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Molecular Transport Behavior of Substituted Aromatic Solvents through Biobased Chain Extended Polyurethane

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Molecular Transport Behavior of Substituted Aromatic Solvents through Biobased Chain Extended Polyurethane

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The biobased chain extended polyurethane (PU) was obtained by reacting castor oil based polyol with toluene-2,4-diisocyanate (TDI) and chain extender such as glutaric acid. The effect of incorporation of chain extender into PU on the molecular transport of substituted aromatic solvent penetrants (benzene, chlorobenzene and nitrobenzene) was studied in comparison with a neat PU. Sorption (S) studies were carried out at different temperatures viz., 25, 40 and 60°C. From the sorption results, the diffusion (D) and permeation (P) coefficients of penetrants have been calculated. A significant increase in the diffusion and permeation coefficients were observed with an increase in the temperature of the sorption experiments. Higher values of diffusion and permeation coefficients were noticed for chain extended PUs as compared to PU. Attempts were made to estimate the empirical parameters like n, which suggests the mode of transport and K is a constant depends on the structural characteristics of the composite in addition to its interaction with penetrants. The temperature dependence of the transport coefficients has been used to estimate the activation energy parameters for diffusion (E_D) and permeation (E_p) processes from Arrhenius plots.

Keywords: biopolyurethane, castor oil, sorption, diffusion, aromatic solvents, penetrant

1 Introduction

Polyurethane (PU) elastomers are known to exhibit unique mechanical properties, primarily as a result of two phase morphology (1). These materials are alternating block copolymers made up of hard segments from the diisocyanate/chain extender and soft segments from the polyol (ether or ester, castor oil). The hard and soft segments are chemically incompatible and micro phase separation of the hard segments dispersed in a matrix of soft segment can occur in varying degrees (2, 3). The PU materials are becoming popular as membranes to remove or recover the hazardous chemicals from the liquid effluents discharged from various processing industries (4–6). The transport behavior of various solvents into PU has received considerable attention as it helps to design the barrier material or tubes for transporting the liquids and gases.

In view of the importance of PU as a barrier material in several emerging engineering areas (7, 8), it is important to know its transport characteristics with respect to common organic solvents. The knowledge of the transport mechanisms as manifested by sorption, diffusion and permeation of organic liquid penetrants in PU will be helpful for establishing the structure-property relationship. A numerous research publications are available in the literature on the transport behavior of various organic solvents into PUs (9–15). The diffusion of water and ethanol through PU membrane was studied by Huang et al. (16). The migration of substituted aromatic solvents into polyurethane/polystyrene (PU/PS) semi-interpenetrating polymer network (SIPN) was investigated by Kumar and Siddaramaiah (17). Wolinska-Grabczyk (18) studied the transport behavior of liquid hydrocarbons through poly (oxytetramethylene) diol chain extended PU. In general, the authors have noticed a Fickian sorption rate curves for PU/benzene systems and non-Fickian anomalies for *n*-hexane and cyclohexane penetrants. Lue and Liaw (19) employed PU-zeolite as composite membranes for the separation of xylene mixtures. The observed xylene vapor sorption isotherms exhibited a Henry's law relationship in PU–zeolite blend system. Ajithkumar et al. (20) reported the anomalous behavior of sorption and diffusion of organic solvents through PU and unsaturated polyester based interpenetrating polymer networks. Aminabhavi et al (21, 22)

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Table 1. Some typical properties of aromatic solvents

Penetrants	Molecular mass	Molar volume (cm^3/mol)	Boiling point ($°C$)	Viscosity ($MPa\,s$)	Solubility parameter ($cal/cm^3)^{1/2}$
Benzene	78	88.7	80.09	647	9.2
Chlorobenzene	112	101.3	132.0	830	9.7
Nitrobenzene	123	102.2	210.0	1980	10.0

have carried out extensive studies on sorption and diffusion behavior of organic probe molecules through various polymeric systems. A detailed literature survey revealed that, the transport behavior of substituted aromatic solvent penetrants through gluataric acid (GA) based bio based polyurethane has not yet been studied. In the previous communication (22), authors have reported on the transport behavior of n-alkane penetrants through maleic and citric acid based chain extended bio PUs. In the present study, the authors have selected the substituted aromatic solvent penetrants (benzene, nitrobenzene and chlorobenzene) as probe molecules to investigate the transport behavior of these probe molecules through both neat and chain extended PU.

