Sorption and Diffusion of Substituted Aromatic Organic Penetrants into Carboxylic Acid-Based Chain Extended Polyurethane Membranes

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3-Carboxy-3-hydroxy pentanedioic acid (otherwise known as citric acid, CA) and (*Z*)-butenedioic acid (otherwise known as maleic acid, MA) based chain extended polyurethane (CEPU) membranes have been prepared using castor oil and hexamethylene diisocyanate (HDI). The molecular transport of a series of organic probe molecules through CEPU membranes had been studied in the temperature range (298 to 333) K using the sorption-gravimetric method. The coefficients of sorption S, diffusion D, and permeation P have been calculated for CEPU-aromatic penetrants. The sorption and diffusion results measured at different temperatures, namely, (298 to 333) K, are found to follow Ficks Law. The transport data are affected by the nature of the interacting probe molecule rather than its size and also by the structural variations of the polymer membrane. It was found that the penetrant of the comparable solubility parameter with CEPU interact more and thus there is an increase in sorption. In all of the liquid penetrants, the transport phenomenon was found to follow the Fickian mode of transport. From the temperature dependence of diffusion and permeation coefficients, the Arrhenius activation parameters, such as the activation energy for diffusion, E_D, and permeation, E_P, processes, have been estimated. Furthermore, the sorption results have been interpreted in terms of thermodynamic parameters such as the change in enthalpy, ΔH.

Introduction

The diffusion of small molecular liquids into a polymer membrane is a subject of intense study. This type of diffusion process plays an important role in several important areas of engineering and industry.[1,2] Membrane separation of liquids in the industry has become widespread as more traditional methods are based on absorption, pressure-swing adsorption, or cryogenics. The membrane process has certain benefits compared to the cryogenics process, for example, lower investment cost and easier operation. The effects of interaction between polymers and small molecules are of practical interest to chemical engineers. The penetration of the solvent into the polymer membrane depends on the length of storage and nature of the solvent. The behavior of the solvent with the membrane for a considerable length of time has to be studied. Hence, for the sorption of solvents it is very essential to know the diffusion and permeation characteristics of polymer membranes.

In view of the importance of polyurethane (PU) in several areas such as biomedical applications, coating, adhesives, and so forth, it is important to know its transport characteristics with respect to organic solvents. The sorption of chain extended polyurethane (CEPU) depends very much on their chemical structure and morphology. The structure and molecular weight of the reactants of CEPU significantly influence the phase separation behavior.

PU elastomers are known to exhibit unique mechanical properties, primarily as a result of two-phase morphology.[3] These materials are alternating block copolymers made of hard segments from the diisocyanate/chain extender and soft segments from the polyol (ether or ester, castor oil, etc.). The hard and soft segments are chemically incompatible, and microphase separation of the hard segments into domains dispersed in a matrix of soft segment can occur in varying degrees. In view of the importance of PU as a barrier material in several engineering sectors,[4] it is important to know its transport characteristics with respect to common organic solvents. Thus, knowledge of the transport mechanisms as manifested by sorption, diffusion, and permeation of organic liquid penetrants in the PU matrix is helpful for establishing the structure−property relationships under severe application conditions.

Several studies have been reported in the literature regarding the transport and sorption of liquids into polymer membranes.[5−8] Rzeszutek and Chow[5] investigated the sorption behavior of monobromobenzoic acid by a PU membrane. Igwe et al.[6] studied the diffusion characteristics of some aromatic solvents into polypropylene (PP) film. Sreenivasan[7] studied the sorption behavior of the PU-β-cyclodextra blend. Aminabhavi and Khinnavar[8] studied the diffusion and sorption of organic liquids through the polymer membrane.

Siddaramaiah et al.[9,10] have investigated the sorption and diffusion behaviors of castor oil-based PUs, its interpenetrating polymer networks (IPNs), and diol-based CEPU membranes with several organic liquids. They found that transport behavior depends not only on the size of the penetrants but also on the nature of liquid molecules and membranes. These studies are extremely important for the design of new polymer materials, which would greatly benefit the development of high-performance membranes. Polyether-based PU foam is being studied by many scientists for the isolation of heavy metal ions like cobalt and antimony and the absorption of phenol compounds in aqueous solutions.[11]

Although many studies have been reported on solvent transport through PU membrane, there is ample scope for a better understanding of thermodynamic interactions between the polymer membrane and the solvent.[12,13] A CEPU membrane

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Table 1. Chemical Composition of Castor Oil[14]

acid	molecular formula	mass fraction
palmitic	$C_{16}H_{32}O_2$	0.008 to 0.011
stearic	$C_{18}H_{36}O_2$	0.007 to 0.010
oleic	$C_{18}H_{34}O_2$	0.022 to 0.033
linoleic	$C_{18}H_{32}O_2$	0.041 to 0.047
linolenic	$C_{18}H_{30}O_2$	0.005 to 0.007
ricinoleic	$C_{18}H_{34}O_3$	0.877 to 0.904

Table 2. Molar Mass M, Molar Volume V_m, Boiling Point T_b, Viscosity η, and Solubility Parameter δ of the Aromatic Penetrants Benzene C_6H_6, Chlorobenzene C_6H_5Cl, and Nitrobenzene $C_6H_5NO_2$

	M	$V_m \cdot 10^5$	T_b	η	δ
solvent	$g \cdot mol^{-1}$	$m^3 \cdot mol^{-1}$	K	mPa·s	$MPa^{1/2}$
C_6H_6	78.11	8.87	353	0.652	18.81
C_6H_5Cl	112.56	10.13	405	0.753	19.84
$C_6H_5NO_2$	123.06	10.22	483	1.86	20.46

has been chosen in this study because of its good mechanical properties and wide variety of industrial engineering and biomedical applications. However, the acceptability of PUs for any specific applications depends on its performance requirements before using these materials for commercial or engineering applications. Aromatic solvents have been chosen as probe molecules as they have diverse applications in process industries and in manufacturing of perfumes, dyes, bulk drug formulations, and so forth.

