

Sorption/Desorption and Diffusion Kinetics of Ketones and Nitriles into Fluoropolymer Membranes

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Received 20 September 1996; accepted 30 December 1996

ABSTRACT: Analysis of sorption/desorption and diffusion kinetics of ketones and nitriles at 25, 44, and 60°C into three Du Pont's VITON fluoropolymer membranes loaded with different amounts of carbon black has been undertaken by use of a sorption/desorption technique. The transport results are affected by the percent loading of carbon blacks. Diffusion coefficients have been calculated from Fick's equation. These results show a decrease with increasing amount of carbon black. Experimental results have been analyzed by considering swelling of the membranes. Sorption/desorption results have been analyzed from a calculation of the concentration profiles, which are obtained from the analytical solution of Fick's equation. These results have been compared with a numerical solution based on the finite difference method. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 635–647, 1997

Key words: fluoropolymer; diffusion; sorption; ketones; nitriles

INTRODUCTION

Sorption/desorption and diffusion kinetics of liquids into polymer membranes has been the subject of intense study in our laboratories for the past several years.^{1–6} Such a study has great relevance in membrane applications of polymeric materials in a variety of separation processes.^{7–9} In particular, the success of rubbery polymers in pervaporation separation studies on organic liquid mixtures caused an intensive search for tailor-made polymers exhibiting improved selective mass transport properties.^{10,11} However, mass transport into polymer membranes can be described by the solution-diffusion model, i.e., penetrant molecules get sorbed in the polymer matrix at one side of the barrier with the highest chemi-

cal potential and then diffuse within the matrix in the direction of lower chemical potential.¹² Thus, sorption (S), desorption (D), resorption (RS), and redesorption (RD), i.e., S–D–RS–RD testing of the polymer–solvent systems is important in membrane applications.¹³ Over the years, many theories have been developed which describe the sorption/desorption processes into solid polymer matrices.^{14–16}

The fluoropolymer membranes used are Du Pont's VITON A-201C series with the designated sample numbers 2093, 2094, and 2095 containing, respectively, 10, 20, and 30% of carbon blacks. These polymers are known for their excellent fuel, solvent, and chemical resistivity properties in addition to outstanding environmental stability over a wide range of temperature. The VITON A-type fluoropolymers¹⁷ are based on the copolymerization of vinylidene fluoride, $\text{CH}_2=\text{CF}_2$ (VF_2), and hexafluoropropylene, $\text{CF}_2=\text{CF}-\text{CF}_3$ (HFP), with the general polymer structure $-(\text{CH}_2-\text{CF}_2-)_n-(\text{CF}_2-\text{CF}-\text{CF}_2-)_n-$. These polymers prepared by the emulsion polymerization method^{18,19}

This article is dedicated to Dr. Patrick E. Cassidy, Department of Chemistry and Associate Vice President for Academic Affairs, Southwest Texas State University, San Marcos, TX 78666, on the occasion of his 60th birthday.

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are primarily developed for military applications. The VF₂ monomers with a homopolymer glass transition temperature (T_g) of -40°C and the HFP with a homopolymer T_g of 165°C have been used to synthesize the copolymer membranes. Here, the low T_g of VF₂ helps to retain the elastomeric properties and tends to crystallize with the hydrocarbon portion of the polymer that swells in organic liquids. However, the higher T_g HFP portion breaks up crystallinity to give the elastomeric behavior. The fluorine content of the polymers is 66%, and the Mooney viscosity as measured by ML 1 ± 10 at 100°C is around 65, with the number and mass average molar masses, \bar{M}_n and \bar{M}_w , as 64,000 and 327,000, respectively. This study is concerned about the evaluation of sorption-desorption phenomena and investigates the diffusion kinetics of organic ketones and nitriles into three fluoropolymer membranes having different carbon black contents in the temperature interval $25\text{--}60^\circ\text{C}$. The ketones used are: acetone, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), and cyclohexanone, whereas acetonitrile and acrylonitrile are the examples of nitriles.

EXPERIMENTAL

Rubber formulations were mixed in a "B" Banbury mixer with an upside-down mix procedure. All of the dry ingredients were preblended before being added to the mixing chamber, and the polymer was added last. The ram was lowered, and the compounds were mixed for 2–2.5 min. The stocks were discharged at an indicated temperature of 93°C , but the actual stock temperature was around 121°C . The stocks were milled on a 16-inch two-rolled mill for 2 min; they were sheeted off the mill and allowed to rest overnight at 24°C before being resheeted on the mill to have samples die cut for curing. Samples were cured for 10 min at 177°C in an electric press. The next day, these were postcured at 232°C for 24 h. Mix compositions and some representative mechanical properties are given in Table I.

Sheets of fluoropolymers (sample designation 2093, 2094, and 2095) were fabricated at Du Pont Chemical Laboratory, Cincinnati, OH (courtesy of Mr. Bill Stahl) in dimensions of 15×15 cm slabs, with the initial thicknesses ranging from 0.214 to 0.239 cm. Circular disc-shaped samples with a diameter of 1.976 cm were cut from large sheets

with 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 the start of the sorption experiments.

Reagent-grade acetone, MEK, MIBK, and acrylonitrile (all from S.D. Fine Chemicals, Mumbai, India) and cyclohexanone and acetonitrile (both from Qualigens, Mumbai, India) were used without further purification. Solvent structures and their molar volumes are given in Table II.

