

Sorption Kinetics and Diffusion of Alkanes into Tetrafluoroethylene/Propylene Copolymer Membranes

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SYNOPSIS

Sorption kinetics and diffusion of hexane, heptane, octane, nonane, decane, cyclohexane, and 2,2,4-trimethylpentane through tetrafluoroethylene/propylene copolymer membranes were studied using the gravimetric sorption method at 30, 45, and 60°C. Coefficients of diffusion were calculated from Fick's equation. From these data, the permeability coefficients were obtained. Analytical solutions of Fick's relations were used to estimate the liquid concentration profiles into the polymeric membranes at different times. The profiles of liquid concentrations were also simulated for the polymer-solvent systems using the numerical simulation method. Activation parameters for diffusion and sorption were evaluated and these results are discussed in terms of the molecular sizes and geometries of liquids (i.e., shape) as well as temperature. The diffusion coefficients follow a systematic decrease with increasing size of the penetrant molecules. The activation energies i.e., E_D values, increase with increasing size of *n*-alkanes. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The molecular transport of low molecular weight liquids into polymeric sheet membranes is a subject of great practical importance in a variety of areas such as food packaging,¹ drug and pesticide release,²⁻⁴ reverse osmosis,⁵ and pervaporation.⁶ The main research activities in these areas have been to achieve a quantitative understanding of the factors influencing diffusion phenomena in terms of transport parameters such as sorption, diffusion, and permeation. A comprehensive understanding of the phenomena of molecular transport into polymeric sheet membranes is very essential before we envisage practical applications of these materials. An analysis of the diffusion processes in terms of concentration profiles is equally important in these areas and especially in food-packaging industries. Diffusion of small molecules into the polymer matrix is a complex theoretical problem with diverse applications. Several experimental techniques have been used to study the solvent transport characteristics of polymer mem-

branes.⁷⁻¹² Of these, the sorption gravimetric method, though simple, yields reliable data.^{13,14}

The recently developed tetrafluoroethylene (TFE)/propylene copolymer membranes (Aflas[®] FA 100S and FA 150P TFE elastomers, manufactured by 3M) exhibit a unique combination of high-temperature, chemical, and electrical resistance properties. These elastomers are designed for use in molded goods and extruded shapes and profiles, which find applications where compression-set resistance as well as gas (e.g., N₂ and CO₂) blistering and antiextrusion resistance are important. The TFE elastomers provide service life advantages in acids, bases, steam/hot water, amines, oils, and hydraulic fluids. Other important applications of these elastomers include O-rings, seals used in hydraulic and brake systems, jet engines, cable clamps, electrical connectors and boots, wire and cable insulation, hose, and pipeline patches. Its good property, retention, and moderate volume swell prompted us to study the molecular transport of alkanes into these membranes. These liquids are used particularly in view of their importance in petrochemical industries.

In our earlier articles,¹⁵⁻²¹ we addressed different aspects of diffusion anomalies for different polymer-solvent systems. In continuation of these studies and

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as a further contribution in this area, we report here experimental results of sorption and diffusion of alkanes, viz., hexane, heptane, octane, nonane, decane, cyclohexane, and 2,2,4-trimethylpentane into TFE/propylene copolymer (TFE polymers) sheet membranes at 30, 45, and 60°C. These liquids are chosen particularly in view of their importance in petrochemical and other related industries and, hence, their migration into the polymeric sheet membranes has great practical relevance in chemical engineering areas. Moreover, from a fundamental viewpoint, an understanding of the molecular interactions between alkanes and the chosen polymer membrane is important.

In the present study, the molecular transport parameters viz., diffusion, D , permeation, P , sorption, S , and kinetic rate constant, k , were obtained in addition to activation parameters for these processes. From a knowledge of these parameters and from an analysis of the experimental and calculated results, the molecular transport phenomenon has been found to follow the anomalous-type behavior. Furthermore, the transport results have been discussed in terms of the penetrant shapes and their interactions with the polymer chain segments. Complex analytical solutions of Fick's equations and the numerical solutions based on the finite difference method have been used to obtain liquid concentration profiles into the membrane materials.^{22,23} These profiles have been studied in terms of diffusion parameters.

EXPERIMENTAL

Materials

FA 100S- and FA 150P-grade Aflas TFE polymer sheets in dimensions of $14.7 \times 14.7 \times 0.225$ cm were obtained from 3M Industrial Chemical Products Division, St. Paul, MN. These TFE elastomers are mixed with curatives, fillers, and other compounding ingredients by a conventional mill or internal mixing methods. In typical formulations, the peroxide curing agent and coagent are preblended with dry powders prior to adding to the base gum on the mill. For internally mixed compounds, a two-pass procedure is recommended with peroxide being added in the second pass. Care should be taken to avoid mixing temperatures above 121°C. After mixing, the stock solution should be cooled rapidly by either an air or water cooling technique and the mixed catalyzed compound should be stored in a cool dry place prior to use. Elastomer compositions along with some of their representative physical/mechanical properties are given in Table I.

