

Chemical compatibility of PU/PAN interpenetrating polymer network membrane with substituted aromatic solvents

H. Kumar^a, Siddaramaiah^{b,*}

^a Department of Chemistry, R.V. College of Engineering, Bangalore 560 059, India

^b Department of Polymer Science and Technology, S.J. College of Engineering, Mysore 570 006, India

Received 21 July 2006; received in revised form 24 February 2007; accepted 28 February 2007

Available online 3 March 2007

Abstract

Polyethylene glycol (PEG)-based polyurethane/polyacrylonitrile (PU/PAN, 50/50) semi-interpenetrating polymer network (SIPN) membrane has been studied from sorption/desorption cycles and diffusion behaviour with substituted aromatic probe molecules at 20, 40 and 60 °C. Sorption/desorption cycles have been repeated to evaluate polymer–solvent interaction. Organic solvents taken up or given out by IPN are measured periodically till equilibrium. Using these data, sorption (*S*), diffusion (*D*) and permeation (*P*) coefficients have been calculated from Fick's equation. Sorption data is correlated with solubility parameter of solvents and polymer. It was found that solvents of comparable solubility parameter with IPN interact more and thus there is an increase in sorption. Molecular mass between cross-link has been calculated using Flory Rehner equation. The cross-link density and degree of cross-linking of the membrane is calculated. From the temperature dependence of sorption and diffusion coefficients, the Arrhenius activation parameters like activation energy for diffusion (E_D) and permeation (E_P) processes have been calculated. Furthermore, the sorption results have been interpreted in terms of thermodynamic parameters such as change in enthalpy (ΔH) and entropy (ΔS). Concentration profiles of penetrants at different penetration depths in the polymer sample at different time intervals have also been calculated theoretically from a solution of Fick's equation under appropriate initial boundary conditions.

© 2007 Elsevier B.V. All rights reserved.

Keywords: PU/PAN; Probe molecules; Sorption; Transport data; Permeation

1. Introduction

In many areas of science and technology, i.e., chemical engineering, environmental engineering, biotechnology processing and design operations physico-mechanical methods are necessary to remove or recover the hazardous chemical ingredients present in liquid effluents discharged from electroplating, pesticide, fertilizer, pharmaceutical, chemical plant, dyes and pigments and other process industries. The use of geomembranes in hazardous waste treatment has been increased in the recent past [1–5]. Polyether-based polyurethane (PU) foam are being studied by many scientists for the isolation of heavy metal ions like cobalt and antimony and absorption of phenol compounds in aqueous solutions [6–8]. Generally, the hazardous materials are to be stored in holding tanks or open ponds before the

treatment. The holding tank must be impervious to these hazardous chemicals. At the same time lining of open pond must be impermeable; otherwise these pollutants will percolate into earth and contaminate the ground water. The increase in awareness of general public and strict enforcement of environmental law has made it compulsory to look into aspect of interaction and penetration of hazardous solvent with geomembranes. The penetration of hazardous solvent into polymer membrane depends on length of storage and nature of the solvent. The behaviour of solvent with the membrane for considerable length of time has to be studied. Hence, sorption/desorption of solvents and its repetition of the process is very essential to know the diffusion and permeation characteristics of polymer membranes. PU/PAN (50/50) interpenetrating polymer network (IPN) membrane has been chosen in this study because of its good mechanical properties and wide variety of industrial engineering and biomedical applications. However, acceptability of IPNs for any specific applications depends on its performance requirements before these materials seek commercial or engineering applica-

* Corresponding author.

E-mail address: siddaramaiah@yahoo.com (Siddaramaiah).

tions. Aromatic solvents have been chosen as probe molecules as these have diverse applications in process industries and in manufacture of perfumes, dyes, bulk drug, formulations, etc.

In our previous publications [9–12], the behaviour of castor oil-based polyurethane (PU), chain extended PU and its IPNs have been studied for molecular transport with several organic liquids. In continuation of our research program, we now present the resistivity data of some of the substituted aromatic solvents with polyethylene glycol (PEG)-based PU/PAN IPN. Sorption (S)–desorption (D)–resorption (RS)–redesorption (RD), i.e., S–D–RS–RD experiments were conducted to probe the polymer–solvent interactions. The equilibrium swelling at 20 °C is taken to evaluate the solvent–polymer interactions. The sorption and desorption data measured at different temperature 20 °C and higher temperatures viz., 40 and 60 °C are used to simulate and assess the behaviour of IPN membrane under accelerated conditions [13,14]. The solvent uptake results were used to calculate the diffusion coefficients using Fick's equation [15]. The Arrhenius parameters and thermodynamic parameters were estimated for both sorption and resorption processes. To know the possible concentration distribution of probe molecules in the body of membrane, concentration profiles were simulated [16]. These simulation data could be useful for chemist and engineers for real time applications at site.

2. Experimental

2.1. Materials

Polyurethane/polyacrylonitrile (PU/PAN, 50/50) SIPN has been prepared using polyethylene glycol-400 (PEG), 4,4'-diphenyl methane diisocyanate (MDI) and acrylonitrile as reported elsewhere [17]. The tensile strength and percentage elongation at break for tough and transparent sheets are 4.2 MPa and 80, respectively. The positron annihilation lifetime spectroscopy studies have revealed that PU/PAN IPN possess 17.5% free volume with average hole size of (V_f) 69.7 Å³ in the network and thus fractional free volume in the network would be (F_v) 12.3% [18]. The solubility parameter of PU/PAN is 13.11 (cal/cm³)^{1/2}, which is obtained by group additive method. 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. Sorption (S)–desorption (D)–resorption (RS)–redesorption (RD) experiments

The polymer membrane is exposed to different chemical environments for definite period of time and the changes in mass of the samples are measured. The mass gain due to sorption and mass loss due to desorption processes are monitored periodically until equilibrium is reached. These data are then used to calculate diffusion, sorption and permeability coefficients.