The principle objective of this research article is to study the transport behavior of aromatic probe molecules through dicarboxylic acid {(*Z*)-butenedioic acid (MA) and 3-carboxy-3-hydroxypentanedioic acid (CA)} based CEPU membranes. It is expected that a systematic change in solvent power would lead to results which could be interpreted by considering the possible interactions with soft and hard segments of the PU. Transport properties, namely, sorption S, diffusion D, and permeation P coefficients have been evaluated for CEPUs over an interval of temperatures from (298 to 333) K. The temperature dependence of the sorption and diffusion coefficients has been studied using the Arrhenius equation to estimate the activation parameters.

Experimental Section

Materials. Castor oil (CO) was procured from the SD. Fine Chemicals Ltd. Regardless of its country of origin or season in which it was grown, its chemical composition remains relatively constant and is listed in Table 1.[14] Its molar mass M_n was 930 $g \cdot mol^{-1}$, and its other properties such as hydroxyl group per molecule (2.24), acid number (1.48), and isocyanate equivalent (330) were determined as per standard procedure.[15] Hexamethylene diisocyanate (HDI) ($C_8H_{12}N_2O_2$), dibutyl tin dilaurate (DBTL), CA ($C_6H_8O_7$), and MA ($C_4H_4O_4$) were obtained from Sigma (USA) and used as received. The organic solvents such as methyl ethyl ketone (MEK), benzene, chlorobenzene, and nitrobenzene of mass fraction purity greater than 0.99 were distilled before use. Some physical properties of solvents used as penetrants are tabulated in Table 2.

Castor oil-based chain extended PUs were prepared using HDIs and carboxylic acids such as MA and CA as chain extenders as per the procedure reported elsewhere.[16] The tough and transparent PU sheets formed were used for sorption behavior. The tensile strength of CA- and MA-based chain extended PUs are (6.23 and 7.04) MPa, respectively.

Sorption Measurements. The PU membranes were exposed to the aromatic probe molecules for a definite period of time, and the changes in mass of the membranes are monitored gravimetrically. Sorption experiments were performed at (298 to 333) K using an electrically controlled oven maintained at the desired temperature with an accuracy of ± 2 K. The PU samples were cut circularly (0.015 m diameter) using sharp edged steel die. The initial thickness of the specimens were measured at several points using a digital screw gauge (Mitutoyo, Japan with a precision of ± 0.001 mm) and then dried in a vacuum desiccator for one day over anhydrous $CaCl_2$ before the experimental investigation. Dry weights of specimen were recorded before immersion into the penetrant. The cut specimens were immersed into the aromatic solvents taken in the screw tight metal cap bottle, kept in a thermostatically controlled oven. At specified intervals of time, the membrane is removed from the containers; surface-adhered liquid drops were removed by using soft tissue paper and then weighed immediately using an analytical balance. The sample is then placed back immediately into the test liquid and transferred to the temperature-controlled oven. The total time spent by the PU membrane outside the penetrant was within (20 to 30) s to minimize the possible experimental error. The weighing of the samples continued until the equilibrium value is reached. The membrane after attaining equilibrium sorption did not change its weight significantly even after keeping PU membranes inside the liquids for a further period of one or two days. The time taken for the attainment of equilibrium for different penetrants varied from (52 to 73) h. Two independent readings were taken, and the average value was used in all of the calculations. The sorption coefficient, S, was obtained from the true equilibrium values for the sorption process (calculated as the mass fraction of solvents sorbed by the polymer) in the investigated temperature interval.[16,17]

Results and Discussion

Transport Behavior. Transport behavior of substituted aromatic penetrants such as benzene, chlorobenzene, and nitrobenzene into CA- and MA-based CEPU membranes have been studied at temperatures from (298 to 333) K by an immersion mass gain method. The mass gain during the sorption process was expressed as the mass fraction of the solvent uptake by the polymer sample (C_t), and it was calculated using the following equation;

$$C_t = \left(\frac{W_t - W_0}{W_0}\right) \tag{1}$$

where W_0 is the initial mass of the sample; W_t is the mass at time t, which is the immersion period.

The solvent uptake was monitored until the specimens attained the equilibrium values. Some typical plots of sorption curves for CA- and MA-based CEPUs in nitrobenzene at temperatures from (298 to 333) K are shown in Figure 1.