Reagents

Alkanes are particularly selected because of their industrial importance and in view of their applications as solvent media in various petrochemical and industrial processes. These solvents were purchased from S.D. Fine Chemicals, Bombay. Hexane, heptane, octane, nonane, and decane were used directly. Cyclohexane and 2,2,4-trimethylpentane were double-distilled before use. The chemical formulas along with some important properties of these solvents are listed in Table II.

Sorption Experiments

Circular disc-shaped sheet membrane samples of a diameter of 1.96 cm were cut from the large polymer sheets using a sharp-edged carbon-tipped steel die. The cut samples were dried by storing them in a vacuum oven at 25°C, for 48 h before use. These samples were then soaked in screw-tight test bottles containing 15–20 mL of the respective solvents maintained at the desired temperature ($\pm 0.5^\circ\text{C}$) in a hot-air oven (WTB Binder, Germany). Polymer 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 ± 0.01 mg. The other experimental details are the same as given in our earlier articles.^{15–21}

When the samples attained equilibrium saturation, no more weight gain was observed and this did not change significantly over a further period of 1 or 2 days. The wt % gain, M_t , of the polymer samples by solvent molecules was calculated as

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

where W_0 is initial weight of the polymer sample, and W_t , its weight at time t for the immersion period.

RESULTS AND DISCUSSION

Sorption Behavior

The initial sorption results of this study, i.e., before the attainment of 50–55% equilibrium sorption, were analyzed by using an empirical equation^{24–26}:

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

Table I Compound Formulation and Some Representative Physical/Mechanical Properties of TFE Elastomers

Compounds	Low Compression Set Formulation (phr) ^a	Regular Formulation (phr) ^a	
		FA 100S	FA 150P
Aflas™ FA 100S/FA 150P	100	100	100
MT black (N-990)	15	30	30
Austin Black™ 325	15	—	—
Peroxide (Vul-Cup™ 40 KE)	4	4	4
Coagent (100% active TAIC)	5	4	4
Process aid (sodium stearate)	1	1	1

Properties	FA 100S		FA 150P	
Rheological Properties				
(at 177°C, 100 cpm, 3° arc, microdie)				
Minimum torque, in-lbs (N-m)	24.0	(2.71)	14.4	(1.63)
Time to 50% cure, min	3.0		3.5	
Maximum torque at 12 min, in-lbs (N-m)	69.5	(7.85)	60.0	(6.78)
Physical Properties				
Press cure 10 min at 177°C				
Tensile, psi (MPa) ASTM D-412	2170	(14.9)	1660	(11.4)
Elongation %, ASTM D-412	325		315	
Modulus at 100%, psi (MPa), ASTM D-42	465	(3.2)	425	(2.9)
Hardness, Shore A, ASTM D-2240	68		67	
Oven cure, 16 h at 200°C				
Tensile, psi (MPa)	2440	(17.3)	2050	(14.3)
Elongation %	285		270	
Modulus at 100%, psi (MPa)	660	(4.6)	680	(4.7)
Hardness, Shore A	72		72	
Brittle point, °C, ASTM D-2137	-40		-40	
Specific gravity	1.55		1.55	
Color	Dark brown		Dark brown	

^a phr, parts per hundred of rubber.

The parameters K and n were obtained by the method of least-squares. The M_t and M_∞ are the sorption values at time t and at equilibrium time.

The value of the exponent, n , indicates the type of transport mechanism. For a Fickian transport, the value of n is 0.50, while for non-Fickian transport,

Table II Some Properties of Solvents

Liquid	Chemical Formula	Molar Volume (cm ³ mol ⁻¹)	Solubility Parameter (J cm ⁻³) ^{1/2}
Hexane	H ₃ C(CH ₂) ₄ CH ₃	131.6	14.87
Cyclohexane	C ₆ H ₁₂	108.8	16.78
Heptane	H ₃ C(CH ₂) ₅ CH ₃	147.5	15.20
Octane	H ₃ C(CH ₂) ₆ CH ₃	163.5	15.48
2,2,4-Trimethylpentane	(CH ₃) ₃ CCH ₂ CH(CH ₃) ₂	166.1	14.01
Nonane	H ₃ C(CH ₂) ₇ CH ₃	179.7	15.65
Decane	H ₃ C(CH ₂) ₈ CH ₃	195.9	15.79

Table III Estimated Parameters of Eq. (2)