2 Experimental

2.1 Materials

Castor oil was procured from the local market. Its average molecular weight (M_n) is 930 and hydroxyl group per molecule is 2.24. Toluene-2, 4-diisocyanate (TDI) and dibutyl tin dilaurate (DBTL) were obtained from Sigma (USA) and were used as received. The AR grade organic solvent, methyl ethyl ketone (MEK), glutaric acid (GA), benzene, nitrobenzene and chlorobenzene were procured from S.D. Fine Chem. Ltd., Mumbai, India. These solvents except GA were distilled before being used. Some of the typical properties of solvents are given in Table 1.

2.2 Preparation of Glutaric Acid Based Chain Extended Bio Polyurethane

The preparation of glutaric acid based chain extended bio PU involves two step procedure as described elsewhere (23). In the first step, pre PU polymer was obtained by reacting two moles of diisocyanates into one mole of castor oil dissolved in MEK in a three-necked round bottomed flask equipped with a reflux condenser at 80°C for one hour under N_2 gas atmosphere. In the second step, one mole of glutaric acid was added into the formed pre PU polymer and the reaction was carried out with continuous stirring at 80°C for 30 min. The reaction mixture was poured into the glass molds coated with silicone releasing agent to cast the chain extended PU sheets. For the comparison studies,

the neat PU without chain extender was also cast in the similar procedure as described above and labelled as PU. The sample with GA chain extender was labelled as PU +GA.

2.3 Technique

2.3.1. *Sorption test*

Both neat PU and chain extended PU were cut circularly (diameter = 1.6 cm) using a sharp-edged steel die. Sorption experiments were performed at different temperatures viz., 25, 40 and 60°C by immersing the specimens in distilled water in the metal-capped bottles maintained at the desired constant temperature (±0.5°C) in a thermostatically controlled oven. At specified intervals of time, specimens were removed from the containers, penetrant adhered on to the surfaces were removed using soft filter paper and weighed immediately using analytical balance having ±0.1 mg accuracy. The weighing continued until the specimens attain the equilibrium values. The weight gain during sorption process is expressed as moles of solvent uptake by 100 g of polymer sample (C_t, mol %):

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

(1)

