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Transport of Aromatic Liquids, and a Ketone into Fluoroelastomer Membrane

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ABSTRACT: Molecular transport of substituted aromatic liquids, through a fluoro- elastomer membrane sample was studied at 25, 35, and 45ºC. Sorption results were obtained by using a gravimetric method and concentration-independent diffu- sion coefficients were calculated using Fick's diffusion equa- tion. Permeability coefficients were calculated from sorption and diffusion data. Concentration profiles of the liquid pen- etrants were calculated by solving the Fick's equation under appropriate initial and boundary conditions and these plots are displayed to show the variations in liquid concentrations with reference to the nature of liquids chosen, membrane thickness, as well as the time of polymer immersion in the liquids. Arrhenius activation parameters were also esti- mated from a temperature dependence of diffusion and sorption coeffic

Key words: diffusion; activation energy

INTRODUCTION

Molecular transport of organic liquids into elastomeric membranes has been a subject of great technological importance and such a study is useful in understand- ing the fundamental aspects of sorption and diffusion phenomena, especially when seeking their applica- tions in engineering and other areas.[1–5] Particularly, such a study is valuable in membrane-based separa- tion processes like reverse osmosis,[6] pervaporation,[7] and ultrafiltration.[8] These processes depend ulti- mately on the type of membranes used in a particular application to act as a barrier under specified experi- mental conditions such as temperature and pressure. Sorption and diffusion of liquid penetrants are also important in membrane-based applications, particu- larly in areas like hazardous waste-pond linings[9] where solvent resistivity to aggressive organic liquids is important. The barrier membranes under such an aggressive environment should retain their mechani- cal strength and dimensional stability. trants of industrial importance. In continuation of this study, herein we report sorption and diffusion results of the same organic liquids . The liquid penetrants chosen for this research are chlorobenzene, dichlorobenzene, nitrobenzene, and cyclohexanone. Sorption experiments were car- ried out at 25, 35 and45ºC. From a temperature dependency of sorption, diffusion, and permeation, the Arrhenius activation parameters were estimated.

EXPERIMENTAL

Reagents/chemicals

The reagent-grade chemicals, nam dichlorobenzene, chlorobenzene, a were obtained from S.D. Fine Chemi- cals (Mumbai, India).

TABLE I
Molar Volume and Sorption Coefficients of Liquids

Liquids	Molar volume (cm^3/mol)	Sorption coefficients mol %		
		25°C	35°C	45°C
Dichlorobenzene	112.56	0.027	0.034	0.044
Nitrobenzene	102.93	0.276	0.299	0.323
Chlorobenzene	101.68	0.034	0.047	0.054
Cyclohexanone	103.64	0.071	0.080	0.090

components, especially in O-ring applications. A gift

sample was received from Ms. Nina McAllum (3M Co., St. Paul, MN). The typical properties of the elas- tomer are a specific gravity of 1.80, off-white color, solubility in ketones and esters, and Mooney viscosity of 23 ML1+10 at 121°C. The press-cured sample for 30 min at 160°C possesses the following mechanical properties: tensile strength, 1350 psi; percent elonga- tion at break, 260; and hardness (Shore A), 75. The sample was compounded with standard fillers and ingredients utilized in typical fluoroelastomer formu- lations.

Sorption experiments

Sorption experiments were performed at 25, 35and 45°C in an air-circulating electronic oven (WTB Binder, Germany) maintained at the respective tem- peratures within an accuracy of ±0.5°C. Circularly cut disc-shaped sheet membranes having diameter of ≈2 cm were kept in a vacuum oven at 25°C for 45 h before being used in the sorption experiments. These samples were then immersed in about 15–25 mL of liquid placed in airtight bottles maintained at the constant desired temperature (±0.5°C). The bottles were placed inside the electronically controlled oven calibrated with a quartz thermometer for precise temperature control. Mass measurements were done at the selected time intervals by removing the samples and immedi- ately after wiping the surface-adhered solvent drops using a soft tissue paper. Samples were placed on a top-loading digital Mettler balance (Model AE 240, Switzerland) sensitive to ±0.01 mg and the mass mea- surements made at regular time intervals. When the samples attained equilibrium sorption, no more mass gain occurred and this did not change significantly over a further period of 1 or 2 days.

