

Evaluation of Solvent Resistivity of Fluoropolymers for Use as Backup Membranes in Isocyanate Samplers

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SYNOPSIS

Four types of fluoroelastomer (VITON) membranes were tested for their resistivity toward dimethyl sulfoxide, dioxane, and toluene at 25, 45, and 60°C, using a gravimetric method. Coefficients of diffusion and permeation were calculated from the sorption results. Analytical solutions of Fick's equation as well as a numerical method were used to calculate the concentration profiles of liquids in the membrane materials at different penetration depths and exposure times. Activation parameters for diffusion, permeation, and sorption were obtained from the Arrhenius equation. These membrane materials were evaluated for their ability to serve as a barrier to solvent permeation in a composite membrane sampler for the analytical determination of isocyanates generated during spray-painting operations. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The National Institute for Occupational Safety and Health (NIOSH) is currently looking at alternative sampling approaches for the collection of isocyanate monomers and oligomers generated during polyurethane spray-painting operations.¹ The currently accepted analytical methods use an impinger filled with either 1-(2-methoxyphenyl)piperazine in toluene² or tryptamine in dimethyl sulfoxide (DMSO).³ Rando et al.⁴ also suggested a procedure which uses 9-(methylaminomethyl)anthracene in a 50 : 50 solution of 1,4-dioxane : DMSO in an impinger. In an effort to devise a more convenient approach which obviates the spilling problems associated with an impinger, we developed a solid sorbent sampler which consists of a microporous polyurethane or polyester substrate backed up by a thin fluoroelastomer (VITON) membrane. The composite membrane assembly is then supported on an aluminum mesh screen and mounted within a sampling cassette. This novel polymeric membrane system is designed to trap isocyanate vapor

and aerosol in the liquid emulsion phase, permeate air effectively, and, at the same time, be resistant to some of the organics used to solvate the derivatizing reagent.

In the present article, we tested four fluoroelastomers for use as membranes in our isocyanate samplers. We tested their solvent resistivity against the most commonly employed solvents used in sampling by calculating the diffusion and permeation coefficients from sorption data. The solvent resistivity of the membranes was substantiated by calculating the concentration profiles at different membrane thicknesses and different exposure times by solving Fick's equation and by using a numerical method.⁵

EXPERIMENTAL

Materials

The solvents, DMSO, 1,4-dioxane, and toluene (all purchased from S. D. Fine Chemicals, Bombay), were used as supplied. The VITONs in four grades, viz., VITON-5507, VITON-5508, VITON-5509, and VITON-5510, were obtained from DuPont (courtesy of Bill Stahl) as films with dimensions of 14.7 × 14.7 × 0.075 cm. The fluoroelastomers were mixed with curatives, fillers, and other compounding ingredients

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by either the conventional mill or internal mixing methods.

In typical formulations, the peroxide curing agent and the coagent are preblended with dry powders prior to adding to the base-gum on the mill, the peroxide being added in the second pass. Care was taken to avoid mixing temperatures above 121°C. After mixing, the stock solution was cooled rapidly by either an air- or water-cooling technique and the mixed-catalyzed compound was stored in a cool dry place prior to use. Elastomer compositions along with some representative physical/mechanical properties are given in Table I.

Methods

The circular disc-shaped polymer membranes (diameter = 1.983 cm) were cut from the large sheets using a sharp-edged carbon-tipped steel die. The cut samples were dried by storing them in a vacuum oven at 25°C for 48 h before use and soaked in screw-tight test bottles containing 15–20 mL of the respective solvent maintained at the desired temperature ($\pm 0.5^\circ\text{C}$) in an electronically controlled hot-air oven (Memmert, Germany). The samples were removed periodically, the solvent drops adhering to the membrane wiped off by gently pressing between two pieces of filter paper, then weighed immediately on a digital Mettler balance (Model AE 240, Switzerland) with a precision of ± 0.01 mg. Other experimental details remain the same as described earlier.^{6–9}

When the samples attained equilibrium saturation, no further weight gain was observed over an extended period of 1 or 2 days. The weight percent uptake, M_t , by the samples of the solvent molecules was calculated as

$$M_t = \left[\frac{W_t - W_0}{W_0} \right] \times 100 \quad (1)$$

where W_0 is the initial weight of the sample, and W_t , its weight after time, t , during solvent exposure.