The sorption behavior is a thermodynamic parameter, which depends on the strength of the interaction in polymer−probe molecule and describes the initial penetration and diffusion of probe molecules into the polymeric membranes. The sorption (S), that is, maximum mass uptake (obtained from the plateau region of the sorption plots) of CA- and MA-based CEPUs in nitrobenzene, follows the order CA > MA. A similar behavior was observed for all penetrants and temperatures. This could be due to the presence of additional polar groups like −COOH and −OH in the CA-based CEPU as compared to the MA-based CEPU, which leads to more interaction with the polar solvent and, hence, higher penetrant uptake. During the initial sorption stages, that is, up to 50 % of the completion of the sorption, penetrant uptake increased linearly with $t^{1/2}$ values. Deviations from the Fickian sorption were associated with the time taken

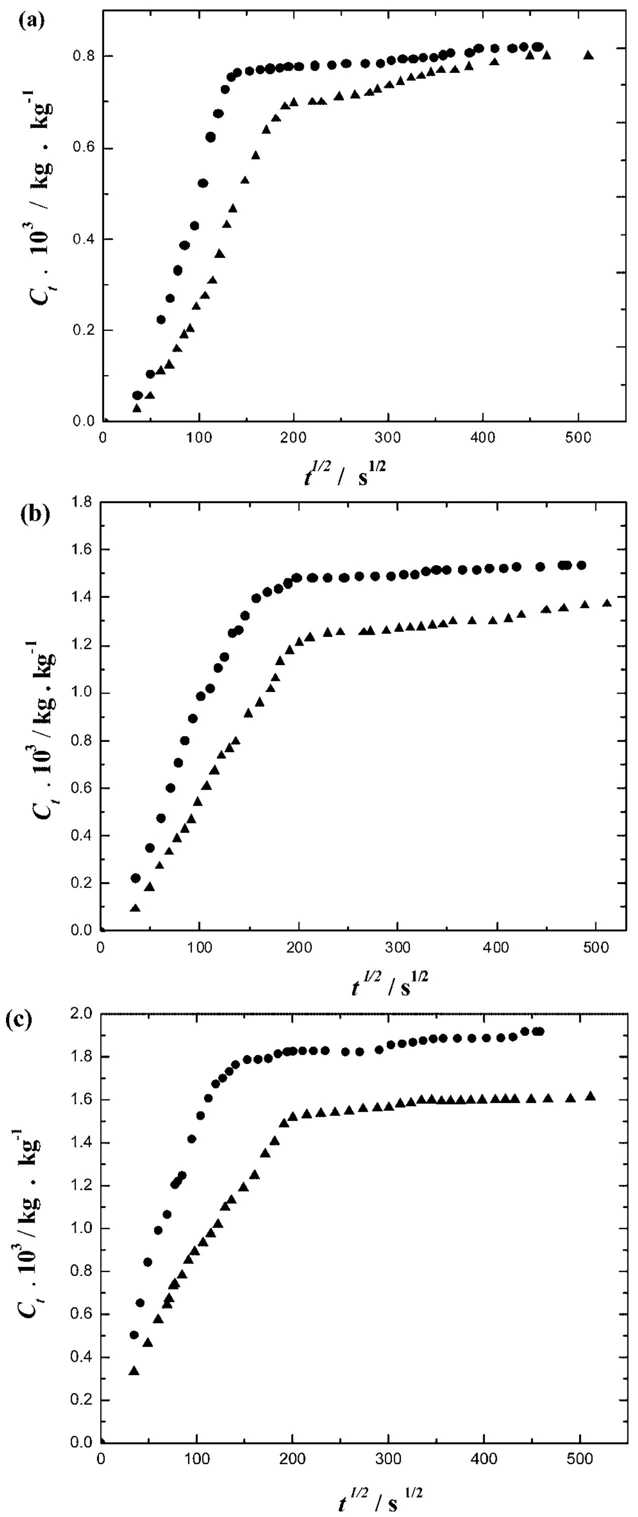

Figure 1. Weight fraction C_t vs square root of time $t^{1/2}$ of ●, CA; ▲, MA in nitrobenzene at three temperatures. (a) $T = 298$ K, (b) $T = 313$ K, (c) $T = 333$ K.

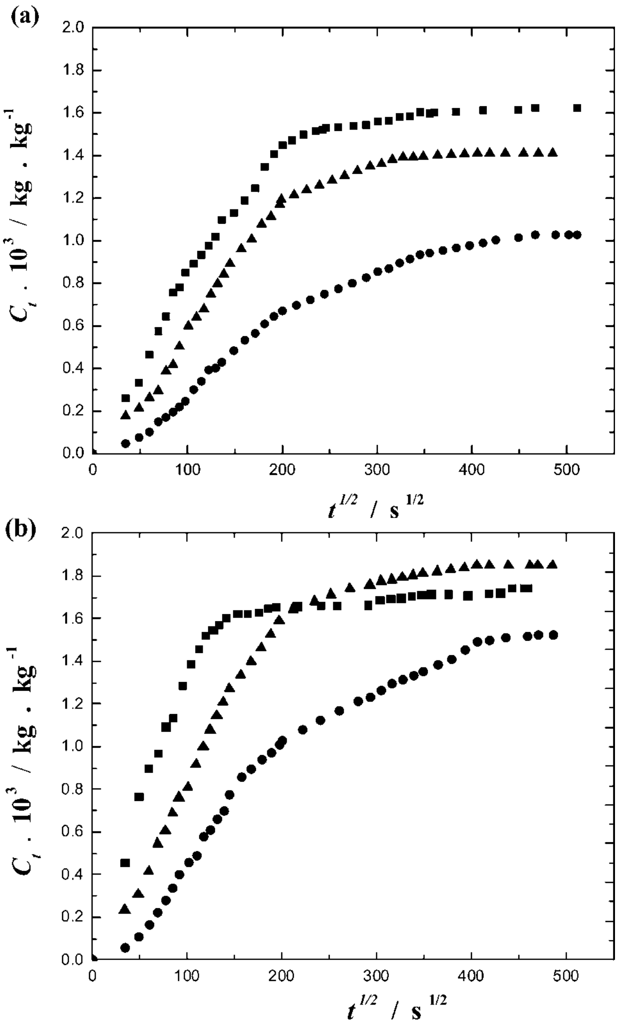

Figure 2. Weight fraction C_t vs square root of time $t^{1/2}$ of (a) MA and (b) CA in different solvents; ●, benzene; ▲, chlorobenzene; ■, nitrobenzene at the temperature of 333 K.