Liquid	n			$K \cdot 10^2$ (g/g min ⁿ)		
	30°C	45°C	60°C	30°C	45°C	60°C
Aflas FA 100S						
Hexane	0.56	0.51	0.54	2.51	4.14	3.75
Cyclohexane	0.51	0.52	0.51	0.91	1.65	2.40
Heptane	0.53	0.54	0.50	1.72	1.89	4.03
Octane	0.50	0.51	0.50	1.58	2.16	2.94
2,2,4-Trimethylpentane	0.51	0.56	0.54	1.55	1.96	2.46
Nonane	0.52	0.50	0.50	1.05	1.76	3.07
Aflas FA 150P						
Hexane	0.52	0.55	0.50	2.88	2.94	3.96
Cyclohexane	0.52	0.65	0.50	0.94	0.78	3.13
Heptane	0.50	0.56	0.50	2.53	2.22	4.31
Octane	0.50	0.62	0.51	2.73	1.10	2.76
2,2,4-Trimethylpentane	0.54	0.58	0.53	1.14	1.44	2.15
Nonane	0.50	0.54	0.51	2.00	1.58	2.76
Decane	0.52	0.51	0.50	3.12	1.28	2.04

n approaches unity. For rubbery polymers with organic solvents, the values of n range generally between 0.50 and 1.00, which is indicative of the anomalous transport behavior.

The estimated values of K and n are given in Table III. The values of n are accurate to ± 0.01 and those of K are accurate to ± 0.0005 . For the polymer FA 100S, the values of n range from 0.50 to 0.56, while for FA 150P, n varies between 0.50 and 0.65,

signifying higher deviation from Fickian behavior, particularly with FA 150P than with FA 100S polymer. However, in both cases, the values of n do not show any dependence on temperature. This suggests that transport phenomenon is very close to the Fickian mechanism. This is also supported by the initial linear plots of M_t vs. $t^{1/2}$ shown in Figures 1 and 2. On the other hand, the magnitude of K depends on the nature of the penetrant molecule. For

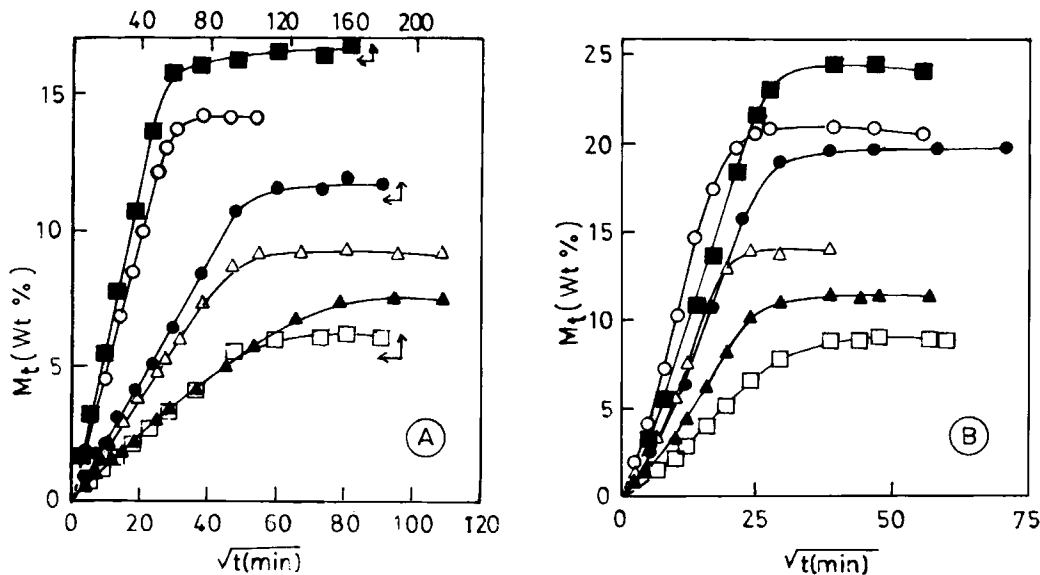


Figure 1 Sorption curves of FA 100S elastomer at (A) 30°C and (B) 60°C for (○) hexane, (●) cyclohexane, (△) heptane, (▲) octane, (■) 2,2,4-trimethylpentane, and (□) nonane.

