

# Transport characteristics of fluoroelastomers by ketones and nitriles

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*(Received 15 April 1996; revised 2 July 1996)*

Solvent resistivity and diffusion of the 3M fluoroelastomers, viz. FC-2179 and FLS-2650 have been studied over the temperature interval of 30–60°C using a gravimetric sorption method. Fick's equation was used to calculate diffusion coefficients. The activation parameters for diffusion have been obtained from a temperature dependency of diffusion coefficients using the Arrhenius relationship. Concentration profiles of liquids at different penetration depths of the polymer samples for different times have been obtained both from an analytical solution of Fick's equation and by using a numerical method. Experimental sorption results and the computed quantities have been discussed in terms of the nature of the penetrant molecules and the morphology of the polymers. © 1997 Elsevier Science Ltd.

(Keywords: fluoroelastomers; Fickian; transport; diffusion)

## INTRODUCTION

Fluoroelastomers are the highly fluorinated synthetic polymers developed by 3M Chemical Company for long service applications under severe temperature and chemical exposure conditions<sup>1</sup>. Their composition and molecular weight are carefully controlled to combine easy processing with high mechanical strength, fuel and solvent resistivity in addition to their good thermal stability. Non-flammability and resistance to oxidation, ozone and weathering of the polymers make them useful in aerospace, automotive, pollution control and chemical industries. A large variety of fluoroelastomers under the trade name, Fluorel<sup>®</sup> have been developed and marketed by 3M. Amongst these, the Fluorel<sup>®</sup> FC-2179 and Fluorel<sup>®</sup> FLS-2650 polymers find widespread applications in engineering and industrial areas. The FC-2179 is a high viscosity fluoroelastomer gum stock developed for sealing applications that demand maximum resistance to compression set. It is a copolymer of tetrafluoroethylene and propylene, with a 65% by weight of fluorine in addition to other ingredients. The Fluorel<sup>®</sup> FLS-2650 (70% of fluorine by weight) is a terpolymer of tetrafluoroethylene, propylene and vinylidene fluoride vulcanized by peroxides, diphenols and diamines. Both the polymers have the good processing characteristics and are more resistant to chemicals than the conventional fluoroelastomers. Some typical applications of FLS-2650 include diesel engine cylinder liner seals, downhole sealing elements, fuel system components and non-metallic flue dust expansion joints. Generally, the Fluorel<sup>®</sup> FC and FLS polymers are resistant to acids, bases, hydraulic fluids of all types, brake fluids,

oils and lubricants, alcohols and various industrial solvents.

Due to the widespread use of ketones and nitriles in chemical industries, a program of research was undertaken to study the resistivity of the other types of fluoroelastomers for ketones and nitriles<sup>2</sup>. In continuation of our ongoing program of research concerning the molecular transport of liquids into elastomers<sup>2–8</sup>, we now present sorption and diffusion properties of ketones, viz. acetone, methyl ethyl ketone (MEK), cyclohexanone and methyl isobutyl ketone (MIBK), and nitriles, viz. acetonitrile and acrylonitrile in the temperature interval between 30 and 60°C using a gravimetric sorption technique for the polymers FC-2179 and FLS-2650. Experimental results of sorption and diffusion along with the activation energy values are presented to achieve a better understanding of the resistivity of the polymers to the presence of the chosen liquids.

## EXPERIMENTAL

Fluorel<sup>®</sup> FC-2179 can be milled or internally mixed with the standard fillers and other ingredients utilized in typical fluoroelastomer formulations. The 'dry' ingredients are blended before adding to the masticated gum. Once mixed, the compounded stocks display excellent processing safety and storage stability. Press cure conditions of 175°C to 205°C for 3–5 min are recommended, with a post cure cycle of 16–24 h at 230–260°C to produce the optimum physical properties.

Fluorel<sup>®</sup> FLS-2650 can be mixed with curatives, fillers and other compounding ingredients on a conventional two-roll mill or by the internal mixing methods. In typical formulations, it is recommended that peroxide and co-agent be preblended with the dry powders prior

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**Table 1** Chemical structure, molar volume ( $v_s$ ) and dipole moment ( $\mu$ ) of solvents at 25°C

Solvent	Structure	$v_s$ (cm <sup>3</sup> mol <sup>-1</sup> )	$\mu$
Acetone		74	2.69
Methyl ethyl ketone		90	2.76
Cyclohexanone		104	3.08
Methyl isobutyl ketone		126	"
Acetonitrile		52	3.53
Acrylonitrile		66	3.67