by the polymer segments to respond to swelling stress and to rearrange themselves to accommodate the solvent molecules.[18] This usually results in the sigmoidal shapes for the sorption curves. Thus, non-Fickian diffusion involves the tension between the swollen (soft segments) and the unswollen (hard segments) parts of CEPU as the latter tends to resist further swelling. However, during the early stages of sorption, the samples may not reach the true equilibrium concentration of the penetrant, and thus, the rate of sorption builds up slowly to produce slight curvatures as shown in Figures 1 and 2. This was an indication of the departure from the Fickian mode and is further confirmed from an analysis of sorption data. At later stages of sorption experiments, due to the saturation equilibrium, the sorption values for all penetrants and at all temperatures attained plateau regions, and obtained values were given in Table 3.

From Figures 1 and 2, it can also be observed that the initial portion of the sorption curves was linear after which the mechanism changes. When a polymer interacts with solvents, the surface of the polymer membrane swells immediately, but the swelling will not take place in the underlying unswollen material. Thus, a two-dimensional compressive stress was exerted on the surface. The swelling stresses are either relaxed or dissipated by further swelling and rearrangement of the segments. The diffusion of low molecular weight probe molecules was found to lead the typical phenomenon of membrane swelling and physical relaxation.

The dynamic sorption curves of MA- and CA-based CEPUs with different aromatic probe molecules at $T = 333$ K are shown in Figure 2. A perusal of the sorption curves shown in Figure 2 suggests a systematic trend with respect to the molecular volume of penetrants in the sorption behavior of aromatic probe molecules. The sorption curve in benzene was found to be lower as compared to other penetrants. This can be attributed to the nonpolar nature of benzene which leads to less interaction with a polar CEPU membrane. The sorption and diffusion processes

Table 3. Diffusion *D*, Sorption *S*, and Permeation *P* Coefficients of CA- and MA-Based CEPUs in Benzene C_6H_6, Chlorobenzene C_6H_5Cl, and Nitrobenzene $C_6H_5NO_2$ at Temperatures from (298 to 333) K

		C_6H_6			C_6H_5Cl			$C_6H_5NO_2$		
CEPU	T / K	$D\cdot10^{10}$ / $m^2\cdot s^{-1}$	$S\cdot10^3$ / $kg\cdot kg^{-1}$	$P\cdot10^{13}$ / $m^2\cdot s^{-1}$	$D\cdot10^{10}$ / $m^2\cdot s^{-1}$	$S\cdot10^3$ / $kg\cdot kg^{-1}$	$P\cdot10^{13}$ / $m^2\cdot s^{-1}$	$D\cdot10^{10}$ / $m^2\cdot s^{-1}$	$S\cdot10^3$ / $kg\cdot kg^{-1}$	$P\cdot10^{13}$ / $m^2\cdot s^{-1}$
CA	298	2.50	0.59	1.46	3.23	0.94	3.04	4.00	1.00	4.0
	313	4.52	1.08	4.88	5.05	1.38	6.70	5.72	1.53	8.75
	333	4.90	1.51	7.40	5.72	1.84	10.50	6.12	1.91	11.68
MA	298	2.11	0.33	0.69	3.19	0.66	2.10	3.72	0.80	2.96
	313	3.37	0.90	3.03	3.62	1.33	4.81	4.0	1.36	5.44
	333	3.94	1.17	4.60	4.15	1.40	5.81	5.0	1.61	8.00

are influenced by factors such as molecular size, interaction parameter between the polymer and the solvent, and the solubility parameters of the membranes and the solvents. Here sorption increases with the increase in the solubility parameter of the penetrant. There is a competition between the size of the penetrants and the interaction parameter of the polymers and the solvents.[17] The difference in solubility parameters overcomes the molecular size and, hence, influences the sorption process.[19]

The equilibrium solvent uptake for sorption as a function of molecular volume and the solubility parameter of probe molecules was shown in Figure 3a,b, respectively. As the solubility parameter of nitrobenzene is closer to the solubility parameter of CEPU, it leads to higher values of equilibrium mass uptake of nitrobenzene. Similarly, benzene with a low solubility parameter exhibits less sorption into the polymer network. The sequence of sorption behavior with reference to the penetrants is benzene < chlorobenzene < nitrobenzene. In this experimental investigation, the solvent uptake behavior was significantly dependent (linear behavior) on the solubility parameter of the solvent. This indicates that there are more interactions between solvent and polymer, which lead to solvation followed by diffusion into membrane.

Recently Siddaramaiah et al.[20,21] have been reported a correlation between the sorption coefficient and the solubility parameter of probe molecules for IPN with aromatic penetrants. Aithal and Aminabhavi[22] also made a similar kind of observation for the PU system. The pattern of curves in Figure 3a,b indicates that there is a clear-cut interaction between CEPU and probe molecules, which depends on the solubility parameter.

Sorption data also serve as a guide to study the effect of temperature on the observed transport behavior. The effect of temperature on the uptake of nitrobenzene for CA-based CEPU is shown in Figure 4. The rate of diffusion and permeation of all CEPU−penetrant systems increases with an increase in temperature.[23] This effect follows the conventional theory that at higher temperatures an increase in free volume occurs due to an increased movement of the chain segments of the PU.[24] An increase in temperature reduces the tortuous route of the solvent and also reduces the time required to attain equilibrium.