S-D-RS-RD Testing

S-D-RS-RD testing of the polymer-liquid systems was done by placing the known dry weights of the cut polymer samples into specially designed screw-tight test bottles containing about $15\text{--}20$ cm³ of the test liquids. At regular intervals (initially, these intervals were within 2–3 min), the submerged samples were removed from the test bottles; the surface-adhered liquid drops were removed by slowly pressing them between smooth filter paper wraps, weighed immediately on a digital Mettler Balance (Model AE 240, Zurich, Switzerland) within the precision of ± 0.01 mg, and placed back into the test bottles. Since the time required for this operation was less than 30 s, this procedure did not introduce large errors in the weight uptake data of the samples. All of the samples reached equilibrium sorption within 48 h, and this remained constant over an extended period of 3–4 days. After the completion of sorption runs, the sorbed samples were placed in a vacuum for desorption measurements. The percent mass gain or loss of the samples was calculated as before.¹⁵ The resorption runs at 25°C were performed in the same manner as those of sorption tests. Dimensional changes of the polymer samples at 25°C were monitored by measuring any changes in the thickness and diameter of the samples during swelling. The thickness (± 0.001 cm) of the samples was measured with a micrometer screw gauge (Frankfurt, Germany) and vernier calipers (Switzerland).

RESULTS AND DISCUSSION

Sorption results expressed in mass percent units at 25, 44, and 60°C , along with the values of desorption, resorption, and redesorption at 25°C , are

Table I Mix Compositions and Properties of Elastomers

Characteristics	Samples		
	2093	2094	2095
Ingredients			
VITON A-201C	100	100	100
Magnalite D ^a	3	3	3
Calcium hydroxide	6	6	6
Carnauba wax ^a	1	1	1
Carbon black N990	10	20	30
Properties (slabs cured at 177°C for 10 min)			
Mooney viscosity (ML 1 + 10, at 121°C)			
ASTM D1646-90	42	50	65
100% Modulus (MPa) ^b	3.0	4.0	5.0
Tensile strength (MPa) ^b	8.8	10.8	12.6
Elongation at break (%) ^b	191	205	261
Hardness, durometer ASTM D2240-87	75	76	77
Specific gravity	1.82	1.82	1.82

^a Magnalite D is a trademark of Marine Magnesium Company. It is a high-activity magnesium oxide. Carnauba wax is a natural wax used for processing.

^b ASTM D412-87, Pulled at 8.5 mm/sec (20 inch/min).

presented in Table III. For ketones, sorption decreases with increasing temperature, indicating either the possible mass loss of the samples or morphological changes of the materials. The former possibility was ruled out because no detect-

able ingredients were found after the completion of sorption runs. However, this effect may be due to the low T_g of the vinylidene fluoride portion of the copolymer, which might shrink in relation to the hydrocarbon portion of the network polymer.²⁰

Table II Structure and Molar Volume of Solvents at 25°C

Liquid	Structure	V_s (cm ³ /mol)
Acetone	$\begin{array}{c} \text{O} \\ \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \end{array}$	74.0
MEK	$\begin{array}{c} \text{O} \\ \\ \text{H}_5\text{C}_2-\text{C}-\text{CH}_3 \end{array}$	90.2
Cyclohexanone	$\begin{array}{c} \text{CH}_2-\text{CH}_2 \\ / \quad \backslash \\ \text{H}_2\text{C} \quad \text{C}=\text{O} \\ \backslash \quad / \\ \text{CH}_2-\text{CH}_2 \end{array}$	103.8
MIBK	$\begin{array}{c} \text{O} \\ \\ \text{H}_3\text{C}-\text{C}-\text{CH}_2-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	125.8
Acetonitrile	$\text{CH}_3-\text{C}\equiv\text{N}$	52.9
Acrylonitrile	$\text{CH}_2=\text{CH}\equiv\text{CN}$	66.3

Table III Weight Percent Uptake Results (Mass %) for Sorption/Desorption Runs of Fluoropolymer Membranes with Ketones and Nitriles

Liquid	S			D	RS	RD
	25°C	44°C	60°C	25°C		
Sample 2093 (10% carbon black)						
Acetone	138.3	133.2 ^a	131.0 ^b	57.3	115.2	52.4
MEK	145.3	137.3	131.7	58.2	146.1	58.4
Cyclohexanone	152.4	147.8	142.1	56.5	143.2	57.1
MIBK	145.8	134.7	128.4	57.0	144.1	57.4
Acetonitrile	69.6	70.4	71.1	36.8	62.8	36.0
Acrylonitrile	75.6	78.2	78.6	42.2	77.6	42.8
Sample 2094 (20% carbon black)						
Acetone	113.5	110.4 ^a	109.5 ^b	52.5	140.3	57.2
MEK	118.9	114.7	109.1	53.3	121.4	53.8
Cyclohexanone	128.8	124.8	119.5	52.0	116.0	52.3
MIBK	121.6	114.5	107.4	52.8	121.6	53.5
Acetonitrile	59.4	59.3	59.9	35.4	61.0	37.0
Acrylonitrile	66.4	66.0	65.5	39.2	67.0	39.3
Sample 2095 (30% carbon black)						
Acetone	95.8	92.7 ^a	90.0 ^b	48.2	97.8	48.2
MEK	103.1	95.8	92.6	50.1	104.0	49.9
Cyclohexanone	111.2	105.4	101.1	49.8	104.9	49.3
MIBK	102.5	94.8	90.5	48.7	101.7	48.7
Acetonitrile	51.5	52.2	54.2	32.8	50.6	32.6
Acrylonitrile	56.0	57.3	56.6	35.4	57.3	35.5

^a Results obtained at 40°C.^b Results obtained at 50°C.

Another plausible explanation would be that the polymer chain segments might have relaxed faster than the rate of the molecular transport of ketones. This type of anomaly was not observed for acetonitrile and acrylonitrile. For nitriles, sorption increases with increasing temperature, indicating the entry of more solvent molecules into the free volume spaces of the matrix polymer.

Sorption/desorption results are influenced by the amount of carbon black present in the samples. For instance, the mass percent sorption values decrease considerably with increasing amount of carbon black at all temperatures. This might be attributed to the filling up of the available void volumes in the polymers by the carbon black particles. Among the ketones, cyclohexanone exhibits the highest sorption at all temperatures. However, the sorption values of MEK and MIBK (even though these molecules have different molar volumes) are quite identical. Acetone exhibits lower sorption than all of the other ketones, but because of its low boiling temperature, sorption experiments were performed up to 50°C. Between aceto-

nitrile and acrylonitrile, the latter (being a more polar and larger molecule) exhibits higher sorption than the former. In comparison to ketones, both of the nitriles exhibit considerably lower sorption values, suggesting somewhat better resistivity of the polymer membranes to nitriles than ketones.

