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A study of sorption/desorption and diffusion of substituted aromatic probe molecules into semi interpenetrating polymer network of polyurethane/polymethyl methacrylate

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Abstract

The sorption–desorption–resorption–redesorption experiments have been conducted to evaluate the transport behaviour of polyethylene glycol (PEG) based polyurethane/polymethyl methacrylate (PU/PMMA, 50/50) semi interpenetrating polymer network (SIPN) with aromatic probe molecules. Molecular migration depends on the nature of the organic solvent, membrane–solvent interaction, temperature, solubility parameter, molecular volume and free volume available within the polymer matrix. The transport parameters like sorption (S), diffusion (D) and permeation (P) coefficients have been calculated for IPN-aromatic probe molecule systems. Sorption and diffusion results measured at different temperatures viz. 20, 40 and 60 °C are found to follow Fickian mechanism. The liquid concentration profiles in the membranes during sorption and resorption processes have been simulated by solving Fick's diffusion equations and by using numerical method. Equilibrium swelling results have been used to measure the molecular mass between cross links, degree of cross linking and cross link density using Flory–Rehner theory. It is found that the mass uptake values decreased with increase in cross link density during polymer–solvent interactions. The estimated Arrhenius activation energy for diffusion (E_D) and permeation (E_P) are indicative of nature of liquid and their interaction with membrane. Thermodynamic parameters like change in entropy (ΔS) and enthalpy (ΔH) have been calculated using van't Hoffs equation. The rate of evaporation of liquids have been calculated for desorption and redesorption runs, and these results depend on volatility of solvents.

Keywords: PU/PMMA; IPN; Migration

1. Introduction

Interpenetrating polymer networks (IPNs) are specialty blends, have attracted the attention in recent years [1–7]. Though, the term IPNs implies some kind of interpenetration of two polymer networks, molecular interpenetration occurs in the case of mutual solubility only [8,9]. The IPNs have been characterized by studying the morphology, mechanical properties, thermal behaviour, transport phenomena etc. [1–9].

The transport behaviour of various organic solvents and gases through polymer membranes is of great importance, because they are widely used for various barrier applications [10]. These transport studies becomes utmost importance while designing barrier material or tubes for transporting liquids and gases. Nghiem et al. [11] have studied nanofiltration (NF) with membranes of different permeability. It was demonstrated that nanofiltration membranes can be used to remove pesticides and that the removal mechanism are mainly influenced by stearic and electrostatic interactions [12,13]. When the interaction between membrane and adsorbing solute is important for separation, then the nature of solute has something to reveal about membrane. Van de Bruggen et al. [14] notices that physico–chemical properties of solute and membranes influences separation behaviour. The use of probe molecules to infer the detailed structure of polymer system is in extensive practice in recent times [15–17]. It was found that

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Table 1
Physical properties of substituted aromatic solvents

Penetrants	Molecular mass	Molar volume (cm^3/mol)	Density (g/cm^3)	Viscosity (MPa s)	Solubility parameter $(cal/cm^3)^{1/2}$
Benzene	78	88.7	0.879	647	9.2
Toluene	92	106.1	0.867	590	8.9
Chlorobenzene	112	101.3	1.106	830	9.7
Nitrobenzene	123	102.2	1.2033	1980	10.0

the physical and chemical structure of polymers, their morphology, crosslink density, the shape and size of solvent molecules and temperature influence the molecular transport of the solvents through polymers. Ajithkumar et al. [18,19] reported the anomalous behaviour of sorption and diffusion of organic solvents through polyurethane and unsaturated polyester based IPNs. Aminabhavi et al. have carried out extensive studies on sorption and diffusion behaviour of organic probe molecules through various polymeric systems [20,21]. In our earlier communications, we have reported the sorption and diffusion behaviour of castor oil based polyurethane (PU) IPNs and chain extended PUs [22–24].

In the present article, transport phenomenon of polyethylene glycol (PEG) based PU and polymethyl methacrylate (PMMA) SIPN membrane has been studied. The systematic studies of sorption–desorption–resorption–redesorption of substituted aromatic solvents such as benzene, toluene, chlorobenzene and nitrobenzene through PU/PMMA (50/50) IPN membrane have been studied. The sorption, diffusion and permeation coefficients were calculated. The mechanism of sorption was determined and is compared with theoretical values. Furthermore, under the suitable boundary conditions Fick's equation was solved to compute the concentration profiles based on the finite-difference method [25]. This approach is useful to predict the liquid concentration profiles within the polymer network at different time intervals. It was observed that the sorption (S), desorption (D), resorption (RS) and redesorption (RD) cycles, i.e. S–D–RS–RD processes of solvents into polymer is important to predict its suitability as barrier material in the chosen chemical environment.

2. Experimental

2.1. Materials and sample preparation

Semi interpenetrating polymer network (SIPN) of polyurethane/polymethyl methacrylate (50/50 weight ratio) were prepared by sequential polymerization method, using analytical grade polyethylene glycol-400 (PEG), 4,4′-diphenyl methane diisocyanate (MDI) and methyl methacrylate as reported elsewhere [26]. The tensile strength and percentage elongation at break for tough and transparent PU/PMMA sheet was found to be 11.94 and 56 MPa, respectively. The solubility parameter of the resulting PU/PMMA (50/50) IPN was calculated as per group additive method and it is found to be 11.56 $(cal/cm^3)^{1/2}$.

The analytical grade benzene, toluene, chlorobenzene and nitrobenzene were procured from SD Fine Chem. Ltd, Mumbai, India. These solvents were distilled before being used. Some of the typical properties of solvents are given in Table 1.

2.2. Measurements

2.2.1. Sorption (S)–desorption (D)–resorption (RS)–redesorption (RD) experiments

The circular disc shaped samples of diameter ranging from 1.609 to 1.618 cm and thickness ranging from 0.051 to 0.083 cm were cut from IPN sheets using sharp edged carbon tipped steel die. The samples were initially dried in vacuum desiccator over anhydrous calcium chloride at room temperature for 24 h before the experiments. The previously weighed dry and circular shaped samples are immersed in screw-tight bottles containing about 15–20 cm^3 of the liquids maintained at the desired temperature (±0.5 °C) in thermostatically controlled oven (M/s Tempo Laboratories, Mumbai). IPN samples are removed periodically, the solvent drops adhering to the surface were wiped off using soft filter paper wraps, and samples are weighed immediately on a digital analytical balance (Mettler Toledo, Switzerland) with an accuracy of ±0.01 mg. Swollen samples reached equilibrium saturation within 40 h, which did not change significantly over an extended immersion period of 1–2 days. The weight gain during sorption is expressed as moles of solvent uptake by 100 g of polymer sample (C_t mol%).

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

After sorption experiments, the swollen samples were taken out of solvent and placed in ambient condition for desorption. 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_t mol%).

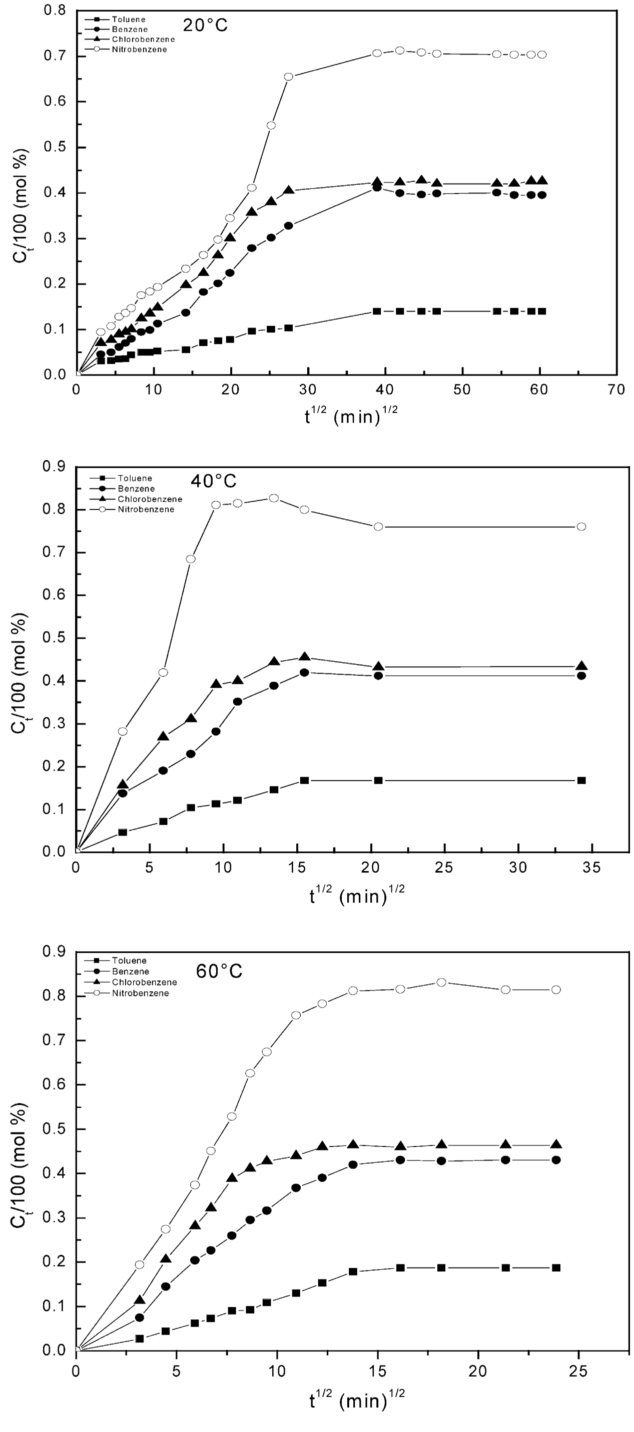


Fig. 1. The mol% uptake of different problem molecules in to PU/PMMA membrane as function of square root of time at different temperatures for sorption process.