Sorption coefficients were expressed in mol percent units and calculated by using the equation

$$M = \frac{W_t - W_0}{W_0} \times 100 \quad (1)$$

where W_0 is the initial mass of the sample; W_t, the mass at time t, that is, the immersion period; and M, the molar mass of the solvent. Sorption results are presented in Table

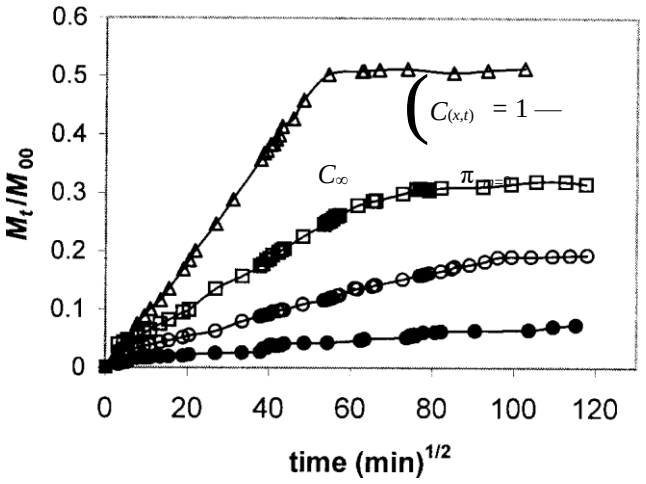

Figure 2 Plots of M_t/M_∞ versus square root of time for fluoroelastomer membrane at 30°C with (,) propionalde- hyde, (□) benzaldehyde, (E) salicylaldehyde, and (F) cyclo- hexanone.

Diffusion coefficients and concentration profiles

There are many different methods to deduce diffusion coefficients of small penetrant molecules within the polymeric systems. One of the most direct methods is the mass gain probe wherein one can monitor the mass of an amorphous polymer sample immersed in a liquid bath. To simplify the boundary conditions, an approximate geometry is chosen to effect a one-di- mensional diffusion process with the use of a film configuration such that the film thickness is h and the mass of liquid absorbed at time t is given by

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

Here, C_∞ is the mass sorbed at an equilibrium state when the chemical potential of the liquid penetrant in the polymer sample is equalized to that in the bath such that the sorption process ceases. Equation (2) is applicable only during the early stages of penetrant sorption, that is, well before reaching the saturation level and, hence, the D calculated this way becomes concentration independent. The symbol θ represents the slope of the initial linear portion of the sorption curve. The sorption results initially followed linear trends nearly up to 50 –55% attainment of equilibrium in all the cases. The calculated values of D are pre- sented in Table II. Permeability coefficients calculated using the relation $P = D \times S$ are also included in Table II.

To predict solvent resistivity of the fluoroelastomer used, it is important to know the depth of solvent migration inside the polymer. This can be done by calculating the concentration profiles of liquids inside the membrane and this can be done by solving Fick's diffusion equation under appropriate initial and boundary conditions,[11–13] which gives

$$\frac{C_{(x,t)}}{C_\infty} = 1 - \frac{4}{\pi} \sum_{m=0}^{\infty} \frac{1}{(2m+1)} \times \exp\left[-\frac{D(2m+1)^2\pi^2 t}{h^2} \right] \sin\left[\frac{(2m+1)\pi x}{h} \right] \quad (3)$$

Here, m is an integer, and $C_{(x,t)}$ and C_∞, the concentra- tions at time t and at infinite time t_∞. The concentration profiles developed within the membranes were calcu- lated using eq. (3). These data for some typical pene- trants are presented in Figures 4 –7.