The desorption (D), resorption (RS), and redesorption (RD) data presented at 25°C in Table III also show a systematic decrease with an increasing amount of carbon black in all the cases except acetone for desorption and redesorption runs. However, the maximum percent mass losses of the samples during desorption and redesorption runs are almost identical for the majority of liquids. On the other hand, sorption and resorption uptake values at 25°C are not quite comparable for many liquids. The differences in sorption and resorption uptake values of acetone and cyclohexanone are higher for 2093 and 2094 membranes than 2095. For the remaining liquids, the maximum uptake values of sorption and resorption are somewhat comparable.

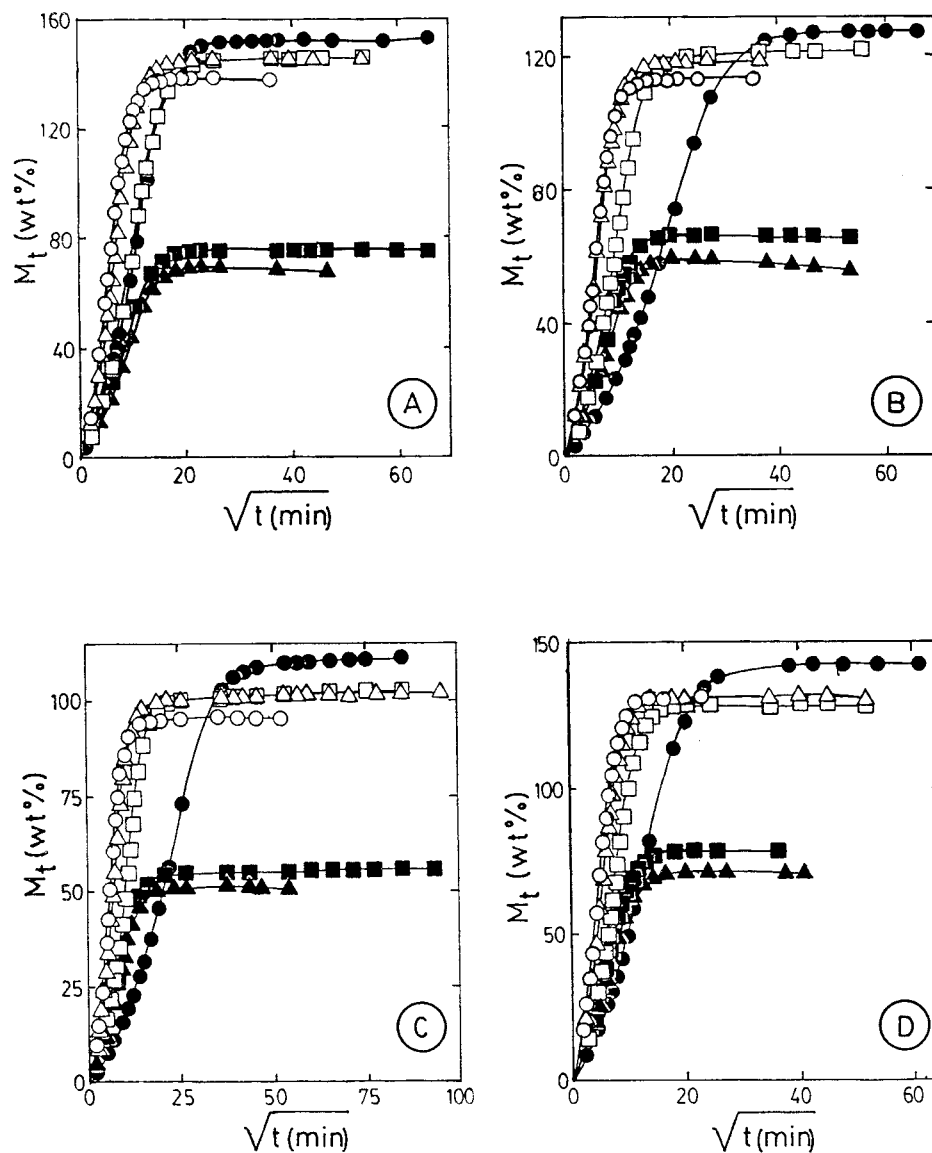


Figure 1 Sorption plots of VITON (A) 2093, (B) 2094, and (C) 2095 membranes at 25°C and (D) 2093 at 60°C with ketones and nitriles. Symbols: (○) acetone, (△) MEK, (●) cyclohexanone, (□) MIBK, (▲) acetonitrile, and (■) acrylonitrile.

Sorption results for 2093, 2094, and 2095 membranes at 25°C are displayed graphically in Figure 1. Also included in the same figure is a comparison of the sorption plot for the 2093 membrane at 60°C. For all liquids except cyclohexanone with 2093, 2094, and 2095 membranes, initially sorption increases in a linear manner with $t^{1/2}$ and later reaches equilibrium. However, the sorption of cyclohexanone depends on the type of polymer used. For instance, with the 2093 membrane with 10% carbon black, the sorption curves of cyclohexanone and MIBK are almost identical initially,

but near equilibrium, the sorption of cyclohexanone becomes higher than that of MIBK. On the other hand, with membranes 2094 and 2095, the sorption curves for cyclohexanone deviate differently than that observed for MIBK. Also, the times required to attain equilibrium sorption for the 2094 and 2095 membranes are higher than those observed for the 2093 membrane.