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

The resorption experiments have been carried out in the same manner as sorption. The resorbed samples were subjected to redesorption as explained earlier. The results of S–R–RS–RD runs help us to know the migration behaviour of organic solvent and parameters that are responsible for the same. The results are so important for the material to be used as engineering polymer and to establish structure–property relationship.

3. Results and discussion

3.1. Transport behavior

The transport behavior of PU/PMMA (50/50) semi interpenetrating polymer network with substituted aromatic solvents was analyzed. The mol% uptake (C_t) of different probe molecules into PU/PMMA membranes as function of square root of time at different temperatures are shown in Fig. 1. The order of mol% uptake into PU/PMMA IPN at equilibrium is; toluene < benzene < chlorobenzene < nitrobenzene. This sorption trend is probably due to similarity in the solubility parameter of PU/PMMA and solvents. The equilibrium mol% uptake for sorption as a function of solubility parameter of probe molecules is shown in Fig. 2. As the solubility parameter of nitrobenzene is closer to solubility parameter of PU/PMMA IPN the equilibrium mol uptake of nitrobenzene into the IPN is more. Similarly toluene with low solubility parameter shows less sorption into the polymer network. The order of solubility parameter and equilibrium uptake into the IPN is; nitrobenzene > chlorobenzene > benzene > toluene. From Fig. 2 it is evident that, lesser the difference between the solubility parameter of IPN and solvent more will be the equilibrium sorption value. Aithal et al. [27] noticed similar trend with polyurethane system. The pattern of curves shown in Fig. 1 indicates that, there is clear-cut interaction between IPN and probe molecules that depends on solubility, size, viscosity and temperature.

Desorption of probe molecules from the swollen PU/PMMA is shown in Fig. 3. The sorption and desorption curves follows the same trend. However, mol% desorption of benzene and chlorobenzene is almost identical. The solvent uptake into PU/PMMA as a function of square root of time at different temperatures during resorption is shown in Fig. 4. The equilibrium mol% uptake during resorption is more than that of sorption [28] but the trend is same as that of sorption. At 20 °C the difference between equilibrium mol% uptake of toluene (9.05%) and nitrobenzene (48.3%) was found to be high. The time and temperature dependence of redesorption is shown in Fig. 5. The redesorption results follows the trend; nitrobenzene > benzene > chlorobenzene > toluene. In the first desorption process (Fig. 3), desorption of benzene and chlorobenzene were almost identical, but in redesorption process mol% of benzene desorbed is more than that of chlorobenzene. The mol% of nitrobenzene desorbed is highest and toluene is lowest.

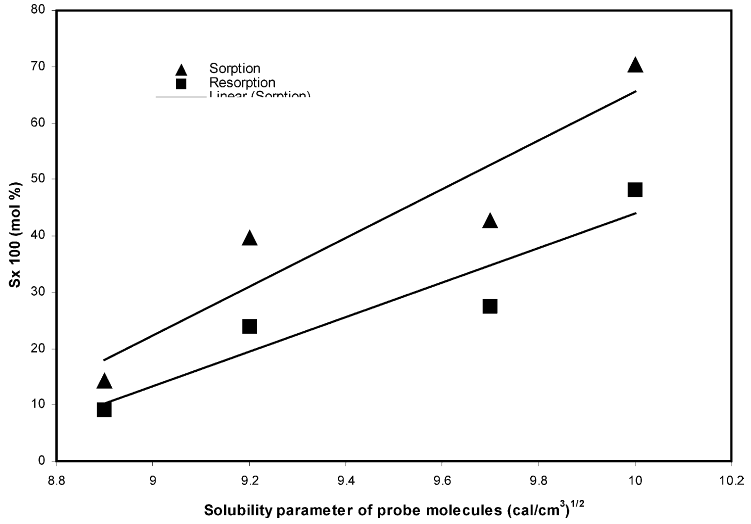


Fig. 2. Sorption coefficient with respect to solubility parameter of probe molecules.

The mechanism of transport of PU/PMMA was examined using the empirical formula [29];

$$\log\left(\frac{C_t}{C_\infty}\right) = \log K + n \log t \tag{3}$$

where, C_t and C_∞ are the mol% sorption at time t and at equilibrium, respectively, n tells about mode of transport and K is constant that depends on the structural characteristics of the polymer and gives information about interaction of polymer and solvent. The values of n and K are obtained by regression analysis of $\log(C_t/C_\infty)$ versus $\log t$ plot. The estimated values of n and K for the sorption and resorption processes are compiled in Table 2. The values of n are accurate to (± 0.01 units. The magnitude of n denotes the transport mode. For a normal Fickian mode of transport, where the rate of polymer chain relaxation is higher compared to the diffusion rate of the probe molecules, the value of n is 0.5. When $n=1$, (nonFickian mode of transport) chain relaxation is slower than the liquid diffusion. The value of n for sorption and resorption processes are lie in the range 0.41–0.55 and 0.40–0.55, respectively. The mode of transport is near Fickian because n values of PU/PMMA-aromatic solvents fall in the range 0.40–0.55. For the Fickian modes of transport, the rate of diffusion of probe molecules are much less than the relaxation rate of the polymer chains. Generally rubbers and semi crystalline polymers exhibit Fickian mode of diffusion [30]. The values of n or K for sorption and resorption processes did not show any systematic dependence. But at higher temperature, K value was smaller for all IPN-probe molecule systems. The values of K for resorption process were smaller than the corresponding sorption indicating mild PU/PMMA-probe molecule interactions.

The transport of small molecules through polymers generally occurs through a solution diffusion mechanism, i.e. the solvent molecules are first sorbed by the polymer followed by diffusion through the polymer membrane. The net diffusion through polymer depends on the difference in the amount of probe molecules between the two successive layers. Hence, the permeability [31];

Table 2
System parameters n and K for PU/PMMA (50/50) IPN

Probe molecules	Temperature (°C)	$n \pm 0.01$		$K \times 10^2 \pm 0.04$ (g/g min^n)	
		Sorption	Resorption	Sorption	Resorption
Nitrobenzene	20	0.49	0.52	0.36	0.26
	40	0.56	0.54	0.13	0.13
	60	0.55	0.49	0.15	0.11
Chlorobenzene	20	0.52	0.50	0.32	0.21
	40	0.42	0.55	0.12	0.10
	60	0.51	0.40	0.11	0.04
Toluene	20	0.47	0.41	0.27	0.16
	40	0.43	0.55	0.18	0.17
	60	0.51	0.47	0.20	0.11
Benzene	20	0.52	0.50	0.38	0.25
	40	0.51	0.53	0.17	0.15
	60	0.52	0.50	0.15	0.12