Circular disc-shaped samples of diameter ranging from 1.608 to 1.616 cm and thickness ranging from 0.076 to 0.1097 cm were cut from IPN 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 IPN is soaked in screw-tight bottles containing about 15–20 cm³ of liquid maintained at 20, 40 and 60 °C (±0.5 °C) in thermostatically controlled oven (M/S Tempo Laboratories, Mumbai). Polymer samples are removed periodically, the solvent drops adhering to the surface were wiped off using soft filter paper wraps, and samples weighed immediately on a digital analytical balance (Mettler Toledo, Switzerland) within the accuracy of 0.01 mg and immediately placed back into the test bottle. Since the time of this operation was less than 30 s, the method did not introduce large errors in weight uptake values. Samples reached equilibrium saturation within 76 h, which did not change significantly over a further period of 1 or 2 days. The weight gain during sorption is expressed as moles of solvent uptake by 100 g of polymer sample (C_t , mol%):

$$C_s \text{ (mol\%)} = \frac{\text{mass of solvent sorbed} \times 100}{(\text{molar mass of solvent})(\text{mass of polymer})} \quad (1)$$

After sorption experiments, the sorbed 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 from swollen membrane was expressed as moles of solvent lost by 100 g of polymer sample (C_d , mol%):

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

The resorption experiment was carried out in the same manner as sorption. The resorbed samples were subjected to desorption as explained earlier. The result of S–D–RS–RD of a polymer is important to predict its compatibility and suitability as a barrier in the chosen chemical environment.

Table 1
Some typical properties of aromatic solvents

Penetrants	Molecular mass	Molar volume (cm ³ /mol)	Boiling point (°C)	Viscosity (MPas)	Solubility parameter (cal/cm ³) ^{1/2}
Benzene	78	88.7	80.09	647	9.2
Toluene	92	106.1	110.8	590	8.9
Chlorobenzene	112	101.3	132.0	830	9.7
Nitrobenzene	123	102.2	210.0	1980	10.0

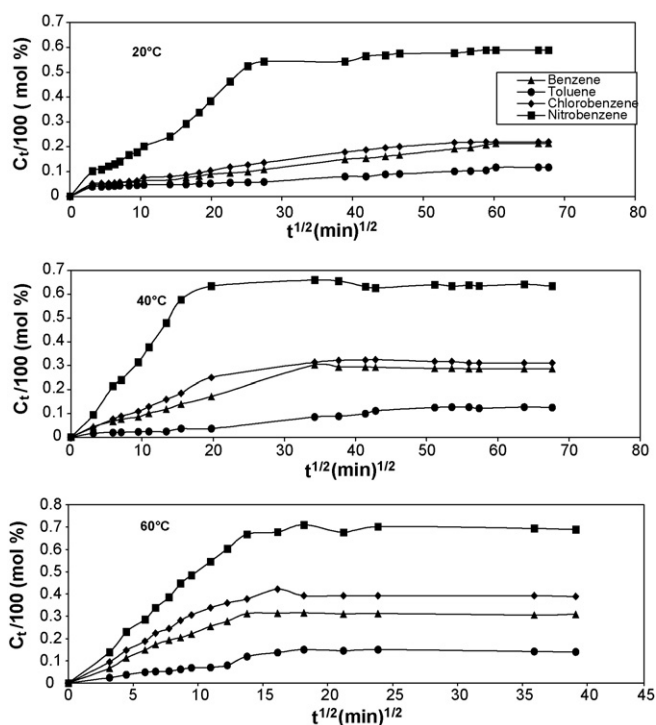


Fig. 1. The mol% uptake of substituted aromatic solvents into PU/PAN IPN during sorption at 20, 40 and 60 °C.

3. Results and discussion

3.1. Sorption

The mass uptake values expressed in weight percent units, i.e., mass of solvent sorbed by the polymer membrane often referred to as sorption or sorption coefficient, for PU/PAN (50/50) IPN with aromatic solvents are given in Fig. 1. From the figure it is found that nitrobenzene uptake is highest at all the measured temperatures, i.e., 20, 40 and 60 °C. The increase in order of mol% uptake of solvents into PU/PAN IPN is toluene < benzene < chlorobenzene < nitrobenzene. The lowest mol% uptake of toluene by PU/PAN can be justifi-

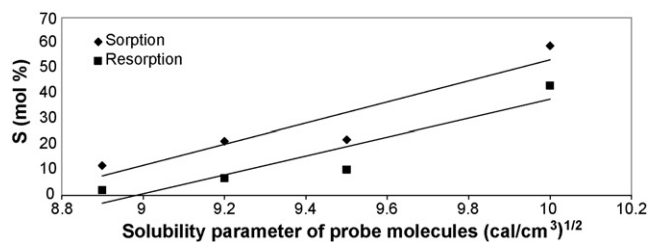


Fig. 2. Sorption coefficient (S) as a function of solubility parameter of probe molecules.

able as molar volume of toluene is higher than that of other solvents. The order of molar volume of the solvents are toluene > nitrobenzene > chlorobenzene > benzene. The solvent uptake into PU/PAN membrane is probably due to free volume in the IPN network and size of the penetrant. If size of the penetrant is the matter of concern then, mol% uptake for benzene would have been highest but, it is not so. Highest mol% of bulkier and polar nitrobenzene into polar PU/PAN, revealed that polarity of the penetrant molecules plays a major role in sorption.

The sorption coefficient S , number moles of solvent sorbed at equilibrium for every 100 g of polymer for sorption and resorption processes are given in Table 2. The S values depend on the chemical nature of the solvent rather than their size [19]. At 20 °C the S value of chlorobenzene and benzene are almost same. From Fig. 1, sorption curves at lower temperature are crowded within a narrow range whereas at higher temperature sorption curves are somewhat widely spaced owing to temperature dependence of sorption.

Variation of sorption coefficient with solubility parameter of probe molecules is shown in Fig. 2. It shows that as solubility parameter of solvent approaches the solubility parameter of PU/PAN IPN, the value of S increases [20]. This observation confirms that chemical interaction is the main reason for sorption.

