

Sorption, Diffusion, and Permeation of Esters, Aldehydes, Ketones, and Aromatic Liquids into Tetrafluoroethylene/Propylene at 30, 40, and 50°C

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Received 26 January 2002; accepted 2 December 2002

ABSTRACT: The coefficients of sorption, diffusion, and permeation for five organic esters, three aldehydes, one cyclic ketone, and three substituted aromatic liquids have been calculated for tetrafluoroethylene/propylene copolymer membranes at 30, 40, and 50°C with the sorption–gravimetric technique. With the sorption data, the concentration-independent diffusion coefficients have been calculated from Fick’s diffusion equation. Analytical solutions of Fick’s equation under suitable boundary conditions have been obtained so that the liquid concentration

profiles in the polymeric membranes at different times and different depths of liquid penetration could be computed. Because of the linearly increasing trend of the diffusion coefficients with temperature, efforts have been made to estimate Arrhenius parameters. Experimental values and the computed quantities have been used to determine the membrane–solvent interactions and to propose suitable applications for the membranes under investigation in various situations. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3201–3209, 2003

INTRODUCTION

Over the past several years, considerable efforts have been made in our laboratory to understand the fundamental aspects of the molecular transport of organic liquids through polymer membranes.^{1–5} Such studies have great relevance to many applied areas of science and engineering, including those of separation processes.⁶ Moreover, efforts in this direction have greatly benefited our understanding of the technological problems related to membrane-based separation processes, including pervaporation separation,⁷ reverse osmosis,⁸ and microfiltration.⁹ For a successful operation of these processes, it is important to have an accurate knowledge of the sorption, diffusion, and permeation of small molecules through flat membrane materials acting as barriers.^{10–12} From an experimental viewpoint, molecular transport is greatly influenced by the membrane structure, polymer morphology, and its interaction with the liquid molecules. Therefore, an understanding of the sorption kinetics in terms of diffusion anomalies and the permeation of liquid molecules through membrane materials is very

important before we seek industrial applications for these polymers as barrier materials in aggressive environments, including organic solvents.¹³

In earlier studies,^{14–16} efforts were made to compute the concentration profiles of organic liquids through a variety of membrane materials of interest to engineering. In a continuation of this research program, we present here results on the sorption, diffusion, and permeation of organic esters, a ketone, aldehydes, and aromatic liquids through tetrafluoroethylene/propylene copolymer membranes (FC-2121) obtained from 3M Co. (St. Paul, Minnesota). This is a well-known engineering polymer that exhibits unique combinations of high-temperature, chemical, and electrical resistivity with good dimensional stability. It is used in applications for which compression set resistance and gas-blistering properties are important. The polymer is known to be resistant to acids, bases, hot water, amines, oils, and hydraulic fluids. However, its interactions with organic liquids is not known precisely, and so from a technological viewpoint, such studies are important.

In this study, esters such as amyl acetate, phenyl acetate, diethyl oxalate, propyl acetate, and ethyl benzoate; aldehydes such as benzaldehyde, salicylaldehyde, and propionaldehyde, the ketone cyclohexanone, and substituted aromatics such as chlorobenzene, dichlorobenzene, and nitrobenzene have been used as liquid permeants. Sorption experiments have been performed at 30, 40, and 50°C. The liquids have been chosen on the basis of their wide diversity and relevance in chemical engineering and other related

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CEPS Communication #12.

Contract grant sponsor: Department of Science and Technology (New Delhi, India); contract grant number: SP/S1/H-31/2000.

TABLE I
Results of Molar Volume and S Data of Liquids Through Membranes

Liquid	Molar volume (cm ³ /mol)	% S (g/g)		
		30°C	40°C	50°C
Amyl acetate	148.4	108.8	107.1	105.1
Ethyl benzoate	144.7	64.3	57.8	52.8
Diethyl oxalate	135.6	115.1	114.6	105.4
Phenyl acetate	126.8	34.6	37.0	38.7
Propyl acetate	115.7	111.5	113.4	115.6
Dichlorobenzene	113.0	2.6	3.6	4.9
Salicylaldehyde	104.6	35.0	38.1	40.0
Cyclohexanone	103.5	7.7	10.9	12.8
Nitrobenzene	102.9	34.8	36.7	38.8
Benzaldehyde	102.2	38.6	42.8	54.0
Chlorobenzene	102.2	2.2	5.9	9.4
Propionaldehyde	72.0	22.2	25.9	27.9

areas. Sorption data have been used to compute the concentration-independent diffusion coefficient (D) from Fick's diffusion equation. In addition, the analytical solutions of Fick's equation have been obtained to calculate the liquid concentration profiles at different times and depths of liquid penetration inside the membrane material. These profiles, as well as the calculated Arrhenius parameters, have been used to examine the nature of the diffusion anomalies in terms of the size and shape of the liquid molecules.

EXPERIMENTAL

Materials

Fluorel FC 2121 is a low-viscosity incorporated cure copolymer designed for injection-molding sealing components that meet the major requirements of fluoroelastomer O-ring specifications. A gift sample was received from Nina McAllum (3M Co.). Typically, the elastomer has a specific gravity of 1.80, is off-white, is soluble in ketones and esters, and has a Mooney viscosity approximately 25 ML1 + 10 at 121°C. A sample press-cured for 10 min at 177°C had the following mechanical properties: tensile strength, 1260 psi; elongation at break, 235%; and hardness (Shore A), 75. The sample was compounded with standard fillers and ingredients used in typical fluoroelastomer formulations.

