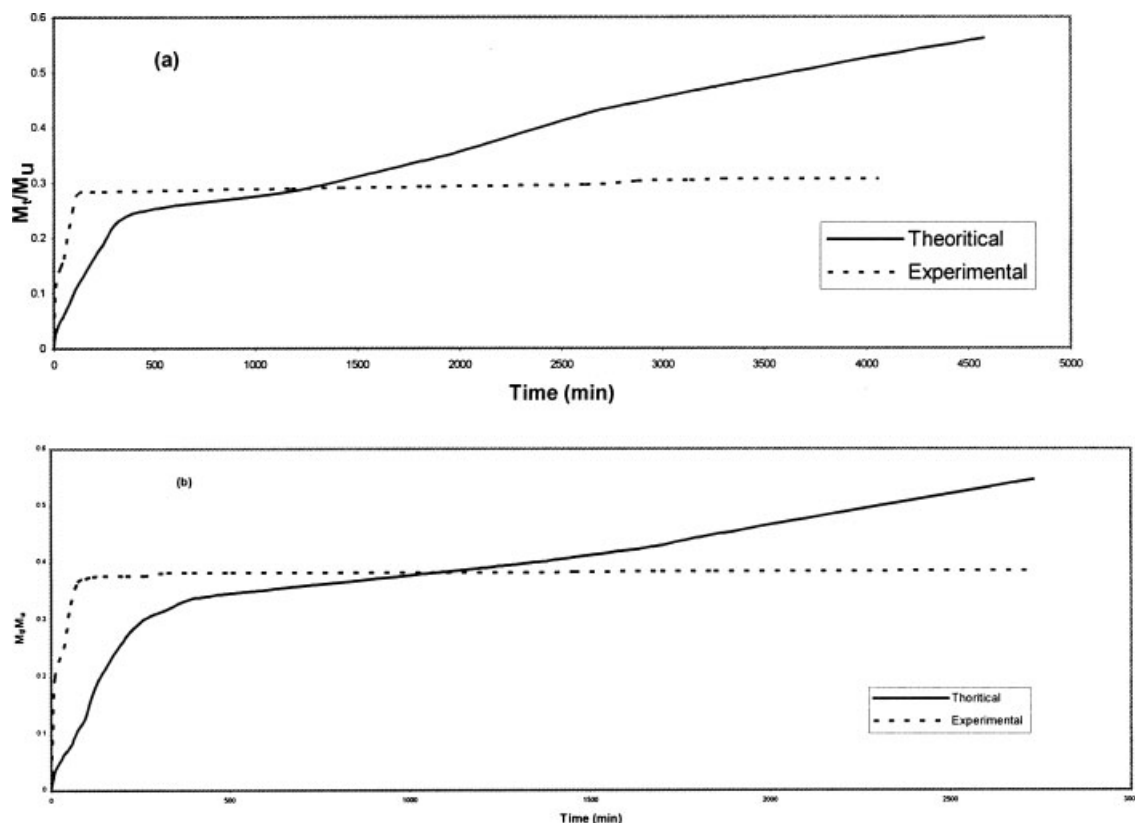


Figure 7 Comparison of theoretical M_t/M_∞ with experimental for nitrobenzene in PU/PS at 40°C during (a) sorption and (b) desorption.

to predict the concentration profiles rather than mere calculation of the values of D .

It may further be demonstrated that with an increasing immersion time the concentration profile also increases drastically. Wherein it is found that the variations are quite drastic and these variations confirm that the D value in these system exhibit considerable concentration dependency, a fact that has been a formidable problem in the literature²⁸ and especially more so in complicated systems such as IPN membranes used in this study. At any rate, the present simulation method is convenient and helpful to predict the liquid concentration profiles, provided that the diffusion data of the liquid-polymer systems are available.