" Data not available

**Table 2** Estimated parameters of equation (1)

Solvents	$n$			$K \times 10^2$ (g/g min <sup>n</sup> )		
	30°C	45°C	60°C	30°C	45°C	60°C
Copolymer (FC-2179)						
Acetone	0.65	0.66 <sup>a</sup>	0.68 <sup>b</sup>	5.66	5.54 <sup>a</sup>	5.82 <sup>b</sup>
Methyl ethyl ketone	0.64	0.65	0.63	4.47	5.38	6.13
Cyclohexanone	0.60	0.61	0.57	1.29	1.64	2.12
Methyl isobutyl ketone	0.65	0.64	0.62	2.66	3.05	3.57
Acetonitrile	0.58	0.58	0.59	5.28	5.69	5.76
Acrylonitrile	0.60	0.61	0.61	4.95	4.85	5.22
Terpolymer (FLS-2650)						
Acetone	0.64	0.64 <sup>a</sup>	0.65 <sup>b</sup>	4.28	4.39 <sup>a</sup>	5.08 <sup>b</sup>
Methyl ethyl ketone	0.62	0.62	0.64	3.79	4.24	4.43
Cyclohexanone	0.52	0.53	0.53	1.40	1.63	1.80
Methyl isobutyl ketone	0.58	0.61	0.60	2.59	2.79	3.08
Acetonitrile	0.51	0.50	0.50	4.00	4.66	5.22
Acrylonitrile	0.52	0.50	0.51	4.56	5.34	5.16

<sup>a</sup> Results obtained at 40°C and <sup>b</sup> at 50°C

**Table 3** Sorption  $S$  (mass %) values for fluoroelastomers with ketones and nitriles

Solvents	Copolymer (FC-2179)			Terpolymer (FLS-2650)		
	30°C	45°C	60°C	30°C	45°C	60°C
Acetone	88.8	85.5 <sup>a</sup>	83.8 <sup>b</sup>	71.2	69.5 <sup>a</sup>	69.3 <sup>b</sup>
Methyl ethyl ketone	91.2	89.9	81.5	72.4	70.9	67.6
Cyclohexanone	98.3	95.4	94.8	48.1	48.2	48.8
Methyl isobutyl ketone	90.8	85.7	85.1	73.7	71.2	68.0
Acetonitrile	46.6	48.4	49.2	13.6	15.3	16.4
Acrylonitrile	54.2	53.8	53.1	19.1	20.6	22.4

<sup>a</sup> Results obtained at 40°C and <sup>b</sup> at 50°C

to adding to the FLS-2650. Care should be taken to avoid mixing temperatures above 121°C. After mixing, the stock solution should be cooled rapidly by either air or water cooling techniques. Mixed catalysed compound (cure incorporated) is then stored in a cool dry place prior to use. The Mooney viscosity values of FC-2179 and FLS-2650 grade samples as measured by ML 1+10 at 121°C by the ASTM D1646 method are 22 and 60 respectively. The weight average molar mass,  $\bar{M}_w$ , of the polymers FC-2179 and FLS-2650 are 185 600 and 246 900 respectively. The fluoroelastomer compositions and their representative physical/mechanical properties have been given in our earlier paper<sup>8</sup>.

FC-2179 and FLS-2650 grade fluoroelastomer sheets in dimensions of 55 cm × 30 cm slabs with the initial thickness ranging from 0.210 cm to 0.237 cm were obtained from 3M Industrial Chemical Products Division, St. Paul, MN, USA (courtesy of Ms Nena McCallum). The circular disc-shaped samples with a diameter of 1.980 cm were cut from large sheets using a sharp-edged carbon-tipped steel die. The cut samples were dried in vacuum desiccators over anhydrous calcium chloride at room temperature for at least 24 h before start of the sorption experiments.

The reagent grade solvents, viz. acetone (s.d. Fine Chemicals, Mumbai, India), MEK and MIBK (both from Ranbaxy Laboratories Ltd., India), cyclohexanone and acetonitrile (both from Qualigens, India) and acrylonitrile (BDH, England) were used without further purification. Structure and molar volume of the solvents are given in Table 1. Details about the sorption experiments have been given earlier<sup>2-8</sup>.