Reagents and chemicals

The reagent-grade chemicals amyl acetate, cyclohexanone, dichlorobenzene, chlorobenzene, benzaldehyde, and ethyl benzoate were obtained from S.D. Fine Chemicals (Mumbai, India). Phenyl acetate and diethyl oxalate were procured from Sisco Chem. Industries (Mumbai, India). Propyl acetate (Lancaster Chemicals, Manchester, United Kingdom) and nitrobenzene (Ranbaxy Chemicals, Mumbai, India) were

used as received. Salicylaldehyde was purchased from Sarabhai Chemicals (Baroda, India). Propionaldehyde was procured from Riedel Chemicals (Germany). All these chemicals were used directly as supplied and are listed in Table I.

Sorption-gravimetric experiments

Circularly cut, disc-shaped sheet membranes 1.96 cm in diameter were first dried in a vacuum desiccator for 48 h over anhydrous CaCl₂ before use. The initial dry mass of the sample was measured to an accuracy of ± 0.01 mg on a Mettler model AE240 microbalance (Switzerland). The samples were soaked in the respective liquids placed in airtight test bottles and were maintained at the desired temperature in an electronically controlled hot air incubator (WTB Binder, Germany). The samples were removed periodically from the liquid containers. The surface-adhered liquid drops were wiped off by gentle pressing between the tissue papers and were weighed immediately with an accuracy of ±0.01 mg. We took care to minimize the loss of liquids from the membrane by covering it with a watch glass. The mass measurements were done within 20 s to minimize any evaporation losses. When the polymer samples attained equilibrium sorption, no more mass gain was observed, and this did not change significantly even when the samples were kept over an extended period of 1 or 2 days. Three independent readings were taken, and the average value was used in all calculations.

RESULTS AND DISCUSSION

Sorption kinetics

The dynamic sorption results of all the liquid penetrants with tetrafluoroethylene/propylene copolymer membranes at 30°C are displayed in Figures 1–3, whereas the sorption coefficients (S) of all the liquids

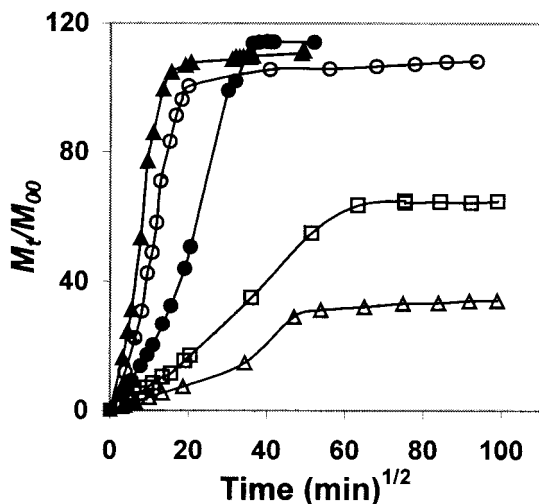


Figure 1 Plots of M_t/M_∞ versus the square root of time for tetrafluoroethylene/propylene at 30°C with (○) amyl acetate, (□) ethyl benzoate, (●) diethyl oxalate, (△) phenyl acetate, and (▲) propyl acetate.

at different temperatures are included in Table I. As can be seen in Figure 1, among all the esters, the sorption of diethyl oxalate is higher than propyl acetate and amyl acetate. The sorption trends of these esters do not follow any systematic trend with the size of the liquid molecules but are more dependent on the nature or type of their interaction with the polymer. For ethyl benzoate and phenyl acetate, the sorption values are quite small; the lowest sorption is observed for phenyl acetate. The sorption curves for phenyl acetate and ethyl benzoate show sigmoidal trends, suggesting that their migration follows a non-Fickian trend. Such trends have generally been explained in terms of different types of diffusion anomalies, as

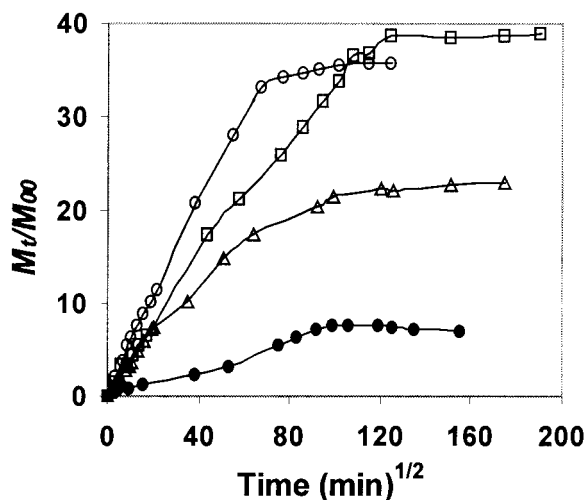


Figure 2 Plots of M_t/M_∞ versus the square root of time for tetrafluoroethylene/propylene at 30°C with (○) salicylaldehyde, (●) cyclohexanone, (□) benzaldehyde, and (△) propionaldehyde.

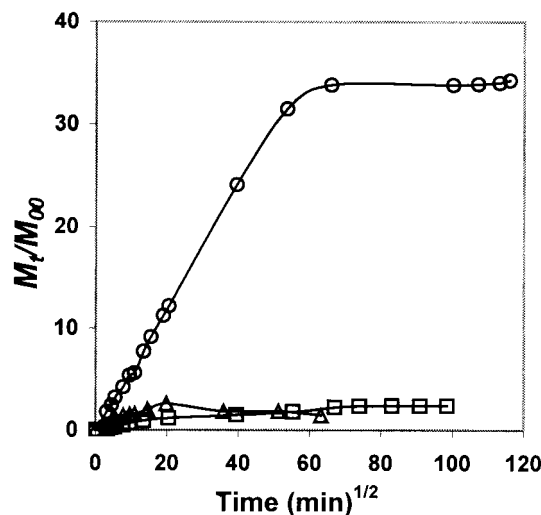


Figure 3 Plots of M_t/M_∞ versus the square root of time for tetrafluoroethylene/propylene at 30°C with (△) dichlorobenzene, (○) nitrobenzene, and (□) chlorobenzene.

discussed by Crank.¹⁷ For propyl acetate, amyl acetate, and diethyl oxalate, sorption increases rapidly within much shorter times than observed for ethyl benzoate or phenyl acetate. This can be explained by the presence of bulky aromatic rings of ethyl benzoate and phenyl acetate, which make the migration much slower. This may further lead to the non-Fickian transport of these molecules.