Desorption

For desorption, it is important to calculate the rate of mass loss of the membrane due to solvent evaporation²⁹:

$$-D(\partial C/\partial t) = F_0(C_0 - C_{\text{ext}}) \quad (15)$$

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_{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. (15) to give²⁹

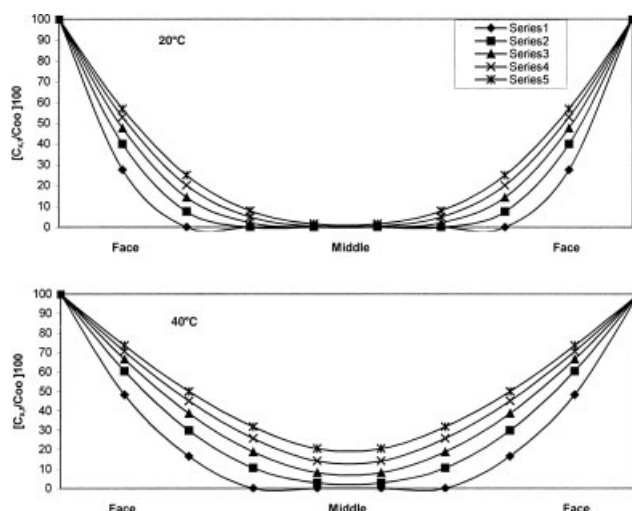


Figure 8 Concentration profiles of chlorobenzene in PU/PS at different temperatures during sorption at series (1) 10 min, (2) 20 min, (3) 30 min, (4) 40 min, and (5) 50 min.

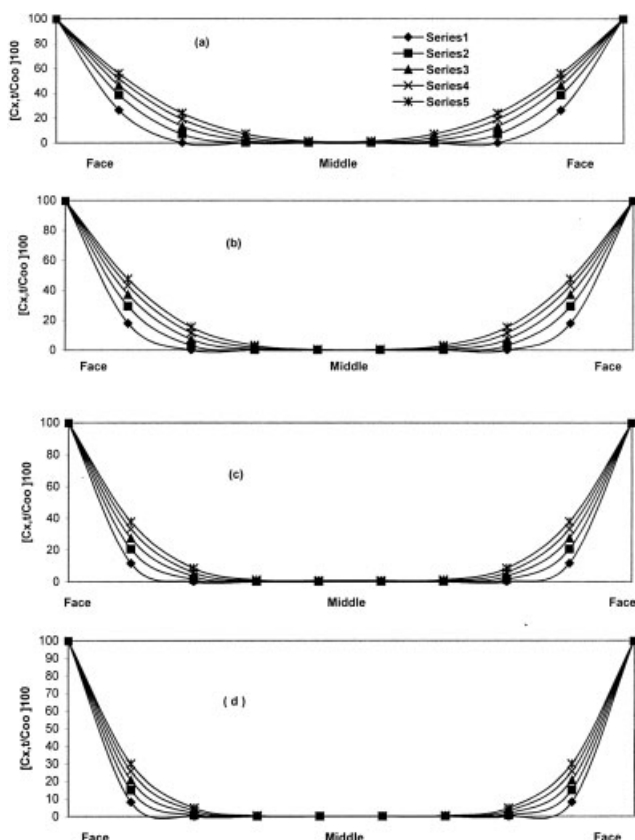


Figure 9 Concentration profiles of (a) nitrobenzene (b) chlorobenzene (c) toluene, and (d) benzene in PU/PS at 20°C during resorption at series (1) 10 min, (2) 20 min, (3) 30 min, (4) 40 min, and (5) 50 min.

$$C_{\infty} - C_{(ext)}/C_{\infty} - C_0 = \sum_{n=0}^{\infty} [2M \cos(\beta_n x/h)/(\beta_n^2 + M^2 + M) \cos \beta_n] \exp(-\beta_n^2 Dt/h^2) \quad (16)$$

where the β_n values are the positive roots of

$$\beta \tan \beta = M \quad (17)$$

with the dimensionless parameter M given by

$$M = hF_0/D \quad (18)$$

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

$$M_{\infty} - M_t/M_{\infty} = \sum_{n=0}^{\infty} [2M^2/\beta_n^2(\beta_n^2 + M^2 + M)] (\exp(-\beta_n^2 Dt/h^2)) \quad (19)$$