## RESULTS AND DISCUSSION

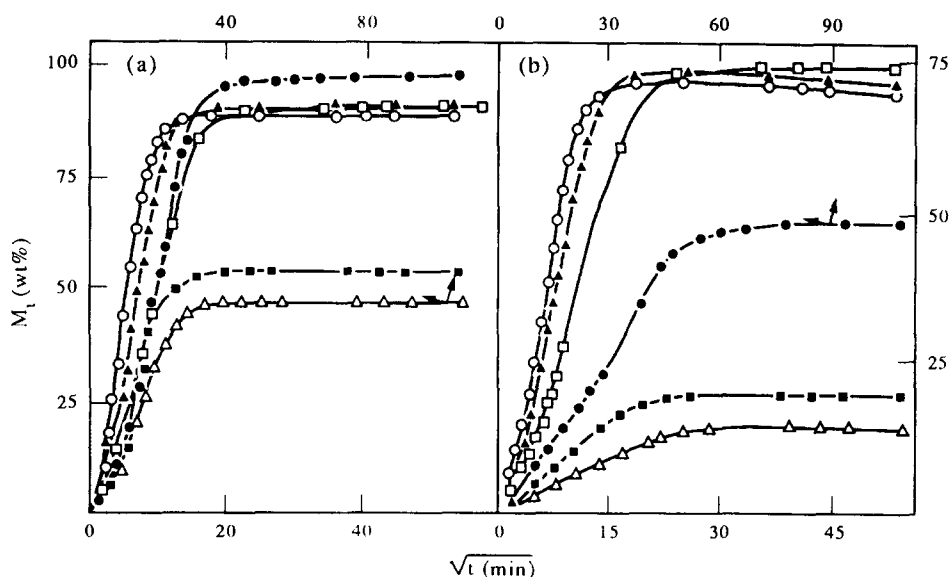
The sorption results of the polymer samples have been fitted to the empirical equation<sup>9</sup>

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

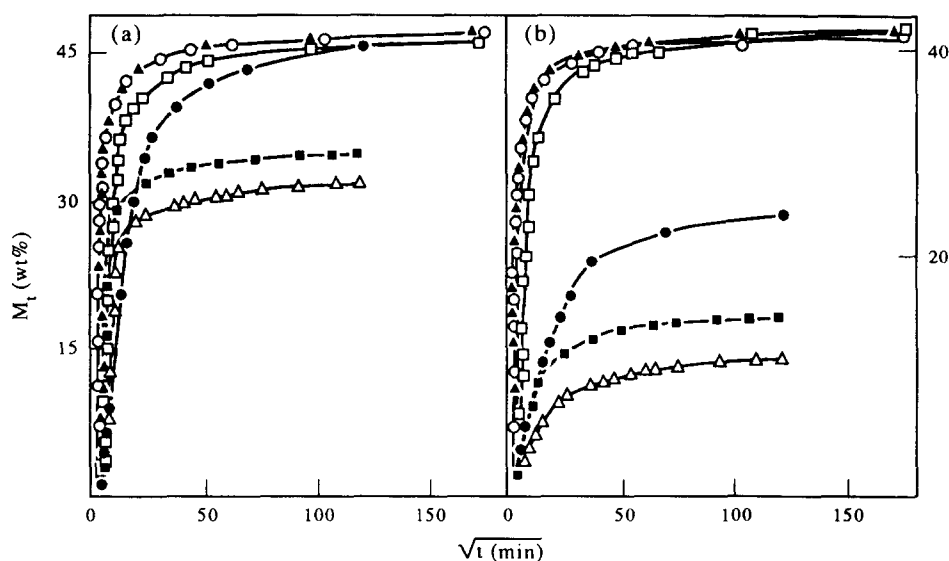
Here, the parameter  $K$  is a closely related function of polymer type and nature of the solvent molecules. Further, it has been shown<sup>2-8</sup> to be related to the diffusion parameters and polymer-solvent interactions.  $M_t$  is the amount of liquid sorbed by the polymer at time  $t$  in sorption experiments or the amount of liquid desorbed in desorption experiments;  $M_\infty$  is the equilibrium amount of liquid sorbed or desorbed that is at infinite time. The exponent value  $n$  indicates the type of transport kinetics. If the values of  $n$  are around 0.5, then the kinetic is said to be Fickian. If the value of  $n = 1.0$ , then the transport kinetics follow the non-Fickian or case-II type mechanism. When the values of  $n$  vary between 0.5 and 1.0, the transport is considered to be of anomalous type. For the majority of rubbery polymer-solvent systems, the anomalous type behaviour is predicted<sup>2-8</sup>.

The calculated values of  $K$  and  $n$  by the least-squares method at 95% confidence level are given in Table 2. The values of  $n$  for FC-2179 are between 0.57 and 0.68, whereas for FLS-2650,  $n$  varies between 0.50 and 0.65. No systematic dependence of  $n$  with temperature is observed for both the polymers. The results of  $K$  are higher for FC-2179 than FLS-2650 indicating higher interactive ability of the solvents with the copolymer than the terpolymer. In all cases, the values of  $K$  increase with increasing temperature suggesting increased molecular interactions of ketones and nitriles with the polymer chain segments. Nitriles being more polar than ketones exhibit higher  $K$  values for both the polymers. Similarly, the more polar and a smaller molecule such as acetone exhibits higher interactions as indicated by the higher  $K$  values than the other ketones. A cyclic molecule, such as cyclohexanone has the smallest value of  $K$  for both the polymers at all the temperatures. This may be the result of its sluggish movement within the polymer matrices.