Desorption curves for the different solvents at different temperatures are presented in Fig. 3. As the temperature increases the extent of desorption of solvents from the membrane will also increase. This shows the temperature dependence of desorp-

Table 2
Sorption (S), diffusion (D) and permeation coefficients of PU/PAN IPN membranes during sorption and resorption processes

Penetrants	Temperature (°C)	S ($\times 10^2$ mol%)		D ($\times 10^8 \pm 0.04$ cm ² /s)		P ($\times 10^8$ cm ² /s mol%)	
		Sorption	Resorption	Sorption	Resorption	Sorption	Resorption
Benzene	20	21.43	6.87	3.98	2.32	0.85	0.15
	40	28.65	27.41	6.04	5.08	1.73	1.39
	60	29.99	41.05	7.30	8.60	2.25	3.53
Toluene	20	11.75	2.08	6.87	5.05	0.81	0.11
	40	12.53	13.05	7.30	5.15	0.92	0.67
	60	14.08	21.19	13.50	6.37	1.90	1.35
Chlorobenzene	20	22.01	10.20	7.05	2.77	1.55	0.28
	40	31.05	32.31	7.16	4.81	2.22	1.55
	60	39.22	45.30	7.84	18.41	3.08	8.34
Nitrobenzene	20	58.9	43.16	3.65	2.48	2.15	1.07
	40	63.5	65.53	6.01	6.71	3.82	4.40
	60	66.46	68.42	6.44	11.75	4.28	8.04

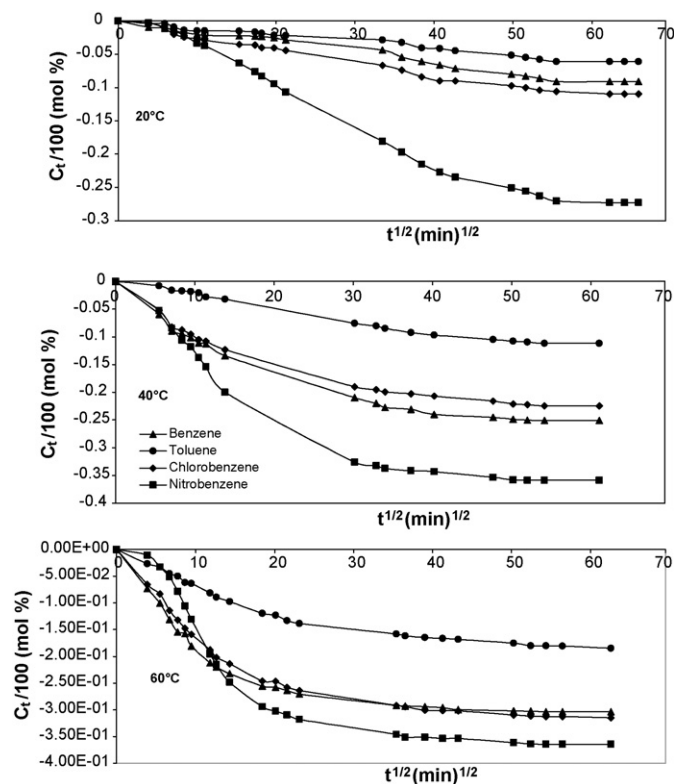


Fig. 3. Desorption of sorbed solvents from swollen PU/PAN IPN at different temperatures.

tion. There is a small difference between desorption of benzene and chlorobenzene at all temperatures [20]. The similar trend is observed during sorption process also.

The mol% uptakes for resorption process, i.e., second sorption at different temperatures are presented in Fig. 4. At low temperature mol% uptake is in the order; toluene < benzene < chlorobenzene < nitrobenzene. Like sorption, resorption curves are also crowded within a narrow range at lower temperature but are widely spaced at higher temperature showing a clear-cut dependence of sorption on temperature. At low temperature mol% uptake during resorption is lower than sorption values. At higher temperatures mol% uptake value for resorption is more than sorption process. The sorption and desorption processes would result in relaxation of SIPN chains. The relaxation is more in the network due to absence in cross-linking. At higher temperature relaxation is more, and thus almost all the solvent could be evaporated from the membrane during desorption. Further for resorption process, solvent uptake will be more due to more cavities and molecular entanglement is under strain. At lower temperature the quantum of solvent desorbed would be less, thus uptake of solvent into this membrane will be less and at the same time this system reaches equilibrium is short span of time. Hence, mol% uptake during resorption is less compared to sorption at low temperature.

The amount of material desorbed from resorbed polymer membrane is expressed as mol% and is shown in Fig. 5. From the figure it is clear that, redesorption results is almost same as that of desorption indicating consistency in interaction of IPN with aromatic solvents.

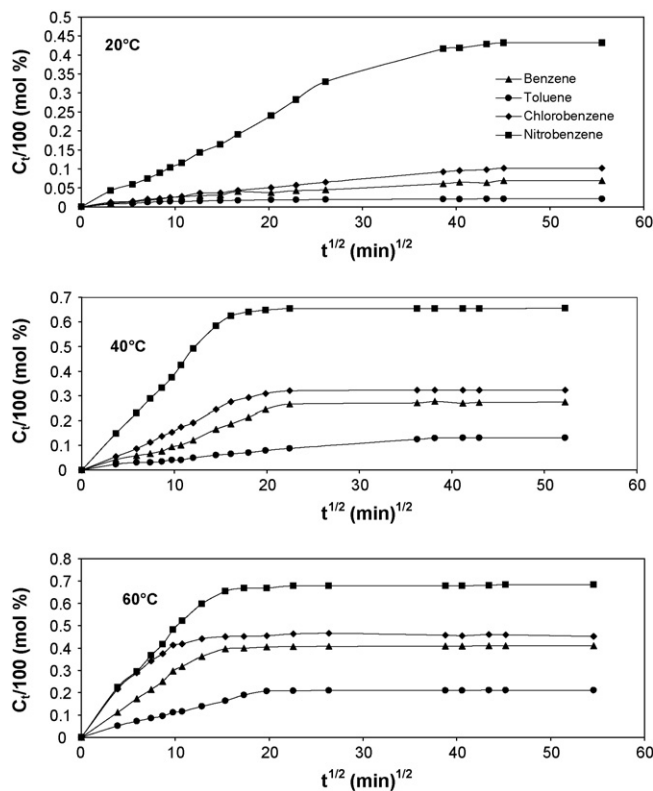


Fig. 4. The mol% uptake of probe molecules in to PU/PAN IPN for resorption at 20, 40 and 60 °C.