To solve eq. (19), the values of β_n were taken from the literature.²⁹ The diffusivity was then calculated for long times, when only the first term of the series is considered to give

$$\ln(M_{\infty} - M_t/M_{\infty}) = (\beta_n^2/h^2)Dt + \ln\{2h^2/[\beta_n^2(\beta_n^2 + M^2 + M)]\} \quad (20)$$

However, it is possible to calculate the value of the diffusion coefficients from eq. (18) by an alternative 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 liquid by diffusion through the membrane near the surface per unit area.

$$-D(\partial C/\partial t)_{\text{surface}} = F_0(C_0 - C_{\text{ext}}) \quad (21)$$

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

$$(dM_t/dt)_{t=0} = F_0(C_0 - C_{\text{ext}}) \quad (22)$$

so that

$$F_0 = [(dM_t/dt)]/(C_0 - C_{\text{ext}}) \quad (23)$$

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

The rate of evaporation (F_0) for desorption and redesorption per unit area of the polymer were calculated by using the initial rate of desorption and rede-

TABLE V
Rate of Evaporation of Penetrants During Desorption and Redesorption for PU/PS (50/50) IPN

Temp (°C)	$F_0 \times 10^4$ ($\pm 4\%$) (g/cm ² s)							
	Benzene		Toluene		Chlorobenzene		Nitrobenzene	
	Desorption	Redesorption	Desorption	Redesorption	Desorption	Redesorption	Desorption	Redesorption
20	1.17	56.4	1.16	0.91	0.65	1.13	1.2	1.51
40	84.43	99.9	2.57	3.15	1.93	2.22	2.73	2.19
60	145.1	196.2	4.46	5.75	8.5	2.78	6.88	2.49

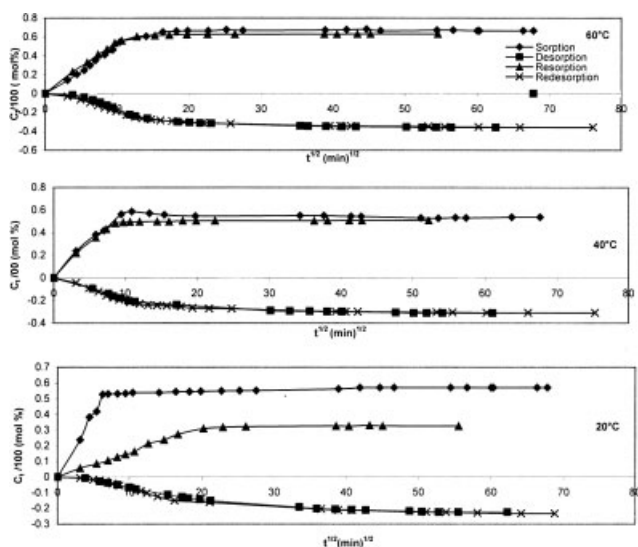


Figure 10 S-D-RS-RD of nitrobenzene into PU/PS at different temperatures.

sorption from eq. (23) and the obtained values are given in Table V. These values show a decreasing trend with size of penetrant molecules. The representative plots for S-D-RS-RD runs for nitrobenzene at 20, 40, and 60°C are given in Figure 10. From the figure it is clear that increase in temperature increases the sorption, resorption, desorption, and redesorption phenomenon. At lower temperature the mass uptake value for sorption is much higher than resorption.³⁰ As the temperature increases, the difference between sorption and resorption decreases. This suggests that increase in temperature rearrange the polymer segments and creates more free volume.^{17,31} Though desorption and redesorption increases with temperature, the weight loss during desorption and redesorption is almost same. The rate of desorption and amount of desorbed solvent at equilibrium is almost same in both the operation, indicating that the relaxation caused by the penetration of solvent molecule will persist till the removal of solvent and thus there will be free flow of solvent from the polymer system. This consistency in desorption will be very handy in using these material for pervaporation technique.