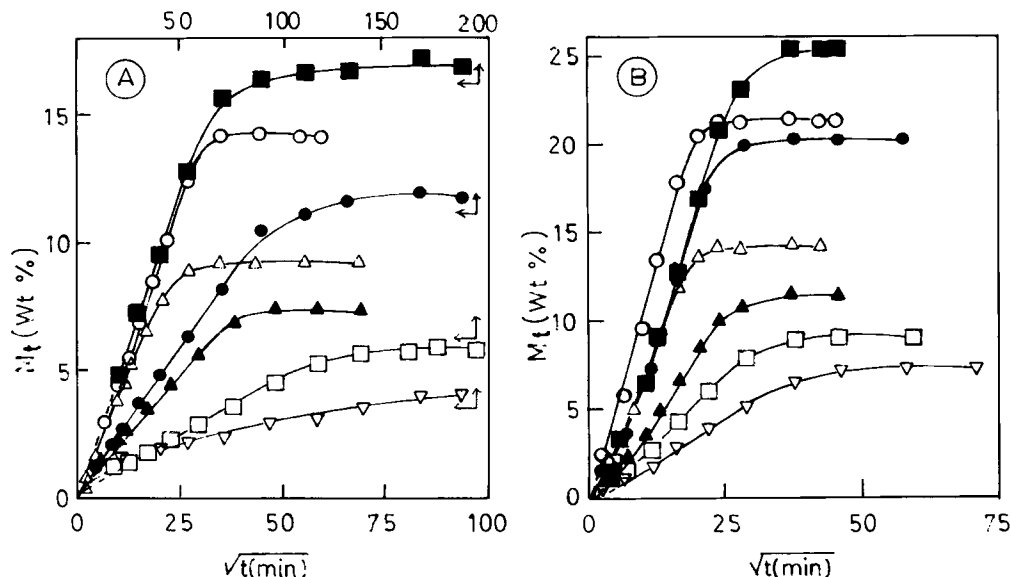


Figure 2 Sorption curves of FA 150P elastomer at (A) 30°C and (B) 60°C for the same liquids given in Figure 1. (▽) is the symbol for decane.

instance, these values are generally higher for a small molecule like hexane and, also, K shows an increasing trend with temperature except in a few cases. This suggests increased molecular interactions between solvent molecules and the polymer chain segments. Also, the values of K are higher for FA 150P polymer than for FA 100S, suggesting increased solvent interactions with FA 150P polymer than with FA 100S.

The results of sorption coefficients, S (which are calculated in wt % units from the M_∞ values of the sorption curves) are given in Table IV. From the experimental sorption curves for FA 100S polymer membranes with all the solvents at 30 and 60°C given in Figure 1, it is noticed that the shapes of the sorption curves, the equilibrium sorption values, and the time required to attain equilibrium saturation depend upon the size of the solvent molecules. For instance, nonane takes a longer time than do the lower alkanes. In between hexane and cyclohexane, the transport of the latter is slower than the former and also hexane exhibits a higher equilibrium sorption than does cyclohexane. Similarly, 2,2,4-trimethylpentane shows a higher equilibrium sorption than does octane. At 30°C, the initial sorption behaviors of hexane and 2,2,4-trimethylpentane are identical. A similar dependency is observed for cyclohexane and heptane as well as for nonane and octane. At 60°C, the sorption curves tend to become more sigmoidal than at lower temperatures. This suggests that deviation from the Fickian behavior becomes more significant at higher temperatures.

However, at 60°C, the attainment of equilibrium sorption is quick and also higher equilibrium sorption values are shown by all the solvents.

Sorption curves for FA 150P at 30 and 60°C are presented in Figure 2. The values of S decrease with increase in the chain length of alkanes and the S values for both the polymer samples are almost identical, suggesting that the transport within these two membrane systems are almost identical. Due to extremely smaller values of sorption for decane by the FA 100S membrane, the experiments for this system were not performed. For both polymers, there is a systematic increase of S with temperature. The increase in equilibrium sorption with increasing temperature indicates the increased molecular mobility of the polymer chain segments. The initial shapes of the M_t vs. $t^{1/2}$ plots change with increase in temperature, indicating that the molecular transport phenomenon is clearly influenced by temperature.

Diffusion and Permeation Behavior

The following assumptions have been made to calculate the diffusion coefficients of solvent molecules into the Aflas FA 100S and FA 150P sheet membranes:

- (i) Diffusion through thin-sheet membranes is assumed to be unidirectional.
- (ii) Sorption takes place under transient conditions with a constant diffusivity.

Table IV Sorption and Diffusion Coefficients of Aflas Membranes with Alkanes

Liquid	$D \cdot 10^7$ (cm ² s ⁻¹)								
	S (Wt %)			From Eq. (8)			From Eq. (11)		
	30°C	45°C	60°C	30°C	45°C	60°C	30°C	45°C	60°C
Aflas FA 100S									
Hexane	14.12	17.51	20.93	1.59	2.56	4.34	1.38	2.57	3.77
Cyclohexane	11.97	15.38	19.87	0.16	0.78	1.51	0.13	0.63	1.15
Heptane	9.23	11.60	14.00	0.84	1.31	2.64	0.75	1.00	2.53
Octane	7.41	9.32	11.35	0.35	1.10	1.78	0.39	1.01	1.45
2,2,4-Trimethylpentane	16.79	21.42	24.44	0.41	1.31	1.82	0.40	1.13	1.50
Nonane	6.07	7.39	9.05	0.10	0.57	1.02	0.10	0.56	1.32
Aflas FA 150P									
Hexane	14.21	17.77	21.57	1.76	3.09	3.55	1.74	2.54	3.56
Cyclohexane	11.96	15.38	20.28	0.17	0.87	1.11	0.16	0.38	1.21
Heptane	9.20	11.60	14.16	0.79	2.12	2.41	1.05	1.61	2.58
Octane	7.41	9.34	11.37	0.28	1.21	1.76	0.72	0.70	1.45
2,2,4-Trimethylpentane	17.26	20.72	25.28	0.48	0.87	2.01	0.43	0.74	1.59
Nonane	5.90	7.48	8.95	0.11	0.56	1.09	0.32	0.57	1.07
Decane	4.02	7.05	7.26	0.12	0.22	0.89	1.27	0.40	0.76