From the slope, θ, of the initial linear portion of the sorption curves, that is, Q_t versus $t^{1/2}$, the diffusion coefficients have been calculated by using eq 2. The values of D determined in this manner can be regarded as independent of concentration and are thus applicable for the Fickian mode of transport.[19]

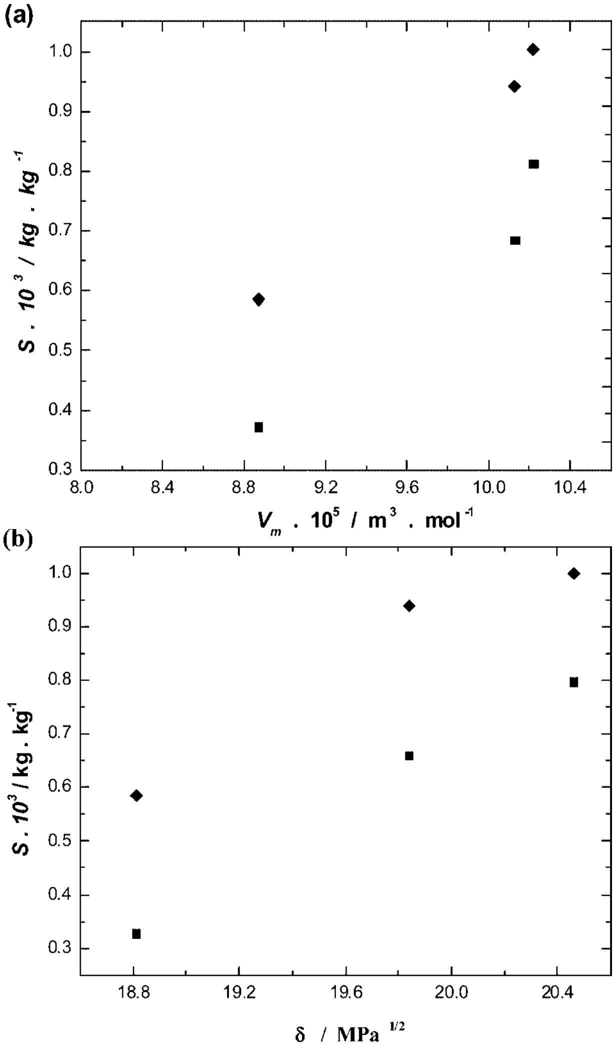

Figure 3. Sorption coefficient S, as a function of (a) molar volume V_m and (b) the solubility parameter δ/MPa$^{1/2}$ of probe molecules for CEPU membranes of ◆, CA; ■, MA.

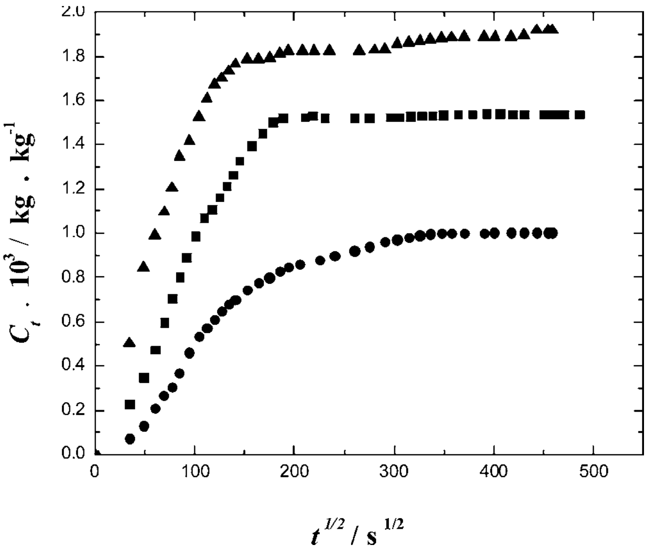

Figure 4. Weight fraction C_t vs the square root of time $t^{1/2}$ of CA in nitrobenzene at different temperatures; ●, 298 K; ■, 313 K; ▲, 333 K.

The diffusion coefficient was calculated using Fick's equation;

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

where h is the thickness of the material, M_∞ is the mass uptake at infinite time, and θ is the slope of the initial linear portion of the sorption curves, that is, Q_t versus $t^{1/2}$. Calculated values of D from eq 2 for all chain-extended PUs are given in Table 3.

The evaluation of D from sorption curves gave D with an uncertainty of $\pm$ 0.004 $m^2 \cdot s$ at $T = 298$ K, $\pm$ 0.0048 $m^2 \cdot s$ at $T = 313$ K, and $\pm$ 0.0057 $m^2 \cdot s$ at $T = 333$ K for all polymer−penetrant systems. These uncertainty estimates regarding diffusion coefficients suggest that the half times were very reproducible (to within a few tens of seconds). The variation in the diffusion coefficient also depends on the nature of the penetrant molecules in addition to the structural characteristics of the CEPUs.