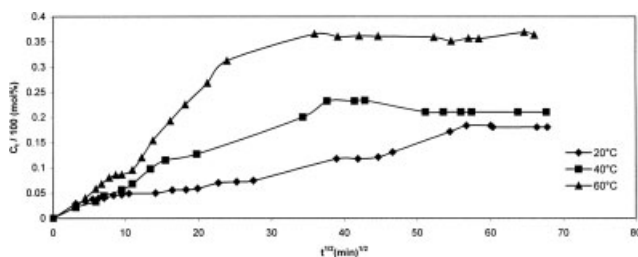


Figure 11 Temperature dependence of percentage mol uptake of toluene during sorption process.

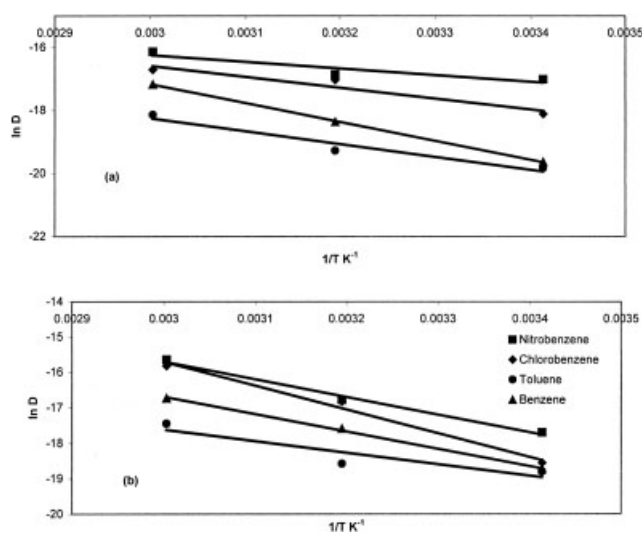


Figure 12 Arrhenius plots for the dependence of $\log D$ versus $1/T$ for PU/PS IPNs with penetrants during (a) sorption and (b) resorption processes.

Effect of temperature

The effect of temperature on mol % uptake of toluene into PU/PS is shown in Figure 11. The figure indicates the typical temperature dependency of mol % uptake of solvent into IPN, i.e., uptake of solvent increases with temperature. The rate of diffusion and permeation increases with increase in temperature.³² The temperature dependence of transport properties can be used to evaluate the activation energy for the

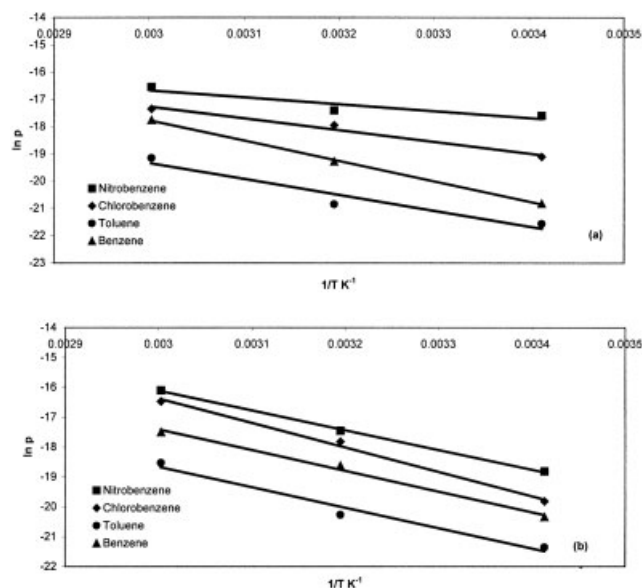


Figure 13 Arrhenius plots for the dependence of $\log P$ versus $1/T$ for PU/PS IPNs with penetrants for (a) sorption and (b) resorption processes.