RESULTS AND DISCUSSION

Sorption kinetics

Molecular transport of liquids through elastomer membranes can be studied in terms of sorption/dif- fusion phenomena. Sorption data generated at three different temperatures are presented in Table I, while the mol percent sorption plots at 30°C are displayed in Figures 1–3, since we believe that this would give us an easy comparison. From a close inspection of the sorption data of the esters presented in Figure 1, it is found that the mol percent sorption shows a some- what systematic effect on the size (molar volume) of the esters. For instance, amyl acetate, having a molar volume of 149 cm^3/mol, shows higher mol percent sorption values than those of all the esters. On the other hand, propyl acetate exhibits higher values of mol percent sorption than those of diethyl oxalate and cases, the sorption curves increase linearly with time,

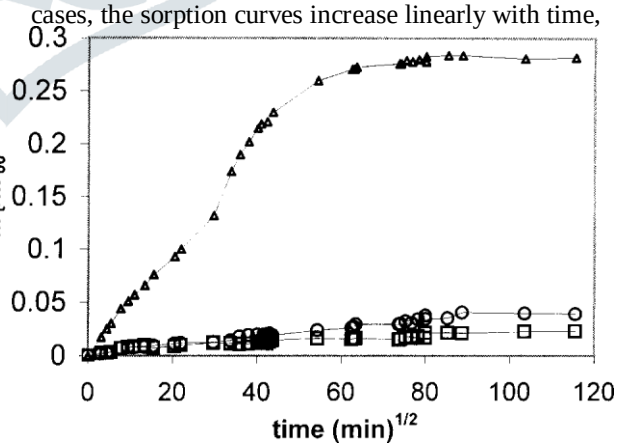

Figure 3 Plots of M_t/M_∞ versus square root of time for fluoroelastomer membrane at 30°C with (,) nitrobenzene, (E) chlorobenzene, and (□) dichlorobenzene.

TABLE II
Diffusion (*D*) and Permeation (*P*) Coefficients ofAromatics, andinto Fluoroelastomer Membrane at Different Temperatures

	D (10^7) cm^2/s			P (10^8) cm^2/s		
		25°C		35°C	45°C	50°C
Dichlorobenzene	0.44	0.50	0.84	0.11	0.19	0.43
Nitrobenzene	0.30	0.58	1.00	1.05	2.16	3.98
Chlorobenzene	0.27	0.30	0.79	0.16	0.28	0.84
Cyclohexanone	0.16	0.18	0.21	0.11	0.16	0.24

In Figure 3 are displayed the mol percent sorption data of the substituted aromatic liquids. Even though the size of both chlorobenzene and nitrobenzene are quite identical (i.e., 102 cm^3/mol), sorption values of nitrobenzene are much higher than those of chloro- benzene and dichlorobenzene. However, dichloroben- zene, whose molar volume is much higher than that of chlorobenzene or nitrobenzene, shows lower mol per- cent sorption values.

The results of diffusion and permeation coefficients are presented in Table II. The values of the diffusion coefficients from amyl acetate to phenyl acetate show a decrease, but the *D* values of amyl acetate are higher than those of propyl acetate as well as those of diethy- loxalate. In the case of esters, the observed *D* values are not dependent on the size of the migrating liquid, signifying that transport depends more on molecular interactions between liquids and the membrane. Chlo- robenzene exhibits the lowest *D* values when com- pared to all the other substituted benzenes (i.e., nitro- and dichlorobenzenes). On the contrary, the diffusion coefficient of nitrobenzene is slightly higher than that of chlorobenzene and diffusion data remain the same at all temperaturesIn areas where polymeric membranes act as barrier membranes toward aggressive liquids, it is important to know the liquid penetration rates calculated in terms of the liquid concentration profiles. These are calculated from eq. (3) at different exposure times and membrane thickness for all the liquids. However, only a few typical graphs are displayed in Figures 4 –7. These plotts show a clear-cut dependence on the tem- perature, the depth of penetration chosen, as well as the nature of the liquid. For instance, diffusivity of amyl acetate is higher than that of benzaldehyde and, hence, its concentration profiles are also higher at all the temperatures (see Fig. 4). In the case of benzalde- hyde, diffusivity is quite small and so are its concen- tration profile values (see Fig. 5). However, we could not observe a clear-cut dependence of *D* at higher temperatures. Similar effects were observed in the case of cyclohexanone and nitrobenzene as displayed in Figures 6 and 7, respectively.

