

# Sorption and Migration of Aliphatic Organic Esters into VITON Fluoroelastomer Membranes

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**ABSTRACT:** Sorption and migration of six aliphatic esters into four VITON fluoroelastomers were studied by a gravimetric sorption method in the temperature interval of 30–60°C. Fick's equation was used to obtain diffusion coefficients. The dependence of fluorine contents and the polymer morphology on the sorption and diffusion characteristics of esters was investigated. The permeability coefficients were obtained from the sorption and diffusion data. Fick's equation was solved to compute the concentration profiles of liquids at various locations within the membrane materials using initial and boundary conditions. These profiles were compared with those obtained from the numerical method based on finite difference technique. Activation parameters for diffusion and sorption were calculated using the Arrhenius relationship. These results were discussed in terms of molecular size and shapes of the esters. For higher esters, namely, *n*- and iso-amyl acetates, a concentration dependency of the diffusion coefficient was investigated. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1223–1235, 1997

**Key words:** VITON fluoroelastomer; esters; membranes; sorption

## INTRODUCTION

Sorption kinetics and migration of organic liquids into high-performance engineering polymer membranes has been the subject of continuous interest in our laboratories,<sup>1–10</sup> due to their widespread application in a variety of areas such as food packaging,<sup>11</sup> reverse osmosis,<sup>12</sup> pervaporation,<sup>13</sup> ultrafiltration,<sup>14</sup> electro dialysis,<sup>15</sup> hazardous chemical pond lining,<sup>16–19</sup> etc. Fluorinated elastomers are a class of synthetic elastomers that are designed for demanding service applications in environments where extremes in temperature and requirements for chemical resistance are encountered. They are also used in seals for the oil field, and in the chemical processing, pollution

control, and aerospace industries.<sup>20</sup> Their superior thermal and chemical stability compared to other well-established hydrocarbon elastomers is attributed to the very high strength of the carbon—fluorine (C—F) bond.<sup>21</sup> The carbon—carbon (C—C) bond distance is 1.54 Å, whereas that of the C—F bond is 1.32 Å. The C—F bonds are also extremely stable as evidenced by their high heat of formation. For instance, the bond energy of C—F is 116 kcal mol<sup>-1</sup> whereas that of the C—C bond is 83 kcal mol<sup>-1</sup>.

VITONs are known to be resistant to oils, fuels, lubricants, most mineral acids, hydraulic fluids, and aliphatic and aromatic hydrocarbons that act as solvents for other commercial rubbers. The polymers remain tough and elastic indefinitely when exposed to oil, even up to 150°C. However, the resistivity of VITON polymers to the presence of esters has not been studied in detail. This

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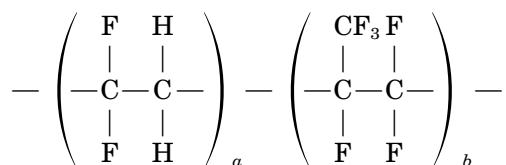
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prompted us to undertake a detailed investigation of the interaction of these membranes with methyl acetate, ethyl acetate, *n*-propyl acetate, *n*-butyl acetate, *n*-amyl acetate, and iso-amyl acetate. Sorption experiments were carried out with four different fluoropolymers over the temperature interval of 30–60°C. The diffusion coefficients and related parameters were obtained. The first-order kinetic equation was used to analyze the sorption data. Arrhenius parameters have been estimated, and the results are discussed in terms of the nature of polymer-solvent interactions.

## EXPERIMENTAL

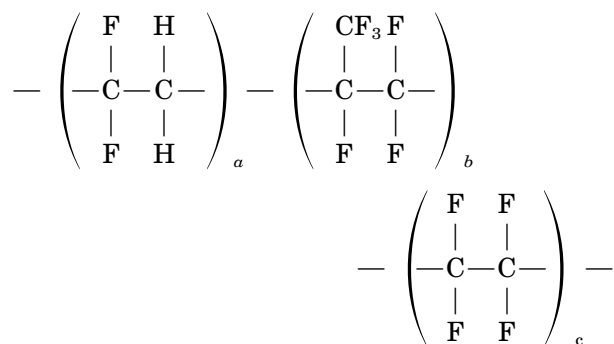
### Materials

There are three major VITON fluoropolymers, viz., A, B, and F developed by Du Pont. The A-type family belongs to a copolymer of vinylidene fluoride (VF<sub>2</sub>) and hexafluoropropylene (HFP) with a 66% fluorine content designated as Sample #1360 having the following structure:



where *a* and *b* represent the degree of polymerization for each homopolymer. The weight average molar mass,  $\bar{M}_w$  of the polymer is  $185.6 \times 10^3$ . The Mooney viscosity as measured by ML 1 + 10 at 121°C by the ASTM D1646 method is 22. However, the exact composition of the monomers is proprietary information.

The B- and F-type families belong to the terpolymers obtained from various combinations of VF<sub>2</sub>, HFP, and tetrafluoroethylene (TFE) with the following structure:



where the subscripts *a*, *b*, and *c* are the degree of polymerization of each of the monomers. Three samples have been used in this category, viz., VITON B200 with a fluorine content of 68% (Sample #1361), VITON GF with 70% fluorine (Sample #1362), and VITON GFLT with 67% fluorine (Sample #1363). Among these, VITON GF (Sample #1362) contained a cure-site monomer such as bromoperfluoropropylene (BPPF) in addition to VF<sub>2</sub>, HFP, and TFE moieties. For Sample #1361, the Mooney viscosity and  $\bar{M}_w$  values are 65 and 261100, respectively. For Samples #1362 and #1363, the Mooney viscosities are respectively, 60 and 67, while their respective  $\bar{M}_w$  values are 246900 and 370500.

These fluoropolymers are prepared by fairly similar manufacturing processes consisting of emulsion polymerization. However, a small variation in the polymerization conditions can result in polymers of the same type which are not identical in molar mass averages. As a matter of fact, Mooney viscosity values are related to the molar mass of the polymers. VITON fluoropolymers and products based on them present no health hazards. However, certain hazards may arise during the compounding and processing of raw polymers into finished products or during service at temperatures above 200°C. For example, toxic vapors, including hydrogen fluoride, are evolved at temperatures above 200°C; therefore experiments should be conducted under hoods. The four elastomers used in this research were obtained in sheets with dimensions of 15 × 15 cm and thicknesses ranging from 0.07–0.095 cm. The mix compositions and some of the useful engineering properties are given in Table I.