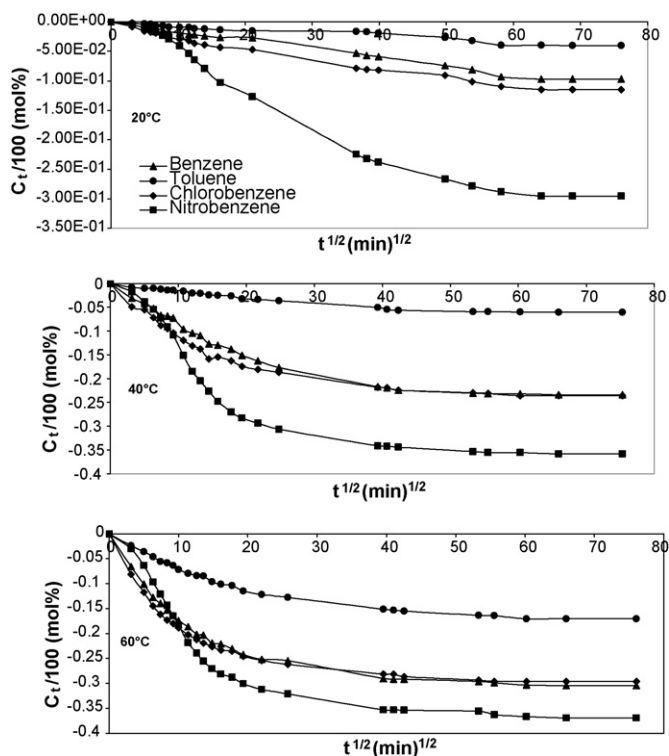


Fig. 5. The mol% solvents desorbed from swollen IPNs at different temperatures for redesorption.

Table 3
System parameters n and K for PU/PAN IPN membranes at different temperatures

Penetrants	Temperature (°C)	$n \pm 0.01$		$K (\times 10^2 \pm 0.04 \text{ g/g min}^n)$	
		Sorption	Resorption	Sorption	Resorption
Benzene	20	0.41	0.52	0.28	0.31
	40	0.52	0.54	0.28	0.53
	60	0.50	0.52	0.13	0.15
Toluene	20	0.40	0.41	0.26	0.09
	40	0.52	0.50	0.62	0.61
	60	0.51	0.43	0.19	0.14
Chlorobenzene	20	0.40	0.51	0.23	0.39
	40	0.51	0.47	0.28	0.17
	60	0.51	0.41	0.13	0.12
Nitrobenzene	20	0.50	0.55	0.32	0.50
	40	0.52	0.52	0.20	0.21
	60	0.52	0.48	0.60	0.13

3.2. Diffusion

The Fickian diffusion theory is used to calculate diffusion coefficient, D , of liquid in a membrane [15,21]. According to Fick's law of diffusion, mass transport occurs in the direction of concentration gradient and this will generate concentration profiles in the polymer membrane. Thus, from a solution of the one-dimensional Fick's equation, we get an expression for the concentration-independent D as

$$D = \pi \left[\frac{h\theta}{4C_\infty} \right]^2 \quad (3)$$

where h is the sample thickness; θ the slope of the initial linear portion of sorption curves, i.e., before the attainment of 50% of equilibrium uptake; C_∞ is equilibrium mole uptake. The calculated values of diffusion coefficient (D) are tabulated in Table 2. At 20 °C the value of D is highest for chlorobenzene ($7.05 \times 10^{-8} \text{ cm}^2/\text{s}$) and lowest for nitrobenzene ($3.65 \times 10^{-8} \text{ cm}^2/\text{s}$). As temperature increases D values also increases. For chlorobenzene, increase in D is marginal. These data show dependence on the nature of the liquid molecules, but not on their sizes [19]. Diffusion coefficient (D) values for resorption are found to be lower than corresponding sorption value at 20 and 40 °C (except with nitrobenzene), whereas at 60 °C it is more. Diffusion into this membrane at low temperature will be less during resorption, because there is already some solvent inside the membrane due to incomplete desorption and this will inhibit the diffusion of solvent. In case of interaction with nitrobenzene, difference in solubility parameter of solvent and polymer membrane plays an important role, as this difference is very less, the rate of diffusion is also more. However, the values of D do not show any systematic dependence on the size of penetrant.

The dynamic penetrant sorption results were analyzed using the empirical equation [22,23];

$$\frac{C_t}{C_\infty} = Kt^n \quad (4)$$

where C_t and C_∞ are the mol% sorption at time t and at equilibrium, respectively. Exponent n is constant and it tells about mode of transport, and K is constant that depends on the structural characteristics of the polymer. It gives information about interaction of polymer and solvents. The value of n and K are obtained by regression analysis of $\log(C_t/C_\infty)$ versus $\log t$ plot. The estimated values of K and n in Table 3 are accurate to ± 0.01 and ± 0.04 , respectively. The value of n for sorption and resorption processes are lies in the range 0.40–0.52 and 0.41–0.55, respectively. As the value of n falls in the range 0.40–0.55 for PU/PAN IPN, this indicates that the mode of transport is near Fickian. For the Fickian mode of transport, the rate of diffusion of permeate molecules are much less than the relaxation rate of the polymer chains. Generally rubbers and semi-crystalline polymers exhibit Fickian mode of diffusion [24]. The variation of n and K did not show any systematic changes.

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. The net diffusion through polymer depends on the difference in the amount of penetrant molecules between the two successive layers.

Hence, the permeability [25]:

$$P = DxS \quad (5)$$

where D is diffusivity and S is the solubility, and the value of S are taken as grams of solvent sorbed per gram of IPN. The permeability coefficient derived from Eq. (5) is given in Table 2. Though the value of D for nitrobenzene at 20 °C is low, P value for it is highest, whereas for toluene it is lowest. This indicates that, solubility parameter probe molecules plays an important role in permeation and thus affinity of PU/PAN IPN is more towards nitrobenzene. From the Table 2 it is clear that, the order of permeability is: nitrobenzene > chlorobenzene > benzene > toluene. Interestingly the order of solubility parameter of probe molecules (Table 1) is nitrobenzene > chlorobenzene > benzene > toluene. As the solubility parameter of nitrobenzene is closer to that of polymer, there will be more solubility due to interaction of

nitrobenzene with polymer and hence, high permeability. P value also increases with increases in the temperature. Permeability of resorption is lower than the corresponding P values of sorption process.