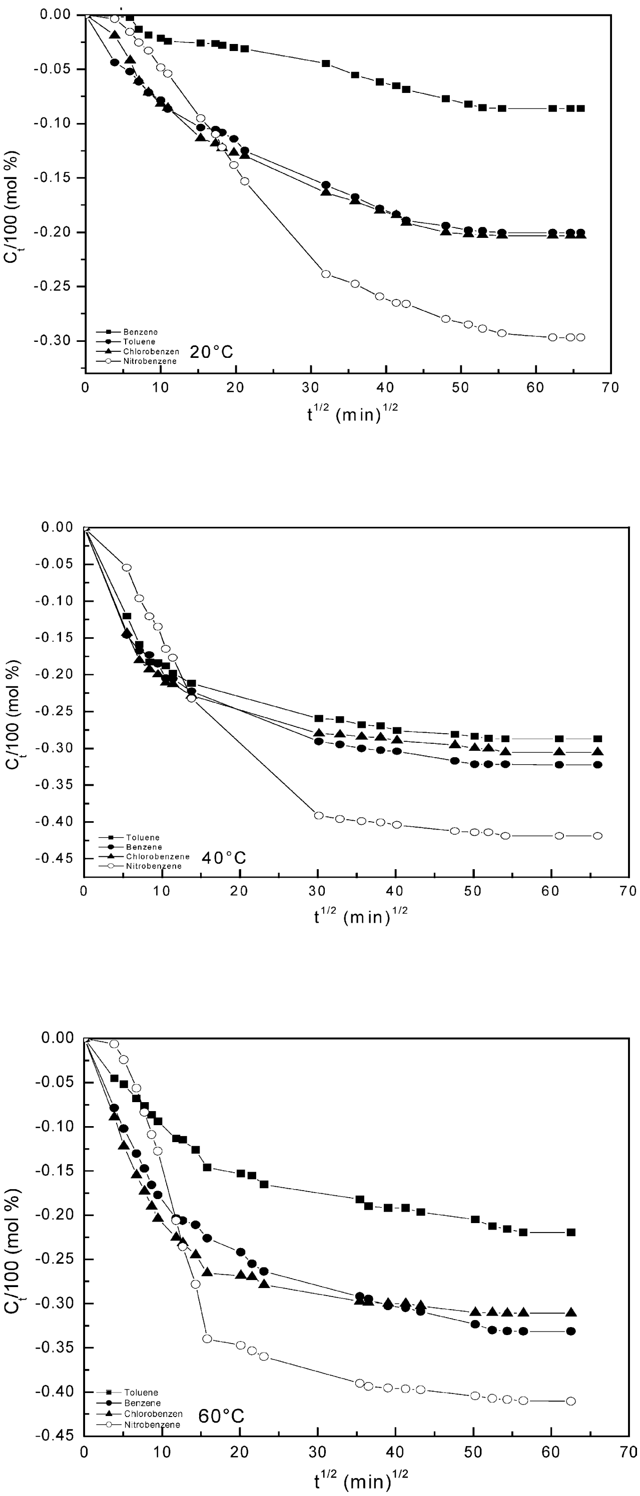


Fig. 3. The mol% of probe molecules desorbed from PU/PMMA membrane as function of square root of time at different temperatures for desorption.

$$P = D \times S \tag{4}$$

where, D is diffusivity and S, the solubility. The value of S are taken as grams of solvent sorbed per gram of IPN.

The diffusion coefficient D can be calculated using the equation [31];

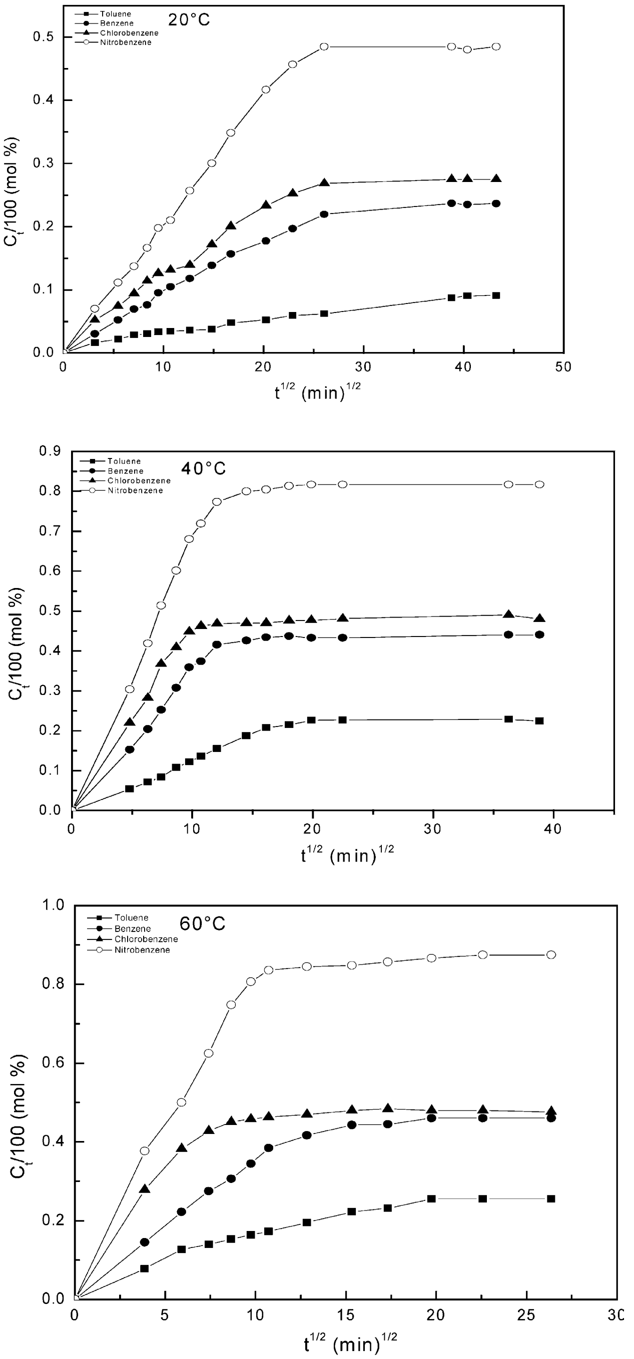


Fig. 4. The mol% uptake (C_t) of different probe molecules as function of square root of time at different temperatures for resorption.

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

where, t is the time and h is the initial thickness of the polymer membrane, C_t and C_∞ has the same meaning as explained earlier. The diffusivity at short times is calculated

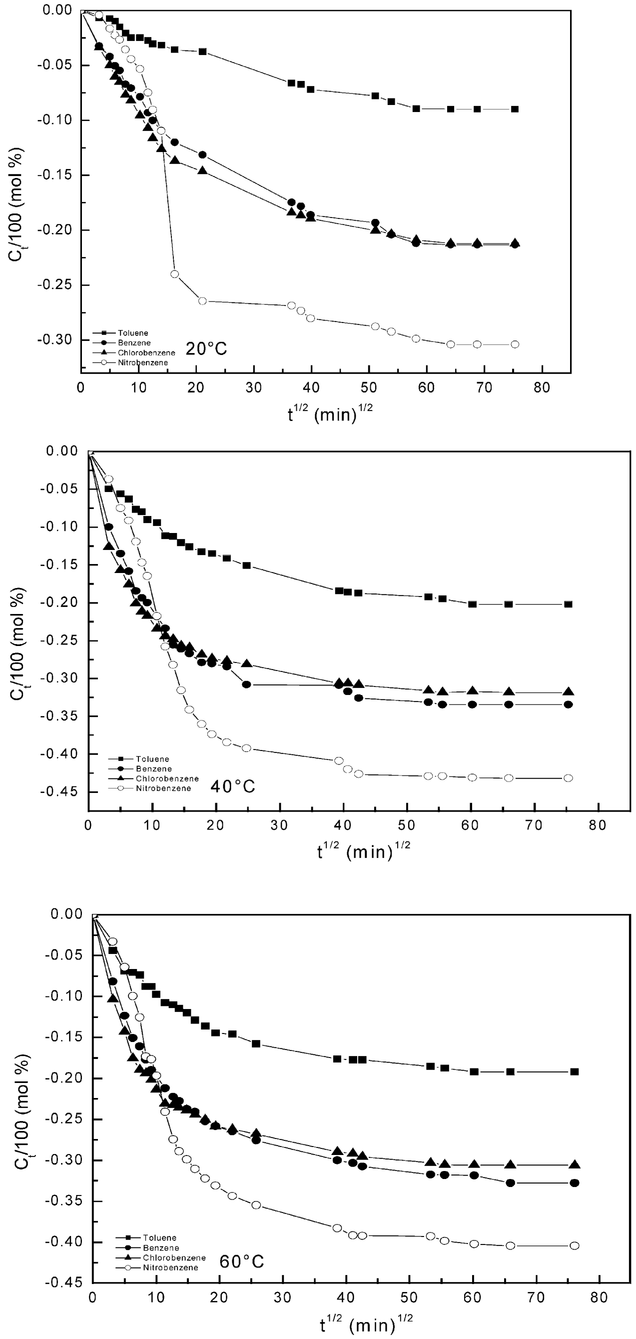


Fig. 5. The mol% of probe molecules desorbed from PU/PMMA membrane as function of square root of time at different temperatures for redesorption.

by using;

$$\frac{C_t}{C_\infty} = \frac{4}{h}\left[\left(\frac{Dt}{\pi}\right)^{1/2}\right] \tag{6}$$

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. (6) as;

$$D = \pi\left[\frac{h\theta}{4C_\infty}\right]^2 \tag{7}$$

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% equilibrium uptake. The calculated diffusion (D) and permeation (P) coefficients under working temperatures are given in Table 3. The D value for toluene at 20 °C is highest whereas that of benzene is lowest. However, P value at 20 °C for nitrobenzene is highest whereas for toluene is lowest. This indicates that, solubility parameter of IPN and probe molecules play an important role in permeation and thus affinity of PU/PMMA IPN is more towards nitrobenzene. From the Tables 1 and 3, it is observed that, the permeability and solubility parameter of solvents are in the same order; nitrobenzene > chlorobenzene > benzene > toluene. Since the solubility parameter of nitrobenzene is closer to that of PU/PMMA, the solubility of nitrobenzene into PU/PMMA IPN is more and hence the permeability. In all cases, diffusion increases with increase in temperature, but the value of D did not show any systematic dependence on the size of probe molecules.