When the rate of diffusion of solvents is comparable to the relaxation rate of the polymers, the analysis of



**Figure 1** Sorption results of (a) FC-2179 and (b) FLS-2650 polymers with liquids at 30°C. Symbols for liquids: acetone (○); methyl ethyl ketone (▲); cyclohexanone (●); methyl isobutyl ketone (□); acetonitrile (Δ); acrylonitrile (■)



**Figure 2** Desorption curves for (a) FC-2179 and (b) FLS-2650 polymers at 30°C for the same liquids given in Figure 1

solvent uptake kinetics becomes more complicated as it deviates from the  $M_t/M_\infty$  vs  $t^{1/2}$  relationship, thus giving the anomalous transport<sup>10</sup>. From the results of  $S$  given in Table 3 it is observed that the copolymer FC-2179 is less resistant to ketones and nitriles than the terpolymer FLS-2650. Generally, sorption values of nitriles with FLS-2650 polymer are lower than those observed for FC-2179 samples at all the temperatures. For FC-2179 polymer, except acetonitrile, other liquids show a decrease with increasing temperature. On the other hand, with FLS-2650 polymer, cyclohexanone, acetonitrile and acrylonitrile exhibit an increase in sorption with increasing temperature.

Sorption curves of the FC-2179 and FLS-2650 polymers for all the liquids at 30°C are presented in Figure 1. Generally, the sorption curves for FLS-2650 polymer are more sigmoidal than observed for FC-2179, indicating a slower response of the terpolymer to the presence of liquids when compared to the copolymer. However, for both the polymers, cyclohexanone shows

greater sigmoidal trends than other liquids due to its cyclic structure and thereby accounting for the deviations from Fick's diffusion kinetics. Since sorption curves at other temperatures (45 and 60°C) exhibit the same trends, but with different magnitudes, such data are not presented graphically so as to reduce the number of graphs. With nitriles, sorption varies linearly with square root of time and the equilibrium values for the nitriles are smaller than observed for ketones. At all temperatures, the equilibrium sorption values (expressed as mass% sorption coefficients,  $S$ ) of acetonitrile are smaller than acrylonitrile for both the polymers. The presence of unsaturation in acrylonitrile increases its affinity towards the polymer chain segments. Another plausible explanation may be that acetonitrile ( $\delta = 24.77 \text{ (J cm}^{-3})^{1/2}$ ) has a higher solubility parameter than acrylonitrile ( $\delta = 21.50 \text{ (J cm}^{-3})^{1/2}$ ) which increases its ability to establish the intermolecular contact interactions with the polar polymer segments. In the case of other liquids, sorption decreases with increasing temperature. This may be due

to the presence of the crystalline tetrafluoroethylene regions that are more susceptible to reordering by an interacting liquid molecule<sup>11</sup>.

The desorption curves (presented in this paper as uptake values) of the polymers for all the liquids are shown in *Figure 2*. Such curves for acetone and MEK are quite identical for both the polymers, but the values are slightly smaller for FLS-2650 than FC-2179 polymer. Also, the equilibrium desorption values of MIBK are quite identical to those of acetone and MEK for both the polymers. An interesting observation is that the desorption curve for cyclohexanone in the FC-2179 polymer is very different and the uptake values are higher than those observed for FLS-2650. Moreover, cyclohexanone in FC-2179 attains equilibrium values identical to other ketones, but this trend is not observed in FLS-2650 polymer. Also, its equilibrium sorption values are about 50% smaller than those observed for FC-2179. Trends in the desorption behaviour of acetonitrile and acrylonitrile are very much different in both the polymers, i.e. the desorption equilibrium values of nitriles in FC-2179 are nearly twice as high as those observed for FLS-2650.

Diffusion coefficient,  $D$ , provides a measure of the rate at which the liquid molecular diffusion occurs within the polymer matrices. Fick's second law<sup>12</sup> was used to evaluate the values of  $D$  as

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

where  $t$  is time and  $C$  is the solvent concentration within the polymer. This equation neglects the frame of reference term due to convection, and in all subsequent derivations, this term will be neglected because it will not be considered in this study. According to Crank and Park<sup>13</sup>, the average value of diffusivity,  $D_{av}$  provides a good approximation of the variable diffusion coefficient averaged over the entire range of concentration. Thus, when  $D$  varies moderately with concentration  $C$ , the integral value of  $D$  can be calculated using

$$D_{av} = \frac{1}{C_f - C_0} \int_{C_0}^{C_f} D \partial C \quad (3)$$

where  $C_0$  to  $C_f$  is the concentration range existing within the polymer during sorption.