- (iii) During sorption, when the membrane comes into contact with the solvent, the solvent concentration on the membrane surface reaches the equilibrium value soon after the sample is immersed in the solvent.
- (iv) The time required for the polymer to establish thermal equilibrium is negligible when compared to the time of sorption.
- (v) Changes in polymer dimensions are negligible during the immersion experiment.

The one-dimensional diffusion equation is described by Fick's second law of diffusion for a constant diffusivity as²⁷

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

where C is the liquid concentration in the polymer matrix at a time, t , and distance, x , with the following initial and boundary conditions:

$$t = 0 \quad 0 < x < h \quad C = 0 \quad (4)$$

$$t > 0 \quad x = 0, x = h \quad C = C_{\infty} \quad (5)$$

The analytical solution of eq. (3) to determine the solvent concentration developed during sorption through the membrane of thickness, h , at a time, t , and distance, x , is given by²⁷

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

where $C_{(t,x)}$ and C_{∞} are solvent concentrations at a time, t , and distance, x , and at equilibrium, respectively. D is the diffusion coefficient and n is an integer.

The concentration profiles at 30 and 60°C for FA 100S and FA 150P samples with octane calculated from eq. (6) at different time intervals are displayed in Figure 3 wherein it can be seen that increased diffusion rates at higher temperature widens the spacings between the concentration profiles. The amount of liquid sorbed by the membrane material is also given by

$$\begin{aligned} \frac{M_t}{M_{\infty}} = & 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \\ & \times \exp \left[- \frac{D(2n+1)^2 \pi^2}{h^2} t \right] \quad (7) \end{aligned}$$