The value of S at all temperatures for sorption is highest for nitrobenzene than other aromatic probe molecules. At higher temperature the S values of resorption will be almost identical with the corresponding S values of sorption. This is due to temperature dependence of solubility parameter. At low temperature, S value for resorption is less than the corresponding sorption process value.

3.2. Desorption

For desorption, it is important to calculate the rate of mass loss of the swollen membrane due to solvent evaporation [25];

$$-D\left(\frac{\partial C}{\partial t}\right) = F_0(C_0 - C_{\text{eq}}) \tag{8}$$

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_{eq} 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. (8) to give [25];

$$\frac{C_\infty - C_{\text{eq}}}{C_\infty - C_0} = \sum_{n=1}^{\infty}\frac{[2M\cos(\beta_n x/h)\exp(-\beta_n^2 Dt/h^2)]}{(\beta_n^2 + M^2 + M)\cos\beta_n} \tag{9}$$

where, the β_n values are the positive roots of;

$$\beta\tan\beta = M \tag{10}$$

with the dimensionless parameter M is given by;

$$M = \frac{hF_0}{D} \tag{11}$$

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;

Table 3
Sorption (S), diffusion (D) and permeation (P) coefficients for sorption and resorption of aromatic solvents into PU/PMMA (50/50) IPN

Probe molecules	Temperature (°C)	$S\times10^2$ (mol%)		$D\times10^8\pm0.04$ (cm^2/s)		$P\times10^8$ (cm^2/s mol%)	
		Sorption	Resorption	Sorption	Resorption	Sorption	Resorption
Nitrobenzene	20	70.32	48.13	2.24	3.67	1.57	1.77
	40	75.61	81.85	3.46	8.39	2.62	6.87
	60	81.54	87.16	14.55	15.80	11.85	13.77
Chlorobenzene	20	42.71	27.52	2.15	4.48	0.92	1.23
	40	43.43	47.69	2.59	8.06	1.12	3.84
	60	46.30	48.27	7.81	14.41	3.61	6.96
Benzene	20	39.60	23.87	1.38	2.70	0.54	0.65
	40	41.41	44.02	1.40	5.21	0.58	2.29
	60	43.07	45.90	5.76	12.09	2.47	5.55
Toluene	20	14.3	9.05	3.28	2.32	0.47	0.21
	40	16.81	22.53	3.56	2.43	0.60	0.55
	60	18.75	25.34	5.71	6.73	1.07	1.71

$$\frac{M_\infty - M_t}{M_\infty} = \sum_{n=1}^{\infty} \frac{2M^2 \exp(-\beta_n^2 Dt/h^2)}{\beta_n^2(\beta_n^2 + M^2 + M)} \tag{12}$$

In order to solve Eq. (12), the values of β_n were taken from the literature [25]. The diffusivity was then calculated for long times, when only the first term of the series is considered to give;

$$\ln\left[\frac{M_\infty - M_t}{M_\infty}\right] = \left(\frac{\beta_n^2}{h^2}\right)Dt + \ln\left\{\frac{2M^2}{\beta_n^2(\beta_n^2 + M^2 + M)}\right\} \tag{13}$$

However, it is possible to calculate the value of the diffusion coefficients from Eq. (13) 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 vapour out of the membrane surface is equal to the rate of transport of the liquid by diffusion through the membrane near the surface per unit area;

$$-D\left(\frac{\partial C}{\partial t}\right)_{\text{surface}} = F_0(C_0 - C_{\text{eq}}) \tag{14}$$

Thus, at the beginning of the process, for $t\to0$, the initial rate of evaporation is;

$$\left(\frac{\mathrm{d}M_t}{\mathrm{d}t}\right)_{t=0} = F_0(C_0 - C_{\text{eq}}) \tag{15}$$

so that;

$$F_0 = \frac{(\mathrm{d}M_t/\mathrm{d}t)}{C_0 - C_{\text{eq}}} \tag{16}$$

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

Table 4
Rate of evaporation of solvent from sorbed PU/PMMA (5050) IPN for desorption and redesorption

Temperature (°C)	$F_0\times10^4$ (g/cm^2 s)							
	Benzene		Toluene		Chlorobenzene		Nitrobenzene	
	Desorption	Redesorption	Desorption	Redesorption	Desorption	Redesorption	Desorption	Redesorption
20	217	230	0.17	0.42	2.7	3.44	2.25	3.29
40	270	269	0.75	2.07	3.29	3.94	3.25	3.45
60	332	330	1.20	3.99	3.35	4.05	3.41	3.88

Table 5
Solvent–PU/PMMA interaction parameters

Solvent	Volume fraction of polymer (ϕ)	Interaction parameter (χ)	Molecular mass between cross link (M_c)	Cross link density (V_e) (10^3 g mol/cm^3)	Degree of cross linking (V)
Benzene	0.7002	0.0275	192	6.13	2.604
Toluene	0.7904	0.0260	156	7.66	3.205
Chlorobenzene	0.6664	0.0412	256	4.67	1.953
Nitrobenzene	0.5488	0.0724	444	2.69	1.126

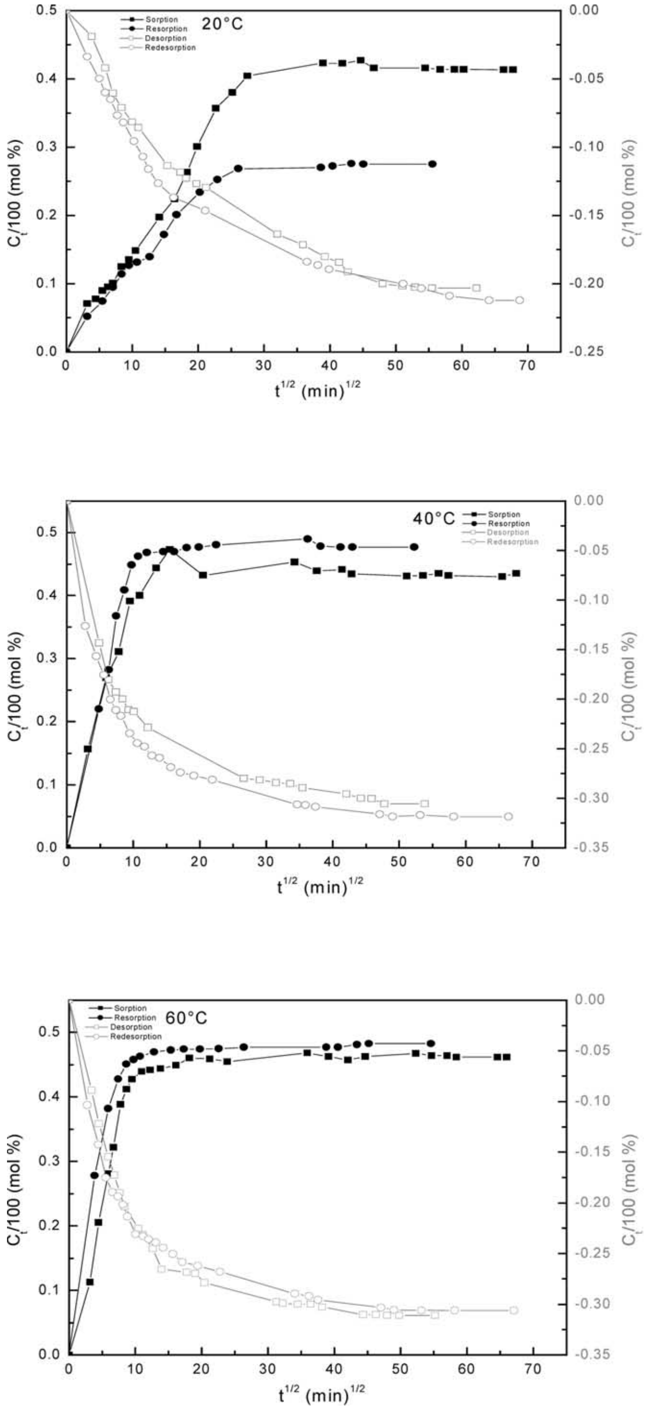


Fig. 6. The effect of temperature on mol% uptake/loss of chlorobenzene for S–D–RS–RD runs at different temperatures.

known. The rate of evaporation for desorption and redesorption per unit area of the polymer was calculated (Table 4) using the initial rate of desorption and redesorption from Eq. (16). The rate of evaporation of benzene from sorbed IPN membrane is higher than other solvents and it reaches equilibrium quickly. This is due to low boiling point of benzene compared to other solvents. Among chlorobenzene and nitrobenzene, the rate of evaporation of chlorobenzene is more than nitrobenzene. From Table 4 it was revealed that, the rate of redesorption of benzene is almost same as that of desorption. In case of toluene, chlorobenzene and nitrobenzene the redesorption values are higher than corresponding desorption values.