RESULTS AND DISCUSSION

The experimental sorption results calculated in weight percent units at 25, 45, and 60°C for all the fluoropolymers with DMSO are presented in Figure 1. These polymers behave differently in the presence of DMSO. For instance, VITON-5509 and VITON-5510 exhibit considerably lower sorption values of around 15 wt % at 25°C. Intermediate sorption val-

ues are exhibited by VITON-5508 at all temperatures. VITON-5507 shows the highest sorption and least resistivity to DMSO at all temperatures. Generally, for all the VITONs, sorption increases with increasing temperature. It is noticed that at 25 and 45°C a slight decrease in sorption is observed for VITON-5507 and VITON-5508 samples, but this effect is not pronounced at 60°C. Such a decrease in sorption is attributed to the slight leaching out of the VITON ingredients by the DMSO. Temperature also shows an effect on the time required to attain equilibrium, and in all cases, sorption increases with increasing temperature. However, all polymers in the presence of DMSO exhibit Fickian transport, i.e., the weight % uptake values increase linearly with square root of time up to about 50% equilibrium.

Sorption curves for all the VITONs at 25, 45, and 60°C with toluene are presented in Figure 2. It is found that at 25°C, even after continuous exposure for 4 days, VITON-5508, VITON-5509, and VITON-5510 samples have not reached equilibrium sorption. On the other hand, VITON-5507 reaches equilibrium within 24 h of immersion. At 45 and 60°C, equilibrium sorption for the other samples was attained within 24 h. However, except for VITON-5507, the sorption curves for the other samples at 45 and 60°C are sigmoidal, suggesting a slight deviation from the Fickian mode of transport. Generally, the equilibrium sorption uptake values for toluene are much smaller than those for DMSO, but the general trends of the shapes of the sorption curves and their variations remain similar.

In Figure 3 are presented the sorption results for 1,4-dioxane in all the VITONs at 25 and 60°C; these results are higher than those observed for DMSO and toluene. In addition, the time to reach equilibrium sorption for dioxane is smaller when compared to DMSO and toluene.

The equilibrium sorption results calculated in weight % units from the plateau regions of the sorption curves are presented in Table II. In almost all cases with the exception of 1,4-dioxane + VITON-5507, equilibrium sorption increased with temperature. The sorption uptake values were fitted to the empirical equation¹⁰

$$M_t/M_\infty = Kt^n \quad (2)$$

where M_t and M_∞ refer to solvent uptake data at time t and at equilibrium; K is an empirical parameter which depends on the structural characteristics of the polymer as well as the polymer-solvent interaction. The value of n depends

Table I Mixing Compositions and Some Typical Properties of VITON Polymers

Ingredients	Samples			
	5507	5508	5509	5510
Viton A 401C	100	—	—	—
Viton B 601C	—	100	—	—
Viton F 601C	—	—	100	—
Viton GF	—	—	—	100
Maglite D	3	3	3	—
Calcium hydroxide	6	6	6	—
Zinc oxide	—	—	—	3
N 990 carbon black	30	30	30	30
Cannauba wax	1	1	1	1
Diak #8	—	—	—	1
Lupenco 101 XL	—	—	—	3
Polymer properties				
Viscosity (mPa s)	40	60	60	60
Fluorine content (wt %)	66.0	68.5	69.5	69.5
Physical properties				
Compression set % (70 h/2°C)	15	20	40	45
Temperature of retention (TR-10)°C	-17	-13	-06	-06
Volume increase (%) (after 7 days/MEOH)	75-105	35-45	5-10	5-10

on the type of transport mechanism. Using eq. (2), the values of n and K were estimated by the method of least-squares and are listed in Table III.

For toluene, the values of n fall in the range 0.50–0.52, suggesting Fickian transport. For DMSO and 1,4-dioxane, these values range from 0.50 to a maximum of 0.67, indicating slight deviations from

Fickian behavior. This is further supported by the slight, sigmoidal shapes of the sorption curves for 1,4-dioxane with VITON-5509 and VITON-5510 (Fig. 3). Generally, no systematic trend in the variation of n with temperature is observed. On the other hand, the values of K systematically increase with temperature in all cases, except for toluene + VITONs.