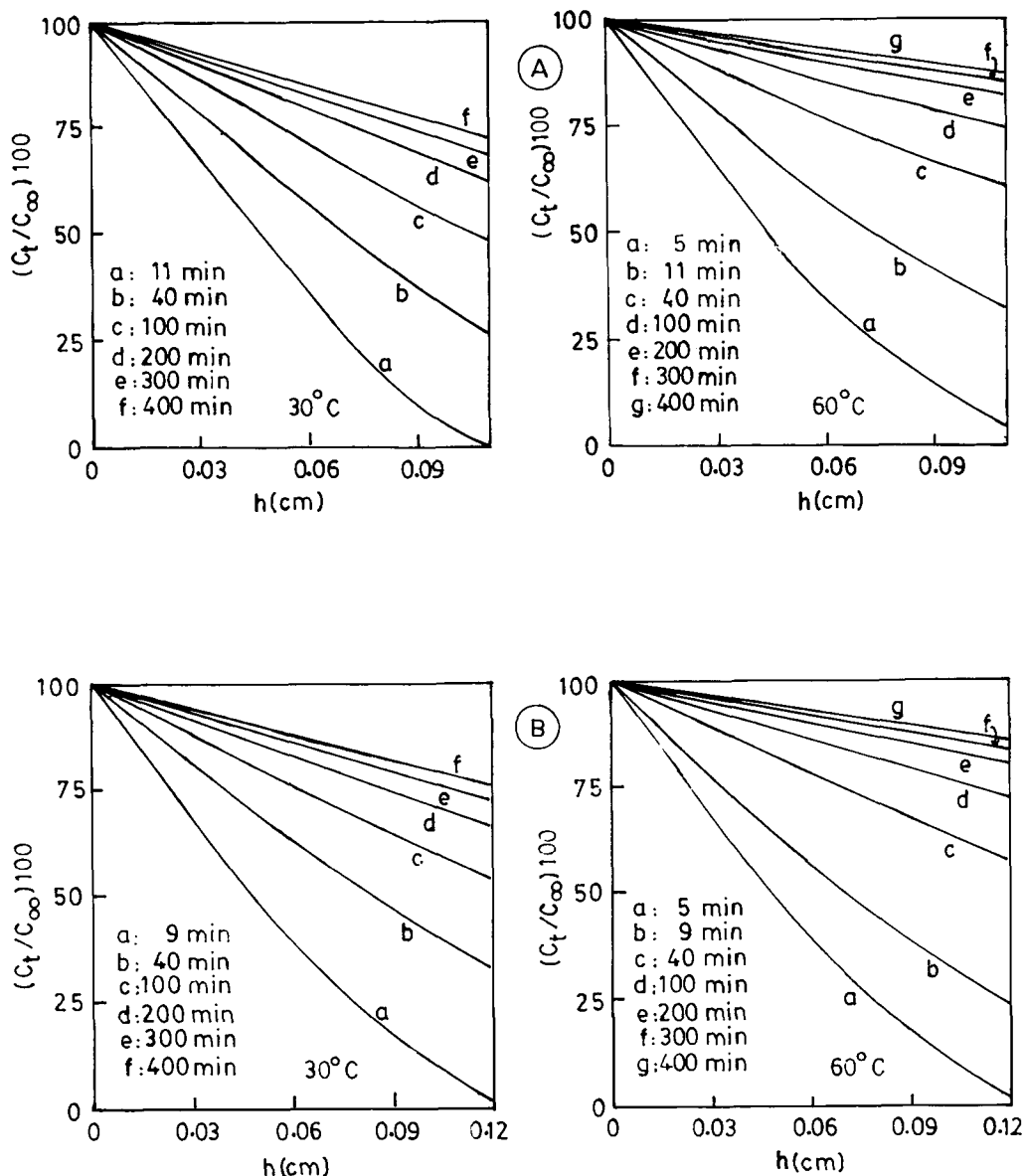


Figure 3 Theoretical concentration profiles calculated from eq. (6) for (A) FA 100S and (B) FA 150P with octane at 30 and 60°C.

However, the diffusivity before completion of 55% equilibrium sorption is then calculated using the short-time equation:

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

The calculated values of diffusion coefficients are also included in Table IV. These values are accurate to $\pm 0.01 \times 10^7 \text{ cm}^2 \text{ s}^{-1}$. It is found that hexane exhibits the highest D value of $1.59 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, while the smallest D of $1.01 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$

is observed for nonane with FA 100S. A similar dependency exists for sample FA 150P. The intermediate values are observed for the remaining solvents. Cyclohexane, due to its cyclic nature, exhibits slower diffusion rates than do many other alkanes. A systematic dependence of diffusion coefficients on the size of n -alkanes is observed for both the polymer samples at all temperatures. The results of the permeability coefficients, P , calculated from $P = D \cdot S$ are presented in Table V. These results are higher for hexane in the investigated range of temperature than for the other liquids. The smallest values of P are ob-

Table V Permeability Coefficients and Kinetic Rate Constants of Aflas Membranes with Alkanes

Liquid	$P \cdot 10^8$ (cm ² s ⁻¹)			$k \cdot 10^3$ (min ⁻¹)		
	30°C	45°C	60°C	30°C	45°C	60°C
<u>Aflas FA 100S</u>						
Hexane	2.24	4.48	9.09	3.02	5.10	5.78
Cyclohexane	0.19	1.20	3.01	0.21	1.24	2.52
Heptane	0.78	1.52	3.70	1.15	1.89	4.62
Octane	0.26	1.02	2.02	0.56	1.47	2.98
2,2,4-Trimethylpentane	0.68	2.81	4.46	0.78	2.05	3.00
Nonane	0.06	0.42	0.92	0.20	0.88	2.05
<u>Aflas FA 150P</u>						
Hexane	2.50	5.50	7.65	2.70	4.12	4.65
Cyclohexane	0.21	1.33	2.24	0.26	1.25	2.65
Heptane	0.72	2.46	3.41	1.17	2.71	4.51
Octane	0.21	1.13	2.01	0.49	1.47	2.79
2,2,4-Trimethylpentane	0.83	1.80	5.09	0.61	1.71	2.29
Nonane	0.07	0.42	0.98	0.18	1.05	1.93
Decane	0.05	0.16	0.65	0.20	0.30	1.37

served for nonane with FA 100S and for decane with FA 150P.

Numerical Analysis

In many cases, numerical schemes using the finite difference method are also used to calculate the liquid concentration profiles into the membrane materials.^{22,23} Such profiles of liquid concentrations at various time intervals for different membrane thicknesses are obtained using the following equation²²:

$$CN_m = \frac{1}{M} [C_{m-1} + (M - 2)C_m + C_{m+1}] \quad (9)$$

with the dimensionless parameter, M , given as

$$M = \frac{(\Delta x)^2}{\Delta t} \frac{1}{D} \quad (10)$$

In the above equation, for computational purposes, we divided the membrane thickness into 10 slices of equal size, Δx . Each slice is characterized by an integer, m . The C_m and CN_m represent the liquid concentrations at a position, m , at a time, t , and after an elapse of time, Δt , respectively. For each position, the liquid concentration curves were generated in the computer for different time inter-

vals. It may be noted that the numerical scheme is built when the liquid is transported into the membrane sheet in one dimension.