Sorption results were analyzed by fitting the sorp- tion data using an empirical equation of the type[14,15]

$$\frac{M_t}{M_\infty} = Kt^n \quad (4)$$

Here, the parameter *K* represents polymer–solvent in- teractions while the exponent value *n* represents the nature of the transport mechanism. For instance, if *n* lies between 0.5 and 0.75, then the transport is anom-

alous, that is, it slightly deviates from the Fickian trend. The results of *n* and *K* are presented in Table III. In the present systems, the values of *n* vary from 0.50 to 0.66, suggesting deviations from the Fickian trans- po

Temperature effects

Sorption, diffusion, and permeation coefficients show a dependence on the temperature and, hence, Arrhe- nius plots of log *D* or log *S* versus 1/*T* for the present systems exhibit linearity (see Fig. 8). This type of linear

behavior suggests that the activation energy for diffu- sion, E_D, permeation, E_P, and sorption, ΔH_S, are con- stant over the investigated range of temperature, so that these parameters can be obtained from the Arrhe- nius equation

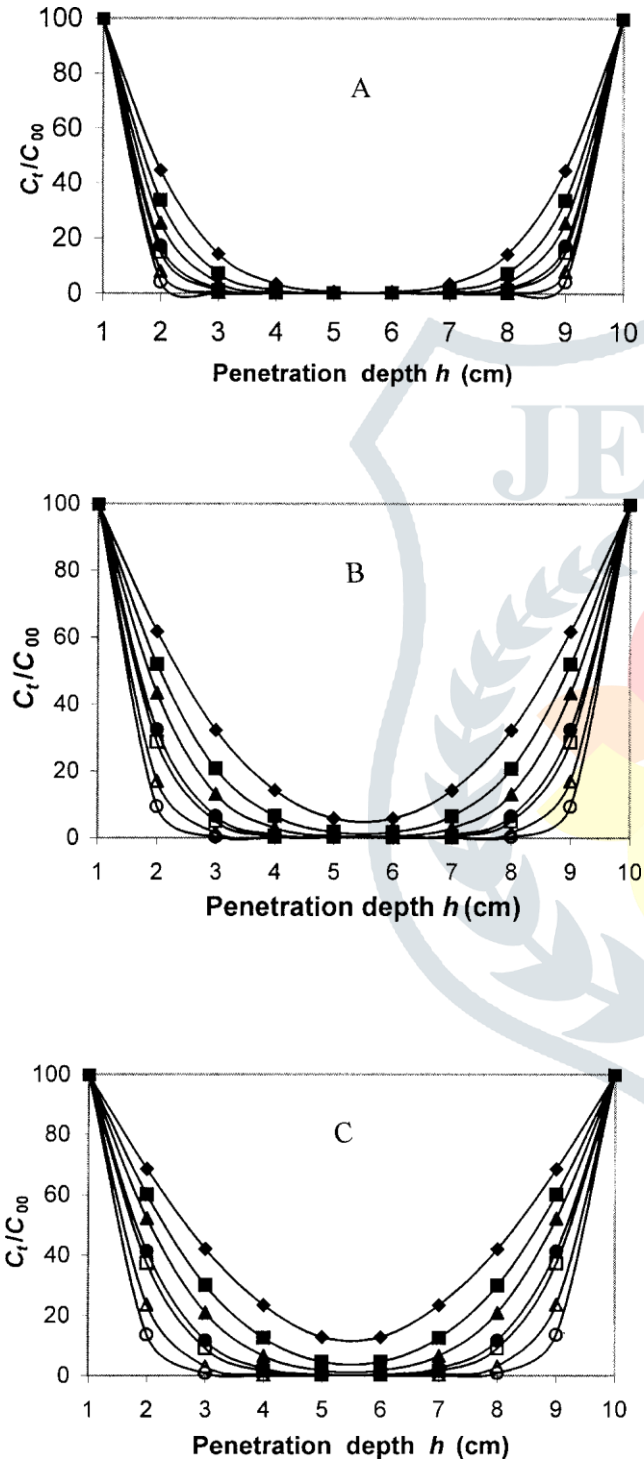

Figure 6 Concentration profiles calculated from eq. (3) for cyclohexanone through fluoroelastomer membrane at (A) 30°C, (B) 40°C, and (C) 50°C: (E) 25 min; (,) 50 min; (□) 100 min; (F) 120 min; (Œ) 200 min; (■) 300 min; (♦) 500 min.

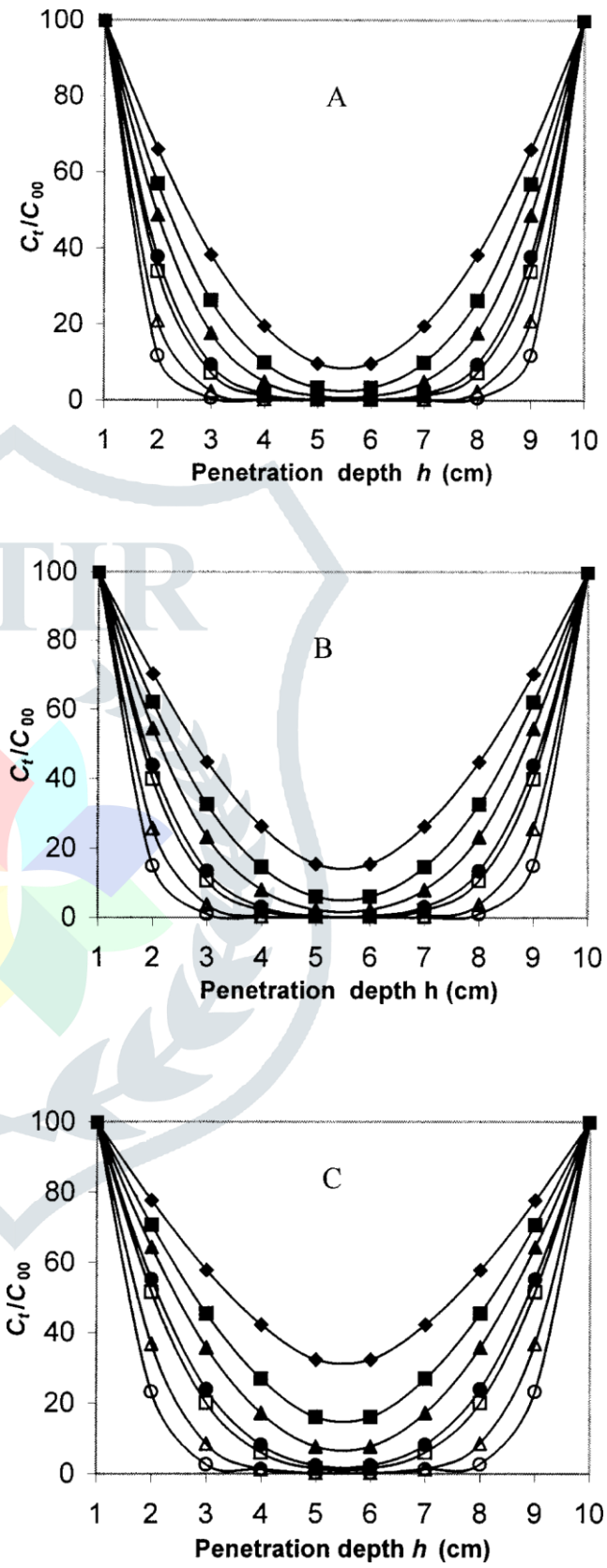

Figure 7 Concentration profiles calculated from eq. (3) for nitrobenzene through fluoroelastomer membrane at (A) 30°C, (B) 40°C, and (C) 50°C: (E) 25 min; (,) 50 min; (□) 100 min; (F) 120 min; (Œ) 200 min; (■) 300 min; (♦) 500 min.