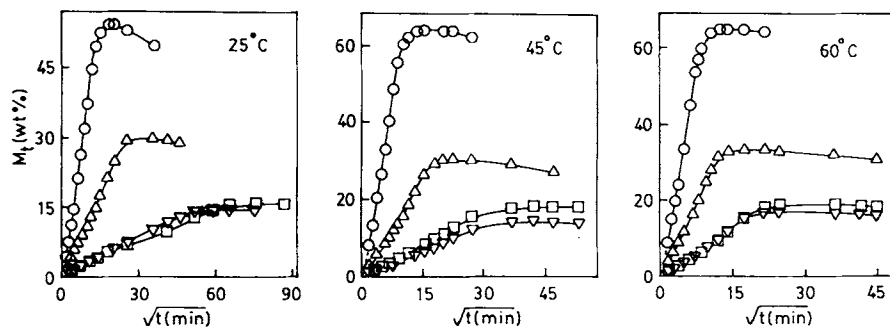


Figure 1 Sorption curves of VITON fluoroelastomers with DMSO at 25, 45, and 60°C. Symbols for polymers: (O) VITON-5507; (Δ) VITON-5508; (∇) VITON-5509; (□) VITON-5510.

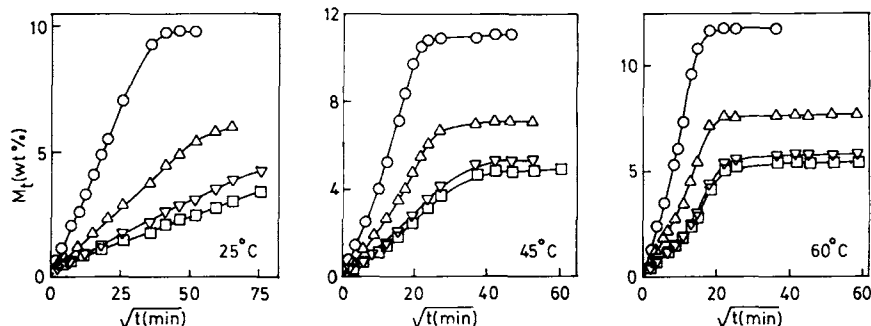


Figure 2 Sorption curves of VITON fluoropolymers with toluene at 25, 45, and 60°C. Symbols for the polymers are the same as in Figure 1.

To predict the molecular migration of the organics into the VITON membranes, we calculated the concentration-independent diffusion coefficients using Fick's second-order differential equation¹¹:

$$\frac{\partial c}{\partial t} = D \left[\frac{\partial^2 c}{\partial x^2} \right] \quad (3)$$

where C is liquid concentration within the polymer at time t and distance x . Using the suitable boundary conditions as explained in ref. 5, eq. (3) was solved for the unidirectional diffusion to give

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

where $C(t, x)$ and C_∞ are the solvent concentrations at time t and distance x and at equilibrium, respectively. The h is the thickness of the membrane and m is an integer.

The liquid uptake by the membrane material is given by

$$\begin{aligned} \frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{k=0}^{\infty} \frac{1}{(2k+1)^2} \\ \times \exp \left[- \frac{D(2k+1)^2 \pi^2}{h^2} t \right] \quad (5) \end{aligned}$$

Diffusivity at short times, i.e., at $M_t/M_\infty < 0.55$, is calculated as⁹

$$\frac{M_t}{M_\infty} = \frac{4}{h} \left[\frac{Dt}{\pi} \right]^{1/2} \quad (6)$$

The calculated values of D are presented in Table IV. Included in the same table are the values of the kinetic rate constants, k_1 , calculated by using¹²

$$k_1 t = \ln [M_\infty / (M_\infty - M_t)] \quad (7)$$

where M_t and M_∞ are sorption values at time t and at equilibrium.

A close inspection of the data presented in Table IV reveals that diffusion coefficients and kinetic rate constants vary according to the sequence 1,4-dioxane > DMSO > toluene. However, the magnitudes of these values depend on the nature of the polymer used. In the majority of cases, the values of D and k_1 are small for VITON-5509 and VITON-5510 membranes. The trend in the variation of these values follows the pattern VITON-5507 > VITON-5508 > VITON-5509. In some cases, the values of D and k_1 for VITON-5510 lie between VITON-5508 and VITON-5509 samples.