3.3. Desorption

During desorption, the rate of loss in polymer weight due to evaporation of penetrant is given by [25]:

$$-D \left(\frac{\partial C}{\partial t} \right) = F_0(C_0 - C_{\text{ext}}) \quad (6)$$

where F_0 is rate of evaporation of pure solvent under the same conditions; C_0 the actual concentration of the liquid on the membrane surface; C_{ext} is the concentration on the surface which is at equilibrium with the surrounding environment. The solution of Eq. (6) is given as [25]:

$$\frac{C_{\infty} - C_{\text{ext}}}{C_{\infty} - C_0} = \sum_{n=0}^{\infty} \frac{2M \cos(\beta_n x/h) \exp(-\beta_n^2 Dt/h^2)}{(\beta_n^2 + M^2 + M) \cos \beta_n} \quad (7)$$

where the β_n values are the positive roots of

$$\beta \tan \beta = M \quad (8)$$

with the dimensionless parameter M is given by

$$M = \frac{hF_0}{D} \quad (9)$$

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

$$\frac{M_{\infty} - M_t}{M_{\infty}} = \sum_{n=0}^{\infty} \frac{2M^2 \exp(-\beta_n^2 Dt/h^2)}{\beta_n^2(\beta_n^2 + M^2 + M)} \quad (10)$$

The β_n values for any M were taken from the literature [25].

The rate of evaporation for desorption and redesorption per unit area of the polymer were calculated by using the initial rate of desorption/redesorption process:

$$F_0 = \frac{dM_t/dt}{C_0 - C_{\text{ext}}} \quad \text{for } t \rightarrow 0 \quad (11)$$

The calculated values of F_0 have been tabulated in Table 4. The rate of evaporation decreased from benzene to toluene and chlorobenzene to nitrobenzene. The dependence of rate of evaporation varies from hydrocarbon to substituted hydrocarbon but there is dependence among the materials of similar family, i.e.,

as molecular mass increased from benzene to toluene, decreases in rate of evaporation is observed, similarly from chlorobenzene to nitrobenzene, decrease in rate of evaporation is observed. Increase in temperature found to increases the rate of evaporation, which is on expected lines. The similar trend is noticed for redesorption process but the rate of evaporation is slightly more for almost all the solvent systems.

3.4. Swelling

The interaction between polymer and solvent can be established by knowing the amount of polymer in the swollen polymer. The volume fraction of polymer Φ in the swollen IPN is calculated using the equation [26]:

$$\Phi = \frac{W_1/\rho_p}{(W_1/\rho_p) + (W_2/\rho_s)} \quad (12)$$

where W_1 is weight of polymer; ρ_p the density of polymer; W_2 the weight of solvent in the swollen sample; ρ_s is the density of solvent. In a given polymer system, low value of Φ , is an indication of higher interaction of PU/PAN IPN with solvent. For a given series of solvents, the value of Φ for nitrobenzene (Table 5) is found to be less. Similarly for toluene, volume fraction of polymer in swollen IPN is high indicating less amount of solvent being taken up. This indicates that there is greater degree of interaction between IPN and nitrobenzene and lesser interaction between toluene and PU/PAN IPN. The interaction of solvent with IPN system could be further evaluated using interaction parameter, given by equation [27]:

$$\chi = \frac{\beta + V}{RT(\delta_A - \delta_B)^2} \quad (13)$$

where V is the molar volume of solvent, δ_A and δ_B the solubility parameters of solvent and polymer, respectively; R the universal gas constant; T the absolute temperature; β is the lattice constant and its value is equal to 0.34. The χ value (Table 5) of nitrobenzene is more compared to other solvents which indicates that, PU/PAN IPN interact more with nitrobenzene than other solvents under consideration. Using χ and Φ values, the molecular mass (M_c) between interlocking (cross-linking), cross-link density (V_c) and degree of cross-linking (V) has been calculated using following equations [27–29]:

$$M_c = \frac{-\rho_p V_s \Phi^{1/3}}{\ln(1 - \Phi) + \Phi + \chi \Phi^2} \quad (14)$$

Table 4
Rate of evaporation (F_0) of penetrants during desorption and redesorption for PU/PAN (50/50) IPN

Temperature (°C)	$F_0 (\times 10^4 \text{ g/cm}^2 \text{ s})$							
	Benzene		Toluene		Chlorobenzene		Nitrobenzene	
	Desorption	Redesorption	Desorption	Redesorption	Desorption	Redesorption	Desorption	Redesorption
20	15.6	90.72	2.98	5.88	2.92	3.43	2.54	2.78
40	185	476	5.87	6.56	4.47	4.15	3.46	4.70
60	227	771	6.63	7.44	5.84	5.61	4.95	5.17

Table 5
Solvent–polymer interaction parameters

Solvent	Volume fraction of polymer (ϕ)	Interaction parameter (χ)	Molecular mass between cross-link (M_c)	Cross-link density (V_e) ($\times 10^3$ g mol/cm ³)	Degree of cross-linking (V)
Benzene	0.8103	0.0100	119	0.0102	0.00420
Toluene	0.8681	0.0104	107	0.0113	0.00465
Chlorobenzene	0.7865	0.0134	152	0.0080	0.00329
Nitrobenzene	0.5594	0.0182	403	0.0030	0.00124

where V_s is the molar volume of solvent, the meaning of χ , Φ and ρ_p is same as defined earlier.

$$V_e = \frac{\rho_p}{M_c} \quad (15)$$

$$V = \frac{1}{2M_c} \quad (16)$$

The calculated values of M_c , V_e and V are given Table 5. The interaction of probe molecules with given PU/PAN IPN indicate higher M_c with nitrobenzene, and low M_c with toluene. At the same time cross-link density (V_e) and degree of cross-linking (V) is found to be high when toluene interacts with PU/PAN IPN and low value when nitrobenzene interacts with IPN. This is an indicative of probable interlocking of polymeric chains in the network. However, M_c values may not be the true molar masses between cross-links, but rather may represent the molar mass between physical entanglements of the polymer. Hence, these values should be regarded as only approximate.