3.3. Effect of interlocking (cross linking)

The physico–mechanical and thermal properties of polymers are found to depend on the nature of interlocking. To know the extent of interlocking it is very much essential to assess the interaction of polymer with solvent. In this paper, authors made an effort to know the extent of interaction of IPN with different solvents using equilibrium swelling values at 20 °C. The molar masses between interlocking of the PU/PMMA have been calculated using Flory–Rehner [32,33] relation;

$$M_c = \frac{-\rho_p V_s \Phi^{1/3}}{[\ln(1-\Phi) + \Phi + \chi\Phi^2]} \tag{17}$$

where, ρ_p is the density of polymer, V_s is the molar volume of solvent, Φ the volume fraction of polymer and χ the interaction parameter.

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

$$\Phi = \frac{(W_1/\rho_p)}{(W_1/\rho_p) + (W_2/\rho_s)} \tag{18}$$

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

The interaction parameter χ is given by the equation [32];

$$\chi = \frac{\beta + V}{RT(\delta_A - \delta_B)^2} \tag{19}$$

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

From the M_c value, the cross-link density (V_e) and degree of cross-linking (V) can be calculated using the equation [33];

$$V_e = \frac{\rho_p}{M_c} \tag{20}$$

$$V = \frac{1}{2M_c} \tag{21}$$

The calculated Φ, χ, M_c, V_e and V are given in Table 5. The cross link density, degree of cross linking and volume fraction of polymer in swollen membrane is found to vary with solvents. These Φ, V_e and V values for PU/PMMA vary in the order of nitrobenzene < chlorobenzene < benzene <

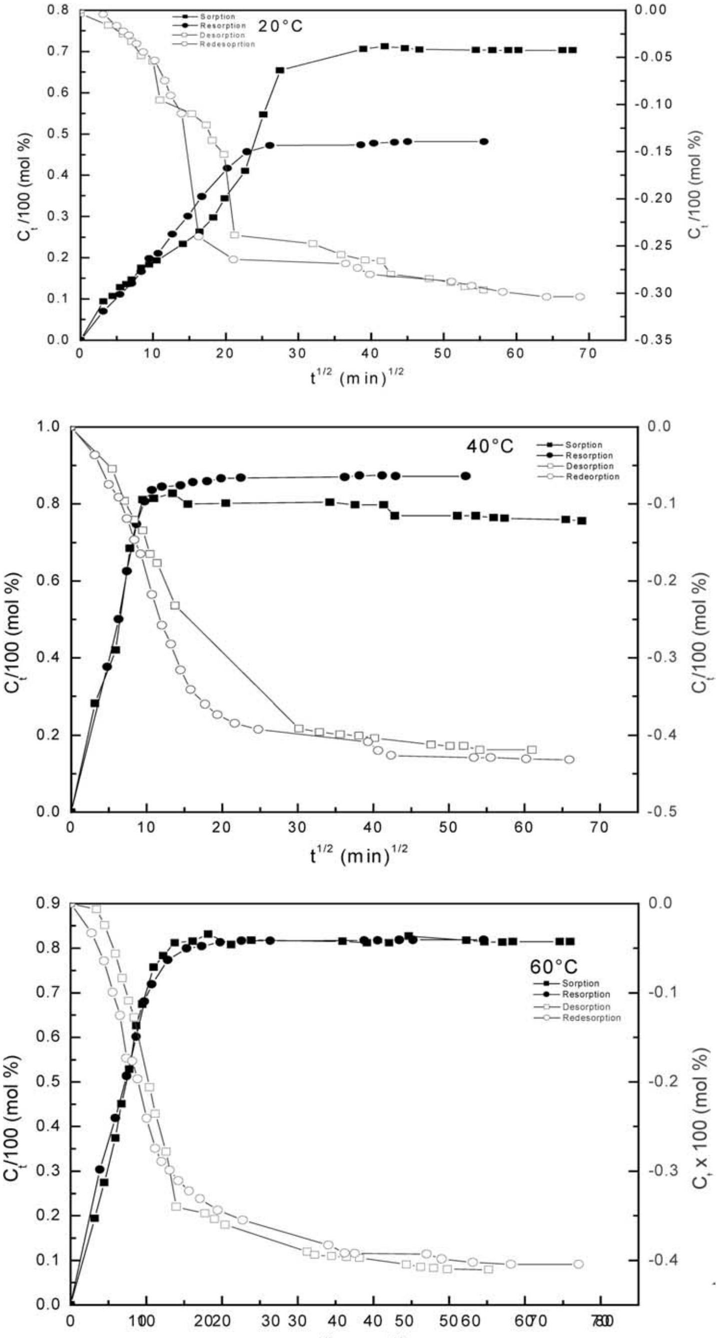


Fig. 7. The effect of temperature on mol% uptake/loss of nitrobenzene for S–D–RS–RD runs at different temperatures.

toluene. However, interaction parameter and molecular mass between cross linking increase in the order toluene < benzene < chlorobenzene < nitrobenzene. The calculated interaction parameter and observed *S* will go together. As the value of interaction parameter increases, interaction between polymer and probe molecules will also increase and thus there will be increase in swelling. In the given semi interpenetrating polymer network of PU/PMMA, the interaction parameter for toluene is found to be less compared to other solvent, thus showing highest degree of interlocking (cross linking) hence, solvent uptake into polymer system is less. Nitrobenzene with higher interaction parameter shows lowers degree of cross-linking and higher mass uptake. This is probably due to structural changes caused by sorbed molecules. The sorbed molecules loosen the polymer structure and make it easier for subsequent molecules to enter the polymer network [34]. The values of M_c lie in the range 156–444. However, M_c values may not be the true molar masses between crosslinks, but rather may represent the molar mass between covalent

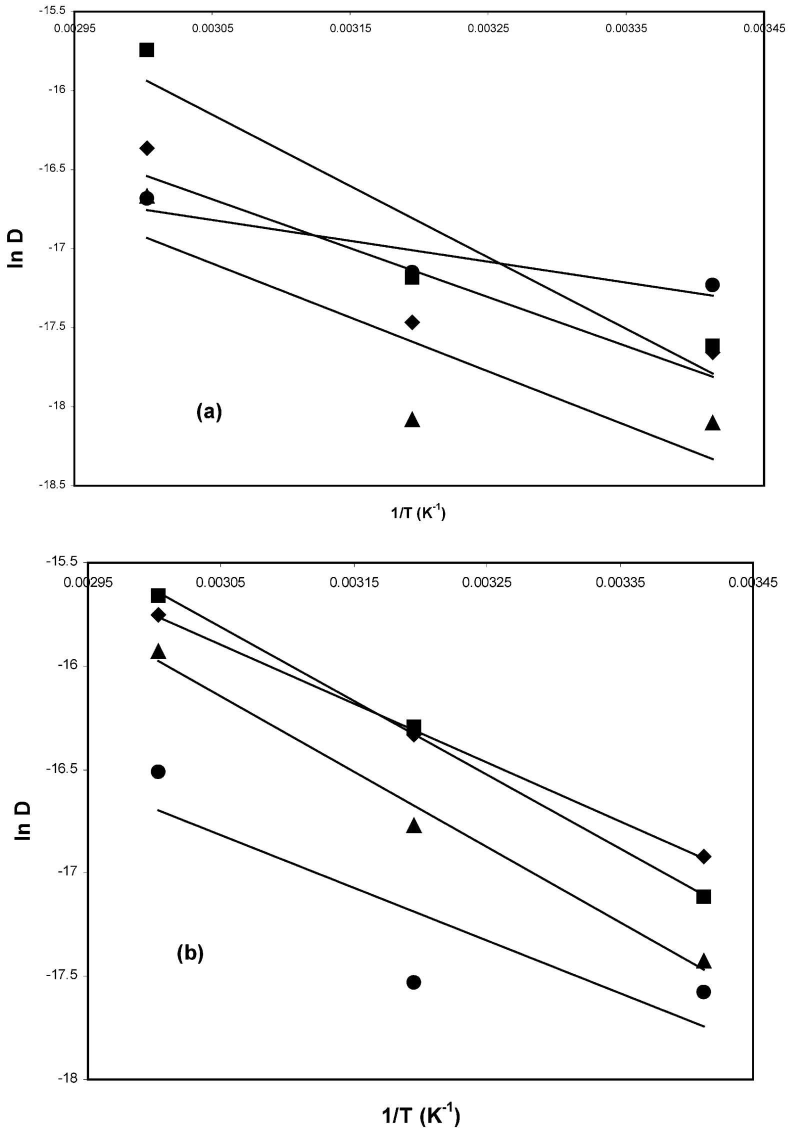


Fig. 8. Arrhenius plots for the dependence of ln D versus $1/T$ for (a) sorption and (b) resorption processes.

physical entanglements of the polymer. Hence, these values should be regarded as only approximate. Interestingly the trends observed as per Flory and Rehner's theory substantiate sorption and permeation behaviour of PU/PMMA IPN.