The sorption plots for all the aldehydes and cyclohexanone at 30°C are presented in Figure 2. We find that the sorption curve for benzaldehyde is slightly higher than those observed for salicylaldehyde and propionaldehyde, and this variation follows the variation in the size of these molecules. The lowest sorption is observed for cyclohexanone, whereas for propionaldehyde, the sorption is higher than for cyclohexanone. For cyclohexanone, the sorption curve follows a slight sigmoidal trend, suggesting non-Fickian transport.

Sorption curves for the substituted aromatics chlorobenzene, dichlorobenzene, and nitrobenzene at 30°C are presented in Figure 3. For nitrobenzene, sorption increases systematically in a Fickian manner, whereas for chlorobenzene and dichlorobenzene, the sorption curves overlap one another, and the uptake values are much smaller than that observed for nitrobenzene. Even though the molecular sizes of nitrobenzene and chlorobenzene are almost identical, they exhibit very different sorption tendencies; this signifies that in this polymer, sorption depends not on the size of the molecule but on the solvent property and the interactions with the polymer membrane.

The sorption curves for the majority of the liquids show a systematic variation with temperature; that is, sorption generally increases with increasing temperature. This indicates an increased molecular mobility

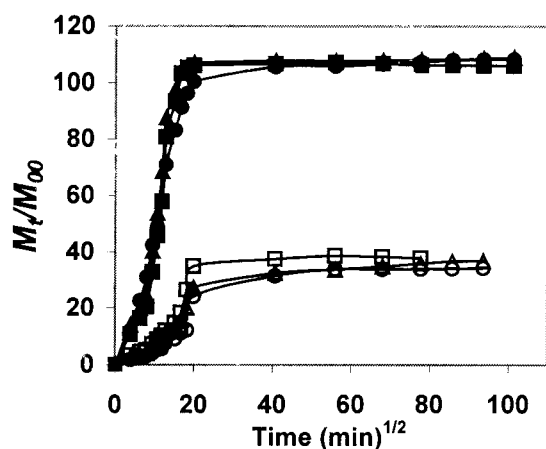


Figure 4 Temperature dependence of the sorption for tetrafluoroethylene/propylene with amyl acetate (filled symbols) and nitrobenzene (open symbols) at (○) 30, (△) 40, and (□) 50°C.

due to polymer chain segmental motion at higher temperatures as a result of the creation of extra free volume within the polymeric matrix. To avoid overcrowding of the plots, we have not displayed the temperature-dependent sorption curves for all the liquids, but only a typical plot is shown in Figure 4 for amyl acetate and nitrobenzene. For nitrobenzene, the sorption curves at the three temperatures are much lower than those observed for amyl acetate.

To investigate the nature of the transport processes, we have fitted the molar percentage sorption data before the completion of 55% equilibrium to an empirical equation of the following type:¹⁻⁴

$$\frac{M_t}{M_\infty} = Kt^n \quad (1)$$

where M_t and M_∞ are mass sorption values (%) at time t and t_∞ , respectively. The parameters K and n have

been estimated by the method of least squares at the 95% confidence limit. These data are presented in Table II. Even though the values of n are indicative of the nature of diffusive transport in these systems, we have been unable to make any distinctive correlation between the values of n and the nature of the sorption curves. In all cases, the values of n range between 0.50 and 0.61, suggesting anomalous transport behavior, as is normally the case for elastomers.¹⁻⁴ Furthermore, the values of n do not show any systematic trend with temperature. However, the magnitude of K implies that the nature of the polymer-liquid interaction varies according to the nature of the liquid. In all cases, K increases with increasing temperature, and this suggests increased molecular interactions between the polymer and liquid molecules.

Calculation of D and concentration profiles

To assess the usefulness of a barrier polymer in field applications involving exposure to aggressive liquids, we should have an accurate knowledge of D for liquid molecules through polymeric sheet membranes. The calculation of the concentration-independent value of D for polymer-liquid systems based on the unidirectional flow of liquids has been calculated with Fick's equation:¹⁷

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

where C is the liquid concentration inside the polymer at time t and x is the distance that the diffusing molecules travel inside the membrane polymer.

In actual applications, the polymer can be exposed to aggressive liquids, and so it is necessary to compute the concentration profiles of liquids inside the membrane material. D has been computed by the solution

TABLE II
Estimated Parameters from Eq. (2) for the Tetrafluoroethylene/Propylene Copolymer Membrane for Different Liquids at Different Temperatures

Liquid	n			K		
	30°C	40°C	50°C	30°C	40°C	50°C
Amyl acetate	0.52	0.55	0.58	1.50	2.10	3.30
Ethyl benzoate	0.56	0.54	0.50	1.40	1.50	2.20
Diethyl oxalate	0.61	0.57	0.57	1.00	1.53	2.17
Phenyl acetate	0.50	0.52	0.51	1.42	1.57	1.69
Propyl acetate	0.53	0.50	0.56	4.92	6.21	7.50
Dichlorobenzene	0.58	0.57	0.56	3.76	3.85	3.93
Salicylaldehyde	0.52	0.55	0.50	1.52	1.64	2.40
Cyclohexanone	0.56	0.52	0.50	2.30	2.41	2.58
Nitrobenzene	0.51	0.50	0.52	1.50	2.01	2.50
Benzaldehyde	0.50	0.51	0.57	1.10	1.87	2.80
Chlorobenzene	0.52	0.50	0.51	1.68	2.10	2.40
Propionaldehyde	0.51	0.50	0.52	1.15	1.49	2.10