TABLE VI
Activation Energy for Diffusion (E_D), Permeation (E_P), Enthalpy of Sorption (ΔH)
and Entropy of Sorption (ΔS) for PU/PS IPN

Activation and thermodynamic parameter	Benzene		Toluene		Chlorobenzene		Nitrobenzene	
	Sorption ^a	Resorption ^b	Sorption ^c	Resorption ^d	Sorption ^e	Resorption ^f	Sorption ^g	Resorption ^h
E_D (10^{-3} kJ/mol)	33.91	26.95	49.95	40.56	28.91	55.67	17.33	41.46
E_P (10^{-3} kJ/mol)	48.25	17.20	61.94	57.73	35.65	68.05	20.93	54.95
ΔS (kJ/mol K)	13.77	19.98	14.30	35.39	6.43	13.66	2.86	16.12
ΔH (kJ/mol)	5.31	7.53	6.07	13.06	2.96	5.36	1.46	5.88

^a E_D, E_P (± 3.3), $\Delta S \pm 0.8$, $\Delta H \pm 0.2$.

^b E_D, E_P (± 3.0), $\Delta S \pm 0.9$, $\Delta H \pm 0.2$.

^c E_D, E_P (± 3.1), $\Delta S \pm 1.0$, $\Delta H \pm 0.6$.

^d E_D, E_P (± 2.5), $\Delta S \pm 1.1$, $\Delta H \pm 0.5$.

^e E_D, E_P (± 1.9), $\Delta S \pm 0.9$, $\Delta H \pm 0.2$.

^f E_D, E_P (± 1.4), $\Delta S \pm 1.9$, $\Delta H \pm 0.3$.

^g E_D, E_P (± 1.5), $\Delta S \pm 0.4$, $\Delta H \pm 0.1$.

^h E_D, E_P (± 0.9), $\Delta S \pm 0.7$, $\Delta H \pm 0.3$.

diffusion and permeation processes using Arrhenius relation:

$$X = X_0 \exp -(E_a/RT) \quad (24)$$

where, X is P or D , E_a is the activation energy, R is the universal gas constant, and T is the absolute temperature. The Arrhenius plot of $\log D$ and $\log P$ versus $1/T$ for IPN are given in Figures 12 and 13, respectively. From the Arrhenius plots, the values of activation energy for permeation E_P and diffusion E_D were calculated using regression analysis and the results are shown in Table VI. The activation energy for diffusion and permeation is lowest for nitrobenzene and highest for toluene during sorption. Activation energy for diffusion and permeation during resorption is found to be highest for chlorobenzene and lowest for benzene.

Thermodynamic parameters

The thermodynamic parameters for diffusion change in enthalpy (ΔH) and entropy (ΔS) can be calculated using van't Hoff's relation

$$\log K_s = (\Delta S/2.303 R) - (\Delta H/2.303 RT) \quad (25)$$

where, K_s is equilibrium sorption constant which is given by

$$K_s = \frac{\text{No. of mols of solvent sorbed at equilibrium}}{\text{mass of the polymer}} \quad (26)$$

The values of ΔS and ΔH are obtained by regression analysis of the plot of $\log K_s$ versus $1/T$ (Fig. 14) and are given in Table VI. ΔH represents heat of sorption and is a composite parameter involving the contributions from Henry's law and Longmuir's hole filling type sorption. The ΔH values are positive and vary

from 1.46 to 6.07 kJ/mol. The positive values of ΔH indicate that the sorption is an endothermic process and is dominated by Henry's mode,³³ i.e., the sorption proceeds through creation of new sites or pores in the polymer.

Interaction parameter (γ)

The volume fraction of polymer Φ in the swollen sample was calculated using following the equation:

$$\Phi = (W_1/\rho_p)/[(W_1/\rho_p) + (W_2/\rho_s)] \quad (27)$$

where, W_1 is weight of polymer, ρ_p is the density of polymer, W_2 is the weight of solvent in the swollen sample, and ρ_s is the density of solvent.