### Reagents

Ethyl acetate (Fischer, India), *n*-propyl acetate (Merck, Germany), *n*-butyl acetate (Sisco, India), *n*-amyl acetate (Merck, Germany), and iso-amyl acetate (Ranbaxy Laboratories Ltd., India) were double-distilled before use, whereas methyl acetate (Sisco, India) was used directly. The structure and molar volumes of these solvents are given in Table II.

The polymer samples were cut into uniform-size circular pieces (diameter = 1.96 cm) using a specially designed sharp-edged steel die and dried overnight in a vacuum oven at 25°C before use. The thickness, *h*, of the samples was measured at several points using a micrometer screw gauge within the precision of ±0.001 cm. The average value was considered in all calculations.

**Table I Elastomer Compositions and Representative Properties**

	Elastomer Sample			
	1360	1361	1362	1363
VITON A-200	97.5	—	—	—
VITON VT-R-6480	—	97.2	—	—
VITON GF	—	—	100	—
VITON GFLT	—	—	—	100
Fluorine content (%)	66	68	70	67
VITON Curative #20	—	0.5	—	—
VITON Curative #50	2.5	2.3	—	—
Magnalite D <sup>a</sup>	3	3	—	—
Calcium hydroxide	6	6	—	—
N-990 Black	30	30	—	—
Carnauba wax	1	1	1	1
RC-R-6156	—	—	0.2	0.2
DIAK #8	—	—	1	1
Lupercol 101XL <sup>b</sup>	—	—	4	4
Specific gravity	1.82	1.82	1.91	1.89
Compression set (%), 70 h/200°C	22	45	34	34
Brittle point, °C	-19.2	-21.4	-36.4	-35.3
TR-10, °C	-15.8	-12.8	-5.2	-24.3
DSC, °C				
mid point	-15.9	-11.7	-3.7	-21.7
end point	-11.4	-9.4	0.2	-19.3
Thickness (cm)	0.085	0.078	0.092	0.085

<sup>a</sup> High-activity magnesium oxide.

<sup>b</sup> An organic peroxide [2,5-dimethyl-2,5-bis(*t*-butyl peroxy)hexane].

### Sorption Experiments

Sorption experiments were performed on circularly-cut polymer samples by immersing them in screw-tight test bottles containing 15–20 mL of the test solvent maintained at the desired temperature in an electronically controlled incubator (WTB Binder, Tuttlingen, Germany, Model: BD-53). Samples were removed periodically, and the surface-adhered solvent drops were wiped off using filter paper wraps and then weighed immediately on a digital Mettler balance, Model AE 240

(Switzerland), within the precision of  $\pm 0.01$  mg. Other experimental details are the same as given earlier.<sup>1–10</sup>

When the samples attained equilibrium saturation, no more weight gain was observed and this did not change significantly over an extended period of one or two days. The mol % weight gain,  $M_t$  during solvent sorption was calculated as

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

**Table II Solvent Properties of Esters at 25°C**

Ester	Structure	Molar volume (cm <sup>3</sup> mol <sup>-1</sup> )	Solubility parameter (cal cm <sup>-3</sup> ) <sup>1/2</sup>
Methyl acetate	CH <sub>3</sub> COOCH <sub>3</sub>	79.8	9.6
Ethyl acetate	CH <sub>3</sub> CH <sub>2</sub> COOCH <sub>3</sub>	98.5	9.1
<i>n</i> -Propyl acetate	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> COOCH <sub>3</sub>	115.7	8.8
<i>n</i> -Butyl acetate	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> COOCH <sub>3</sub>	132.6	8.5
<i>n</i> -Amyl acetate	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> COOCH <sub>3</sub>	147.9	<sup>a</sup>
Iso-amyl acetate	(CH <sub>3</sub> ) <sub>2</sub> CH(CH <sub>2</sub> ) <sub>2</sub> COOCH <sub>3</sub>	150.4	<sup>a</sup>

<sup>a</sup> Not available.

where  $W_0$  is the initial dry weight of the sample,  $W_t$  is the weight of the sample at time  $t$ , and  $M$  is molecular weight of the solvent. This way of expressing mol % concentration was found to be more convenient for comparing sorption by different liquids than were the weight percent results.

## RESULTS AND DISCUSSION

### Sorption Kinetics

To investigate the mechanism of solvent transport within the membrane material, sorption results have been fitted to the equation<sup>22,23</sup>

$$\frac{M_t}{M_\infty} = Kt^n \quad (2)$$

where  $K$  is a constant which depends on the structural characteristics of the polymer in addition to its interaction with the solvent;  $M_t$  and  $M_\infty$  are the mol % uptake values at time  $t$  and at equilibrium time,  $t_\infty$ . The value of the exponent,  $n$ , indicates the type of the transport mechanism. A value of  $n$  of 0.50 implies Fickian transport; a value of  $n$  of 1.00 implies non-Fickian transport; and for values of  $n$  of  $0.50 < n < 1.00$ , anomalous transport is observed.

From the least-squares analysis, the values of  $n$  and  $K$  have been estimated and these are listed in Table III. For the majority of cases, the values of  $n$  vary between 0.53 and 0.86, suggesting the transport mechanism to be of an anomalous type. However, no systematic dependence of  $n$  on temperature is observed. On the other hand,  $K$  shows a systematic trend with the size of esters and temperature. For instance,  $K$  decreases with an increase in molar volume from methyl acetate to  $n$ -amyl acetate. Also, with increasing temperature, the values of  $K$  increase, suggesting increased polymer segmental interactions with the esters. However, we could not observe any systematic variations in the  $K$  values with any of the VITONS.