Increasing sigmoidal trends of the sorption curves for cyclohexanone (Fig. 1) with an increasing amount of carbon black in the membrane samples are clear-cut evidence of the fact that the rate of

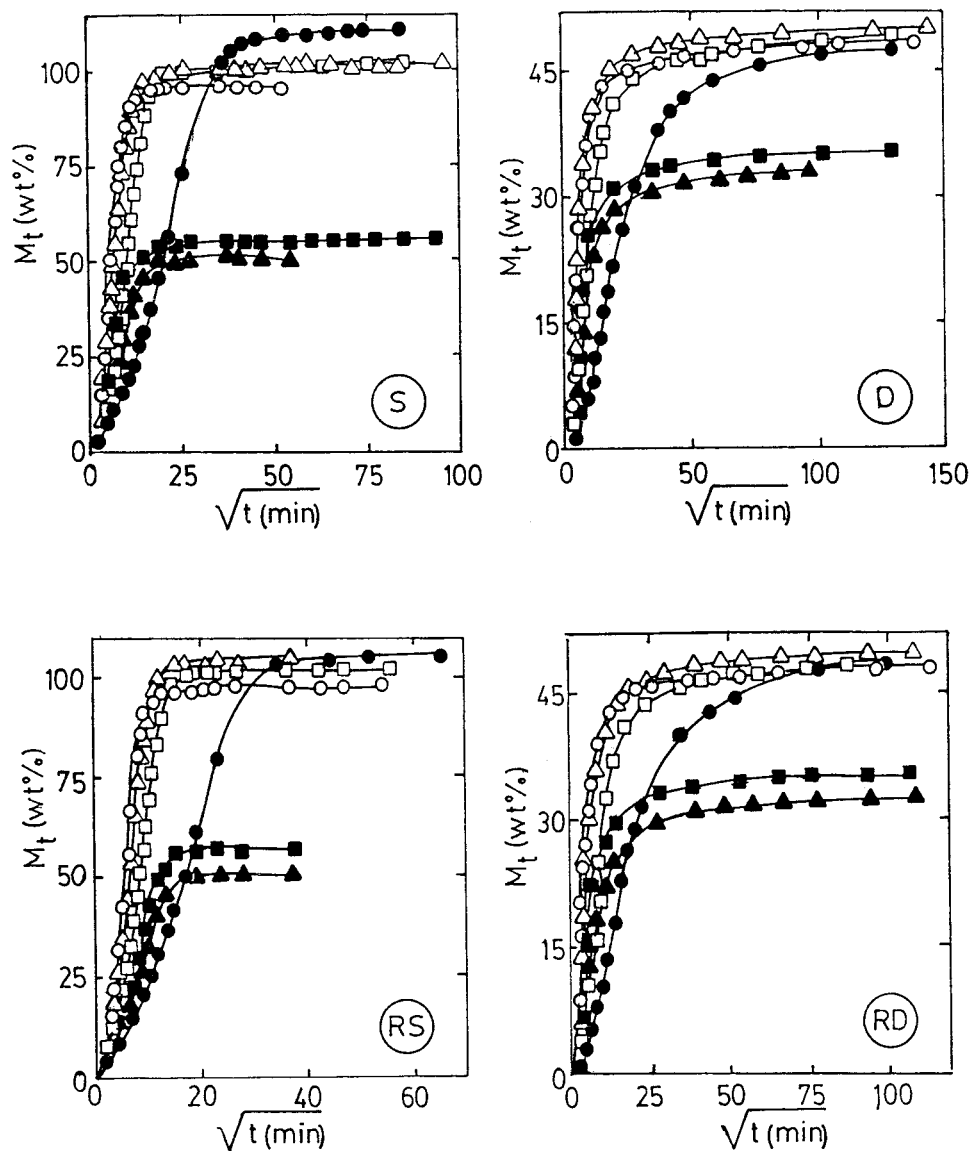


Figure 2 Uptake value of sorption (S), desorption (D), resorption (RS), and redesorption (RD) of VITON 2095 membrane at 25°C with the same liquids as given in Figure 1.

polymer chain relaxation is faster than the rate of the diffusion of cyclohexanone into the network polymers. Even an increase of temperature from 25°C [Fig. 1(A)] to 60°C [Fig. 1(D)] shows the increasing sigmoidal trends for similar reasons. The S-D-RS-RD results of all of the liquids for the 2095 membrane are presented in Figure 2, wherein the same effects as seen in Figure 1 are observed.

In studies of the molecular transport of liquids into polymer membranes, diffusion has been classified as Case I (Fickian), Case II (relaxation controlled), and non-Fickian (anomalous). Excellent

reviews on this subject were given by Thomas and Windle,²¹ Frisch,²² Peterlin,²³ Hansen,²⁴ and Astarita and Sarti.²⁵ When liquids diffuse into a network polymer, a sharp advancing concentration boundary exists between the inner glassy core and the outer swollen layer of the polymer. The depth of the moving boundary or solvent penetration rates can be studied by use of an empirical relation²⁶:

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

Table IV Estimated Parameters of Eq. (1)

Liquids	n			$K \times 10^2$ (g/g min ⁿ)		
	25°C	44°C	60°C	25°C	44°C	60°C
Sample 2093 (10% carbon black)						
Acetone	0.66	0.67 ^a	0.68 ^b	5.03	5.40 ^a	6.08 ^b
MEK	0.68	0.67	0.68	3.83	4.96	5.27
Cyclohexanone	0.61	0.63	0.63	1.06	1.51	2.04
MIBK	0.67	0.68	0.68	2.27	2.77	3.47
Acetonitrile	0.60	0.60	0.59	4.14	5.09	5.88
Acrylonitrile	0.60	0.61	0.62	4.15	4.71	5.39
Sample 2094 (20% carbon black)						
Acetone	0.67	0.68 ^a	0.68 ^b	4.92	5.21 ^a	6.03 ^b
MEK	0.68	0.66	0.67	4.05	5.06	5.83
Cyclohexanone	0.61	0.62	0.61	1.23	1.59	2.07
MIBK	0.69	0.63	0.66	2.26	3.18	3.69
Acetonitrile	0.59	0.58	0.59	4.62	5.51	6.57
Acrylonitrile	0.61	0.61	0.61	4.37	5.48	6.18
Sample 2095 (30% carbon black)						
Acetone	0.66	0.69 ^a	0.69 ^b	4.83	5.07 ^a	5.39 ^b
MEK	0.68	0.67	0.69	4.04	4.46	4.82
Cyclohexanone	0.61	0.62	0.62	1.04	1.44	1.80
MIBK	0.67	0.68	0.68	2.10	2.65	3.05
Acetonitrile	0.59	0.62	0.61	4.28	4.73	5.76
Acrylonitrile	0.60	0.62	0.62	3.81	4.61	5.26