TABLE III
D and *P* Values of Liquids at Different Temperatures Through the Tetrafluoroethylene/Propylene Copolymer Membrane

Liquid	<i>D</i> (10 ⁷ cm ² /s)			<i>P</i> (10 ⁷ cm ² /s)		
	30°C	40°C	50°C	30°C	40°C	50°C
Amyl acetate	4.68	5.00	5.24	4.00	4.68	4.92
Ethyl benzoate	0.10	0.25	1.41	0.89	0.93	1.02
Diethyl oxalate	1.18	1.36	2.66	1.00	1.20	1.68
Phenyl acetate	2.00	3.00	4.00	1.15	2.85	3.57
Propyl acetate	4.35	4.73	5.07	4.00	4.23	4.64
Dichlorobenzene	0.33	0.43	0.48	0.29	0.39	0.39
Salicylaldehyde	0.57	0.67	0.72	0.43	0.59	0.65
Cyclohexanone	0.25	0.46	0.63	0.20	0.36	0.53
Nitrobenzene	2.00	4.14	6.00	0.12	0.35	0.45
Benzaldehyde	1.00	2.02	4.00	1.00	1.44	2.23
Chlorobenzene	0.10	0.11	0.23	0.10	0.11	0.19
Propionaldehyde	2.00	2.99	3.20	1.17	1.90	2.00

of eq. (2) under suitable boundary conditions with the following assumptions: (1) in a sorption experiment, the concentration on the membrane surface reaches equilibrium immediately; (2) the time required to attain thermal equilibrium for the membrane is negligible in comparison with the time required to reach equilibrium sorption; and (3) changes in membrane dimensions due to swelling stresses are negligible during the solvent exposure time. Therefore, with the following boundary conditions, we find

$$t = 0 \quad 0 \leq x \leq h \quad C = 0 \quad (3)$$

$$t > 0 \quad x = 0 \quad x = h \quad C = C_{\infty} \quad (4)$$

$$\partial C / \partial x = 0, \quad x = 0, \quad t > 0 \quad (5)$$

We have solved Fick's diffusion equation to compute liquid concentration profiles inside a membrane of thickness *h* at time *t* and distance *x* to obtain^{5,13}

$$\frac{C_{(t,x)}}{C_{\infty}} = 1 - \frac{4}{\pi} \sum_{m=0}^{\infty} \frac{1}{(2m+1)} \times \exp\left[-\frac{D(2m+1)^2\pi^2 t}{h^2}\right] \sin\left[\frac{(2m+1)\pi x}{h}\right] \quad (6)$$

where *C*_(*t*,*x*) and *C*_∞ are the liquid concentrations at time *t* and distance *x* and at the equilibrium time, respectively; *m* is an integer.

The concentration-independent values of *D* have been calculated by the solution of eq. (2) under appropriate boundary conditions:¹⁷

$$D = \pi \left(\frac{h\theta}{4C_{\infty}} \right)^2 \quad (7)$$

In this equation, *θ* is the slope of the initial linear portion of the sorption curves (shown in Figs. 1–3), and *C*_∞ is the equilibrium (saturation) sorption. The results for *D* obtained this way are compiled in Table III. Included in the same table are the values of the permeation coefficient (*P* = *DS*).

At 30°C, phenyl acetate, nitrobenzene, and propionaldehyde possess identical values of *D* (i.e., ca. 2.0 × 10⁻⁷ cm²/s), but at higher temperatures, these data are not comparable. For chlorobenzene and ethyl benzoate, the *D* values are almost identical at 30 and 40°C, whereas at 50°C, *D* for ethyl benzoate is higher than that for chlorobenzene. Therefore, in this study, the values of *D* are not dependent on the molecular size of the migrating liquid, even though the general rule is that *D* should decrease with the increasing size of the liquids. Such a trend is seen only in a few cases, and this signifies that molecular transport depends more on the interactions between the liquids and the membrane material than on the size of the liquid molecules.

Among aldehydes, propionaldehyde exhibits the highest *D* value of 2.00 × 10⁻⁷ cm²/s at 30°C, whereas salicylaldehyde exhibits the lowest *D* value of 0.57 × 10⁻⁷ cm²/s at 30°C. This is probably due to the polar nature of the hydroxy group on benzene, which might hinder its migration through the membrane. For benzaldehyde, a lower value of *D* of 1.00 × 10⁻⁷ cm²/s at 30°C is observed in comparison of propionaldehyde. This trend agrees with the size of the liquid molecules; that is, salicylaldehyde is a bigger molecule than propionaldehyde. Similarly, benzaldehyde is a bigger molecule than propionaldehyde, and the diffusivity values of aldehydes vary systematically with the size of the penetrant molecules; that is, diffusivity decreases with the increasing molecular size of liquids. Among the aldehydes, the *D* values vary as follows: propionaldehyde > benzaldehyde > salicylaldehyde.