3 Results and Discussion

Sorption of substituted aromatic solvent penetrants such as benzene, chlorobenzene and nitrobenzene into both neat PU and chain extended PU membranes have been studied. Sorption curves are expressed as percent penetrant uptake (C_t) versus square root of time. Typical sorption curves of neat PU and chain extended PU in benzene penetrant at 25, 40 and 60°C are shown in Figure 1. The typical sorption curves of neat PU and chain extended PU at 25°C in all penetrants is shown in Figure 2. From Figure 1, it can be observed that the chain extended PU has higher sorption as compared to neat PU. A similar behaviour was observed in other (chlorobenzene and nitrobenzene) penetrants. The dicarboxylic acid (glutaric acid) based chain extended PU may be more flexible and contain high amount of soft component like glycol based chain extended PU (24). This may be the reason for higher penetrant uptake in chain extended PU as compared to neat PU. From the
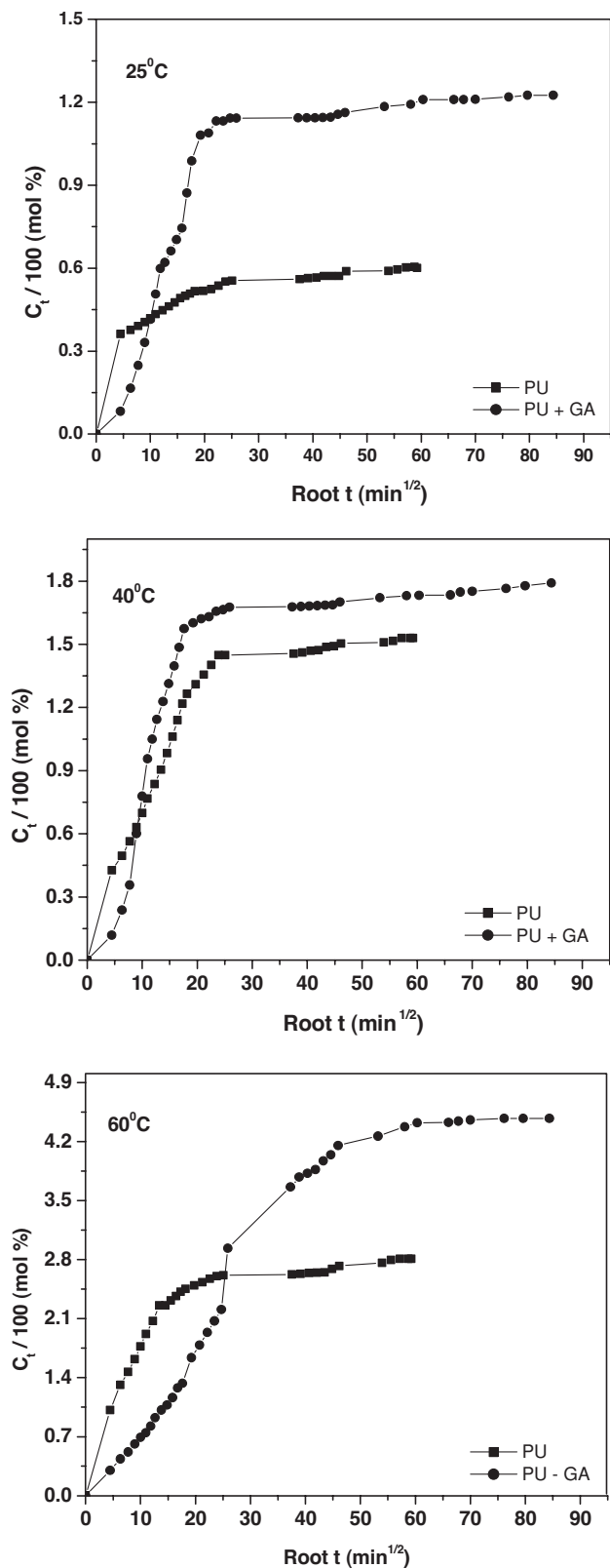
Fig. 1. The mol percentage uptake vs. square root of time for PU and PU + GA in benzene at different temperatures.
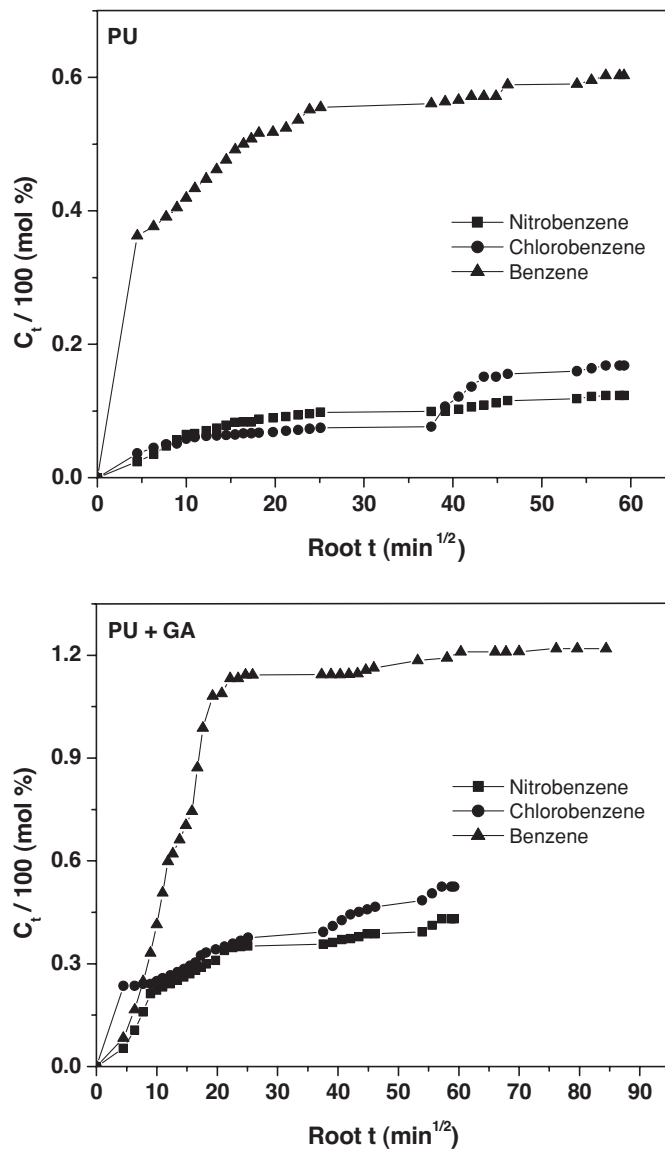