3.5. Effect of temperature

Sorption and diffusion have shown the temperature dependence and hence, the Arrhenius plots of $\log D$ and $\log P$ versus $1/T$ exhibit linear relationship. The activation energy for diffusion E_D , and permeation E_P are calculated using Arrhenius equation [30]:

$$X = X_0 \exp\left(-\frac{E_a}{RT}\right) \quad (17)$$

where X is P or D ; E_a the activation energy; R the universal gas constant; T is the absolute temperature. The energy of activation energies are obtained by least square analysis and are given in Table 6. The energy of activation for diffusion E_D and permeation E_P for chlorobenzene is lowest during sorption and highest during desorption process. Similarly E_D for toluene is highest

for sorption and lowest for desorption process. As expected E_P values for sorption and desorption processes are more than corresponding E_D values. The energy of activation for desorption processes are higher than sorption values, except for toluene where the uptake of solvent into polymer itself is poor. This observation confirms that, the residual solvent present in the membrane hinder the diffusion and permeation of fresh solvent during desorption processes. Hence they require high amount of energy and thus higher E_D and E_P values.

The thermodynamic parameter like change in entropy ΔS and enthalpy ΔH are obtained from Van't Hoff relation:

$$\log K_s = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \quad (18)$$

where K_s is equilibrium sorption constant which is given by

$$K_s = \frac{\text{no. of moles of solvent sorbed at equilibrium}}{\text{mass of the polymer}} \quad (19)$$

The obtained values of ΔS and ΔH are obtained by regression analysis of the plot of $\log K_s$ versus $1/T$ (Fig. 6). The heat of sorption is a composite parameter, which involves contribution from Henry's law mode with the endothermic reaction contribution and Langmuir's (hole-filling) type sorption giving the endothermic heats of sorption. The values of ΔS and ΔH are given in Table 6. The ΔH values for all the solvent–polymer systems are positive, suggesting that sorption may be dominated by Henry's law mode giving an endothermic contribution. The ΔS values for all membrane–solvent systems are negative. This suggests that the structure of the solvent molecules is retained in the sorbed state [31].

3.6. Comparison of D with theoretical value

Attempt has been made to compare the experimental solvent diffusion curves with the theoretical diffusion profile. The the-

Table 6
Activation energy for diffusion ($E_D \pm 2\%$), activation energy for permeation ($E_P \pm 1.6\%$), enthalpy of sorption ($\Delta H \pm 3.5\%$) and entropy of sorption ($\Delta S \pm 1.5\%$) for PU/PAN IPN

Thermodynamic parameter	Benzene		Toluene		Chlorobenzene		Nitrobenzene	
	Sorption	Resorption	Sorption	Resorption	Sorption	Resorption	Sorption	Resorption
E_D (kJ mol ⁻¹)	12.40	27.43	13.46	4.62	2.12	38.01	11.68	31.70
E_P (kJ mol ⁻¹)	19.85	57.73	17.20	17.20	13.87	68.05	14.86	45.27
$-\Delta S$ (kJ/mol K)	12.94	103.88	5.65	131.81	27.84	86.22	6.41	25.86
ΔH (kJ/mol)	7.47	36.63	3.58	47.60	11.79	30.55	3.17	9.50

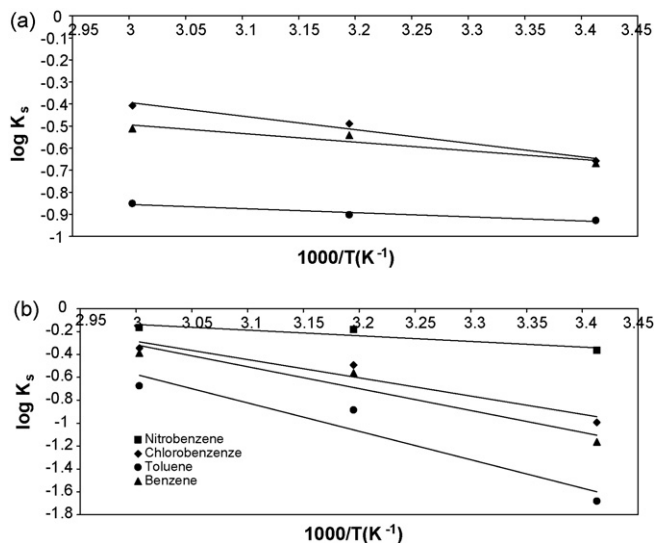


Fig. 6. $\log K_s$ vs. $1000/T$ for probe molecules with PU/PAN for (a) sorption and (b) desorption process.

oretical curves are generated using Fickian diffusion equation:

$$\frac{C_t}{C_\infty} = 1 - \left(\frac{8}{\pi^2}\right) \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(\frac{-D(2n+1)^2\pi^2 t}{h^2}\right) \quad (20)$$

The experimentally determined D values are substituted in Eq. (20) and diffusion curves are generated. Fig. 7 shows theoretical and experimental sorption curves for benzene during sorption and desorption processes. Generally, agreement between the experimental and theoretical curves is fairly good at lower sorption time but, at longer sorption times it deviates. A similar behaviour was observed for other solvents also. Aminabhavi et al. noticed similar trend for diffusion of alkanes into santoprene system [32].