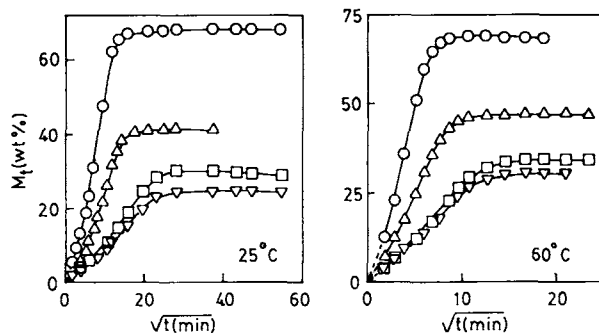


Figure 3 Sorption curves of VITON fluoropolymers with 1,4-dioxane at 25 and 60°C. Symbols for the polymers are the same as in Figure 1.

Table II Sorption and Permeability Coefficients for VITONs with Liquids

Temperature (°C)	<i>S</i> (wt %) for Samples				<i>P</i> × 10 ⁸ (cm ² s ⁻¹) for Samples			
	5507	5508	5509	5510	5507	5508	5509	5510
<u>DMSO</u>								
25	54.35	30.00	14.40	15.83	04.80	01.080	0.15	00.09
45	64.01	30.58	14.64	18.18	08.96	02.090	0.33	00.39
60	65.01	33.36	17.08	18.71	14.61	03.370	0.64	00.69
<u>1,4-Dioxane</u>								
25	68.20	41.54	24.75	30.20	05.82	03.15	00.93	01.19
45	70.25	47.36	30.22	33.55	15.50	07.93	02.77	03.26
60	68.96	47.37	30.64	34.46	26.37	12.44	04.54	04.98
<u>Toluene</u>								
25	09.82	06.03	04.45	03.63	00.12	00.05	00.02	00.01
45	11.06	07.10	05.33	04.88	00.32	00.16	00.10	00.08
60	11.79	07.69	05.80	05.41	00.56	00.29	00.20	00.15

Permeability coefficients, P , of the polymer-solvent systems were calculated from the relation $P = D \cdot S$, and these results are included in Table II. The values of P vary in the same manner as those of D .

The liquid concentration profiles calculated from eq. (4) at various time intervals from face to face of the VITON-5507 membrane with DMSO and toluene at 25°C are presented in Figure 4. These profiles exhibit an effect which is dependent on the size

of the liquid molecules. For instance, the diffusion coefficient of DMSO is higher than that of toluene and, hence, higher concentration profile values are observed for DMSO. These values increase considerably with increasing exposure times, suggesting higher sorption values with longer sorption times.

To test the validity of the analytical approach based on the solution of Fick's equation, we further attempted to calculate the concentration profiles using a numerical method based on the finite dif-

Table III Estimated Parameters of Eq. (2)

Temperature (°C)	<i>n</i> for Samples				<i>K</i> × 10 ² (g/g min ⁿ) for Samples			
	5507	5508	5509	5510	5507	5508	5509	5510
<u>DMSO</u>								
25	0.60	0.50	0.50	0.50	4.07	3.75	2.96	3.30
45	0.58	0.50	0.51	0.50	6.41	5.36	3.77	3.79
60	0.59	0.51	0.52	0.51	8.16	6.78	4.97	4.77
<u>1,4-Dioxane</u>								
25	0.62	0.67	0.55	0.53	3.73	2.48	2.78	3.00
45	0.63	0.59	0.52	0.51	6.11	5.75	4.48	6.07
60	0.65	0.59	0.52	0.53	8.86	7.77	7.04	6.48
<u>Toluene</u>								
25	0.50	0.50	0.51	0.50	3.87	3.80	4.72	7.35
45	0.50	0.51	0.51	0.52	3.78	3.45	2.38	2.08
60	0.50	0.50	0.50	0.52	5.59	4.60	3.28	3.89

Table IV Diffusion Coefficients Calculated from Eq. (7) and Kinetic Rate Constants

Temp (°C)	$D \times 10^8$ (cm ² s ⁻¹) for Samples				$k_1 \times 10^3$ (min ⁻¹) for Samples			
	5507	5508	5509	5510	5507	5508	5509	5510
DMSO								
25	05.75	03.49	01.33	01.17	09.93	03.52	01.08	00.56
45	09.90	06.72	02.71	02.47	18.08	06.05	02.06	02.18
60	15.77	09.33	03.93	03.89	29.36	11.94	05.23	04.31
1,4-Dioxane								
25	05.04	03.77	02.80	03.09	10.80	00.80	03.51	03.48
45	13.15	11.60	08.09	08.91	23.15	16.06	07.21	09.82
60	22.29	18.37	13.47	12.76	43.97	25.96	13.82	12.97
Toluene								
25	01.54	01.50	01.35	02.48	01.92	00.88	00.48	00.43
45	02.72	02.38	01.61	01.30	03.72	02.46	01.72	01.65
60	04.85	04.12	03.04	02.83	06.92	04.24	02.93	02.88