TABLE III
Estimated Parameters from Eq. (4) for Fluoroelastomer Membrane + Liquids at Different Temperatures

	n			*K*		
Liquids	25	35°C	45°C	25°C	35°C	45°C
Dichlorobenzene	0.61	0.56	0.58	1.52	3.30	2.25
Nitrobenzene	0.53	0.55	0.56	1.63	1.60	2.18
Chlorobenzene	0.66	0.58	0.52	0.83	1.60	1.24
Cyclohexanone	0.54	0.53	0.55	4.77	1.85	1.76

$$X = X_0 \exp\left(\frac{-E_X}{}\right) \quad (5)$$

In the above equation, $X = D, P, or S$; $X_0 = D_0, P_0, or S_0$; and $E_X = E_D, E_P, or \Delta H_S$. The estimated values of E_D, E_P, and ΔH_S calculated from the least-squares method are presented in Table IV.

The E_D values of esters range between 18.8 and 35.9 kJ/mol. For aldehydes, E_D values range from 16.8 to 65.6 kJ/mol. For aromatic liquids, E_D values range from 26.1 to 49.0 kJ/mol. The results of the heat of sorption, ΔH_S, are positive in all the cases, suggesting an endothermic contribution (Henry's mode of sorp- tion), except for amyl acetate and propyl acetate, whose ΔH_S values are negative, suggesting an exo- thermic contribution. The ΔH_S values for amyl acetate and propyl acetate range from —1.62 to —2.66 kJ/mol. For aldehydes, the ΔH_S values are positive and range from 2.42 to 11.4 kJ/mol. For aromatics, ΔH_S values are positive and range from 5.17 to 27.8 kJ/mol. In the majority of the cases, the ΔH_S values are positive, suggesting that sorption is dominated mainly by the Henry's mode of sorption, giving an endothermic con- tribution.

CONCLUSIONS

The migration behavior of , aromat- ics, and a membrane was investigated by an immersion/mass gain method over the temperature interval of 30 – 50°C. Molecular transport was found to follow the anomalous-type behavior. Diffusion coefficients were calculated from Fick's equation. Concentration pro- files of liquid penetrants were calculated by solving Fick's equation and displayed graphically to study the effect of the nature of the liquid molecule, depth of penetration, and time of immersion exposure. These profiles follow the trends exhibited by the diffusion/ sorption behavior of penetrant molecules into the polymeric sheet membrane. In all cases, the *D* values do not show any systematic dependence on the size of the penetrant molecule except for those of aldehydes. The activation energy for diffusion and sorption was calculated by studying the temperature dependence of sorption and diffusion. The ΔH_S values are positive, suggesting that sorption is dominated mainly by Hen- ry's mode of sorption with an endothermic contribu- tion. On the whole, such data on the polymer–solvent systems are useful in field applications of the poly- meric me.

TABLE IV
Activation Energy for Diffusion, Permeation, and Enthalpy of Sorption for Fluoroelastomer Membrane with Aldehydes, Esters, Aromatics, and Ketone

Liquids	E_D (kJ/mol)	E_P (kJ/mol)	ΔH_S (kJ/mol)
Dichlorobenzene	26.15 ± 1.32	54.10 ± 2.26	27.80
Nitrobenzene	49.07 ± 8.73	54.29 ± 2.40	5.17
Chlorobenzene	43.33 ± 6.86	67.24 ± 5.65	23.91
Cyclohexanone	11.05 ± 1.27	30.14 ± 1.79	19.15

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