The calculated sorption S, diffusion D, and permeation P coefficients under investigated temperatures for CEPU/aromatic penetrant systems were given in Table 3. The sorption and diffusion coefficients of MA-based CEPUs were lower as compared to CA-based CEPUs. The sorption values increased with an increase in temperature for all solvents. The sorption and diffusion coefficient values for CEPUs followed a sequence: benzene < chlorobenzene < nitrobenzene. This can be attributed to the increase in the solubility parameter of the penetrants (Table 2). As is well-known, the diffusion process is a thermally activated process. An increase in temperature was found to increase the diffusion coefficient of the penetrant molecule. It can also be attributed to the development of micro cracks/voids on the surface and in the bulk of the materials.[25]

The transport of small molecules through polymers generally occurs through a solution diffusion mechanism; that is, the solvent molecules are first sorbed by the polymer followed by diffusion through the polymer. The net diffusion through the polymer depends on the difference in the amount of penetrant molecules between the two successive layers. Permeation is a collective process of diffusion and sorption, and consequently the permeability of liquid molecules into the polymer membrane depends upon both diffusivity and sorptivity. The P was calculated from the relation, $P = DS$. The calculated P also followed the same trends as those of diffusion with reference to the temperature and solubility parameter of the penetrant molecules listed in Table 2. The calculated P values were tabulated in Table 3, and it follows the order of S and D. The highest P values for nitrobenzene and lowest for benzene were noticed. This indicates that P values significantly depend on the solubility parameter of probe molecules and thus the affinity of CEPU is more toward nitrobenzene. From Tables 2 and 3, it was observed that the sequence of variation of the permeability coefficient and solubility parameter of solvents is in the order: nitrobenzene > chlorobenzene > benzene.

To investigate the type of diffusion mechanism, an attempt was made to estimate the values of "n" and "K" from the following empirical equation;[26]

$$M_t/M_\infty = Kt^n \quad \text{or} \quad \ln(M_t/M_\infty) = \ln K + n \ln t \qquad (3)$$

where M_t is the mass of solvent sorbed at time t, M_∞ is the mass of the solvent sorbed at equilibrium time, and K is a parameter that depends on the structural characteristics of the polymer material and on the penetrant−polymer interactions. The exponent value of n suggests the type of transport mechanism and to infer any changes in the macromolecular network. To determine K and n, the plots of $\ln(M_t/M_\infty)$ versus $\ln t$ for CEPUs in nitrobenzene are shown in Figure 5. The estimated values for the empirical parameters n and K were given in Table 4. The uncertainties in the estimation of n and K are $\pm$ 0.007 and $\pm$ 0.04, respectively. The magnitude of n denotes the transport mode.

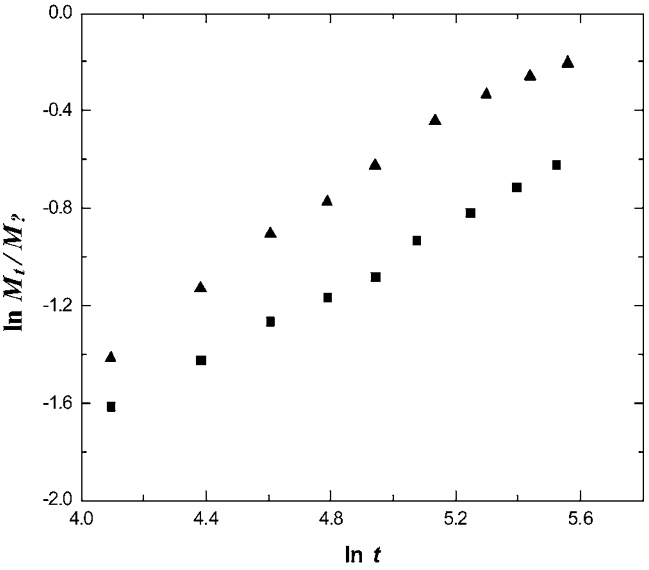

Figure 5. Plots of ln M_t/M_α vs ln t of ▲, CA; ■, MA in nitrobenzene at the temperature of 313 K.

Table 4. Values of n and K for CA- and MA-Based CEPUs for Benzene C_6H_6, Chlorobenzene C_6H_5Cl, and Nitrobenzene $C_6H_5NO_2$ at Temperatures of (298 to 333) K

solvent	T / K		n	$K \cdot 10^7$ / $kg \cdot kg^{-1} \cdot s^n$
C_6H_6	298	CA	0.54	6.0
		MA	0.45	5.8
	313	CA	0.46	8.6
		MA	0.48	6.6
	333	CA	0.50	11.8
		MA	0.51	8.8
C_6H_5Cl	298	CA	0.45	7.5
		MA	0.46	6.1
	313	CA	0.45	9.5
		MA	0.45	6.6
	333	CA	0.51	13.1
		MA	0.45	8.5
$C_6H_5NO_2$	298	CA	0.53	5.8
		MA	0.53	5.0
	313	CA	0.52	6.6
		MA	0.49	6.0
	333	CA	0.44	1.35
		MA	0.48	8.0

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 $n = 1$ (non-Fickian mode of transport), chain relaxation is slower than the liquid diffusion. For 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 the Fickian mode of diffusion. The n values for sorption process lie in the range 0.44 to 0.54. The lower values of n clearly indicate that the molecular transport mechanism of CEPU/aromatic penetrant systems is in the nearly Fickian mode. The increase of K values with the increase in temperature reveals that the interaction of probe molecules with the polymer is high.