Sorption plots, i.e., mol % uptake,  $M_t$ , versus square root time,  $t^{1/2}$ , for methyl acetate and ethyl acetate with all the VITON samples (#1360, #1361, #1362, and #1363) at 30°C are presented in Figure 1. Sorption shows a dependence on both the morphological set-up of VITONS, as well as the amount of fluorine in the polymer. VITON Sample #1360, with a somewhat loose network copolymer structure (66% F) exhibits the highest sorption; whereas the terpolymer VITON Sample

#1362 (70% F), due to its rigid nature, exhibits the lowest sorption for both methyl and ethyl acetates. The shapes of the sorption curves show the Fickian transport trends. VITON Samples #1361 and #1363 with fluorine contents of 68% and 67%, respectively, exhibit intermediary sorption values between those of Samples #1360 and #1362. However, the sorption of Sample #1361 (68% F) is higher than that of Sample #1363 (67% F) because of the large difference in the molar masses of these polymers. The latter polymer has a higher molar mass ( $\bar{M}_w = 370500$ ), thereby restricting the transport of esters when compared to the matrix structure with a lower molar mass (261100).

Figure 2 presents the sorption plots of  $n$ -propyl acetate,  $n$ -butyl acetate,  $n$ -amyl acetate, and iso-amyl acetate for all the VITONS at 30°C. The sorption values of these liquids vary as:  $n$ -propyl acetate >  $n$ -butyl acetate > iso-amyl acetate >  $n$ -amyl acetate. The trends in the shapes of the sorption curves are also different depending on the nature of esters, as well as the barrier polymers. For instance, with  $n$ -propyl acetate and  $n$ -butyl acetate, a Fickian transport is observed. The  $n$ - and iso-amyl acetates exhibit more sigmoidal trends for  $n$ -propyl acetate and  $n$ -butyl acetate. This suggests that, for  $n$ - and iso-amyl acetates, sorption deviates slightly from the Fickian trend. This may be due to a concentration dependency of diffusivity for these liquids. However, the patterns in the variations of sorption curves with  $n$ -propyl acetate,  $n$ -butyl acetate, and iso-amyl acetate with respect to the four VITONS tested remain almost identical. In general, for all the esters, sorption values for different membranes vary as: Sample #1360 (66% fluorine) > Sample #1361 (68% fluorine) > Sample #1363 (67% fluorine) > Sample #1362 (70% fluorine), a trend which does not strictly vary with the fluorine contents of the polymer. Thus, the morphology of the polymer network structure, molar mass, Mooney viscosity, backbone structure, etc., also play a significant role.

A decrease in sorption with increasing size of the esters may be due to the fact that smaller esters occupy less volume and transport more quickly than the larger ones.<sup>24,25</sup> Thus, sorption is governed by the differences in the size and shape of the penetrant molecules. Additionally, the type of the polymer and the shape of the penetrant molecule will also influence the equilibrium sorption data. In any case, solvent transport and polymer segmental movements are intimately related when the polymer swells from its unperturbed state to the solvated state. The increased

**Table III** Estimated Values of  $n$  and  $K$  ( $\text{g/g min}^n$ ) from Eq. (2) for VITON + Ester Systems at Different Temperatures

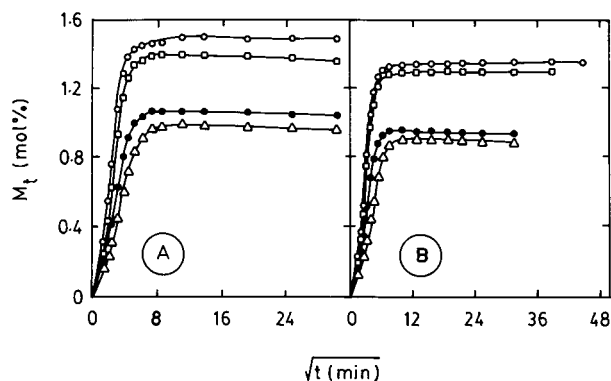
Fluoropolymer Sample	$K \times 10^3$			$n$		
	30°C	45°C	60°C	30°C	45°C	60°C
Methyl Acetate						
1360	11.73	15.49	<sup>a</sup>	0.81	0.77	<sup>a</sup>
1361	9.45	13.71	<sup>a</sup>	0.86	0.77	<sup>a</sup>
1362	9.76	11.73	<sup>a</sup>	0.65	0.64	<sup>a</sup>
1363	12.08	15.17	<sup>a</sup>	0.65	0.69	<sup>a</sup>
Ethyl Acetate						
1360	9.65	12.54	14.45	0.76	0.78	0.74
1361	8.68	10.86	9.99	0.79	0.74	0.79
1362	8.06	9.80	11.07	0.64	0.66	0.65
1363	10.49	14.02	13.47	0.70	0.69	0.67
<i>n</i> -Propyl Acetate						
1360	7.13	8.59	11.08	0.78	0.74	0.77
1361	7.05	9.05	8.38	0.78	0.74	0.81
1362	6.52	7.50	9.50	0.63	0.67	0.68
1363	7.70	9.19	11.06	0.64	0.69	0.66
<i>n</i> -Butyl Acetate						
1360	5.71	6.69	8.76	0.75	0.75	0.73
1361	5.96	6.92	8.57	0.72	0.75	0.72
1362	5.11	6.99	7.35	0.62	0.60	0.63
1363	5.96	8.06	9.03	0.66	0.66	0.65
<i>n</i> -Amyl Acetate						
1360	4.15	4.74	6.53	0.67	0.67	0.67
1361	5.00	5.50	6.63	0.61	0.61	0.65
1362	4.72	6.71	6.76	0.54	0.58	0.55
1363	6.02	7.06	8.01	0.57	0.55	0.59
Iso-amyl Acetate						
1360	5.61	7.31	8.65	0.76	0.75	0.71
1361	5.79	7.02	8.73	0.70	0.73	0.73
1362	5.25	6.60	8.55	0.60	0.60	0.61
1363	6.78	8.59	9.78	0.65	0.65	0.67

<sup>a</sup> Data not obtained due to its low boiling point.

chain mobility due to swelling allows the chain extension, resulting in additional free volume and thus facilitating the solvent transport. This is a dynamic relaxation phenomenon that affects the molecular transport of solvent molecules into the polymer matrix.