Fick's second law is solved to calculate  $D$  by the sorption/desorption method in which the value of  $D$  is determined from the rate of sorption or desorption. The equation is based on the assumption that the concentration within the polymer sheet is initially uniform and the surface concentrations are instantaneously brought to equilibrium so that the final solution to Fick's second law is obtained as<sup>12</sup>

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \exp \left[ -\frac{D(2m+1)^2 \pi^2 t}{h^2} \right] \quad (4)$$

where  $h$  is thickness of the polymer sheet. For long-term sorption, i.e. for values of  $M_t/M_\infty > 0.50$ , equation (4) can be reduced to give

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \exp \left[ -\frac{D\pi^2 t}{h^2} \right] \quad (5)$$

At longer diffusion times, the terms beyond  $m = 0$  become significant and hence, by substituting the value

of 0.5 for  $M_t/M_\infty$  one gets

$$D = \frac{0.049h^2}{t_{1/2}} \quad (6)$$

where  $t_{1/2}$  corresponds to the time at which  $M_t/M_\infty = 0.5$ . Therefore, for a Fickian transport, the value of  $D$  can be obtained by measuring the half-time. Similarly, an expression for  $D$  can be deduced using the initial rates of sorption and desorption. This method yields an average diffusion coefficient,  $D_{av}$  from the initial sorption curve when plotted against  $t^{1/2}$ . Applying Laplace transforms to equation (2), we get

$$\frac{M_t}{M_\infty} = 4 \left( \frac{Dt}{h^2} \right)^{1/2} \left[ \frac{1}{\pi^{1/2}} 2 \sum_{m=0}^{\infty} (-1)^m i \operatorname{erfc} \frac{mh}{(Dt)^{1/2}} \right] \quad (7)$$

For the values of  $M_t/M_\infty \leq 0.5$ , equation (7) is approximated to give<sup>13</sup>

$$\frac{M_t}{M_\infty} = 4 \left( \frac{Dt}{\pi h^2} \right)^{1/2} \quad (8)$$

During early stages of sorption,  $D$  becomes concentration-dependent so that  $D_{av}$  can be obtained from equation (8). This is an approximation corresponding to equation (3). If the sorption curve is linear for up to 50% equilibrium saturation, then equations (6) and (8) are identical.

The calculated values of  $D$  from equations (4) and (8) respectively, are presented in *Table 4*. It is generally observed that the values of  $D$  are smaller for FLS-2650 than FC-2179 polymer, possibly due to the rigid nature of the terpolymer. Except cyclohexanone, for all the other aliphatic ketones, the values of  $D$  decrease with increasing size of the liquid molecules and this observation is valid for all the temperatures. However, in the case of acetonitrile and acrylonitrile, diffusion coefficients do not show any trends with their sizes. For instance, acrylonitrile is a bigger molecule than acetonitrile, but it exhibits higher  $D$  at all the temperatures and for both the polymers for the reasons mentioned before.

An effort was also made to estimate the values of  $D$  from a plot of  $\log(1 - M_t/M_\infty)$  vs  $t$  using equation (5). A typical graph of this dependence for FLS-2650 polymer is shown in *Figure 3*. The results of  $D$  calculated by this method are much closer to the values of  $D$  calculated from equation (8) signifying the validity of equation (8) in estimating  $D$ . In a further attempt to test which of the  $D$  values calculated from different procedures are accurate, we have repeated our calculations to compute the values of  $M_t/M_\infty$  from equation (4) using separately the  $D$  values obtained from equations (4), (5) and (8) respectively. A good agreement is observed between the theoretical  $M_t/M_\infty$  curves and the experimental points when the  $D$  values calculated from equation (8) are used in the simulation of equation (4). A typical plot is shown in *Figure 4* for acetonitrile with both FC-2179 and FLS-2650 polymers at 30°C.

Diffusion results of the polymer-penetrant systems show an increase with increasing temperature. Thus, Arrhenius apparent activation energy for diffusion,  $E_D$ , has been calculated using the relationship

$$\ln D = \ln D_0 - \frac{E_D}{RT} \quad (9)$$

where  $D_0$  is a constant and  $RT$  is the usual energy term.

Table 4 Diffusion coefficients ( $D \times 10^7 \text{ cm}^2 \text{ s}^{-1}$ ) calculated from equations (4) and (8), and activation energy for diffusion ( $E_D$ ) for fluoroelastomers with ketones and nitriles