Activation and Thermodynamic Parameters. Temperature plays a very important role in the diffusion of penetrants through polymeric membranes. The temperature dependence of transport

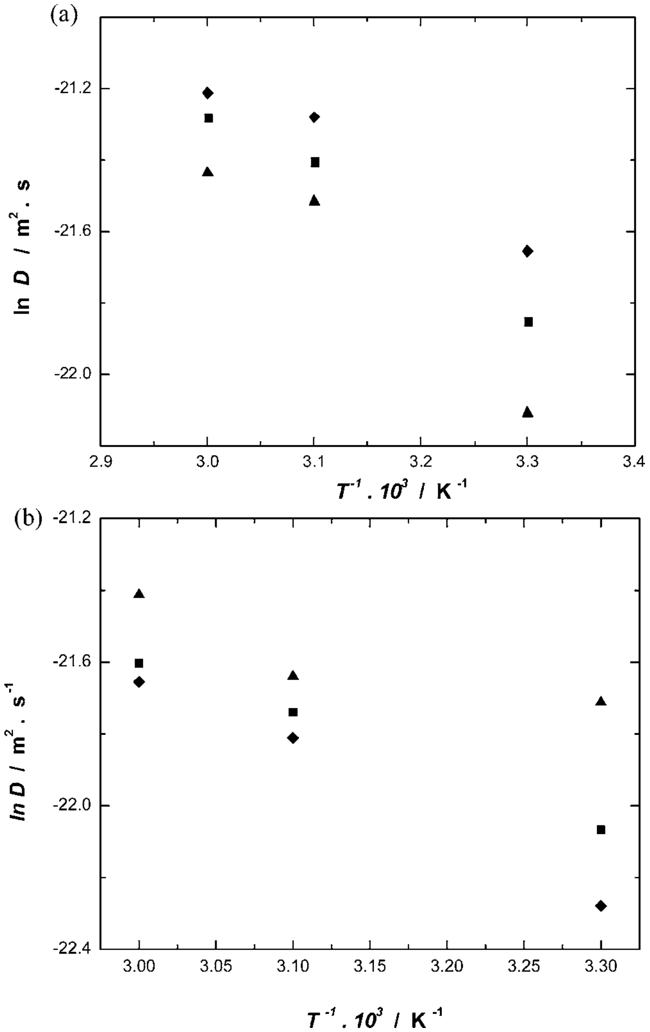

Figure 6. Plot of ln D vs T^{-1} for (a) CA- and (b) MA-based CEPUs in different aromatic penetrants; ◆, nitrobenzene; ■, chlorobenzene; ▲, benzene.

phenomenon can be used to evaluate the activation energy, namely, E_D and E_P, for the diffusion and permeation processes using the Arrhenius relation;

$$X = X_o \exp^{-(E_a/RT)} \tag{4}$$

where X is P or D, E_a is the activation energy, R is the universal gas constant, and T is the temperature. As observed elsewhere,[22] both D and P are found to increase with the increase in temperature. This is mainly attributed to the creation of additional free volume because of the increase in segmental motion of the polymer chain upon the increase in temperature. The estimated activation energy for diffusion and permeation processes which is from the Arrhenius relation was prompted by this effect. The Arrhenius plots of ln D and ln P versus T^{-1} are shown in Figures 6 and 7, respectively. These plots exhibit linear dependency for all systems. The calculated activation energy from regression analysis was tabulated in Table 5. Higher E_D and E_P values were noticed for MA-based CEPUs as compared to CA-based CEPUs. Higher E_D values for benzene and lower values for the nitrobenzene sorption process were noticed. The E_D and E_P values for sorption process lie in the range (1.24 to 2.79) kJ·mol^{-1} and (4.46 to 8.4) kJ·mol^{-1}, respectively. It was also observed that the activation energy E_P will be greater for all liquids, because of the higher degree of cohesive energy in polymer chain.

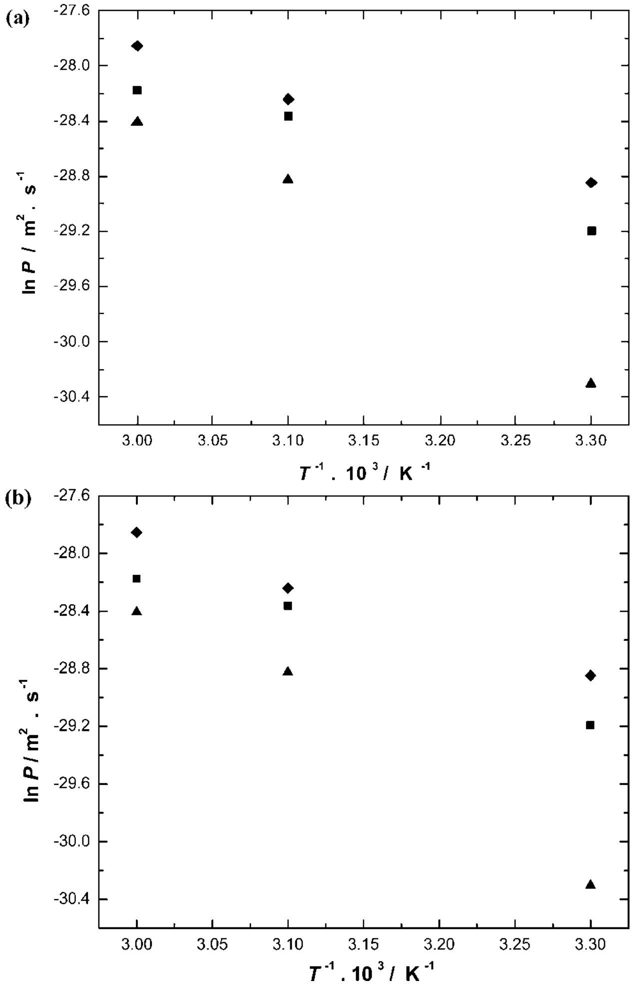

Figure 7. Plot of ln P vs T^{-1} for (a) CA- and (b) MA-based CEPUs in different aromatic penetrants; ◆, nitrobenzene; ■, chlorobenzene; ▲, benzene.