Fig. 2. Mol percentage uptake vs. square root of time for PU and PU + GA in different solvents at 25°C.

figure, it can also be observed that, the initial portion of the sorption curves are linear after which the mechanism changes. According to Southern and Thomas (25), when a polymer interacts with solvents, the surface of the polymer membrane swells immediately, but the swelling will not takes place in the underlying un swollen material. Thus, a two dimensional compressive stress exerts on the surface. The swelling stresses are either relaxed or dissipated by further swelling and rearrangement of the segments. Diffusion of low molecular weight probe molecules found to lead typical phenomena of membrane swelling and physical relaxation.
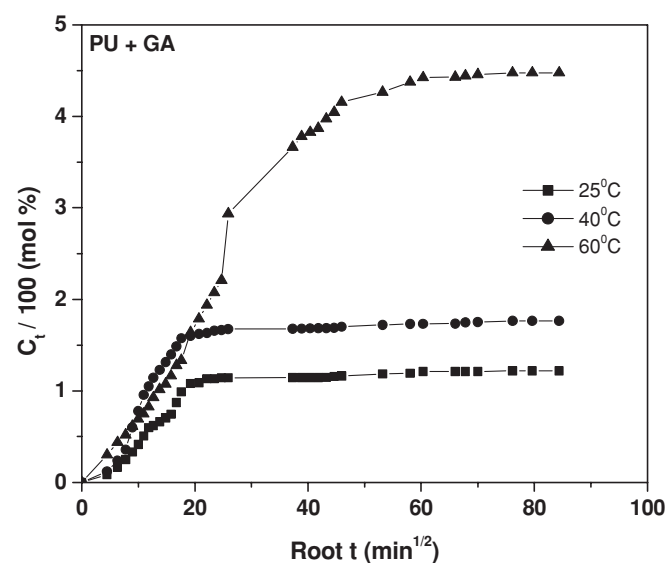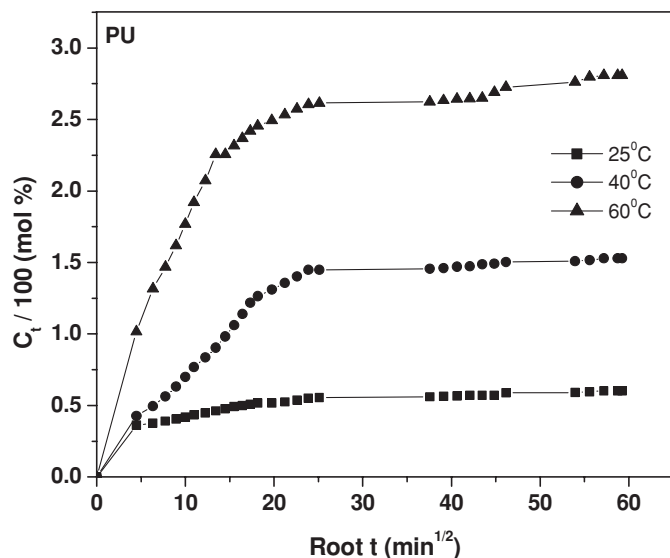
Fig. 3. Mol percentage uptake vs. square root of time for PU and PU + GA in benzene at different temperatures.

The effect of temperature on sorption behavior of neat PU and chain extended PU found to increase with an increase in temperature. This effect is shown typically in Figure 3 for both neat PU and chain extended PU in benzene. This effect follows the conventional theory that, at higher temperatures an increase in free volume occurs due to increased movement of the chain segments of the elastomers (26–28).