Among the aromatic liquids, nitrobenzene has the highest D values (2.00×10^{-7} to 6.00×10^{-7} cm²/s) in the investigated range of temperatures, whereas the chloro-substituted benzenes, monochlorobenzene and dichlorobenzene, exhibit lower D values by an order of magnitude. However, for dichlorobenzene, the D values are slightly higher than those observed for chlorobenzene. This may be because nitrobenzene is more polar than chlorobenzene or dichlorobenzene. A lone pair of electrons of the nitrogen atom in nitrobenzene might interact more strongly with the polymer, giving higher values of D . It is also important to notice that the increase in D is not considerable with increasing temperature for both chlorobenzene and dichlorobenzene, whereas with nitrobenzene, there is a considerable increase in diffusivity with increasing temperature.

The P values (see Table III) exhibit trends similar to those of the D values for the majority of the liquids. This trend suggests that the diffusion values are not greatly influenced by the permeant concentration within the membrane.

Concentration profiles

The concentration profiles [$C_{(t,x)}/C_{\infty}$] have been calculated from eq. (6) with the procedures suggested earlier.^{1-4,13} These profiles have been calculated at different membrane thicknesses (i.e., penetration depths of the liquids) and at different time intervals during the sorption experiments. Some representative graphs at different temperatures are presented in Figures 5-7 for cyclohexanone, benzaldehyde, and nitrobenzene, respectively. The different liquids show different depths of penetration (ingression), and this depends on the time needed to attain equilibrium sorption as well as the temperature. Noticeable effects of the temperature on the shapes of the concentration profiles are prevalent in all cases. For instance, at 50°C, because of the higher diffusivity of the liquids, the concentration profiles also exhibit values higher than those at 30 and 40°C. In addition, the concentration profiles of the liquids vary with their diffusivity values.

In Figures 5-7, we display the concentration profiles of cyclohexanone, benzaldehyde, and nitrobenzene at different temperatures. Cyclohexanone has D values (Fig. 5) that are smaller than those of benzaldehyde (Fig. 6), which, in turn, are smaller than those of nitrobenzene (Fig. 7). It is, therefore, heartening to note the liquid concentration profiles with respect to the diffusion trends of the liquids. For instance, the concentration profiles of cyclohexanone are smaller than those of benzaldehyde, which, in turn, are smaller than those observed for nitrobenzene. Therefore, the profiles vary according to the diffusion val-

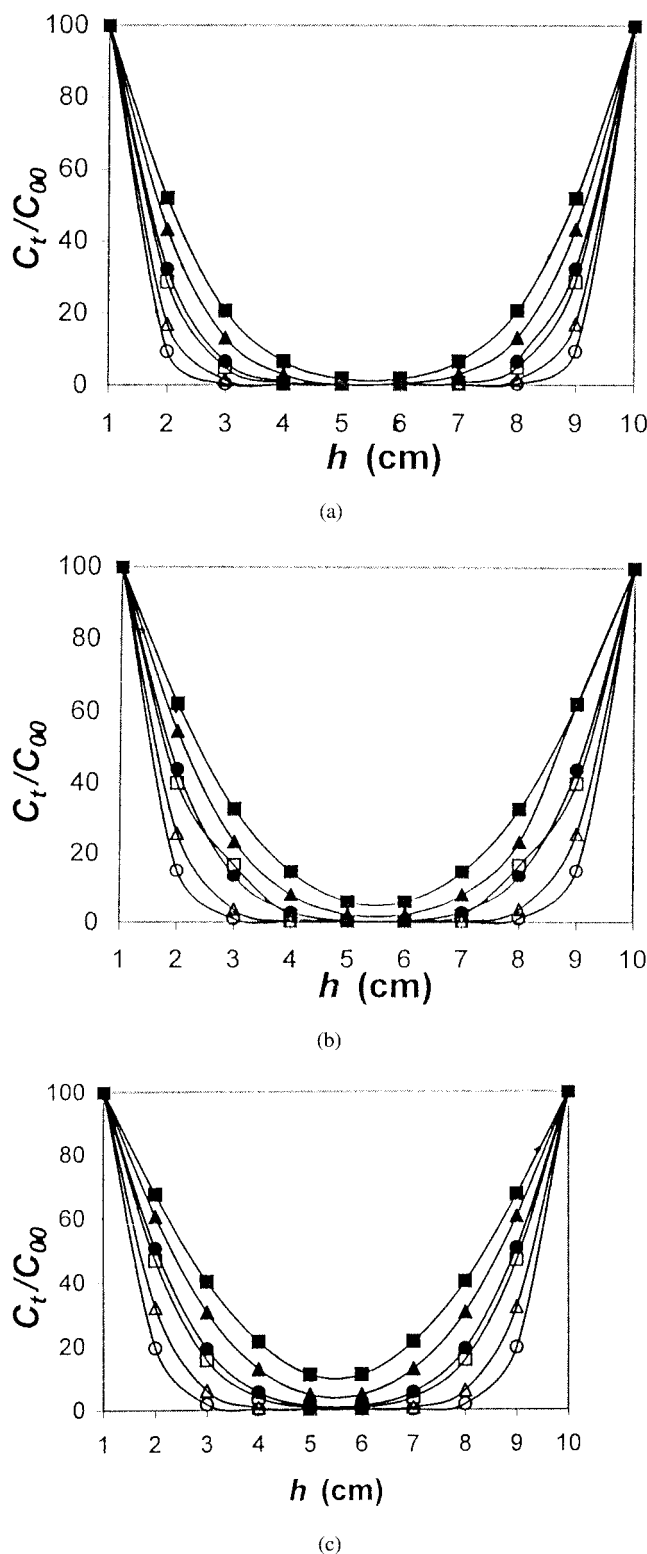
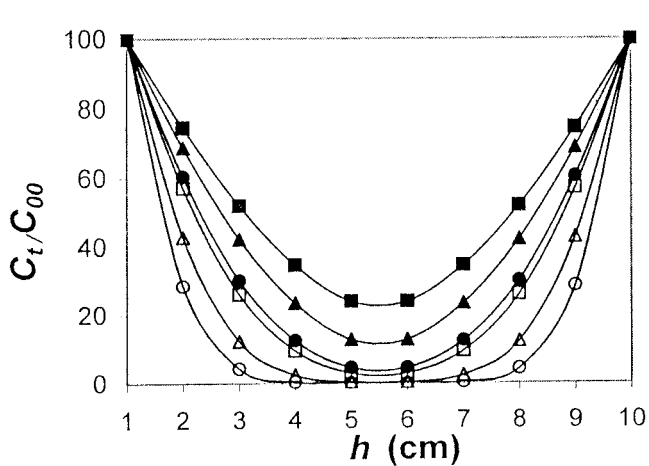
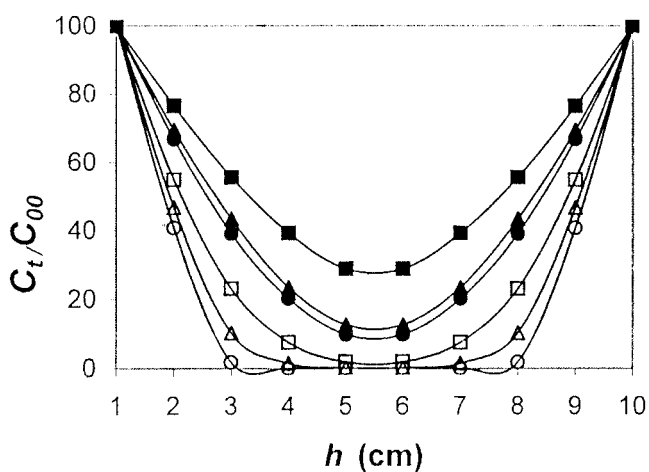