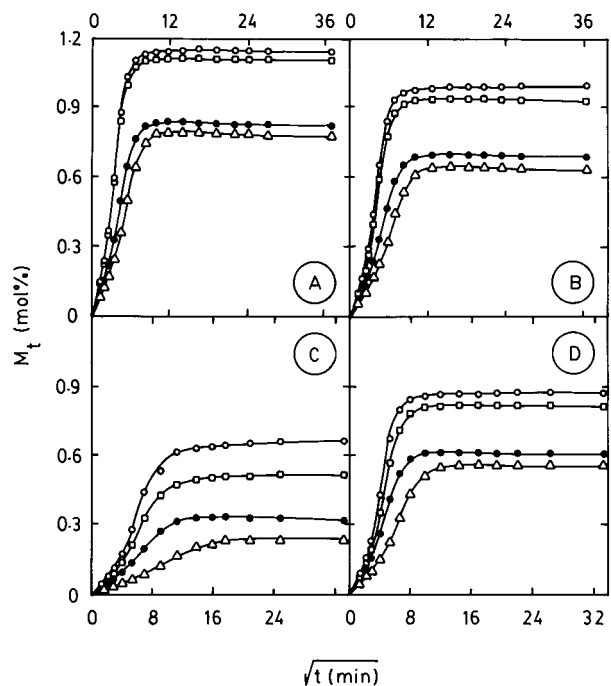
Typical temperature-dependent sorption plots of VITON Sample #1360 with ethyl acetate, *n*-propyl acetate, *n*-butyl acetate, and *n*-amyl acetate are shown in Figure 3. The sorption data

given in Table IV indicate that, for many systems, the sorption values decrease with increasing temperature. The percent volume swell data are also included in Table IV. The volume swells of the membranes show a decrease with increasing weight percent of fluorine in the polymer. The % volume swell in the same compound also decreases with increasing temperature as shown in Figure 4 for ethyl acetate, *n*-propyl acetate, *n*-butyl acetate, and *n*-amyl acetate. These observa-

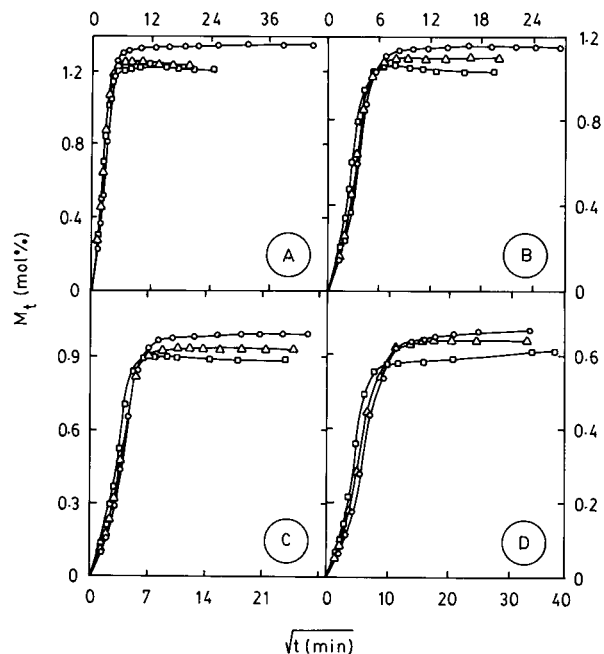


**Figure 1** Mol % sorption ( $M_t$ ) versus square root of time ( $t^{1/2}$ ) at 30°C for (A) methyl acetate and (B) ethyl acetate with fluoroelastomers. Symbols for fluoropolymer samples (○) #1360; (□) #1361; (△) #1362; (●) #1363.

tions may be the result of the fact that the VF<sub>2</sub> homopolymer has a low glass transition ( $T_g = -40^\circ\text{C}$ ) of elastomeric behavior which tends to crystallize while its hydrocarbon portion tends to swell in fluids. On the other hand, HFP breaks up crystallinity to obtain elastomeric behavior, as its homopolymer has a  $T_g$  of 165°C. On the other hand, TFE with its homopolymer  $T_g$  of 127°C ex-



**Figure 2** Mol % sorption ( $M_t$ ) versus square root of time ( $t^{1/2}$ ) at 30°C for (A) *n*-propyl acetate, (B) *n*-butyl acetate, (C) *n*-amyl acetate, and (D) iso-amyl acetate with fluoroelastomers. Symbols for fluoropolymers have the same meaning as in Figure 1.



**Figure 3** Temperature dependence of sorption for elastomer Sample #1360 with (A) ethyl acetate, (B) *n*-propyl acetate, (C) *n*-butyl acetate and (D) *n*-amyl acetate at (○) 30°C, (△) 45°C, and (□) 60°C.

erts a moderate effect on its  $T_g$  thereby increasing its chain stiffness and its ability towards induced crystallization. Although a quantitative study of this effect is not possible at this time, such anomalies have been discussed in the literature.<sup>26</sup>

It may be interesting to comment on the speed to reach equilibrium sorption. With VITON Sample #1360, the attainment of sorption equilibrium is much faster than all the other VITON samples. For VITON Sample #1362, the speed to attain equilibrium is much smaller. VITON Samples #1361 and #1363 exhibit intermediate values. This information may be useful to field engineers and technicians for a better selection of the polymers for varied applications in differing solvent media.

As has been suggested earlier,<sup>27</sup> solvent migration into rubbery polymers can be studied using the first-order kinetic equation to estimate the first-order rate constant,  $k'$  as

$$k't = \ln[M_\infty / (M_\infty - M_t)] \quad (3)$$

These results are given in Table V. For all the VITON-ester systems except ethyl acetate and *n*-propyl acetate, the rate constants vary according to the sequence: Sample #1362 < Sample #1363 < Sample #1361 < Sample #1360. Addi-

**Table IV Sorption Coefficients ( $S$ , mol %) and Percent Volume Swell ( $V_s$ ) for Fluorelastomer + Ester Systems at Different Temperatures**