For Fickian behavior, the plots of C_t vs. $t^{1/2}$ should increase linearly up to about 50% sorption. Deviations from the Fickian sorption are associated with the time taken by the polymer segments to respond to swelling stresses and rearrange themselves to accommodate the solvent molecules (29). During the early stages of sorption, the samples may not reach the true equilibrium concentration of the
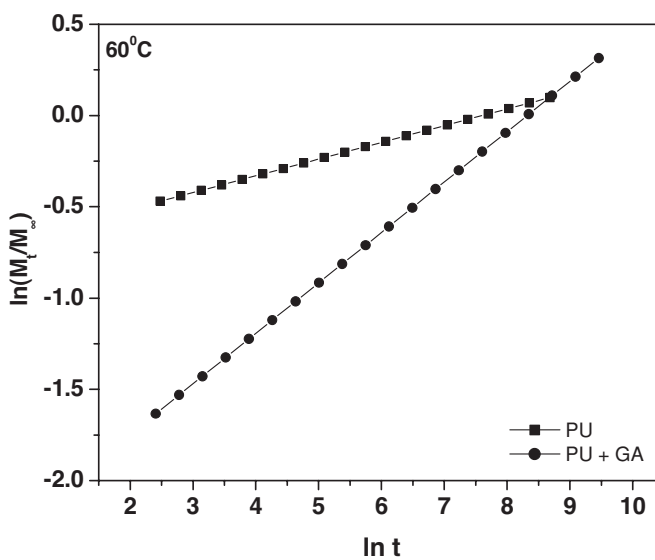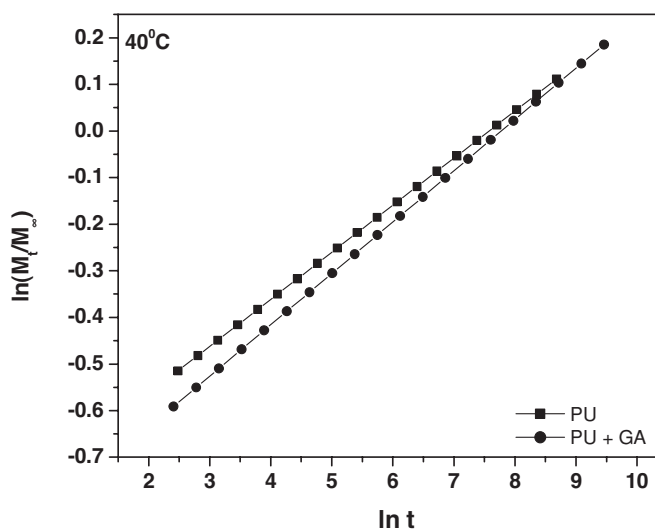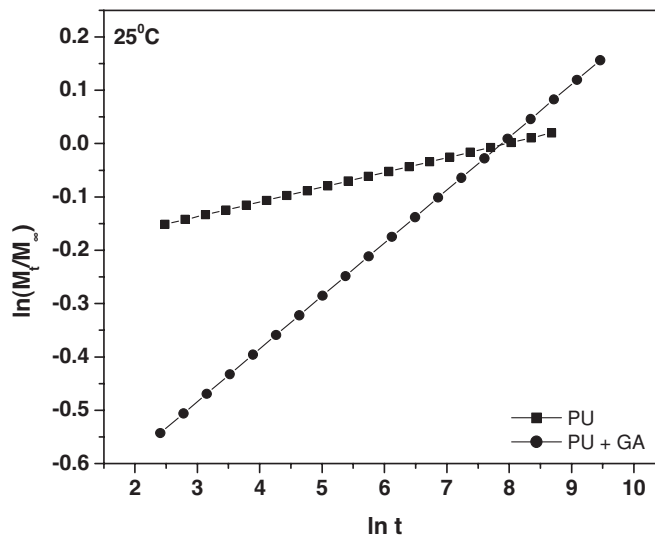

Fig. 4. The plots of ln M_t/M_∞ vs. ln t for PU and PU+GA with benzene penetrant at different temperatures.

Table 2. Values of n and K for neat PU and chain extended PU at different temperatures

Penetrant	Temp. (°C)	Samples	n	K (g/g min)
Benzene	25	PU	0.027	0.465
		PU +GA	0.065	0.358
	40	PU	0.101	0.498
		PU +GA	0.110	0.408
	60	PU	0.091	0.810
		PU +GA	0.276	0.790
Nitrobenzene	25	PU	0.016	0.840
		PU +GA	0.058	0.266
	40	PU	0.016	0.863
		PU +GA	0.166	0.492
	60	PU	0.070	0.890
		PU +GA	0.088	0.658
Chlorobenzene	25	PU	0.026	0.721
		PU +GA	0.050	0.394
	40	PU	0.041	0.795
		PU +GA	0.038	0.745
	60	PU	0.023	0.821
		PU +GA	0.123	0.755

penetrant and thus, the rate of sorption build up slowly to produce slight curvatures as shown in Figures 1–3. This is an indication for the departure from the Fickian mode and is further confirmed from the analysis of sorption data.