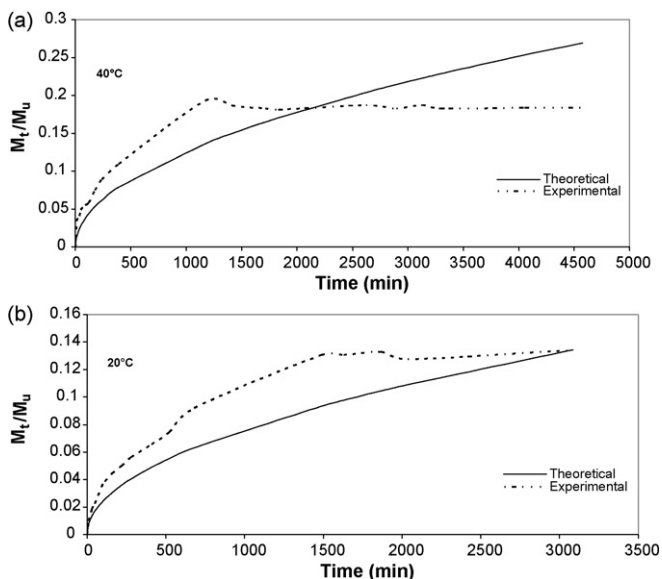


Fig. 7. Comparison of experimental and theoretical M_t/M_∞ of benzene in to PU/PAN for sorption and desorption processes.

3.7. Concentration profile

Diffusion co-efficients have been calculated from Fickian equation. Liquid penetrant ingress into elastomeric membranes is of great technological importance. In many instance, it is important to evaluate the penetrant concentration profiles into barrier polymer membranes. However, their accurate experimental calculations required the use of sophisticated experiments. In the absence of these methods, modified Ficks second law can be used. Hence, the concentration profiles of liquids through PU/PAN IPN membrane have been evaluated by computer-simulated method. To calculate concentration profiles Fick's second order differential equation is used in its most general form [11,16]:

$$\frac{\partial c}{\partial t} = D \left(\frac{\partial^2 c}{\partial x^2} \right) \quad (21)$$

where D is the concentration-independent diffusion coefficient; t the sorption time; c the liquid concentration within the membrane materials; $\partial c/\partial x$ is the concentration gradient along the x direction. Eq. (21) 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

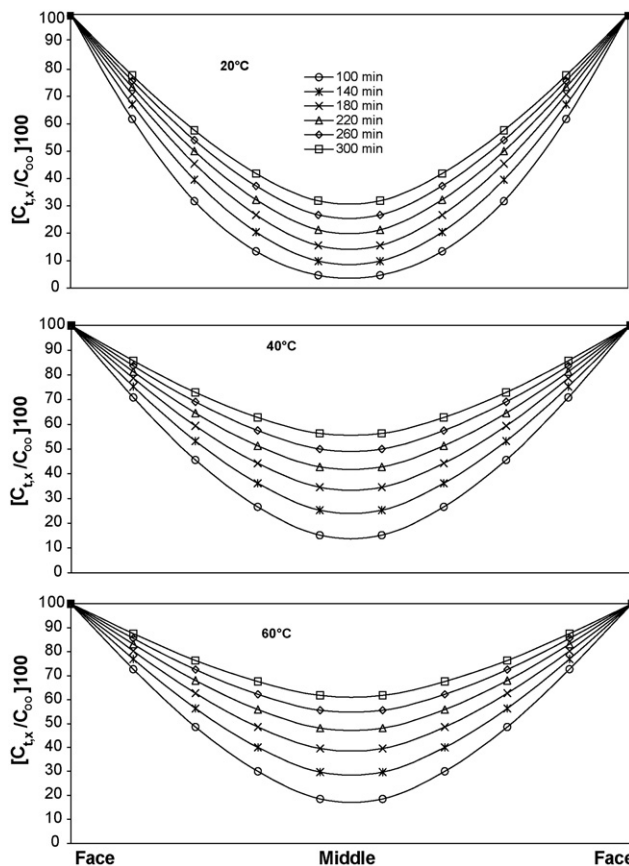


Fig. 8. Concentration profiles of nitrobenzene at different temperatures into PU/PAN for sorption process.

membrane to establish thermal equilibrium is negligible when compared to the time of sorption; (v) the changes in membrane dimensions are negligible during the liquid exposure. The initial boundary conditions are

$$t = 0, \quad 0 \leq x < h; \quad c = 0 \quad (22)$$

$$t \geq 0, \quad x = 0, \quad x = h, \quad c = c_{\infty} \quad (23)$$

$$\frac{\partial c}{\partial x} = 0, \quad x = 0; \quad t > 0 \quad (24)$$

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 :

$$\frac{c_{(t,x)}}{c_{\infty}} = \frac{1 - 4}{\pi \sum 1/(2n + 1)} \exp \left[\frac{-D(2n + 1)^2 \pi^2 t}{h^2} \right] \times \sin \left[\frac{(2n + 1)\pi x}{h} \right] \quad (25)$$

where n is an integer. Solving Eq. (25), 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 representative concentration profiles generated for PU/PAN with nitrobenzene for sorption at 20, 40 and 60 °C, and at different time intervals are given in Fig. 8. From the profiles,

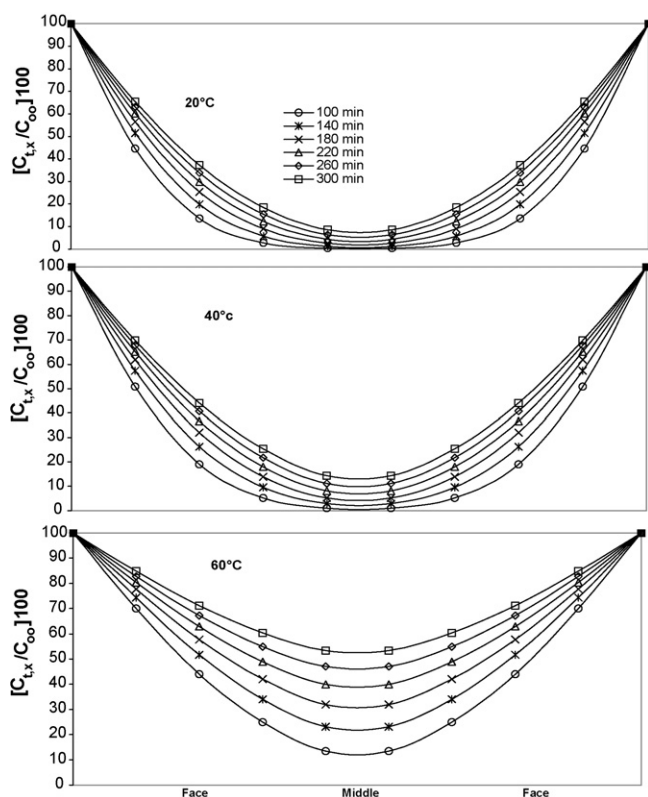


Fig. 9. Concentration profiles of chlorobenzene at different temperatures into PU/PAN for resorption.

the higher values of $c_{(x,t)}/c_{\infty}$, is observed at higher temperatures. The pattern indicates more amount of nitrobenzene in the polymer network than other solvents, indicating more interaction of highly polar nitrobenzene with polar PU/PAN. Fig. 9 shows concentration of chlorobenzene during first 300 min of resorption at 20, 40 and 60 °C. Thus simulations predict the probable distribution of solvent at different time intervals and at different temperatures in IPN. Hence, it will be of much help in engineering applications.