Fluoropolymer Sample	$S$			$V_s$		
	30°C	45°C	60°C	30°C	45°C	60°C
Methyl Acetate						
1360	1.493	1.411	<sup>a</sup>	193	166	<sup>a</sup>
1361	1.391	1.349	<sup>a</sup>	176	157	<sup>a</sup>
1362	0.984	0.971	<sup>a</sup>	133	148	<sup>a</sup>
1363	1.065	1.049	<sup>a</sup>	149	132	<sup>a</sup>
Ethyl Acetate						
1360	1.352	1.256	1.247	213	200	180
1361	1.297	1.221	1.218	199	189	174
1362	0.901	0.899	0.881	170	153	147
1363	0.953	0.939	0.929	157	150	143
<i>n</i> -Propyl Acetate						
1360	1.153	1.099	1.065	217	208	197
1361	1.115	1.077	1.048	213	204	181
1362	0.792	0.764	0.741	159	154	150
1363	0.835	0.804	0.790	169	163	154
<i>n</i> -Butyl Acetate						
1360	0.996	0.935	0.900	230	215	194
1361	0.937	0.891	0.858	215	205	180
1362	0.644	0.603	0.588	165	152	132
1363	0.697	0.666	0.646	170	159	145
<i>n</i> -Amyl Acetate						
1360	0.664	0.638	0.609	170	160	149
1361	0.522	0.518	0.515	132	130	137
1362	0.239	0.230	0.246	68	67	64
1363	0.334	0.334	0.336	92	91	82
Iso-amyl Acetate						
1360	0.877	0.834	0.779	230	208	195
1361	0.821	0.786	0.740	200	202	178
1362	0.561	0.532	0.506	146	146	126
1363	0.614	0.588	0.565	169	146	134

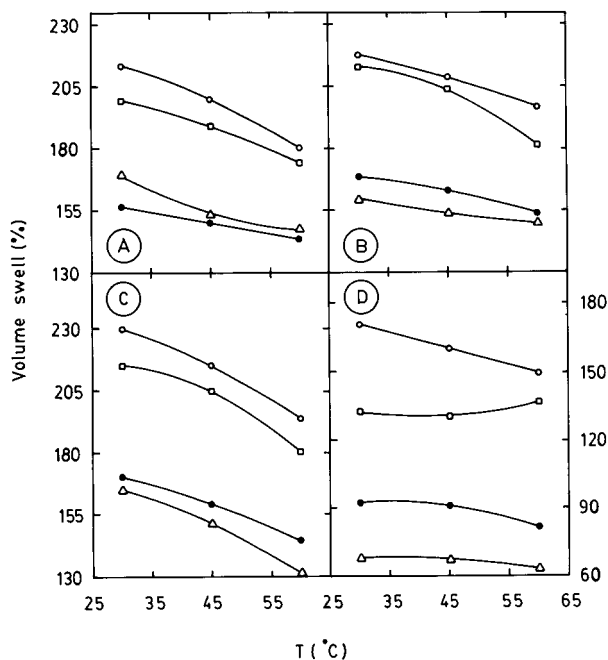
<sup>a</sup> Data not obtained due to its low boiling point.

tional support to justify the use of the first-order sorption kinetics comes from other published reports. For instance, Smith and Fisher<sup>28</sup> related the solvent uptake data to diffusivity, whereas the effect of membrane porosity on sorption kinetics has been studied by Poinescu et al.<sup>29</sup> Similarly, Blow<sup>30</sup> suggested that the mechanism of swelling follows first-order kinetics.

### Computation of Diffusion Coefficients and Concentration Profiles

In order to calculate diffusion coefficients, Fick's equation was solved under suitable initial and boundary conditions using the following assumptions.

1. Sorption occurs under transient conditions with a constant diffusion coefficient.



**Figure 4** Volume % swell ( $V_s$ ) versus temperature ( $T$  in  $^{\circ}\text{C}$ ) for (A) ethyl acetate, (B)  $n$ -propyl acetate, (C)  $n$ -butyl acetate, and (D)  $n$ -amyl acetate with fluoropolymers. Symbols for fluoropolymers have the same meaning as in Figure 1.

- Solvent migration into membranes is considered unidirectional.
- Concentration on membrane surface reaches equilibrium immediately upon exposure to the liquid.
- Dimensional changes of the membrane are considered to be negligibly small during sorption.
- Time required for the membrane to reach thermal equilibrium is negligible when compared to times of solvent migration.
- Solvent migration through the edges of the polymer membrane is considered to be negligible.

The unidirectional diffusion is described by Fick's second law for a constant diffusivity as<sup>31</sup>

$$\frac{\partial C}{\partial t} = \left( D \frac{\partial^2 C}{\partial x^2} \right) \quad (4)$$

where  $C$  is liquid concentration within the membrane material at time  $t$  and distance  $x$ . Under the initial and boundary conditions,

$$t = 0 \quad 0 < x < h \quad C = 0 \quad (5)$$

$$t > 0 \quad x = 0, x = h \quad C = C_{\infty} \quad (6)$$

Equation (4) has been solved for liquid concentration profiles  $C_{(t,x)}/C_{\infty}$  into polymer membrane of thickness  $h$ , at time  $t$  and distance  $x$ , to give<sup>32</sup>

$$\frac{C_{(t,x)}}{C_{\infty}} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{1}{(2n+1)} \times \exp \left[ - \frac{D(2n+1)^2 \pi^2}{h^2} t \right] \times \sin \left[ \frac{(2n+1)\pi}{h} x \right] \quad (7)$$

where  $C_{(t,x)}$  and  $C_{\infty}$  are the sorbed liquid concentrations at time  $t$  and distance  $x$  and at equilibrium, respectively;  $D$  is the diffusion coefficient; and  $n$  is an integer.

The amount of liquid sorbed by the polymer membrane is given by<sup>31</sup>

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

The values of concentration-independent  $D$  have been calculated from the initial slope of the linear portions of sorption curves before 55% of sorption equilibrium.

$$\frac{M_t}{M_{\infty}} = \frac{4}{h} \left( \frac{Dt}{\pi} \right)^{1/2} \quad (9)$$

The calculated values of  $D$  that are accurate to  $\pm 0.01$  units of diffusivity are presented in Table V. Included in the same table are also the values of permeability coefficients,  $P$  calculated as:  $P = D \cdot S$ .