ference technique. The following relation was used to solve for concentration profiles⁵:

$$CN_m = \frac{1}{M} [C_{m-1} + (M-2)C_m + C_{m+1}] \quad (8)$$

with the dimensionless parameter, M , given as

$$M = \frac{(\Delta x)^2}{\Delta t} \frac{1}{D} \quad (9)$$

In the preceding equations, for computational purposes, the membrane thickness is divided into 10 slices of equal size, Δx . Each slice is characterized by an integer, m . C_m and CN_m are the values of liquid concentrations at position m at time t and after time Δt , respectively. For each position within the mem-

brane, the liquid concentration profiles were obtained at different times. The simulated concentration profiles at 25°C for VITON-5507 with DMSO, a highly diffusive liquid, and toluene, a slowly diffusing liquid, are presented in Figure 5. It is gratifying to note that the numerical method predicts that the size of liquid molecules will affect both the shape as well as magnitude of the concentration profiles. Similar results can be seen in Figure 6 for VITON-5508 with dioxane at 25 and 60°C.

To test the reliability of the diffusion results calculated from the short time method, i.e., before < 55% sorption [from eq. (6)], we calculated the theoretical sorption curves from eq. (5) using the diffusion results calculated from eq. (6). A comparison is made in Figure 7 for VITON-5510 between the theoretical curves and the experimental sorption

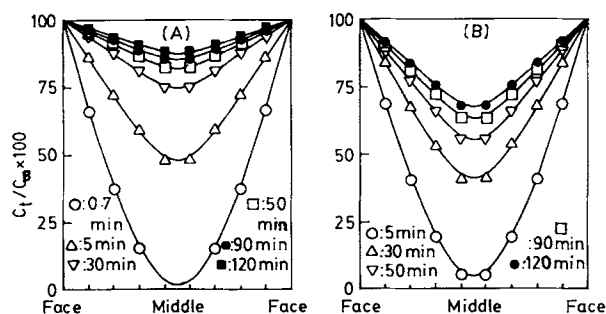


Figure 4 Concentration profiles calculated from eq. (4) for VITON-5507 with (A) DMSO and (B) toluene at 25°C at different time intervals.

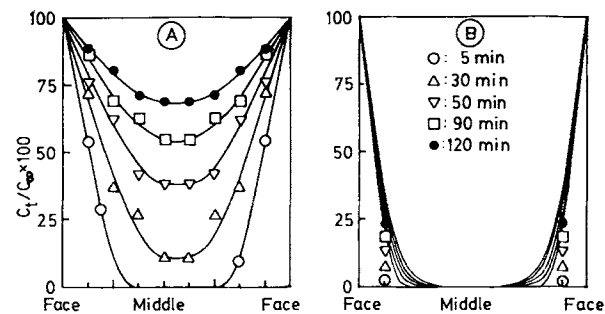


Figure 5 Concentration profiles calculated from eq. (8) for VITON-5507 with (A) DMSO and (B) toluene at different time intervals.

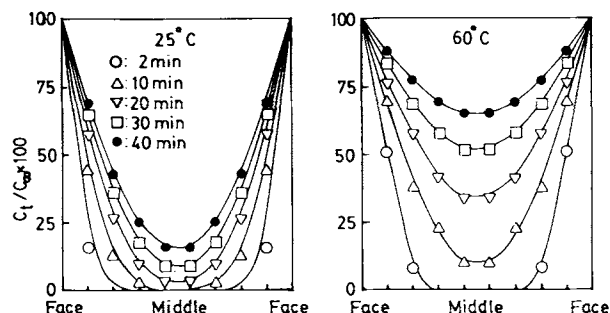


Figure 6 Concentration profiles calculated from eq. (8) for VITON-5508 with 1,4-dioxane at 25 and 60°C for different time intervals.

points. A good agreement is observed between the theoretical curves and the experimental points, justifying the reliability of the diffusion results calculated from eq. (6). However, at longer diffusion times, a slight deviation is observed between the experimental data and the calculated curves.