Figure 5 Concentration profiles calculated from eq. (6) for cyclohexanone through a tetrafluoroethylene/propylene membrane at (a) 30, (b) 40, and (c) 50°C for (○) 25, (△) 50, (□) 100, (●) 120, (▲) 200, and (■) 300 min.

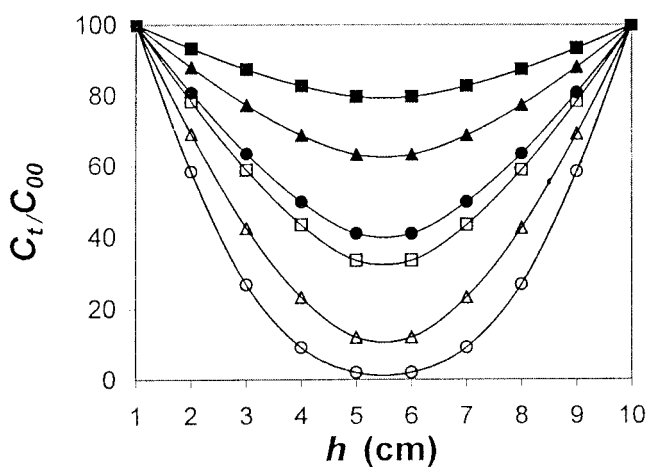
ues of the liquids. The same trend is also observed for other liquids, but these plots are not displayed to reduce the number of plots.



(a)

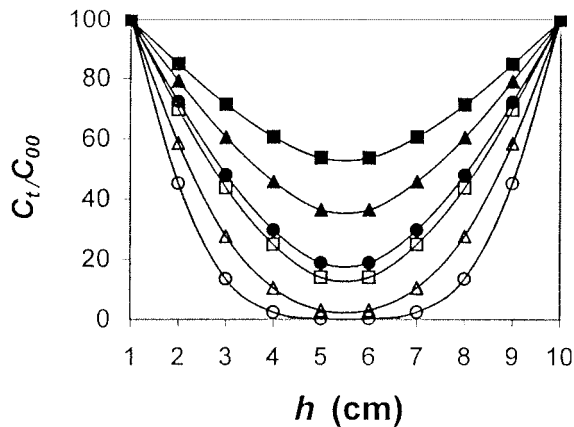


(b)

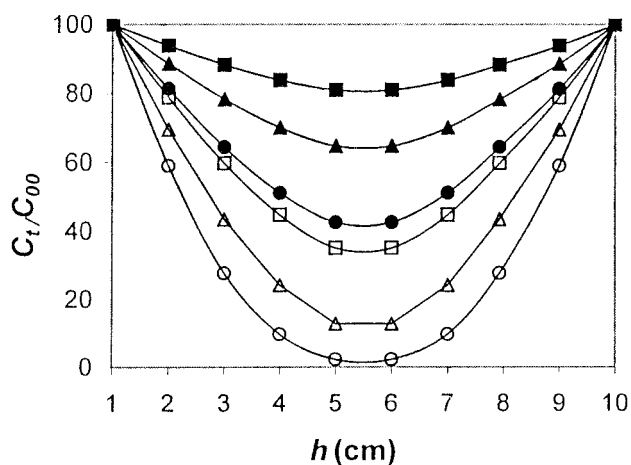


(c)

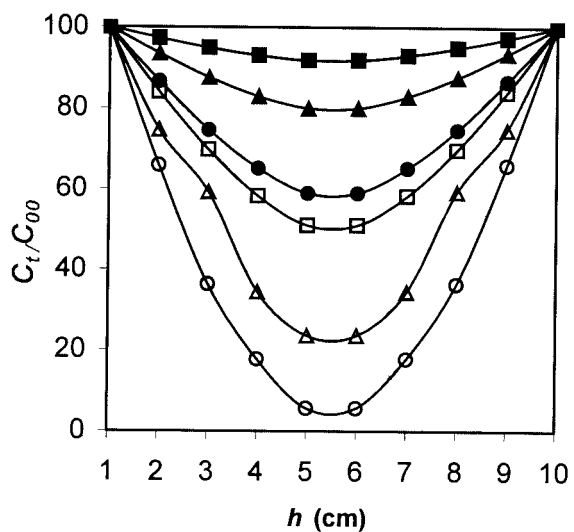
Figure 6 Concentration profiles calculated from eq. (6) for benzaldehyde through a tetrafluoroethylene/propylene membrane at (a) 30, (b) 40, and (c) 50°C for (○) 25, (△) 50, (□) 100, (●) 120, (▲) 200, and (■) 300 min.