Solvents	Equation (4)			Equation (8)			$E_D$ (kJ mol <sup>-1</sup> )
	30°C	45°C	60°C	30°C	45°C	60°C	
Copolymer (FC-2179)							
Acetone	19.0	23.4 <sup>a</sup>	23.6 <sup>b</sup>	10.8	19.1 <sup>a</sup>	19.7 <sup>b</sup>	8.8 ± 4.5
Methyl ethyl ketone	14.2	17.1	19.1	8.2	9.8	16.3	8.3 ± 1.0
Cyclohexanone	1.2	1.8	2.0	0.8	1.0	1.3	13.4 ± 4.8
Methyl isobutyl ketone	5.3	7.6	7.8	3.0	6.9	4.4	10.9 ± 5.4
Acetonitrile	8.3	10.7	12.4	6.1	9.9	11.2	11.3 ± 1.7
Acrylonitrile	9.7	11.3	12.8	6.4	9.7	11.3	7.8 ± 0.3
Terpolymer (FLS-2650)							
Acetone	11.6	13.0 <sup>a</sup>	13.6 <sup>b</sup>	6.5	10.9 <sup>a</sup>	11.3 <sup>b</sup>	7.2 ± 0.8
Methyl ethyl ketone	8.1	10.2	13.1	4.9	6.2	10.2	13.4 ± 0.7
Cyclohexanone	0.5	0.9	1.0	0.4	0.9	1.0	22.8 ± 2.5
Methyl isobutyl ketone	2.3	4.1	7.8	1.7	3.9	3.4	22.5 ± 5.6
Acetonitrile	2.6	3.5	3.6	2.6	3.6	4.5	9.3 ± 3.9
Acrylonitrile	4.0	4.4	4.9	3.6	4.6	5.2	5.6 ± 0.6

<sup>a</sup> Results obtained at 40°C and <sup>b</sup> at 50°C

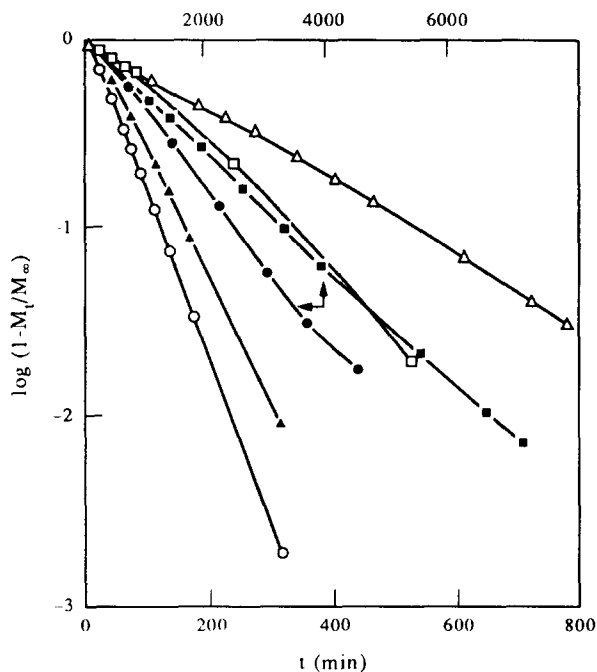


Figure 3 Dependence of  $\log(1 - M_t/M_\infty)$  on  $t$  for FLS-2650 polymer at 30°C with the liquids given in Figure 1

The plots of  $\log D$  vs  $1/T$  shown in Figure 5 are almost linear within the investigated range of temperatures. A least-squares procedure was used to estimate the slopes of the lines from which the  $E_D$  values along with the percentage errors have been calculated and these results are presented in Table 4. The results of  $E_D$  suggest that for molecules with lower  $D$ , the higher  $E_D$  values are observed. This is consistent with Eyring's theory of activated diffusion process. It may be further noted that the values of  $E_D$  are higher for the terpolymer (FLS-2650) than the copolymer (FC-2179). This is expected because the terpolymer structure has higher molar mass and Mooney viscosity values making the terpolymer a more tightly cross-linked structure than the copolymer.

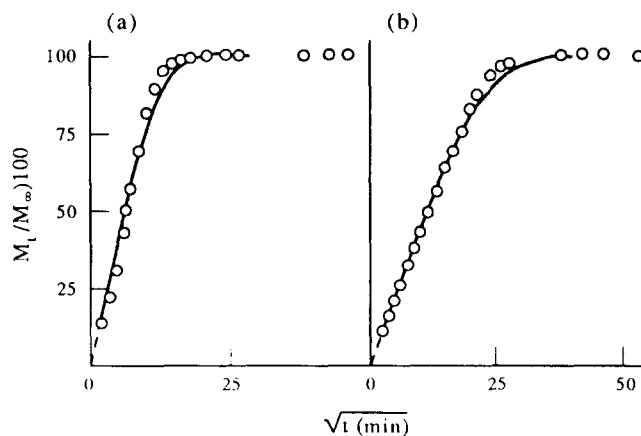
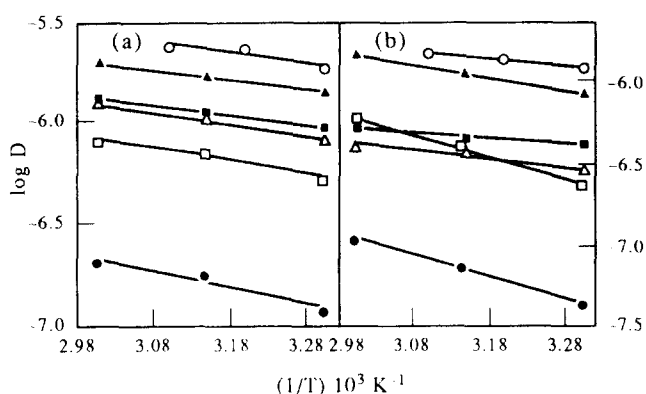