^a Results obtained at 40°C.^b Results obtained at 50°C.

where M_t and M_∞ are the masses of solvent uptake at time t and at equilibrium time, and K is a parameter which depends on the nature of the polymer-solvent interactions. The value of the exponent n indicates the type of transport. For instance, if the values of n vary between 0.5 and 1.0, then such a process is referred to as anomalous diffusion.²⁰ Least-squares estimations of K and n from eq. (1) are presented in Table IV. For all systems, the values of n range between 0.60 and 0.69, indicating the transport to be of anomalous type, but not deviating too far from Fickian mode, for which the value of $n = 0.5$. The values of n presented here are not affected by changes in temperature. On the other hand, the values of K show an increase with increasing temperature, suggesting increased molecular interactions of liquids with the polymer chain segments at higher temperatures. The values of K for cyclohexanone and MIBK are smaller than those observed for other liquids, while for acetone, MEK, and nitriles, the values of K are somewhat higher than those observed for other liquids, suggesting

higher interactions of these liquids with the polymer chain segments.

In the presence of ketones, we noticed slight changes in the dimensions due to the swelling of the membranes. In order to study this effect, we have calculated the increase in volume, ΔV , of the polymer samples by²⁷

$$\Delta V = V_0 \left[1 + \frac{\Delta h}{h_0} \right]^3 \quad (2)$$

where V_0 is the original (unswollen) volume of the polymer, Δh is the change in the thickness of the polymer, and h_0 is its original thickness. Neglecting the second-order and third-order terms at low relative dilations, eq. (2) can be simplified to give

$$\Delta V = V_0 \left[1 + 3 \left(\frac{\Delta h}{h_0} \right) \right] \quad (3)$$

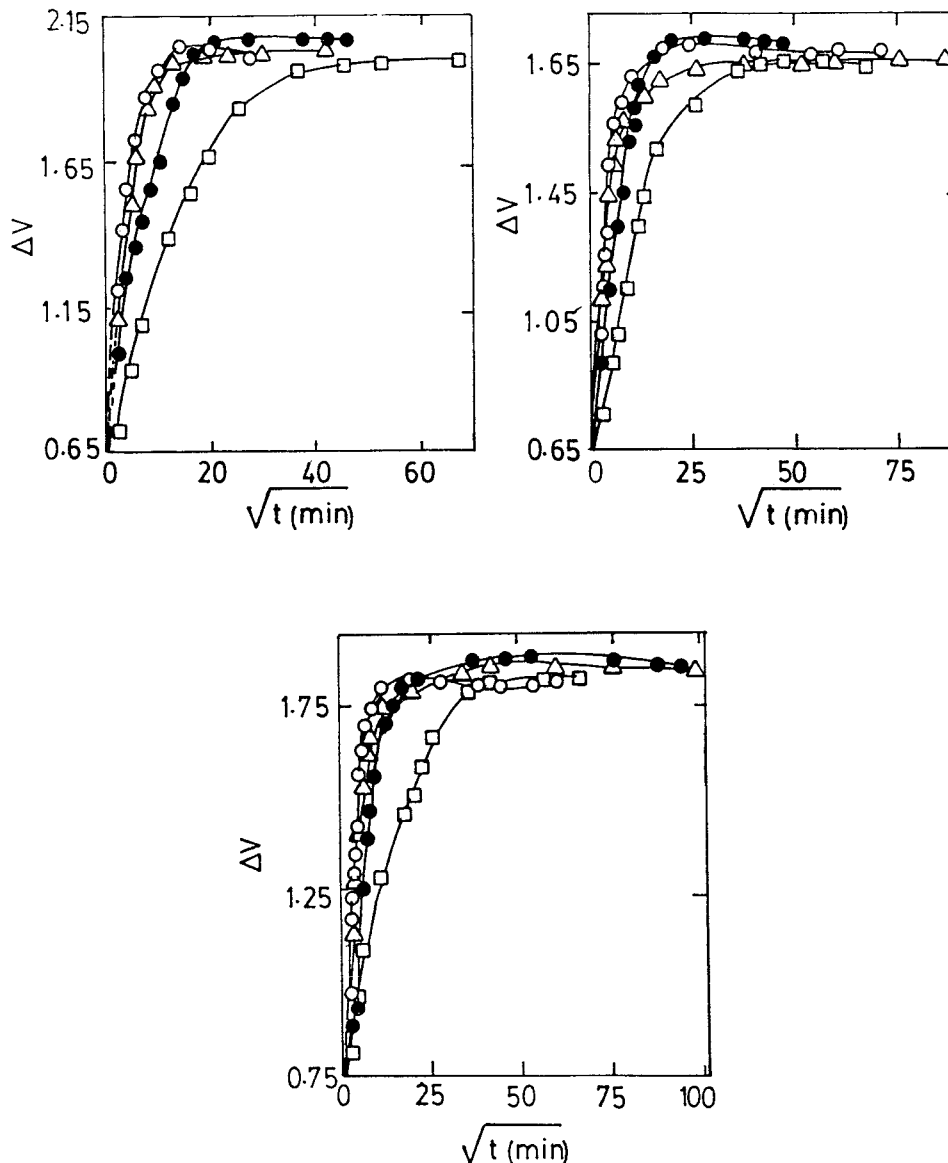


Figure 3 Volume dilation (cm^3) plots for VITON 2093, 2094, and 2095 membranes with ketones at 25°C . Symbols for solvents are the same as given in Figure 1.