The simulated concentration profiles at 30°C for sorption cycles for both FA 100S and FA 150P samples are displayed typically for hexane and nonane in Figures 4 and 5. It is found that these concentration profiles show a dependence on the size of the alkanes rather than on their solvent characteristic properties. For instance, with hexane, these profiles at different times are widely spaced, suggesting the quick transport (i.e., higher diffusivity) of hexane into the membrane sheet. As the size of the liquid molecule increases from hexane to nonane, the concentration profiles are more narrowly spaced, suggesting a slow transport (i.e., lower diffusivity) of bigger molecules into the membrane network systems. It is further gratifying to note that the concentration profiles exhibit a systematic dependence on temperature as shown in Figure 6. The concentration profiles at 30°C for octane are more narrowly spaced than those at 60°C, signifying increased diffusivity at 60°C and thereby attributing it to a free movement of the liquid molecules into the membrane matrix at higher temperature. This dependence is observed for both FA 100S and FA 150P (Fig. 6). A comparison of concentration profiles from the analytical solution of eqs. (6) and (9) is made at 30°C in Figure 7 for the 100S and 150P samples. Linear variations are observed for the calculated

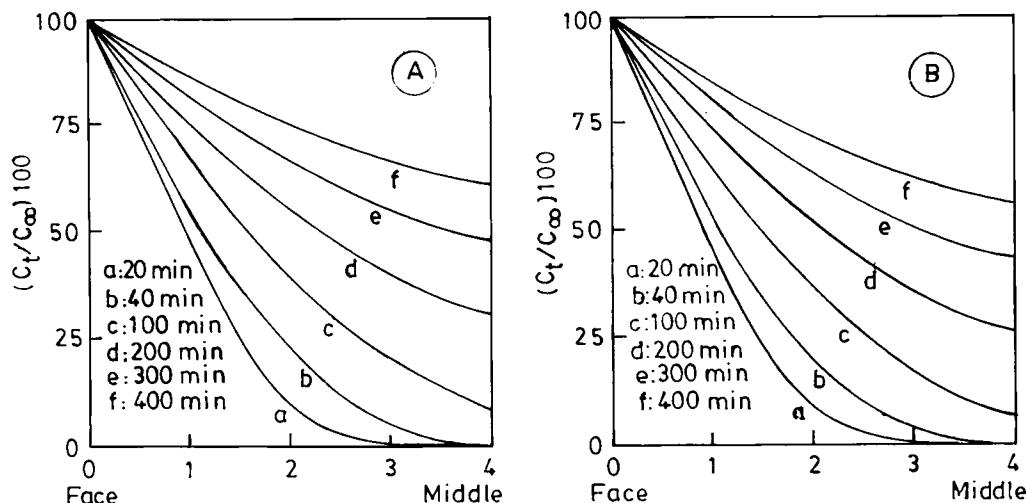


Figure 4 Simulated concentration profiles from numerical eq. (9) for (A) FA 100S and (B) FA 150P with hexane at 30°C, from a face to the middle of the sample for different times.

profiles, and smooth curves are found for the numerical method. A systematic variation based on the chain length of alkanes is observed with 100S, but this is not true in the case of the 150P sample.

Using the values of D as calculated from eq. (8), the theoretical sorption curves were generated from eq. (7). These curves are compared with the experimental sorption kinetic curves in Figure 8 typically for hexane and nonane with FA 100S and FA 150P at 30°C. Excepting 150P with nonane, the agreement between the theoretical and experimental curves in the initial stages is very good, but these curves deviate at later stages, showing a slight concentration dependency of D for these systems. This prompted

us to calculate the average diffusion coefficient and its dependency on solvent concentration.

To test the mathematical relation for the determination of D into the polymer membrane at longer diffusion times, the following relation is deduced from eq. (7) to give²⁸

$$\ln(1 - M_t/M_\infty) = \ln\left(\frac{8}{\pi^2}\right) - \frac{D\pi^2 t}{h^2} \quad (11)$$

Here, a plot of $\ln(1 - M_t/M_\infty)$ vs. t should be linear and the slope is directly proportional to D . Some of our data have been plotted in this format, which are in conformity with eq. (11) (see Fig. 9). The calcu-

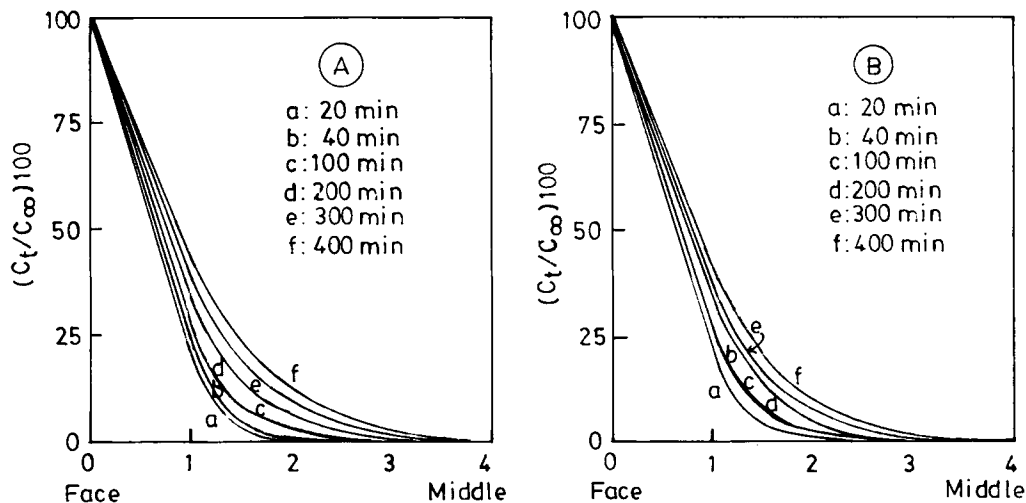


Figure 5 Same as in Figure 4 for nonane at 30°C.