To further investigate this anomaly, the diffusion coefficients were calculated at longer diffusion times using eq. (10) which can be obtained from eq. (5):

$$\ln(1 - M_t/M_\infty) = \ln\left[\frac{8}{\pi^2}\right] - \frac{\pi^2 Dt}{h^2} \quad (10)$$

Thus, a plot of $\ln(1 - M_t/M_\infty)$ vs. t generally should be linear and D can be calculated from the slope. However, the nonlinearity beyond 60% sorption is attributed to the fact that the polymer chains respond quickly to the presence of liquid molecules, thereby introducing a slight deviation from the Fickian mechanism. Some of our data presented in Figure 8 are in conformity with eq. (10). The results of D calculated from eq. (10) are given in Table V. Generally, we found that D values calculated from eq. (10) are lower than those calculated from the short-time method, suggesting slower diffusivity of the liquids near equilibrium saturation. At longer sorption times, the term $n \geq 1$ as well as $\ln(8/\pi^2)$ may be ignored to give

$$\ln\left[\frac{M_\infty}{M_\infty - M_t}\right] \cong \frac{\pi^2 Dt}{h^2} \quad (11)$$

where

$$k_1 = \frac{\pi^2 D}{h^2} \quad (12)$$

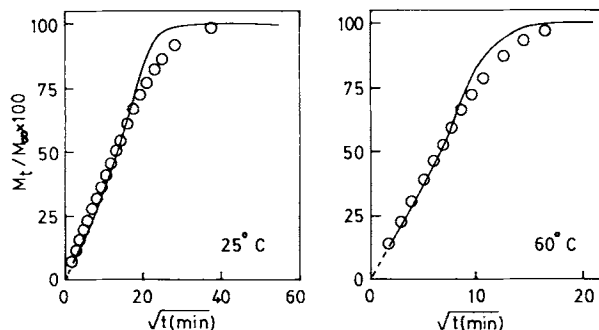


Figure 7 Comparison of experimental sorption data with the theoretical curves computed from eq. (5) for VITON-5510 with dioxane at 25 and 60°C.

This further justifies the use of the first-order chemical kinetics for the present polymer-solvent systems.

It was observed that the sorption, diffusion, and permeation results generally follow a systematic increase with increasing temperature. Activation parameters were estimated from the Arrhenius relationship:

$$X = X_0 \exp(-E_X/RT) \quad (13)$$

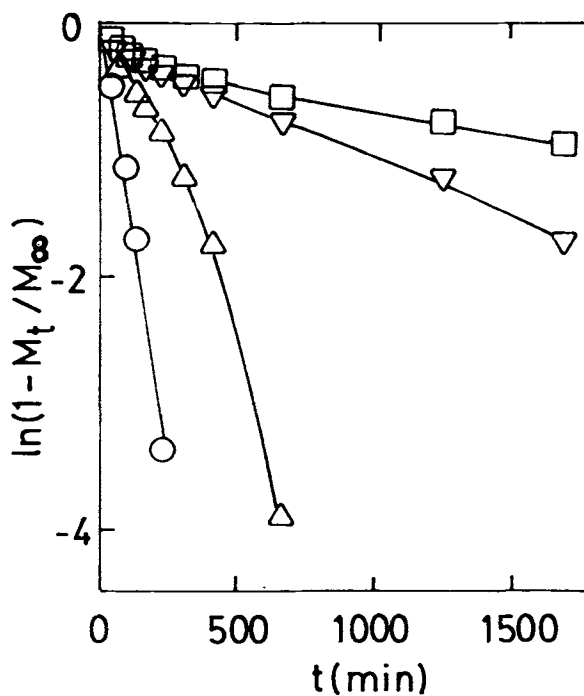


Figure 8 Plots of $\ln(1 - M_t/M_\infty)$ vs. t for VITONs with DMSO at 25°C. Symbols for polymers are the same as in Figure 1.