Figure 4 Comparison between theoretical sorption curve calculated from equation (4) and the experimental uptake points for acetonitrile with (a) FC-2179 and (b) FLS-2650 at 30°C

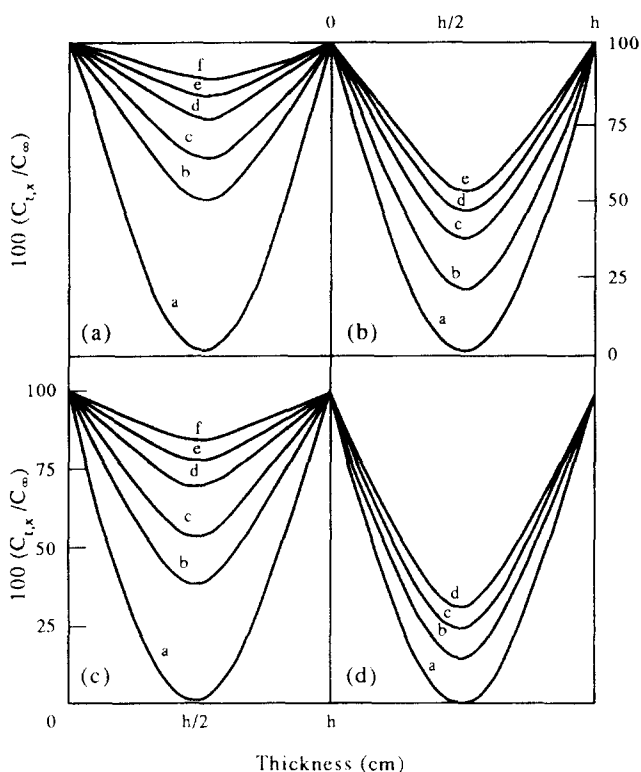
Liquid ingress into the polymeric sheet materials is a phenomenon of great technological importance. In many instances, it would be necessary to know the penetration depths of the liquids into polymers. However, their accurate experimental calculations require the use of sophisticated experiments. In the absence of these tools, we can predict the liquid concentration profiles by solving equation (2) under the suitable initial and boundary conditions to give<sup>13,14</sup>

$$\frac{C_{(t,x)}}{C_\infty} = 1 - \frac{4}{\pi} \sum_{m=0}^{\infty} \frac{1}{(2m+1)} \exp\left[-\frac{D(2m+1)^2\pi^2 t}{h^2}\right] \times \sin\left[\frac{(2m+1)\pi x}{h}\right] \quad (10)$$

where  $C_{(t,x)}$  and  $C_\infty$  are the solvent concentrations expressed in mass% units at time,  $t$  and distance  $x$ , and at sorption equilibrium;  $m$  is an integer. Equation (10) is solved analytically to obtain the concentration profiles  $C_{(t,x)}/C_\infty$  at different penetration depths for different solvent exposure times using the values of  $D$



**Figure 5** Arrhenius plots of  $\log D$  vs  $1/T$  for liquids with (a) FC-2179 and (b) FLS-2650 polymers. Symbols are the same as given in Figure 1