4. Conclusions

When the polymer is used as barrier material in holding and storage tanks, then the polymer membrane should not allow solvent to diffuse and percolate. This can be achieved by using polymer membranes of low diffusivity and permeability. For PU/PAN IPN systems, the sorption coefficient is more for polar nitrobenzene and less for other aromatic hydrocarbons. The permeability of aromatic hydrocarbon is low at all temperatures. However, the rate at which these penetrants evaporate from the surface of swollen PU/PAN is high. Interaction parameter calculated using Flory Rehner theory indicates low interaction of aromatic hydrocarbon with polar PU/PAN. All these observations revealed that PU/PAN has less affinity for aromatic hydrocarbons than polar aromatic solvents. Hence, this membrane could be suitable proposition as a barrier for non-polar aromatic hydrocarbons. The concentration profiles generated using Fick's equation give an idea about quantum of solvents that will be present in the membrane at different time intervals at different depths.

References

- [1] J. Cooke, L. Rebenfeld, *Geotext. Geomembr.* 7 (1988) 7–22.
- [2] N.M.W. John, *Geotextiles*, Blakie & Sons Ltd., London, 1987.
- [3] J. Stastna, D. De Kee, *Transport Properties in Polymers*, Technomic Publishing Co., Lancaster, 1995.
- [4] R. Koerner, *Designing with Geosynthetics*, Prentice Hall, Englewood Cliffs, NJ, 1990.
- [5] M. Sittling, *Pollutant Removal Hand Book*, Noyes Data Corporation, New York, 1973.
- [6] A. Raychaudhuri, S.K. Roy, *Talanta* 41 (1994) 171.
- [7] S.G. Dmitrienko, E.N. Myshak, L.N. Pyatkova, *Talanta* 49 (1999) 309.
- [8] R.J. Cassellaa, V.A. Salima, L.S. Jesuinoa, R.E. Santelli, S.L.C. Ferreirac, M.S. de Carvalhod, *Talanta* 54 (2001) 61.
- [9] Siddaramaiah, P. Mallu, *J. Appl. Polym. Sci.* 67 (1998) 2047–2055.
- [10] B.K. Kendagannaswamy, Siddaramaiah, *J. Appl. Polym. Sci.* 84 (2002) 359–369.
- [11] Siddaramaiah, H. Kumar, S. Roopa, B.K. Kendagannaswamy, T.M. Aminabhavi, *J. Appl. Polym. Sci.* 90 (2003) 122–128.
- [12] M. Begum, Siddaramaiah, H. Kumar, T.M. Aminabhavi, *J. Appl. Polym. Sci.* 90 (2003) 739–746.
- [13] P.E. Cassidy, M. Mores, D.J. Kerwick, K.L. Koeck, Verschoor, D.F. White, *Geotext. Geomembr.* 11 (1992) 61–98.
- [14] T.M. Aminabhavi, U.S. Aithal, S.S. Shukla, *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* C28 (3&4) (1988) 421–474.
- [15] J. Crank, *The Mathematics of Diffusion*, 2nd ed., Clarendon Press, Oxford, 1975.
- [16] H. Kumar, Siddaramaiah, *J. Appl. Polym. Sci.*, in press.
- [17] H. Kumar, Siddaramaiah, *J. Reinf. Plastic Compd.* 24 (2005) 209.

- [18] H. Kumar, Siddaramaiah, G.N. Kumaraswamy, H.B. Ravikumar, Ranganathaiah C., *Polym. Int.* 54 (2005) 1401–1407.
- [19] T.M. Aminabhavi, H.T.S. Phayde, J.D. Ortego, W.E. Rudzinski, *J. Hazard. Mater.* 49 (1996) 125–141.
- [20] H. Kumar, Siddaramaiah, *Polymer* 46 (2005) 7140–7155.
- [21] J.M. Vergnaud, *Liquid Transport Processes in Polymeric Materials*, Prentice Hall, Englewood Cliffs, NJ, 1991.
- [22] N.M. Franson, N.A. Peppas, *J. Appl. Polym. Sci.* 28 (1983) 1299–1310.
- [23] L.M. Lucht, N.A. Peppas, *J. Appl. Polym. Sci.* 33 (1987) 1557–1566.
- [24] H.B. Hopfenberg, D.R. Paul, in: D.R. Paul (Ed.), *Polymer Blends I*, Academic Press, New York, 1976.
- [25] S.B. Haragopad, T.M. Aminabhavi, *Macromolecules* 24 (1991) 2598.
- [26] E. Southern, A.G. Thomas, *Trans. Farad. Soc.* 63 (1967) 1913.
- [27] P.J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.
- [28] P.J. Flory, J. Rehner Jr., *Statistical mechanics of crosslinked polymer networks. Part 2. Swelling*, *J. Chem. Phys.* 11 (1943) 521.
- [29] S. Desai, I.M. Thakore, A. Brennan, S. Devi, *J. Appl. Polym. Sci.* 83 (2002) 1576–1585.
- [30] A.B. Zkia, M.Y. El-Sheikha, J. Evansb, S.A. El-Safty, *J. Colloid Interf. Sci.* 221 (2000) 58.
- [31] S.B. Haragopad, T.M. Aminabhavi, *J. Appl. Polym. Sci.* 42 (1991) 2329.
- [32] T.M. Aminabhavi, H.T.S. Phayde, J.D. Ortego, *Polym. Polym. Compos.* 4 (1996) 103.