(a)



(b)



(c)

Figure 7 Concentration profiles calculated from eq. (6) for nitrobenzene through a tetrafluoroethylene/propylene membrane at (a) 30, (b) 40, and (c) 50°C for (○) 25, (△) 50, (□) 100, (●) 120, (▲) 200, and (■) 300 min.

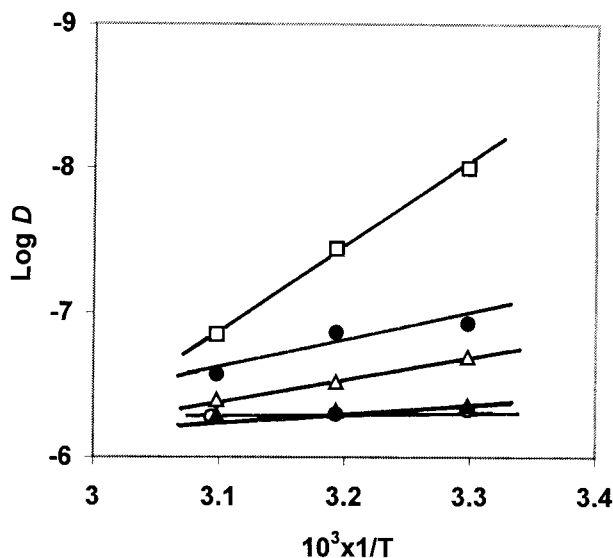


Figure 8 Arrhenius plots of $\log D$ versus $1/T$ for a tetrafluoroethylene/propylene membrane for (○) amyl acetate, (△) phenyl acetate, (□) propyl acetate, (●) diethyl oxalate, and (▲) ethyl benzoate.

Temperature effects

The sorption, diffusion, and permeation results increase with increasing temperature, and so, Arrhenius activation parameters for diffusion (E_D) and permeation (E_P) have been calculated with a general equation of the following type:¹⁷

$$X = X_0 \exp\left(\frac{-E_x}{RT}\right) \quad (8)$$

where X represents D or P and E_x represents E_D or E_P ; RT is the usual energy term. The energy of activation is a function of the nature and size of the permeating liquid within the polymer matrix. With increasing temperature, the segmental motion of the polymer chain also increases; this creates additional free volume and, therefore, increases liquid transport. Figures 8–10 display the Arrhenius plots ($\log D$ vs $1/T$) for all the liquids. The linearity in these plots suggests the validity of the Arrhenius equation over the investigated range of temperatures.

Using the results of E_D and E_P , we have calculated the heat of sorption ($\Delta H_s = E_P - E_D$), which is presented in Table IV. The magnitude of this parameter can be explained in terms of Henry's law, which states that the heat of sorption will be positive for liquid transport leading to the dissolution of chemical species into that site within the membrane giving an endothermic contribution to the sorption process. However, Langmuir sorption requires the pre-existence of a site in which sorption occurs by a hole-filling mechanism, giving an exothermic contribution.

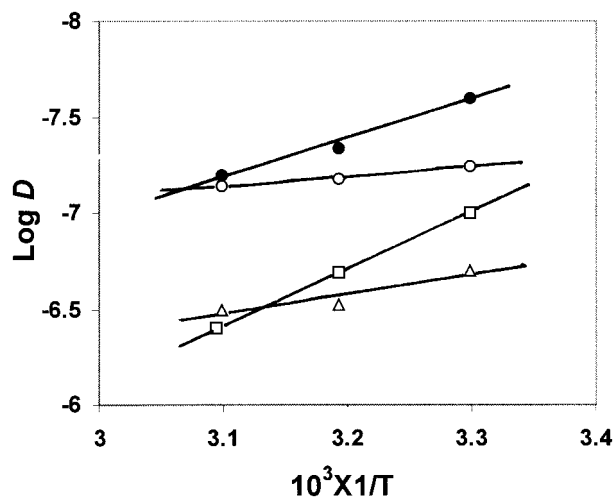


Figure 9 Arrhenius plots of $\log D$ versus $1/T$ for a tetrafluoroethylene/propylene membrane for (○) benzaldehyde, (△) propionaldehyde, (□) salicylaldehyde, and (●) cyclohexanone.

For esters, the E_D values range from 14 to 33 kJ/mol; for aldehydes, they range from 17 to 57 kJ/mol; and for aromatics, they range from 16 to 58 kJ/mol. In all cases, the values of ΔH_s are negative, suggesting an exothermic contribution to the sorption process. For esters, the ΔH_s values range between -6.30 and -11.34 kJ/mol; for aldehydes, they range between -2.05 and -15.01 kJ/mol, and for aromatics, they range between -2.63 and -14.21 kJ/mol. The negative ΔH_s values in all these cases indicate that sorption is mainly dominated by Langmuir's mode with an exothermic contribution.