To investigate the type of diffusion mechanism, an attempt was made to estimate the values of 'n' and 'K' by the following relation;

$$\log(M_t/M_\infty) = \log K + n \log t \qquad (2)$$

where, K and n are empirical parameters, M_t and M_∞ are mass uptake values at time, 't' and at equilibrium. The magnitude of n decides the transport mode, for instance, a value of n = 0.5 suggests the Fickian mode and for n = 1 suggests the non–Fickian diffusion mode. The value of n ranging from 0.5 to 1 suggests the presence of anomalous transport mechanism.

In order to determine the K and n, plots of ln (M_t/M_∞) vs. ln t were plotted (Fig. 4). The calculated values for the empirical parameters n and K are given in Table 2. The average uncertainty in the estimation of n and K are

around ±0.007 and ±0.009, respectively. The increase of K values with an increase in temperature reveals that the interaction of probe molecules with the samples is high. The lower values of n clearly indicates that the mechanism of molecular transport of aromatic penetrants deviates from the Fickian mode.

The sorption values (S) are computed by the following relation;

$$S = M_\infty /M_i \qquad (3)$$

where, M_∞ and M_i represent the maximum penetrant uptake and initial polymer membrane weight, respectively.

The diffusion coefficient 'D' of the penetrant molecules was calculated from the following equation;

$$D = \pi (h\theta/4M_\infty)^2 \qquad (4)$$

where, θ is the slope of the linear portion of the sorption curves, h is the initial thickness of the sample and M_∞ is the mass uptake at infinite time.

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 (30);

$$P = D \times S \qquad (5)$$

where, D and S are diffusion and sorption coefficients, respectively.

The calculated sorption (S), diffusion (D) and permeation (P) coefficients under working temperatures are given in Table 3. The sorption coefficients (S) of neat PU were lower as compared to chain extended PU. The sorption values increased with an increase in the temperature in all solvents. The obtained 'D' values are higher in the case of chain extended PU than the neat PU. The diffusion coefficient values (D) for neat and chain extended PU followed a sequence; benzene > chlorobenzene> nitrobenzene. This can be attributed to the increase in molecular volume of the penetrants (Table 1). As is well known, the diffusion process is a thermally activated process, an increase in temperature was found to increase the diffusion coefficient of

Table 3. Diffusion (D), sorption (S) and permeation (P) coefficients of neat and glutaric acid based chain extended PU