3.4. Effect of temperature

The effect of temperature on mol% uptake of chlorobenzene and nitrobenzene is given in Figs. 6 and 7, respectively. In S–D–RS–RD runs varies with temperature. The rate of diffusion and permeation increases with increase in temperature [34]. Increase in temperature reduces tortuous route of solvent and also reduces the time required to attain equilibrium. The temperature dependence of transport phenomenon can be used to evaluate the activation energy for the diffusion and permeation processes using the

Table 6
Activation energy for diffusion (E_D), permeation (E_P), enthalpy of sorption (ΔH) and entropy of sorption (ΔS) for PU/PMMA (50/50) IPN

Kinetic and thermodynamic parameters	Benzene		Toluene		Chlorobenzene		Nitrobenzene	
	Sorption	Resorption	Sorption	Resorption	Sorption	Resorption	Sorption	Resorption
E_D (kJ/mol)	28.40	30.23	11.03	30.26	25.75	23.66	37.43	29.63
E_P (kJ/mol)	27.35	43.76	17.20	17.20	27.35	35.27	40.30	40.68
ΔS (kJ/mol K)	0.87	15.12	1.39	23.45	0.70	12.83	3.16	14.07
ΔH (kJ/mol)	0.73	5.86	2.37	9.20	0.70	5.04	1.30	4.80

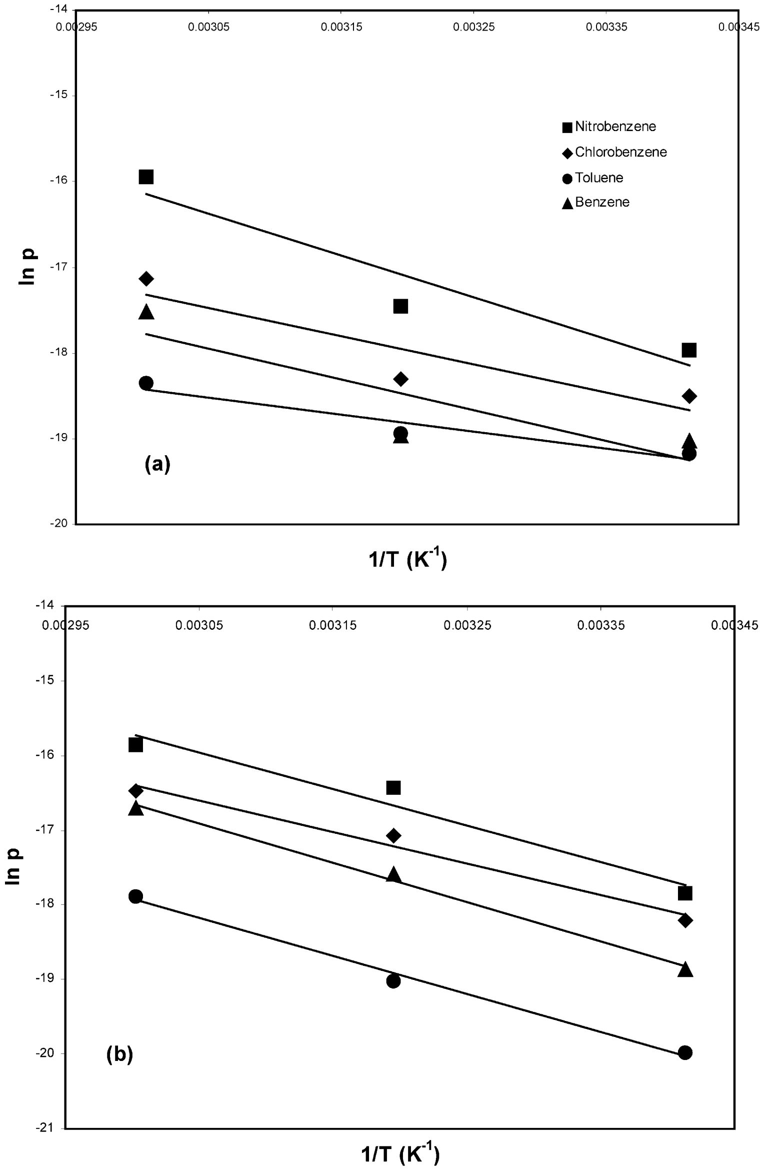


Fig. 9. Arrhenius plots for the dependence of ln P versus $1/T$ for (a) sorption and (b) resorption processes.

Arrhenius relation;

$$X = X_0\exp\left(-\frac{E_a}{RT}\right) \tag{22}$$

where, X is P or D; E_a, the activation energy, R, the universal gas constant and T, the absolute temperature. The Arrhenius plot of log D and log P versus $1/T$ for PU/PMMA (50/50) IPN are shown in Figs. 8 and 9, respectively. The plots of log X against $1/T$ for the IPN-solvent system exhibit linear dependency. From the Arrhenius plots, the values of activation energy for permeation (E_P) and diffusion (E_D) were calculated using regression analysis (Table 6). The lower E_D values was noticed for toluene and higher for nitrobenzene for sorption process. The E_P values lies in the range 17.20–40.46 kJ/mol for sorption. The values of E_D and E_P for resorption process are found to be higher than the corresponding sorption values. Solvent molecules trapped inside the membrane hinder the free flow of solvent and thus require more energy. Hence, higher E_D and E_P values for resorption process. From the table it is noticed that there is no systematic variation in the E_D and E_P values.

3.5. Thermodynamic parameters

The thermodynamic parameters for diffusion, ΔH and ΔS can be calculated using van't Hoff's relation;

$$\log K_s = \left(\frac{\Delta S}{2.303R}\right) - \left(\frac{\Delta H}{2.303RT}\right) \tag{23}$$

where K_s is equilibrium sorption constant which is given by;

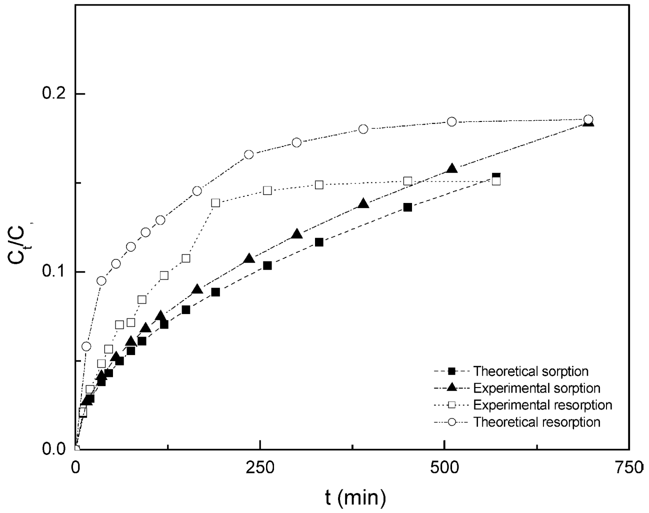


Fig. 10. Experimental and theoretical diffusion curves of toluene at 60 °C for sorption and resorption.

$$K_s = \frac{\text{No. of moles of solvent sorbed at equilibrium}}{\text{mass of the polymer}} \tag{24}$$

The values of ΔS and ΔH are obtained from the plot of log K_s versus I/T and it is given in Table 6. From the table it was noticed that, the ΔH values are positive for all the solvents and vary from 0.70 to 2.37 kJ/mol and 4.80 to 9.20 kJ/mol for sorption and resorption processes respectively. The positive values of ΔH indicate that the sorption and resorption is an endothermic process and is dominated by Henry's mode, i.e. the sorption proceeds through creation of new sites or pores in the polymer [35]. The higher values of ΔH for resorption indicate the fact that, the presence of solvent inside the body of membrane and molecular strain resist the further flow of solvent in to it. To overcome this resistance more amount of energy is required hence, ΔH value is more during resorption.

3.6. Comparison with theory

The diffusion coefficient (D) values calculated from Eq. (6) have been used to generate theoretical sorption curves using Eq. (5). A representative curves for sorption and resorption process of toluene at 60 °C has been shown in Fig. 10. Fig. 11 displays experimental and theoretical diffusion curves of chlorobenzene and benzene at 20 °C. From these figures it was observed that, the agreement between the theoretical and experimental curves are not very good at longer sorption times. But, good agreement in theoretical and experimental curves has been noticed for resorption process as compared to sorption. This suggests the insignificant dependence of D on concentration during resorption. Aminabhavi et al. [36] observed the similar trend.