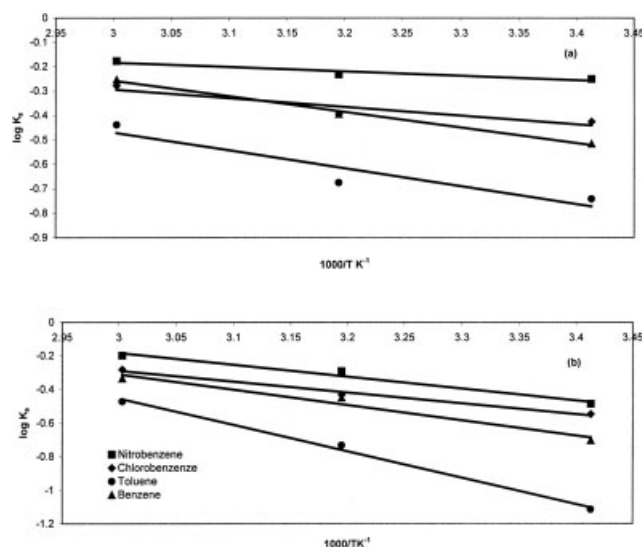


Figure 14 Log K_s versus $1/T$ for PU/PS IPN with aromatic penetrants during (a) sorption and (b) resorption processes.

TABLE VII
Solvent–Polymer Interaction Parameters

Solvent	Volume fraction of polymer (ϕ)	Interaction parameter (χ)
Benzene	0.713	0.0293
Toluene	0.82	0.0275
Chlorobenzene	0.695	0.0443
Nitrobenzene	0.618	0.0799

The interaction parameter χ is given by the equation^{13,14},

$$\chi = \beta + V/RT(\delta_A - \delta_B)^2 \quad (28)$$

where, V is the molar volume of solvent, δ_A and δ_B are the solubility parameter of solvent and polymer, respectively, R is the universal gas constant, and T is the absolute temperature. β is the lattice constant and its value is equal to 0.34.

The interaction behavior such as Φ and χ of PU/PS with different solvents was calculated and the values are given in Table VII. As the affinity between PU/PS IPN and solvents are different, degrees of interaction parameter and volume fraction of polymer in a swollen polymer was also different. The volume fraction of polymer in a swollen polymer was in the order nitrobenzene < chlorobenzene < benzene < toluene. However, interaction of polymer with the solvents was in the order toluene < benzene < chlorobenzene < nitrobenzene. The value of χ is between 0.0275 and 0.0799, which is expected for rubbery polymer and solvent systems. These values are generally lower for the aromatic liquids than for aliphatic ones.³⁴ Interestingly the trends observed as per Flory and Rehner's theory substantiate sorption and diffusion behavior of PU/PS.

CONCLUSIONS

In the present study, S-D-RS-RD trails have been performed to study the interactions of substituted aromatic penetrants with PU/PS (50/50) IPN membrane in view of the importance of the membrane in variety of engineering applications like pervaporators, biomedical applications, storage tanks, etc., The contact times used to generate (S-D-RS-RD) data was around 15 days. The observed transport phenomenon follows a Fickian trend. The mechanism responsible for the impact of solvent on sorption kinetics was postulated to involve changes in polymer conformation, which might be induced by changes in solvent polarity. The effects of solubility parameter of probe molecules on the transport phenomenon were studied. It was found that as the solubility parameter of solvents approaches the solubility parameter of PU/PS, there was an increase in sorption and diffusion coefficients. The repetitive desorption of aromatic substituted

compounds from the sorbed IPN membrane showed consistency in the rate of desorption as well as extent of desorption. This phenomenon will be of much importance for the membranes to be used in pervaporators. Measured sorption coefficients were compared with theoretical value obtained by solving Fick's equation. It is found that both theoretical and experimental values go together in shorter sorption times. The S-D-RS-RD processes were measured at three different temperatures. At higher temperature, mass uptake or loss were higher than the corresponding values at lower temperature. This indicates the temperature dependence of sorption and desorption processes. The activation energy for diffusion E_D and permeation E_P were calculated and found that nitrobenzene showed lower activation energy whereas toluene required more energy to attain equilibrium. The thermodynamic parameters like change in entropy (ΔS) and enthalpy (ΔH) confirm the observed trend. To know diffusion phenomenon, concentration profiles were simulated and presented in this research article. These observations are in the expected range. The effect of temperature on the concentration profiles was also presented.

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