| Samples	Temp (°C)	Benzene D (cm²/sec)	S (×10² g/g)	P (cm²/sec)	Nitrobenzene D (cm²/sec)	S (×10² g/g)	P (cm²/sec)	Chlorobenzene D (cm²/sec)	S (×10² g/g)	P (cm²/sec)
PU	25	3.27E-06	1.47	4.80E-06	2.40E-07	1.12	2.70E-07	1.95E-07	0.85	1.70E-07
	40	3.50E-05	2.19	7.70E-05	2.25E-06	1.69	3.80E-06	8.00E-06	1.64	1.30E-05
	60	2.12 E-03	3.19	6.70E-03	9.22E-05	1.82	1.70E-04	2.35E-05	2.42	5.70E-05
PU-GA	25	1.6E-05	1.95	3.1E-05	7.38E-05	1.53	1.10E-04	2.77 E-06	1.58	4.40E-06
	40	2.20E-05	2.37	5.2E-05	1.47E-05	2.36	3.50E-05	1.37E-05	2.17	3.00E-05
	60	1.10 E-02	4.49	4.93E-02	1.09E-05	1.86	2.00E-05	1.06 E-03	2.75	2.92E-03
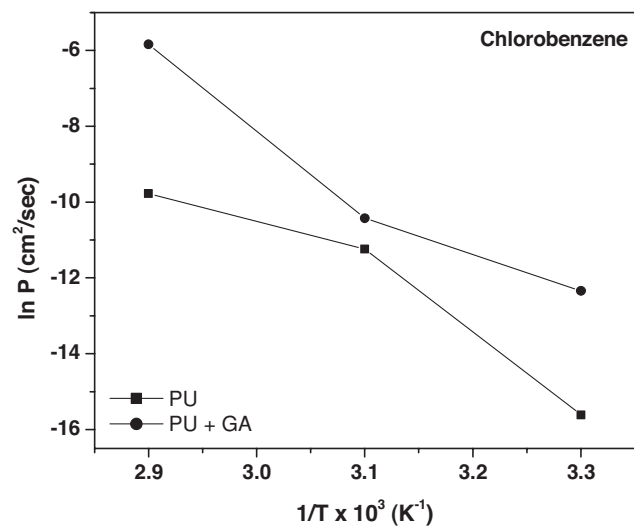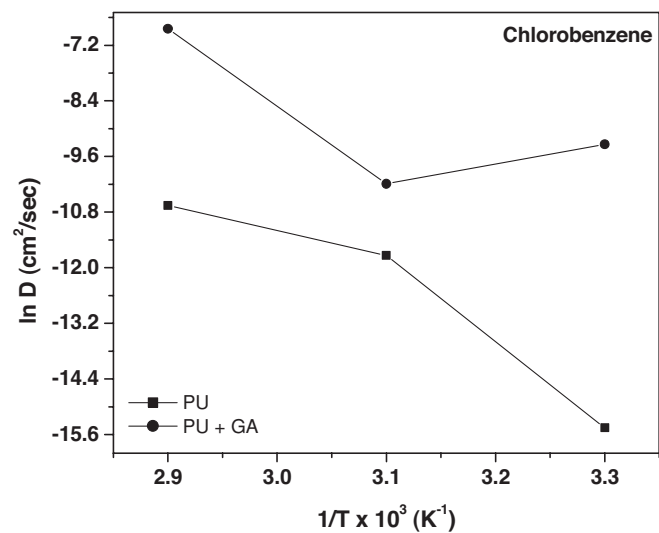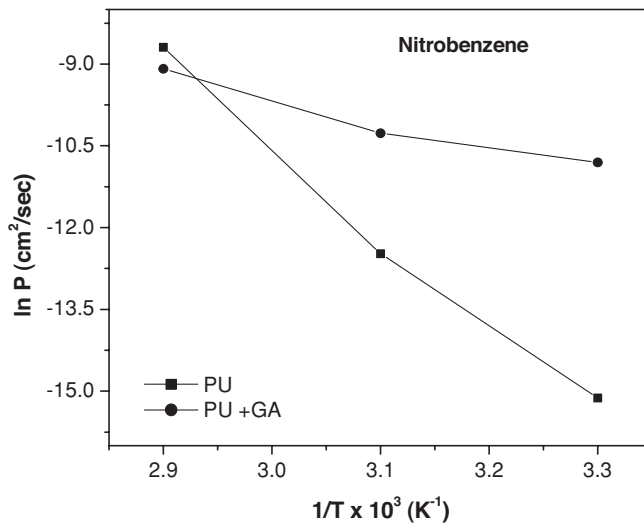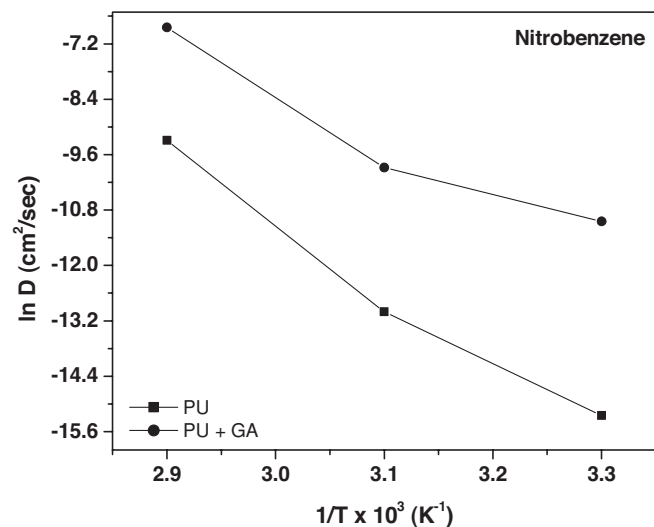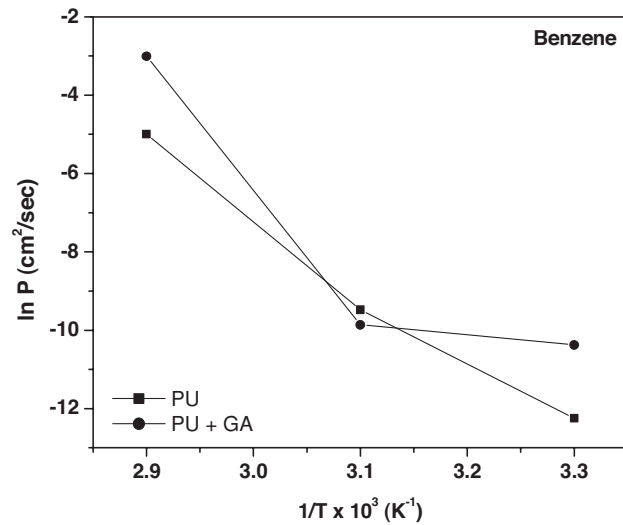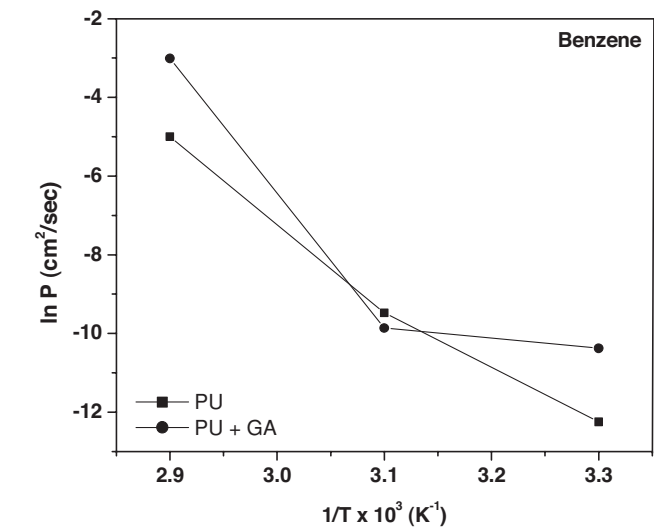
Fig. 5. A plot of ln D vs. 1/T for PU and PU+GA in different solvent penetrants.