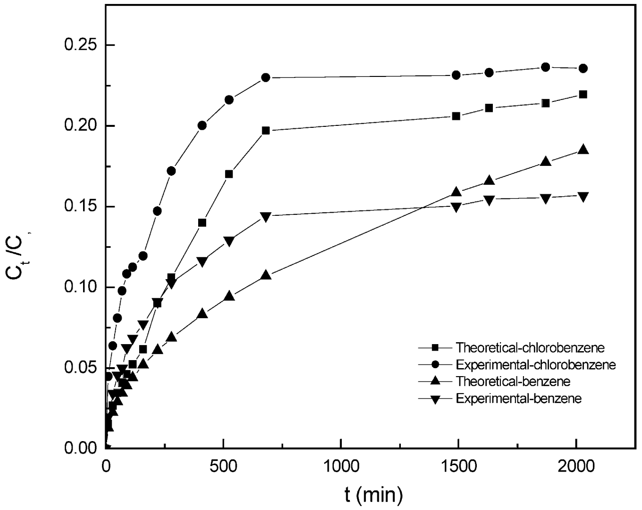


Fig. 11. Experimental and theoretical diffusion curves for chlorobenzene and benzene at 20 °C for resorption processes.

3.7. Concentration profiles

Diffusion co-efficient has been calculated from Fickian equation. It is also realized that the concentration profile of the penetrating liquid molecule plays an important role in the polymer membrane applications. Hence, we have calculated concentration profiles of liquids through PU/PMMA IPN membrane by computer-simulated method. To calculate concentration profiles we use Fick's second order differential equation given in its most general form [25];

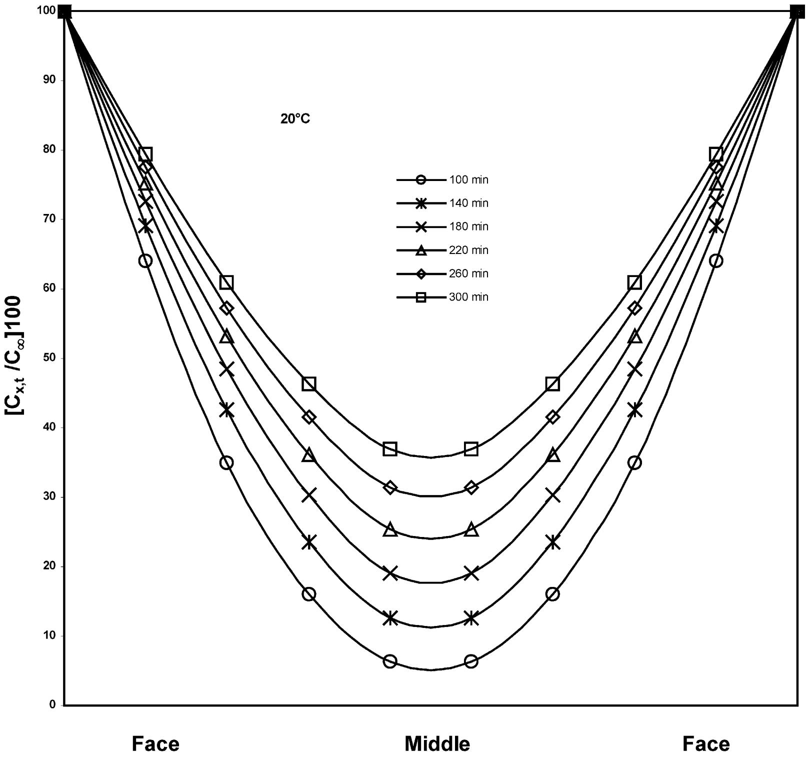
$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2}\right) \tag{25}$$

where, D is the concentration-independent diffusion coefficient, t is the sorption time, c is the liquid concentration within the membrane and $\partial c/\partial x$ is the concentration gradient along the x direction. The Eq. (25) 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 sorption; and (v) changes in the membrane dimensions are negligible during the liquid exposure with the initial boundary conditions, that is;

$$t = 0 \qquad 0 \le x < h \quad c = 0 \tag{26}$$

$$t \ge 0 \quad x = 0, \quad x = h \quad c = c_\infty \tag{27}$$

$$\frac{\partial c}{\partial x} = 0, \qquad x = 0, \quad t > 0 \tag{28}$$



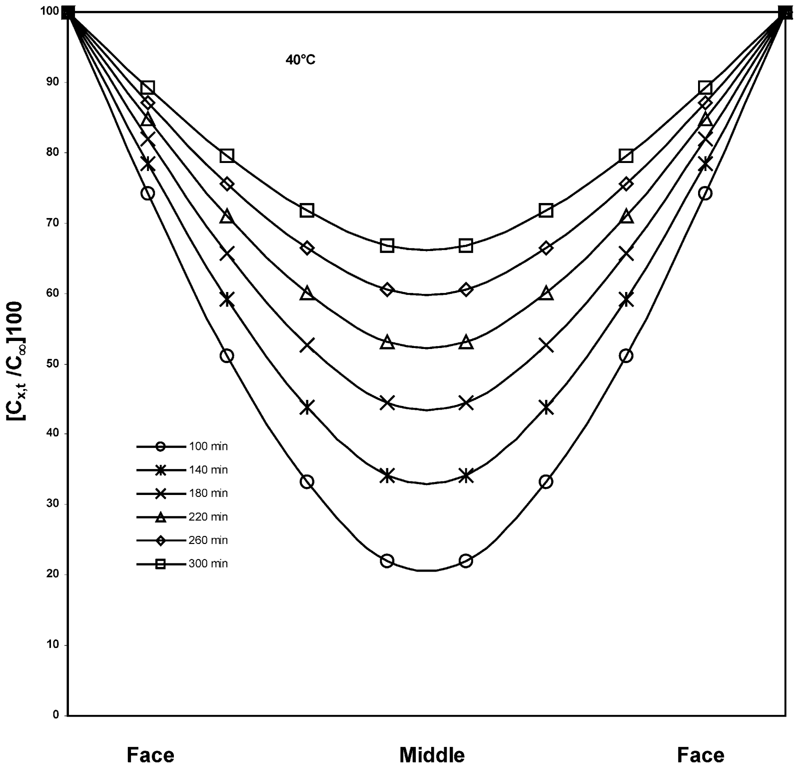


Fig. 12. Concentration profile of nitrobenzene from either sides of PU/PMMA membrane at 20 and 40 °C for sorption.