From the results given in Table V, it is observed that with increase in temperature, the values of  $D$  also increase. For methyl acetate, due to its high volatility, the upper limit of temperature studied was  $45^{\circ}\text{C}$ . However, in the absence of any chemical interactions between the polymer membrane and solvents, diffusion coefficients should generally decrease with the increasing size of penetrants. This is indeed the case from methyl acetate to  $n$ -amyl acetate at all temperatures and



**Table V Diffusion Coefficient, Permeation Coefficient, and Kinetic Rate Constants for Fluoroelastomer + Ester Systems at Different Temperatures**

Elastomer Sample	<i>D</i>			<i>P</i>			<i>k'</i>		
	30°C	45°C	60°C	30°C	45°C	60°C	30°C	45°C	60°C
Methyl Acetate									
1360	17.14	20.68	<sup>a</sup>	18.95	21.61	<sup>a</sup>	11.74	14.49	<sup>a</sup>
1361	13.60	17.48	<sup>a</sup>	14.01	17.46	<sup>a</sup>	9.96	12.80	<sup>a</sup>
1362	7.84	9.74	<sup>a</sup>	5.71	7.01	<sup>a</sup>	5.22	6.52	<sup>a</sup>
1363	9.56	15.57	<sup>a</sup>	7.54	12.10	<sup>a</sup>	7.01	11.38	<sup>a</sup>
Ethyl Acetate									
1360	9.27	13.94	15.70	11.04	13.64	17.25	7.58	11.79	11.94
1361	7.56	11.05	18.89	8.64	11.89	20.28	7.14	8.34	14.22
1362	5.76	7.59	9.27	4.58	6.01	7.20	3.98	5.45	6.21
1363	10.03	12.15	13.83	8.42	10.03	11.32	7.34	10.26	9.02
<i>n</i> -Propyl Acetate									
1360	7.66	8.10	11.43	9.02	9.08	12.43	5.91	6.14	9.45
1361	6.76	7.57	9.51	7.69	8.32	10.18	5.98	6.59	7.47
1362	3.52	5.51	7.09	2.85	4.30	5.36	2.72	4.03	5.70
1363	4.85	7.97	8.61	4.14	6.54	6.94	3.65	5.72	6.61
<i>n</i> -Butyl Acetate									
1360	4.23	6.51	7.58	4.89	7.07	6.88	3.93	4.91	6.08
1361	3.49	5.73	6.46	3.80	5.94	6.24	3.66	5.17	5.71
1362	2.31	2.51	3.80	1.73	1.76	2.59	1.82	2.54	3.12
1363	3.57	4.98	5.64	2.89	3.85	4.24	2.67	4.15	4.72
<i>n</i> -Amyl Acetate									
1360	1.88	2.41	3.09	1.62	2.00	2.45	1.79	2.20	3.29
1361	1.38	1.68	3.15	0.94	1.13	2.11	1.67	1.96	3.03
1362	0.99	1.06	2.20	0.31	0.32	0.71	0.82	1.00	1.72
1363	1.56	1.87	3.30	0.68	0.81	1.44	1.63	1.92	2.93
Iso-amyl Acetate									
1360	4.68	6.62	7.62	5.35	7.18	8.72	4.08	5.42	5.56
1361	3.43	5.04	6.20	3.67	5.15	5.97	3.27	4.65	5.91
1362	1.88	2.84	4.01	1.37	1.97	2.65	1.64	2.35	3.66
1363	3.36	4.72	7.65	2.69	3.61	5.62	3.16	4.27	5.89

<sup>a</sup> Data not obtained due to its low boiling point.

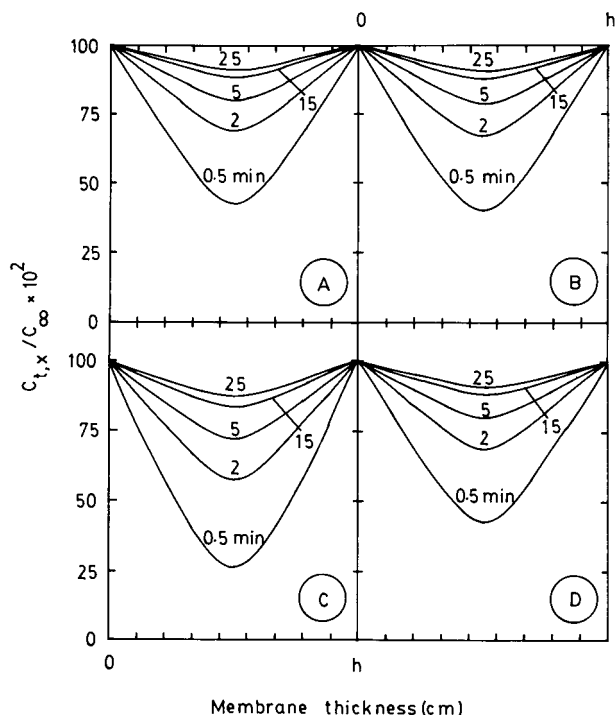
Diffusion coefficient ( $D \times 10^7$ , cm<sup>2</sup> s<sup>-1</sup>), permeation coefficient ( $P \times 10^7$ , cm<sup>2</sup> s<sup>-1</sup>), kinetic rate constants ( $k' \times 10^2$ , min<sup>-1</sup>).

for all the VITONs. The same dependency is also observed for the kinetic rate constants,  $k'$  and permeability coefficients given in Table V. However, the structurally different iso-amyl acetate shows higher values of  $D$ ,  $P$ , and  $k'$  than  $n$ -amyl acetate for all the VITONs and at all the temperatures. Such a dependency is expected due to the fact that at longer sorption times, the term  $n \geq 1$

as well as  $\ln(8/\pi^2)$  in eq. (8), can be ignored to give

$$\ln\left(\frac{M_\infty}{M_\infty - M_t}\right) \cong \frac{\pi^2 D t}{h^2} \quad (10)$$

so that upon comparison with eq. (3), we get



**Figure 5** Profiles of concentration of ethyl acetate calculated from eq. (7) at different depths of fluoropolymer membrane samples (A) #1360; (B) #1361, (C) #1362, and (D) #1363 for different times at 30°C.

$$k = \frac{\pi^2 D}{h^2} \tag{11}$$

Thus, according to eq. (11),  $k'$  is directly related to  $D$ ; hence the variations in  $k'$  values are similar to those of  $D$ .