Plots of ΔV versus $t^{1/2}$ for 2093, 2094, and 2095 membranes with ketones at 25°C are presented in Figure 3. It is observed that the values of ΔV decrease systematically with an increasing amount of carbon black. Thus, polymer dilation is a time-dependent phenomenon that is closely related to the mass transport problem. When liquid molecules first hit the outer surface of the membrane, they get sorbed and later reach the middle of the polymer sample, where sorption increases to a maximum and then levels off at the other side of the membrane.²⁸ Figure 4 illus-

trates schematically the problem of comparing the sorption and volume dilation of the membrane.

Penetrant molecules diffuse into the depth of the membrane until concentration is equal over the whole of membrane thickness. Using the sorption values, we have calculated the relative concentrations $C_{(t,x)}/C_\infty$ of the liquids into the polymer membrane by²⁹

$$\frac{C_{(t,x)}}{C_\infty} = 1 - \frac{4}{\pi} \sum_{m=0}^{\infty} \frac{1}{(2m+1)}$$

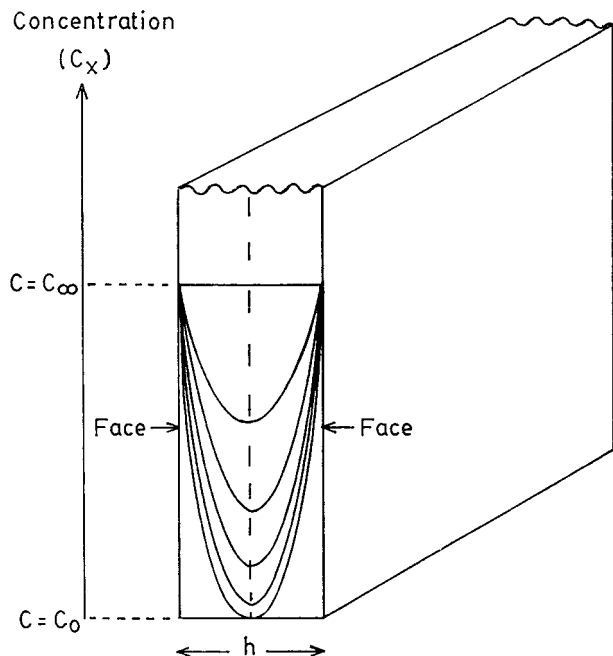


Figure 4 Schematic representation of concentration profiles as the time proceeds in a sorption-dilation experiment.

$$\times \exp \left[-\frac{D(2m+1)^2\pi^2t}{h^2} \right] \sin \left[\frac{(2m+1)\pi x}{h} \right] \quad (4)$$

However, at low concentrations, diffusion coefficients, D , of the polymer-solvent systems have been calculated by¹²

$$\frac{M_t}{M_\infty} = \frac{4}{h} \left(\frac{Dt}{\pi} \right)^{1/2} \quad (5)$$

The calculated values of D from the initial linear slopes of the plots of M_t versus $t^{1/2}$ before the completion of 55% equilibrium are presented in Table V. With these values, the theoretical sorption curves have been generated from a numerical solution of eq. (4).

Another form of the diffusion equation is

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{m=0}^{\infty} \frac{1}{(2m+1)^2} \times \exp \left[-D \frac{(2m+1)^2\pi^2t}{h^2} \right] \quad (6)$$

A typical plot is shown in Figure 5 for the membrane 2093 with MEK at 25 and 60°C. The agreement is good between the solid theoretical curves and the experimental points. This further supports the validity of the diffusion data obtained from eq. (5).

The diffusion results presented in Table V do not show any systematic dependence on the amount of carbon black in the membranes. In a related series of liquids such as with linear ketones, diffusion varies with their sizes and follows the sequence: acetone > MEK > MIBK for S-D-RS-RD runs. However, cyclohexanone, the molar volume of which is smaller than that of MIBK, exhibits lower D than all of the other ketones as well as nitriles; this is probably because of its cyclic structure. Among acrylonitrile and acetonitrile, a somewhat bigger acrylonitrile has slightly higher D than acetonitrile. This may be because it has a higher polarity ($\mu = 3.67$) than acetonitrile ($\mu = 3.53$). For all liquids, diffusion coefficients increase with increasing temperature, suggesting the creation of additional free volume within the polymer chain segments. However, the diffusivity values for D-RS-RD runs are different, suggesting different transport characteristics. The permeability coefficients, P , of the polymer-solvent systems (calculated as $P = DS$) are presented in Table VI. In general, the results of P for sorption decrease with an increasing amount of carbon black in the polymer samples. However, for desorption, resorption, and redesorption runs, no such dependence is observed.

Figure 6 displays the dependence of $C_{(t,x)}/C_\infty$ on the inner thickness values of membrane 2094 at 25°C from one side to the other at different time intervals for acetone and cyclohexanone. Acetone with a $D = 1.94 \times 10^{-6}$ cm²/s shows higher $C_{(t,x)}/C_\infty$ values than cyclohexanone, for which $D = 1.02 \times 10^{-7}$ cm²/s. For instance, at $t = 40$ min, acetone exhibits an M_t/M_∞ value of 82%, whereas cyclohexanone at $t = 40$ min of exposure time exhibits less than 50% sorption; thus, cyclohexanone takes still longer time to attain equilibrium. In a similar manner, an increase of temperature increases diffusivity and thereby exhibits higher values of concentration profiles (these curves are not displayed to avoid redundancy).