Table V Diffusion Coefficients ($D \times 10^8 \text{ cm}^2 \text{ s}^{-1}$) Calculated from Eq. (10)

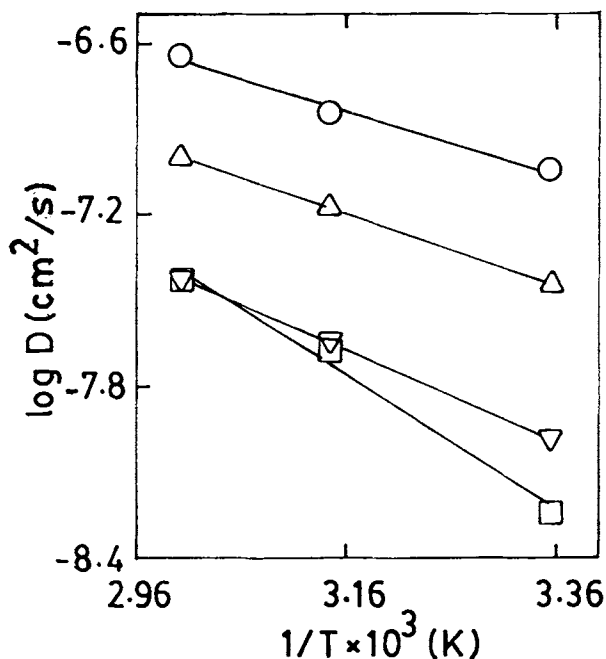
Temp (°C)	Samples			
	5507	5508	5509	5510
<u>DMSO</u>				
25	02.09	02.96	00.38	00.02
45	10.80	09.23	02.09	01.73
60	11.28	17.06	03.66	02.71
<u>Dioxane</u>				
25	05.96	04.62	04.03	04.31
45	10.11	16.93	16.19	15.88
60	07.16	10.75	20.63	20.61
<u>Toluene</u>				
25	00.40	00.32	00.01	00.10
45	04.77	02.97	01.72	01.48
60	06.57	02.84	02.34	02.17

where X represents the property under question, viz., D , P , or S ; X_0 , the preexponential parameter; and E_X , the activation parameter, namely, E_D for diffusion, E_P for permeation, and ΔH_S for the heat of sorption. A typical plot of the dependence of $\log D$ versus $1/T$, shown in Figure 9, displays the applicability of the Arrhenius relationship.

The estimated values of E_D , E_P , and ΔH_S along with the percent swelling data, $\Delta V\%$, are given in Table VI. The activation parameter values do not show any systematic dependence on the size of the liquids, but these values do seem to depend on the nature of liquids and polymer samples. The results of $\Delta V\%$ for the liquids with the membrane materials vary as dioxane > DMSO > toluene. The volume swelling data for dioxane are much higher ($\sim 112\%$) than those observed for other liquids. The positive values of ΔH_S are suggestive of the endothermic contribution to the sorption process as manifested by the Henry's law mode.

CONCLUSIONS

It is anticipated that the four fluoroelastomers used in this study may have applications in the containment of solvents used for sampling isocyanates generated during spray-painting operations. In such operations, the membranes used will come into contact with such solvents as DMSO, dioxane, and toluene. The resistivity of these membranes to such

**Figure 9** Arrhenius plots of $\log D$ vs. $1/T$ for VITONs with DMSO. Symbols for VITONs are the same as in Figure 1.

liquids is of utmost importance to ensure full sample recoveries. The membranes must also exhibit efficient air-flow characteristics. Preliminary experi-

Table VI Activation Energies (kJ/mol) for Diffusion, E_D , Permeation, E_P , and Enthalpy of Sorption, ΔH_S , and Increase in Volume, $\Delta V\%$

Parameters	Samples			
	5507	5508	5509	5510
<u>DMSO</u>				
E_D	21.74	24.29	30.56	44.92
E_P	26.13	26.66	34.33	48.97
ΔH_S	4.40	2.37	3.76	4.05
$\Delta V\%$	76.46	46.19	25.44	24.56
<u>Dioxane</u>				
E_D	35.56	29.50	32.58	30.97
E_P	35.87	2.76	37.83	34.16
ΔH_S	0.33	3.26	5.25	3.19
$\Delta V\%$	112.22	73.53	42.54	53.01
<u>Toluene</u>				
E_D	32.83	37.84	2.52	52.22
E_P	37.18	43.60	58.86	61.82
ΔH_S	4.34	5.78	6.32	9.63
$\Delta V\%$	20.01	13.19	10.88	6.84

ments with these membranes indicate poor air-flow rates because of their thickness. Currently, more prototype membranes are being fabricated with thinner dimensions and these will be tested in actual field studies in the near future. Of the four membranes tested, the VITON-5509 and VITON-5510 proved to be the best barrier materials for toluene.

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