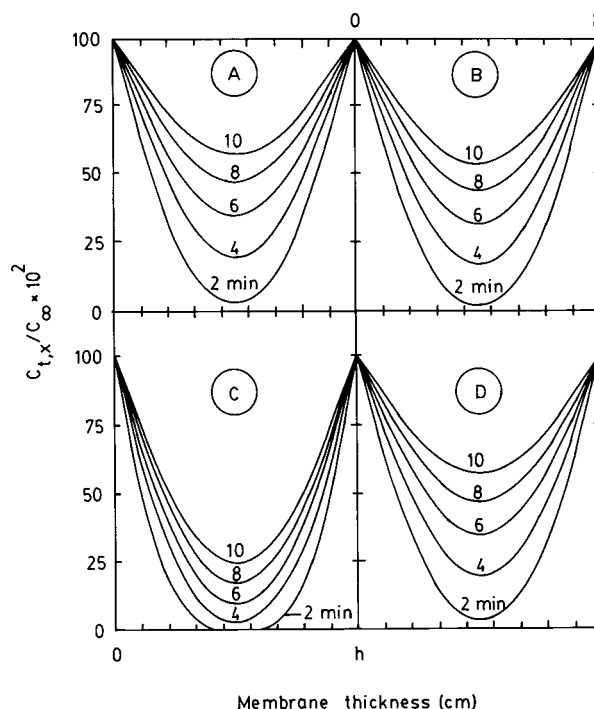
**Computation of Concentration Profiles Using Numerical Method**

A numerical method was also used to simulate the concentration profiles of liquids into polymeric membranes.<sup>32</sup> The computed values of liquid concentration profiles at various time intervals for different depths of the membrane material are obtained using the relation

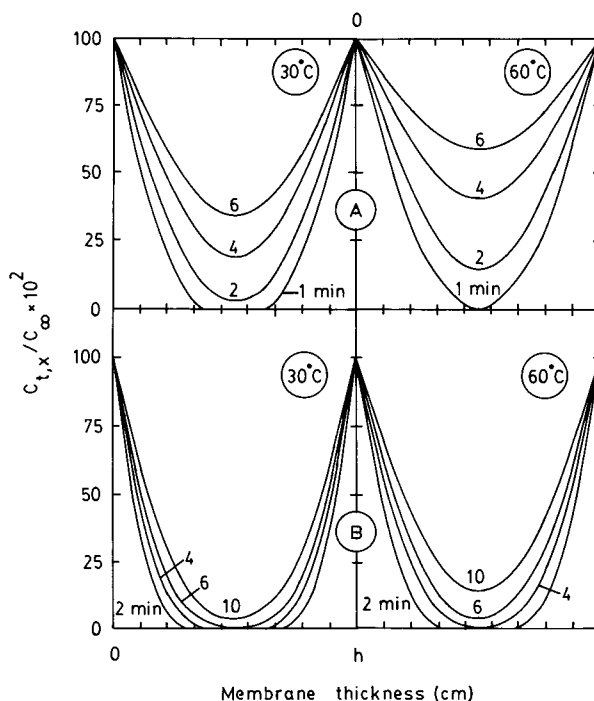
$$CN_m = \frac{1}{M_m} [C_{m-1} + (M_m - 2)C_m + C_{m+1}] \tag{12}$$

where the dimensionless parameter,  $M_m$  is defined as

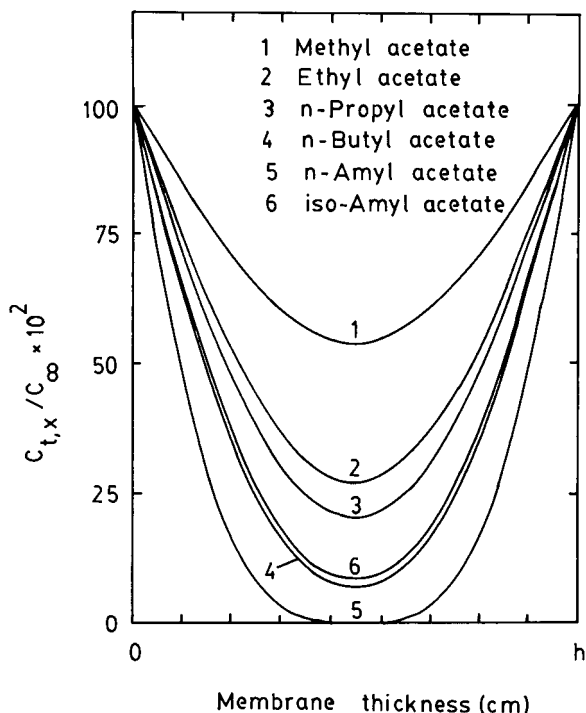
$$M_m = \frac{(\Delta x)^2}{\Delta t} \frac{1}{D} \tag{13}$$



**Figure 6** Profiles of concentration of ethyl acetate calculated from numerical method, i.e., eq. (12), at different depths of fluoropolymer membrane samples (A) #1360; (B) #1361, (C) #1362, and (D) #1363 for different times at 30°C.



**Figure 7** Profiles of concentration of (A) ethyl acetate and (B) *n*-amyl acetate calculated from numerical method, i.e., eq. (12), for fluoropolymer Sample #1360 at different thicknesses at 30 and 60°C.



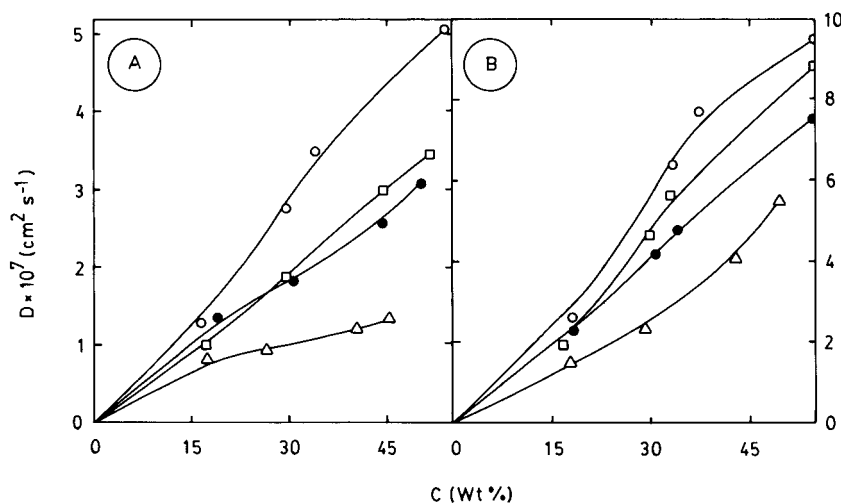
**Figure 8** Profiles of concentration of esters at different depths of elastomer membrane Sample #1360 at 30°C after 5 min.