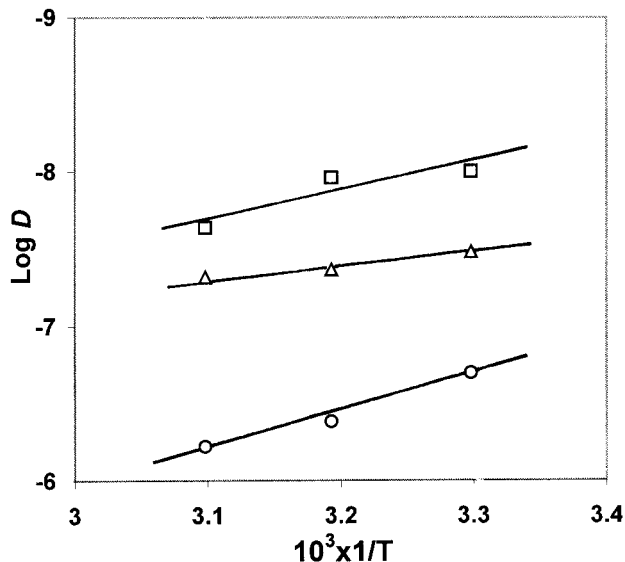


Figure 10 Arrhenius plots of $\log D$ versus $1/T$ for a tetrafluoroethylene/propylene membrane for (○) nitrobenzene, (△) chlorobenzene, and (□) dichlorobenzene.

TABLE IV
 E_D , E_p , and ΔH_s Values for the Tetrafluoroethylene/
 Propylene Copolymer Membrane with Different Liquids

Liquid	E_D (kJ/mol)	E_p (kJ/mol)	$-\Delta H_s$ (kJ/mol)
Amyl acetate	24.52 ± 2.69	13.18 ± 1.11	11.34
Ethyl benzoate	17.38 ± 2.78	7.50 ± 1.24	9.88
Diethyl oxalate	32.86 ± 4.96	22.80 ± 8.41	10.06
Phenyl acetate	28.27 ± 1.51	19.06 ± 1.30	9.21
Propyl acetate	13.46 ± 5.31	5.16 ± 1.15	8.30
Dichlorobenzene	15.31 ± 1.47	12.68 ± 4.58	2.63
Salicylaldehyde	39.81 ± 2.81	24.80 ± 8.41	15.01
Cyclohexanone	37.00 ± 6.28	29.43 ± 1.29	7.57
Nitrobenzene	57.08 ± 1.30	42.79 ± 1.55	14.29
Benzaldehyde	56.44 ± 5.29	51.22 ± 6.12	5.22
Chlorobenzene	31.94 ± 2.94	24.86 ± 1.79	7.08
Propionaldehyde	16.67 ± 1.58	14.62 ± 2.45	2.05

CONCLUSIONS

This investigation is part of our continuing efforts to study the molecular transport of different types of liquids through thin, flat-sheet polymeric membranes that find applications in many areas of engineering. The tetrafluoroethylene/propylene (FC-2121) membrane used in this study exhibits widely varying transport characteristics depending on the nature of the penetrant molecules. The liquids have been chosen from different classes, including aromatics, esters, a ketone, and aldehydes. The polymer is stable in all these media, as evidenced by the lack of chemical degradation. Therefore, the polymer studied here can be used in environments containing these liquids.

Generally, sorption values are higher for esters than for the other liquids studied over the investigated temperature range.

References

- Aminabhavi, T. M.; Munnolli, R. S.; Ortego, J. D. *Waste Manage* 1995, 15, 69.
- Aminabhavi, T. M.; Harlapur, S. F.; Balundgi, R. H.; Ortego, J. D. *J Appl Polym Sci* 1996, 59, 1857.
- Aminabhavi, T. M.; Naik, H. G. *J Hazard Mater* 1998, 60, 175.
- Aminabhavi, T. M.; Naik, H. G. *J Appl Polym Sci* 1999, 72, 349.
- Siddaramaiah, M. P.; Naik, H. G.; Aminabhavi, T. M. *J Appl Polym Sci* 1999, 73, 2051.
- Aminabhavi, T. M.; Naik, H. G.; Toti, U. S.; Balundgi, R. H.; Dave, A. M.; Mehta, M. H. *Polym News* 1999, 24, 294.
- Aminabhavi, T. M.; Khinnavar, R. S.; Harogopad, S. B.; Aithal, U. S.; Nguyen, Q. T.; Hansen, K. C. *J Macromol Sci Rev Macromol Chem Phys* 1994, 34, 139.
- Rangarjan, R.; Mazid, M. A.; Matsuura, T.; Sourirajan, S. *Ind Eng Chem Process Des Dev* 1985, 24, 978.
- Rangarajan, R.; Matsuura, T.; Sourirajan, S. *Reverse Osmosis and Ultrafiltration*; ACS Symposium Series 281; American Chemical Society: Washington, DC, 1985.
- Aithal, U. S.; Aminabhavi, T. M. *J Chem Educ* 1990, 67, 82.
- Aminabhavi, T. M.; Harogopad, S. B. *J Chem Educ* 1991, 68, 543.
- Aboutaybi, A.; Bouzon, J.; Vergnaud, J. M. *Eur Polym J* 1990, 26, 285.
- Vergnaud, J. M. *Liquid Transport Processes in Polymer Materials Modeling and Industrial Application*; Prentice Hall: Englewood Cliffs, NJ, 1991.
- Aminabhavi, T. M.; Naik, H. G. *J Hazard Mater B* 1999, 64, 251.
- Aminabhavi, T. M.; Naik, H. G. *Polym Int* 1999, 48, 373.
- Aminabhavi, T. M.; Naik, H. G. *J Polym Eng* 1999, 19, 315.
- Crank, J. *The Mathematics of Diffusion*, 2nd ed.; Clarendon: Oxford, 1975.