Fig. 6. A plot of ln P vs. 1/T for PU and PU+GA in different solvent penetrants.

Table 4. Values of activation energy for diffusion (E_D, kJ/mol) and permeation (E_P, kJ/mol) of neat PU and glutaric acid based chain extended PU.

Samples	Parameters	Penetrants		
		Benzene	Nitrobenzene	Chlorobenzene
PU	E_D	99	124	124
	E_P	121	134	151
PU+GA	E_D	52	88	135
	E_P	136	140	153

the penetrant molecule. The increase in diffusion with the increase in temperature can be attributed to the development of micro cracks/voids on the surface and in the bulk of the materials (31). This inverse dependence of D on molar volume proves the conjecture that larger molecules in a related series of liquids occupy free volumes, leading to hindered diffusivities through polymer matrix. Kendagannaswamy and Siddaramaiah (32) noticed a similar observation in diol based chain extended PUs. The permeability coefficient (P) followed a similar trend as D.

Diffusivities and permeabilities are dependent on the temperature and their values increases with increase in temperature. The temperature dependence of transport coefficients has been used to compute the values of activation energy for diffusion (E_D) and permeation (E_p) processes, which is estimated from the Arrhenius relation;

$$X = X_0 \exp(-E_a/RT) \qquad (6)$$

where, X_0 is pre-exponential factor, R is the molar gas constant, T is the absolute temperature and X is the coefficient (D for diffusion process and P for permeation process). The Arrhenius plots of ln D and ln P vs. 1/T are shown in Figures 5 and 6, respectively. The calculated values of E_D and E_P are given in Table 4. The higher E_D and E_P values were noticed for neat PU as compared to chain extended PU. The highest and lowest E_D and E_P values were noticed for benzene and nitrobenzene, respectively. It is also observed that $E_P > E_D$ for both neat and chain extended PU membranes in all penetrants. This can also be explained on the fact that, heat of sorption is a composite parameter, which involves contribution from Henry's law mode, with the endothermic reaction contributions to Langmuir's (hole filling) type sorption giving exothermic heats of sorption.

4 Conclusions

The diffusion of substituted aromatic solvents into TDI based chain extended PUs is higher compared to neat PU without chain extender. The diffusion coefficient (D), and permeation coefficient (P) were found to decrease with an increase in molecular volume of the penetrant. The increase in temperature has increased the D, P and S values. The

lower values of 'n' less than 0.5 clearly revealed that the mechanism of solvent transport deviates from the Fickian mode. The increased K value with an increase in the temperature shows more interaction of the penetrant with the PU. The observed E_D and E_p values are higher for neat PU compared to GA based chain extended PU.

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