Table 5. Values of Activation Energy E_a, for Diffusion E_D, Permeation E_P, and Enthalpy of Sorption ΔH for CA- and MA-Based CEPUs with Benzene C_6H_6, Chlorobenzene C_6H_5Cl, and Nitrobenzene $C_6H_5NO_2$ of Probe Molecules

sample		E_D kJ·mol^{-1}	E_P kJ·mol^{-1}	ΔH kJ·mol^{-1}
CA	C_6H_6	2.79	6.74	3.90
	C_6H_5Cl	2.37	5.15	2.31
	$C_6H_5NO_2$	1.84	4.45	2.70
MA	C_6H_6	2.59	7.88	5.19
	C_6H_5Cl	1.09	5.69	3.08
	$C_6H_5NO_2$	1.24	4.13	2.95

The equilibrium sorption constant K_s was calculated from the moles of penetrant sorbed at equilibrium divided by the mass of the polymer. The enthalpy ΔH of sorption values are also estimated from van't Hoff relation using the temperature-dependent equilibrium sorption constant (K_s). van't Hoff plots, namely, ln K_s versus T^{-1}, are presented in Figure 8. These plots are linear within the temperature interval of (298 to 333) K. ΔH and ΔS have been calculated from the slope and intercepts, respectively (Table 5). The estimated uncertainty in ΔH is about ± 4 J·mol^{-1}. From Table 5 it was noticed that ΔH values for all of the solvent−polymer systems were positive, suggesting that sorption may be dominated by Henry's law mode. 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.

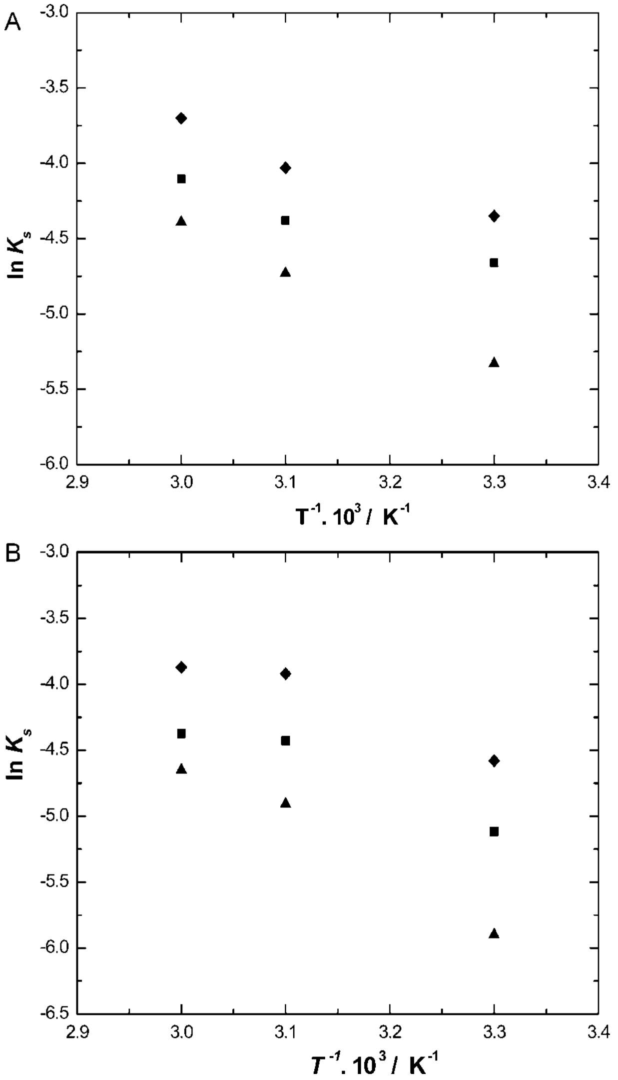

Figure 8. van't Hoff plot of ln K_s vs T^{-1} for all aromatic penetrants: ◆, benzene; ■, chlorobenzene; ▲, nitrobenzene; for (a) CA- and (b) MA-based CEPUs.

Conclusions

The experimental investigation results of sorption and transport behaviors of substituted aromatic penetrants into structurally different CEPUs were reported. It was observed that the factors such as the solvent type (solubility parameter) and chemical nature of the polymer seem to exert significant influence on the molecular transport characteristics. The sorption and diffusion coefficients of substituted aromatic solvents into CA-based CEPU is higher as compared to the MA-based membrane. The diffusion and permeation coefficients were found to increase with the increase in the solubility parameter of the penetrants and temperature. At higher temperatures the increase in diffusion and relaxation rates of the polymer, accompanied by an increase in the polymer free volume, resulted in a higher equilibrium penetrant uptake. The solvent uptake values were found to be highest for nitrobenzene at all temperatures. It was found that, as the difference in the solubility parameter of solvents and polymer membranes is low, 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 the membrane. The values of n lie in the range 0.44 to 0.54 which clearly reveal that the mechanism of transport of aromatic penetrant/CEPU is Fickian mode. The increased K values with increasing temperature for all penetrants indicate more interaction between penetrant and PU membrane.

The temperature dependence of the transport coefficient has been used to compute the activation parameters from the Arrhenius plots. The enthalpy of sorption process for CEPU/aromatic solvents lies in the range (2.31 to 5.19) $\text{kJ}\cdot\text{mol}^{-1}$. For all CEPU−penetrant systems positive ΔH values were observed. The positive ΔH values indicate that the sorption is an endothermic process and is dominated by Henry's mode; that is, the sorption proceeds through the creation of new sites or pores in the polymer. The diffusion coefficient result suggests that when the CEPU membrane is used as a barrier for aromatic probe molecules, sorption behavior depends on several factors, such as nature of the membrane, temperature, and solubility parameter and its compatibility with the probe molecules and also their chemical characteristics.

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