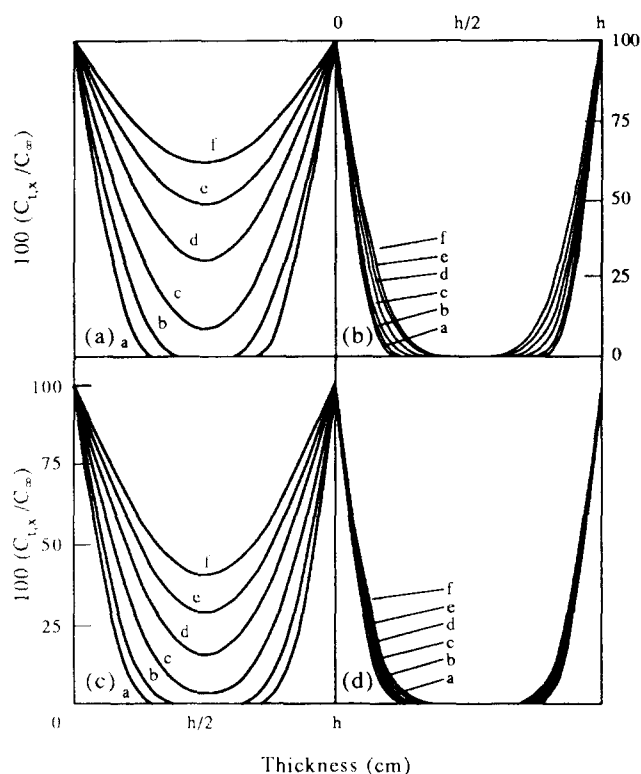


**Figure 6** Concentration profiles of (a) acetone + FC-2179, (b) cyclohexanone + FC-2179, (c) acetone + FLS-2650 and (d) cyclohexanone + FLS-2650 at 30°C at time intervals (a)  $a = 0.21$  min,  $b = 2$  min,  $c = 4$  min,  $d = 10$  min,  $e = 20$  min and  $f = 40$  min, (b)  $a = 3.5$  min,  $b = 10$  min,  $c = 20$  min,  $d = 30$  min and  $e = 40$  min, (c)  $a = 0.35$  min,  $b = 2$  min,  $c = 4$  min,  $d = 10$  min,  $e = 20$  min and  $f = 40$  min and (d)  $a = 5.6$  min,  $b = 20$  min,  $c = 30$  min and  $d = 40$  min calculated from equation (10)

from equation (8). Typical plots of concentration profiles in case of acetone (with high diffusivity  $D = 5.30 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ ) and a low diffusing cyclohexanone ( $D = 2.7 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ ) with FC-2179 and FLS-2650 polymers are compared in Figure 6. For the high diffusing acetone with FC-2179 copolymer, the concentration profiles are higher, but a reverse trend is observed for the low diffusing cyclohexanone with FLS-2650 terpolymer.

The concentration profiles at different penetration depths have also been obtained from a numerical treatment as proposed earlier by Vergnaud<sup>14</sup>, using

$$CN_m = \frac{1}{M} [C_{m-1} + (M-2)C_m + C_{m+1}] \quad (11)$$



**Figure 7** Concentration profiles of (a) acetone + FC-2179, (b) cyclohexanone + FC-2179, (c) acetone + FLS-2650 and (d) cyclohexanone + FLS-2650 at 30°C at time intervals:  $a = 2$  min,  $b = 4$  min,  $c = 10$  min,  $d = 20$  min,  $e = 30$  min and  $f = 40$  min calculated from equation (11)

where the dimensionless parameter  $M$  is defined as

$$M = \frac{(\Delta x)^2}{\Delta t} \frac{1}{D} \quad (12)$$

In the above equation, for computational purposes, we have divided the membrane thickness into 10 slices of equal size,  $\Delta x$ . Each slice is characterized by an integer,  $m$ . The  $C_m$  and  $C_{N_m}$  represent the liquid concentrations for position,  $m$ , at time,  $t$ , and after lapse of time,  $\Delta t$ , respectively. For each position the liquid concentration profiles have been obtained for different times. This numerical scheme is built for the uni-directional transport of liquids into the membrane materials. The calculated profiles for the same systems as shown in Figure 6 are also presented in Figure 7 and the same observations are found.

## CONCLUSIONS

Molecular migration of ketones and nitriles into the 3M Fluorel engineering copolymer and terpolymer membranes has been studied using a gravimetric sorption method in the temperature interval of 30 to 60°C. Sorption of liquids by these Fluorel polymers indicated the Fickian transport kinetics. The diffusion coefficients have been calculated from Fick's equation and these are dependent on the nature of the liquids and their interactions with the polymer chain segments. Diffusion results and the activation parameters for the process of diffusion follow the principle of Eyring's theory of activated diffusion of molecules into the network structures. Concentration profiles of liquids into the network polymers are indicative of the solvent resistivity properties of the polymers. Furthermore, such studies are useful for a preliminary screening of the polymers

before their intended applications in technological and engineering areas.

Fluoroelastomer polymers are a versatile class of thermoplastic elastomers whose major applications are in the automotive and other engineering areas. The present study of the kinetics of sorption/desorption of ketones and nitriles was undertaken to determine the diffusion coefficients as a function of polymer type, nature of solvent molecules and temperature. Two different types of polymers were examined. One is a copolymer of hexafluoropropylene and vinylidene fluoride (FC-2179) and the other is a terpolymer of hexafluoropropylene, vinylidene fluoride and tetrafluoroethylene. The structural differences in these polymers have shown an effect on their solvent transport characteristics.

#### ACKNOWLEDGEMENTS

TMA thanks the All India Council for Technical Education, New Delhi [Grant No. 802/RDII/R&D/94/Rec. 77] for a major financial support of this study. SFH thanks the Department of Science and Technology (Grant No. SP/UR/204/92) for a financial assistance. JDO acknowledges the partial support from the Welch Foundation, Houston, Texas.

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