Concentration profiles have also been calculated by the use of a numerical scheme based on the finite difference method²⁹:

$$CN_m = \frac{1}{M} [C_{m-1} + (M-2)C_m + C_{m+1}] \quad (7)$$

Table V Diffusion Coefficients ($D \cdot 10^6$, cm²/s) for Fluoropolymer Membranes with Ketones and Nitriles

Liquids	S			D	RS	RD
	25°C	44°C	60°C			
Sample 2093 (10% carbon black)						
Acetone	1.80	2.20 ^a	2.56 ^b	7.15	1.79	7.03
MEK	1.28	1.71	2.23	4.26	1.48	4.59
Cyclohexanone	0.10	0.20	0.30	0.26	0.16	0.43
MIBK	0.53	0.85	1.09	1.80	0.71	2.31
Acetonitrile	0.84	1.23	1.54	1.85	0.93	1.64
Acrylonitrile	0.82	1.19	1.44	2.47	0.97	2.68
Sample 2094 (20% carbon black)						
Acetone	1.94	2.30 ^a	2.64 ^b	5.99	1.83	6.12
MEK	1.43	1.68	2.13	4.38	1.38	4.56
Cyclohexanone	0.10	0.19	0.27	0.31	0.17	0.42
MIBK	0.61	0.59	1.05	2.24	0.69	1.85
Acetonitrile	0.90	1.19	1.54	1.90	0.92	2.26
Acrylonitrile	0.94	1.14	1.57	2.54	1.03	2.59
Sample 2095 (30% carbon black)						
Acetone	1.88	2.42 ^a	2.56 ^b	4.56	1.78	5.14
MEK	1.27	1.78	2.31	3.84	1.68	4.36
Cyclohexanone	0.09	0.20	0.30	0.27	0.16	0.41
MIBK	0.51	0.82	1.02	1.63	0.75	2.16
Acetonitrile	0.79	1.26	1.54	1.82	0.94	1.63
Acrylonitrile	0.81	1.26	1.54	2.08	1.02	2.23

^a Results obtained at 40°C.^b Results obtained at 50°C.

where the dimensionless parameter, M , is defined as

$$M = \frac{(\Delta x)^2}{\Delta t} \frac{1}{D} \quad (8)$$

Figure 7 displays the concentration profile curves obtained from such a treatment for the 2094 membrane with acetone and cyclohexanone at 25°C for a maximum immersion time up to 40 min. A comparison of the curves presented in Figures 6 and 7 suggests that the values of concentration profiles calculated from eq. (7) are smaller than those calculated from eq. (4). However, the nature of their variations remains almost identical by both methods.

The results of D and P presented here have shown a systematic dependence on temperature, i.e., the values of D and P increase with increasing temperature, and hence, activation energy values, E_D and E_P , for diffusion and permeation have been calculated from the Arrhenius relation:

$$X = X_0 \exp\left(\frac{-E_X}{RT}\right) \quad (9)$$

where X and X_0 represent D or D_0 and P or P_0 , respectively. E_X refers to E_D for diffusion and E_P

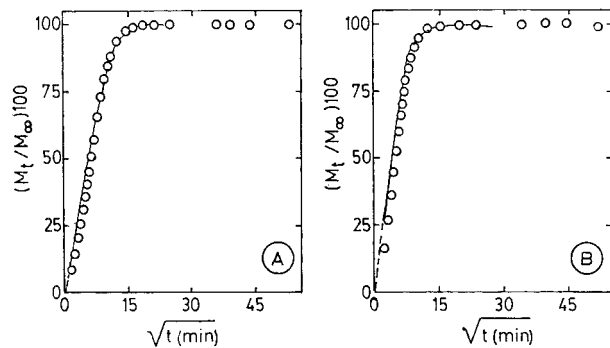


Figure 5 Comparison of the theoretical sorption curve calculated from eq. (6) with the experimental points for VITON 2093 membrane with MEK (A) at 25°C and (B) at 60°C.

Table VI Values of Permeability Coefficients ($P \cdot 10^6$, cm²/s) for Fluoropolymer Membranes with Ketones and Nitriles

Liquids	S			D	RS	RD
	25°C	44°C	60°C	25°C		
Sample 2093 (10% carbon black)						
Acetone	2.49	2.92 ^a	3.35 ^b	4.10	2.06	3.68
MEK	1.86	2.35	2.93	2.48	2.17	2.68
Cyclohexanone	0.15	0.29	0.43	0.15	0.22	0.25
MIBK	0.78	1.15	1.40	1.02	1.02	1.33
Acetonitrile	0.58	0.87	1.09	0.68	0.58	0.59
Acrylonitrile	0.62	0.93	1.14	1.04	0.76	1.15
Sample 2094 (20% carbon black)						
Acetone	2.20	2.54 ^a	2.89 ^b	3.14	2.57	3.50
MEK	1.70	1.92	2.32	2.33	1.67	2.45
Cyclohexanone	0.13	0.24	0.32	0.16	0.20	0.14
MIBK	0.75	0.68	1.13	0.18	0.84	0.99
Acetonitrile	0.54	0.71	0.92	0.67	0.56	0.84
Acrylonitrile	0.62	0.75	1.03	1.00	0.69	1.02
Sample 2095 (30% carbon black)						
Acetone	1.80	2.25 ^a	2.31 ^b	2.20	1.74	2.48
MEK	1.31	1.71	2.13	1.92	1.74	2.17
Cyclohexanone	0.10	0.21	0.30	0.13	0.16	0.20
MIBK	0.52	0.78	0.92	0.79	0.76	1.05
Acetonitrile	0.41	0.66	0.83	0.48	0.60	0.53
Acrylonitrile	0.45	0.72	0.87	0.59	0.74	0.79

^a Results obtained at 40°C.^b Results obtained at 50°C.

for permeation. A representative plot of the dependence of $\log D$ on $1/T$ is displayed in Figure 8. The values of E_D and E_P have been calculated by the method of least squares by fitting the log

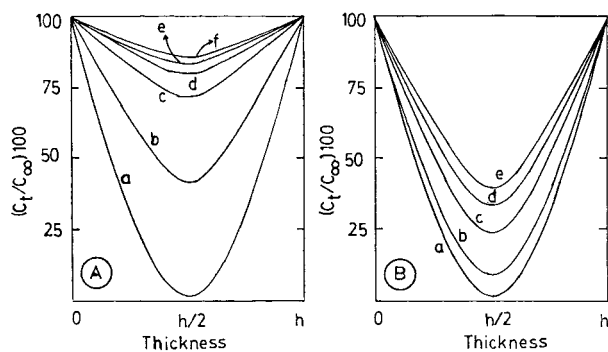


Figure 6 Dependence of concentration profiles on the thickness of the polymer membranes calculated from eq. (4) for VITON 2094 membrane with (A) acetone at time intervals a = 0.3 min, b = 2 min, c = 10 min, d = 20 min, e = 30 min, and f = 40 min and (B) cyclohexanone at time intervals a = 5 min, b = 10 min, c = 20 min, d = 30 min, and e = 40 min at 25°C.