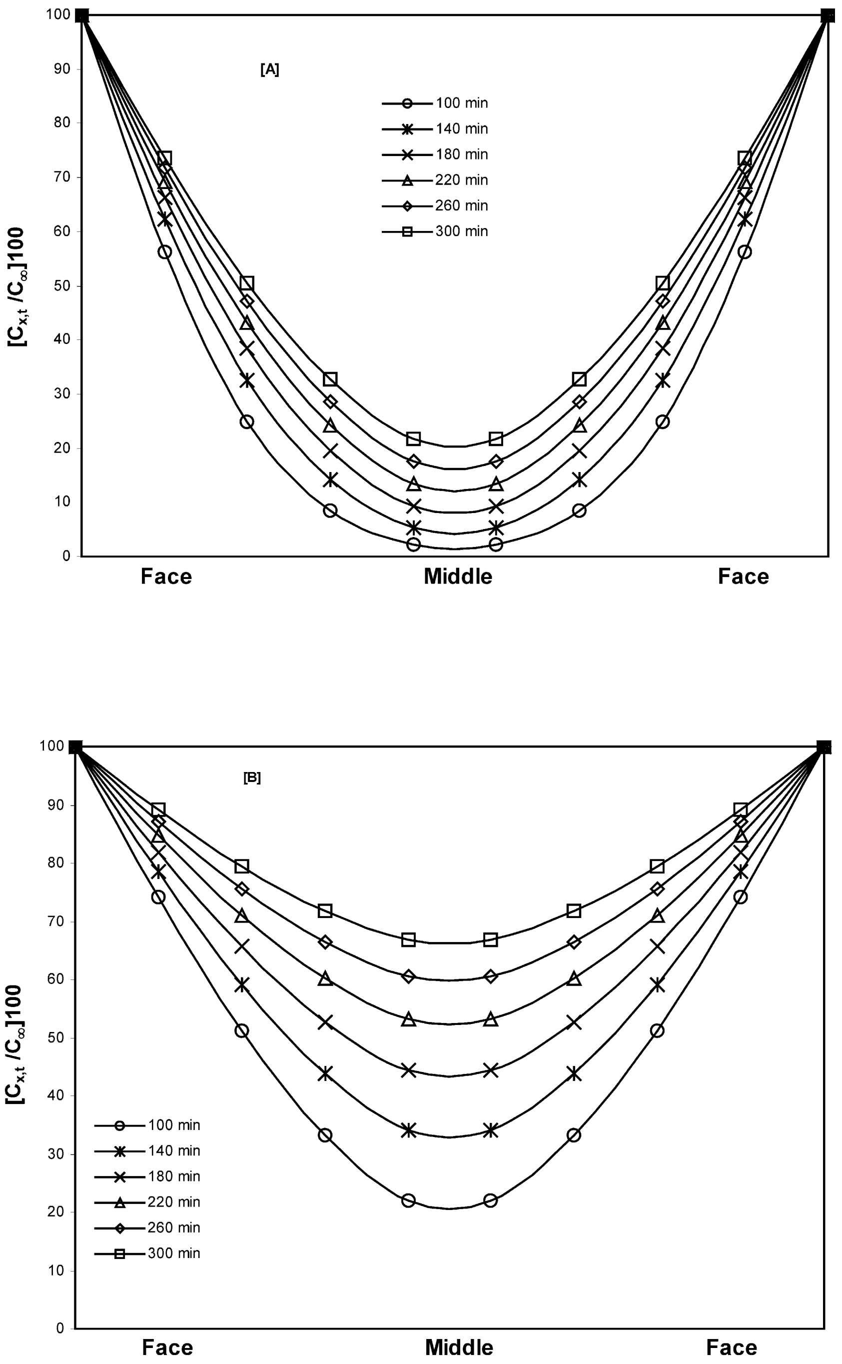


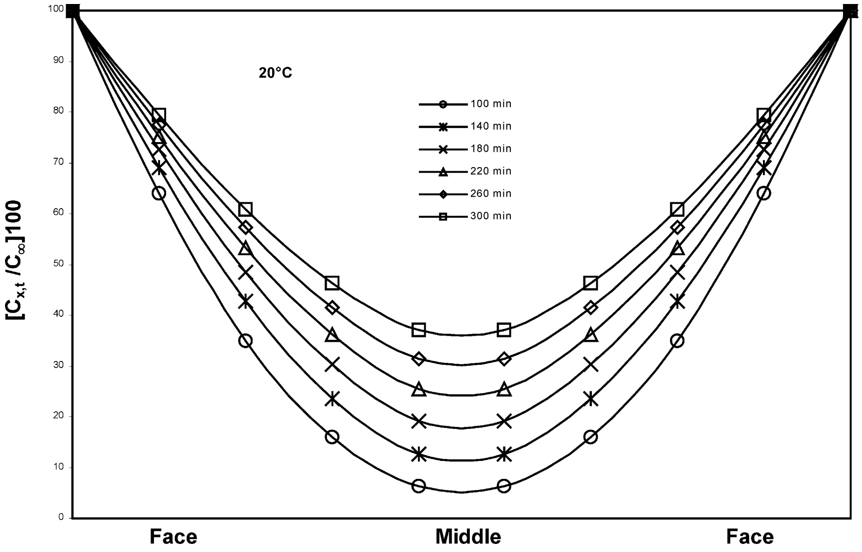
Fig. 13. Concentration profiles from either sides of PU/PMMA membrane at 40 °C for sorption processes; (A) chlorobenzene and (B) nitrobenzene.

To give the concentration profile $c_{(x,\ t)}/c_{\infty}$, of the liquids within the polymer membrane as a function of the penetration depth (i.e. distance x), that is, the thickness of the membrane and time t;

$$\frac{c_{(x,t)}}{c_{\infty}} = 1 - \frac{4}{\pi}\sum\frac{1}{(2n+1)}\exp\left[\frac{-D(2n+1)^2\pi^2 t}{h^2}\right] \times \sin\left[\frac{(2n+1)\pi x}{h}\right] \quad (29)$$

where, n is an integer. Solving Eq. (29), we get concentration profiles of the migrating liquids within the IPN 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 membrane along the thickness direction.

The generated concentration profiles of nitrobenzene across the PU/PMMA membrane for sorption process at 20 and 40 °C with different time intervals are given in Fig. 12. As we move from either sides of membrane the concentration of probe molecules decreases and it reaches minimum $C_{(x,\ t)}/C_{\infty}$ value at the core or middle of the



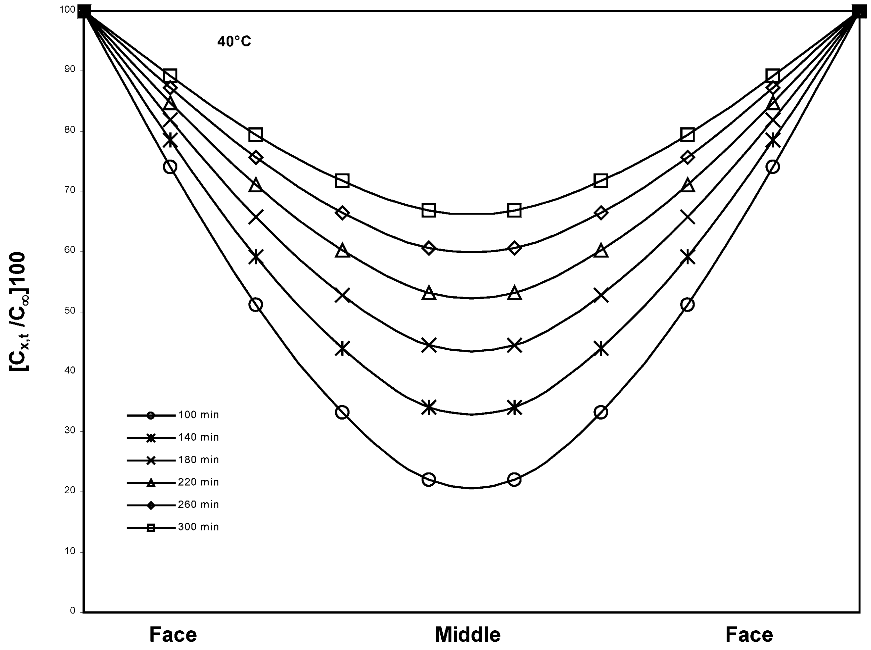


Fig. 14. Concentration profiles of nitrobenzene from either sides of PU/PMMA membrane at 20 and 40 °C for resorption.

membrane. As the time lapses from 100 to 300 min, the values of $C_{(x,\ t)}/C_{\infty}$ increases. The patterns of concentration profiles for nitrobenzene at 20 and 40 °C are found to be different. The Fig. 12 shows higher $C_{(x,\ t)}/C_{\infty}$ value for nitrobenzene at 40 °C. These concentration profiles indicate the temperature dependence of diffusion phenomenon.

The concentration profiles for chlorobenzene and nitrobenzene at 40 °C for sorption is shown in Fig. 13. At the given temperature nitrobenzene shows higher $C_{(x,\ t)}/C_{\infty}$ values than chlorobenzene. This is due to higher interaction of more polar nitrobenzene with PU/PMMA IPN. These concentration profiles comply with experimental observations made in this paper.

The concentration profiles of nitrobenzene at 20 band 40 °C during resorption are shown in Fig. 14. From the Figs. 12 and 14, the concentration profile patterns of nitrobenzene for sorption and resorption processes are almost same. Thus the simulation method appears to be a sensitive test protocol to predict the concentration profiles rather than mere calculation 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 literature [37] and especially more so in complicated systems such as IPN membrane 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.

4. Conclusions

Sorption–desorption–resorption–redesorption processes investigated the transport behaviour of substituted aromatic compounds through PU/PMMA (50/50) IPNs. The transport phenomenon follows a Fickian trend in PU/PMMA membrane. The equilibrium uptake values are found to be highest for nitrobenzene at all temperatures. The effects of solubility parameters of solvents on the transport phenomenon have been studied. It is found that as the difference in solubility parameter of solvents and polymer membrane is less, there is an increase in sorption and permeation coefficients. This indicates that there are more interactions between solvent and polymer, which lead to solvation followed by diffusion into membrane. The equilibrium sorption data have been used to calculate the empirical crosslink density, interaction parameter and molecular mass between interlocking. The molecular mass between interlocking is found to be highest for PU/PMMA-nitrobenzene system compared to other solvents indicating more interaction. The diffusion coefficient result suggests that when PU/PMMA membrane used as barrier for aromatic probe molecules, penetration probe molecules depend on several factors, such as nature of membrane, size, temperature, solubility parameter and its compatibility with probe molecules and also their chemical characteristics. Desorption behaviour of IPN have been measured and the rate of evaporation of benzene during desorption process is found to be highest compared to other penetrants. The effect of temperature on sorption and desorption cycles have been measured. It is found that as temperature increases the mass uptake values during sorption and mass loss values during desorption increases. The activation energy for diffusion E_D and permeation E_P was calculated. The ΔS for sorption and resorption lies in the range of 0.70–3.16 and 12.83–23.45 kJ/mol K, respectively. Similarly ΔH for sorption and resorption processes are 0.70–2.37 and 4.80–9.20 kJ/mol, respectively. These values did not show any regular trend. This may be due to complicated structure and morphology of IPN. For all IPN-penetrant systems positive ΔH values are observed. The positive values of ΔH indicate that the sorption is an endothermic process and is dominated by Henry's mode, i.e. the sorption proceeds through creation of new sites or pores in the polymer. The experimental diffusion coefficients were compared with theoretical predictions. Theoretical and experimental curves are not in good agreement for sorption but fairly good for resorption. The concentration profiles of solvent at different intervals of time and temperatures have been simulated by solving Ficks equation. The simulation indicates the probable concentration of solvent from either side of membrane at different time intervals and at different temperatures.

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