In eq. (12), for computational purposes, the membrane thickness is divided into 10 slices of equal size,  $\Delta x$ . Each slice is characterized by the integer  $m$ .  $C_m$  and  $CN_m$  are concentrations at position  $m$ , at time  $t$  and after the lapse of time  $\Delta t$ , respectively. For each slice, the liquid concentration curves have been generated in the computer for

different time intervals. Numerical method is also solved for liquid transport in one dimension.

The concentration profiles calculated from eqs. (7) and (12) for ethyl acetate at 30°C are given in Figures 5 and 6, respectively. It is evident that sorption or liquid concentration profiles show a dependence on the morphology of the polymers. A comparison of the calculated concentration profiles using eq. (7) at 30°C and 60°C for *n*-amyl acetate (having low  $D$ ) and ethyl acetate (having high  $D$ ) are presented in Figure 7. The profiles at 30°C for the low-diffusing *n*-amyl acetate are more narrowly spaced than those observed at 60°C for the high-diffusing ethyl acetate. Thus, as the size of the ester increases, the concentration profiles become narrowly spaced, suggesting a slower diffusion of the bigger solvent molecules. The calculated concentration profiles from eq. (7) for different esters with VITON Sample #1360 at 30°C presented in Figure 8 suggest that these profiles follow the same trends as those given in Figures 1 and 2.

Realizing the fact that the sorption curves for *n*- and iso-amyl acetates show sigmoidal trends, efforts have been made to study the concentration dependency of diffusivity for these esters. Such plots, generated according to the procedure suggested earlier,<sup>26</sup> are presented in Figure 9 for *n*- and iso-amyl acetates with different polymer membranes. The same types of dependencies are also observed at higher temperatures (i.e., 45 and 60°C), but these curves are not presented in order to minimize the number of graphical presentations.



**Figure 9** Dependence of diffusion coefficient on concentration of (A) *n*-amyl acetate and (B) iso-amyl acetate at 30°C for different polymer membranes. Symbols have the same meaning as in Figure 1.

**Table VI** Activation Parameters  $E_D$ ,  $E_P$ , and  $\Delta H_S$  (all in  $\text{kJ mol}^{-1}$ ) for Fluoroelastomer + Ester Systems

Ester	Parameter	Fluoroelastomer Sample			
		1360	1361	1362	1363
Ethyl acetate	$E_D$	14.86	25.54	13.34	9.01
	$E_P$	12.46	23.77	12.69	8.30
	$-\Delta H_S$	2.28	1.78	0.62	0.71
<i>n</i> -Propyl acetate	$E_D$	11.07	9.49	19.67	16.24
	$E_P$	8.84	7.79	17.75	14.62
	$-\Delta H_S$	2.24	1.75	1.86	1.62
<i>n</i> -Butyl acetate	$E_D$	16.44	17.39	13.77	12.88
	$E_P$	9.72	14.05	11.13	10.80
	$-\Delta H_S$	2.85	2.48	2.56	2.08
<i>n</i> -Amyl acetate	$E_D$	13.90	22.89	22.04	20.78
	$E_P$	11.57	22.42	22.84	20.31
	$-\Delta H_S$	2.41	0.41	-0.77	0.47
Iso-amyl acetate	$E_D$	13.72	16.63	19.88	22.95
	$E_P$	13.71	13.69	17.03	20.54
	$-\Delta H_S$	3.31	2.97	2.85	2.41

### Arrhenius Parameters

The transport coefficients ( $D$ ,  $P$ , and  $S$ ) have shown an increase with temperature. Hence, the activation parameters for diffusion ( $E_D$ ), permeation ( $E_P$ ), and sorption ( $\Delta H_S$ ) have been calculated using the Arrhenius relationship

$$\log X = \log X_0 - E_X/2.303RT \quad (14)$$

where  $X$  represents  $D$ ,  $P$ , or  $S$  and  $E_X$  is  $E_D$ ,  $E_P$ , or  $\Delta H_S$ . The values of  $E_D$  and  $E_P$  as estimated from the Arrhenius plots of  $\log D$  or  $\log P$  versus  $1/T$  are compiled in Table VI. The values of  $E_D$  and  $E_P$  do not seem to bear any direct relationship to the size of the ester molecules. For all the systems, the values of  $\Delta H_S$  are negative, suggesting the presence of a Langmuir mode of sorption.

### CONCLUSIONS

Four du Pont VITON fluoropolymers have been studied with respect to their sorption and diffusion characteristics in the presence of aliphatic esters in the temperature interval of 30–60°C. In all the cases, sorption and migration exhibit the anomalous-type mechanism. However, during the early stages of migration, Fickian behavior was more prevalent; hence diffusion coefficients were calculated from Fick's relation. The dependence of transport coefficients on penetrant size and polymer morphology has been discussed. For the *n*- and iso-

amyl acetates, the dependence of diffusivity on concentration has been studied because the initial sorption curves exhibited the sigmoidal trends.

The gravimetric method used here may have practical applications in obtaining both kinetic and thermodynamic data from sorption experiments, especially when there is a need to evaluate or screen organic liquids as to their potential interactions with the polymer membranes. From the profiles of concentration, it is seen that (1) solvent concentration within the membrane increases with time and (2) liquid concentration increases as the distance from the center of the polymer to its face increases. That is, the solvent concentration at the face of the membrane is 100%, and it decreases steadily from the face to the center of the membrane. In general, the ester migration at infinite time,  $M_\infty$ , is a characteristic of the polymer in question and decreases in the order from Sample #1360 through Samples #1363, #1361, and #1362, respectively. The diffusion coefficients also increase in the same order.

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