D values with $1/T$; these data along with the estimated error values are presented in Table VII. It is found that cyclohexanone, having the lowest values of D , exhibits higher values of both E_D and E_P than the other liquids. However, with the majority of liquids, E_D and E_P values fall within the

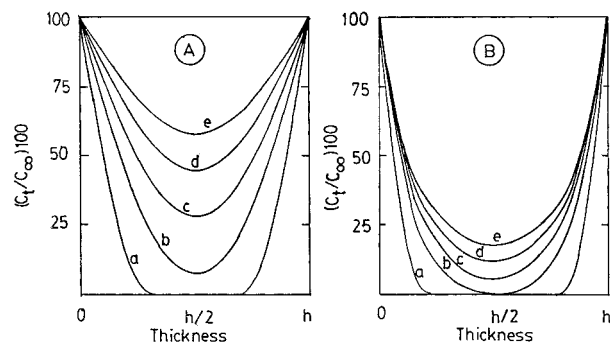


Figure 7 Dependence of concentration profiles on sample thickness from eq. (7) for VITON 2094 membrane with (A) acetone and (B) cyclohexanone at 25°C at time intervals a = 2 min, b = 10 min, c = 20 min, d = 30 min, and e = 40 min.

range expected of the rubbery polymer–organic solvent systems.

CONCLUSIONS

Experimental results of sorption/desorption and diffusion kinetics from 25 to 60°C for four ketones and two nitriles with three fluoropolymer membranes containing 10, 20, and 30% carbon black loadings are presented. The values of sorption and permeation coefficients show a decrease with an increasing amount of carbon black in the polymer. The volume dilation results suggest that expansion of the membranes depends on the amount of carbon black, i.e., lower volume expansions are observed for samples containing higher amounts of carbon black and vice versa. A decrease in sorption with increasing temperature for ketones was attributed to an induced crystallinity and/or morphological changes in the polymers. For nitriles, sorption increases with increasing temperature. From the S–D–RS–RD testing, it is found that the sorption results of D and RD runs are identical. The sorption/desorption results of this study have been analyzed with Fick's equation and also by a numerical method.

T.M.A. appreciates the great encouragement and support he received initially from Prof. P. E. Cassidy in

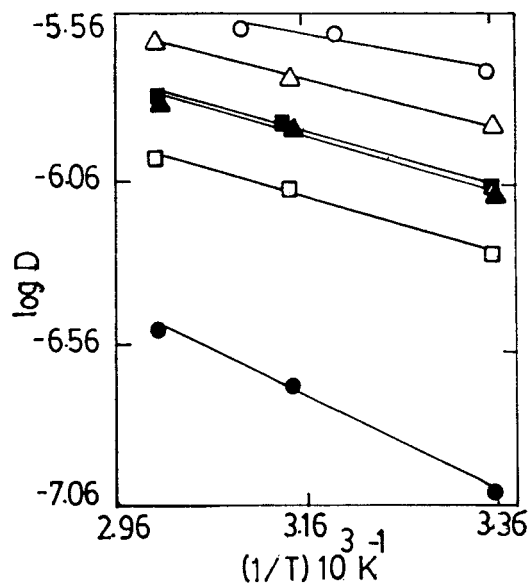


Figure 8 Arrhenius plots of $\log D$ versus $1/T$ for VITON 2095 membrane with the same liquids as given in Figure 1.

Table VII Activation Energy for Diffusion (E_D) and Permeation (E_P) of Fluoropolymer Membranes with Ketones and Nitriles

Liquids	E_D (kJ/mol)	E_P (kJ/mol)
Sample 2093 (10% carbon black)		
Acetone	11.22 ± 0.66	9.44 ± 0.82
MEK	12.92 ± 1.18	10.61 ± 1.05
Cyclohexanone	26.18 ± 0.24	24.56 ± 0.35
MIBK	16.94 ± 1.20	13.94 ± 1.17
Acetonitrile	14.46 ± 0.64	14.92 ± 0.66
Acrylonitrile	13.60 ± 0.96	14.54 ± 1.22
Sample 2094 (20% carbon black)		
Acetone	9.79 ± 0.73	8.60 ± 0.90
MEK	9.23 ± 2.06	7.26 ± 1.67
Cyclohexanone	22.96 ± 1.78	21.22 ± 2.15
MIBK	13.17 ± 1.47	12.87 ± 1.17
Acetonitrile	16.68 ± 2.08	12.72 ± 1.29
Acrylonitrile	11.77 ± 2.96	11.45 ± 2.90
Sample 2095 (30% carbon black)		
Acetone	10.19 ± 2.30	8.23 ± 2.49
MEK	13.97 ± 0.58	11.41 ± 0.79
Cyclohexanone	28.06 ± 2.14	25.81 ± 2.26
MIBK	16.39 ± 1.71	13.44 ± 1.62
Acetonitrile	15.77 ± 1.80	16.92 ± 1.33
Acrylonitrile	15.38 ± 1.52	15.68 ± 1.92

pursuing this field of research. The authors also thank the All India Council for Technical Education, New Delhi (Grant No. 802-1/RDII/R&D/94/Rec.177), for major financial support and the Department of Science and Technology (Project No. SP/UR/204/92) for research assistance to S.F.H.

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