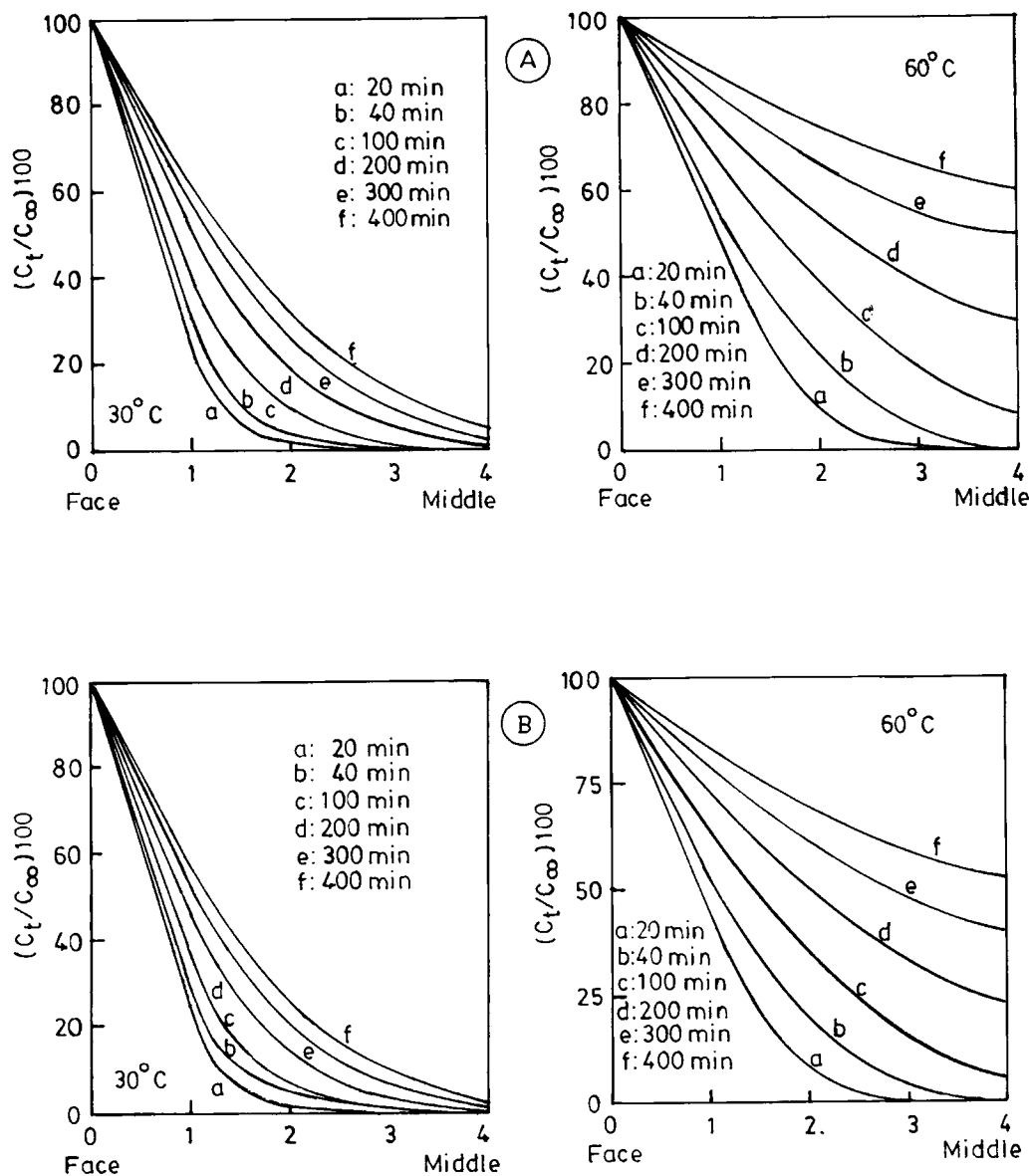


Figure 6 Simulated concentration profiles from numerical eq. (9) for (A) FA 100S and (B) FA 150P for octane at 30 and 60°C.

lated values of D from eq. (11) are compared in Table IV along with those obtained from eq. (8). The agreement is good for all the systems.

Kinetics of Sorption

Crosslinked rubbery polymers are known to exhibit swelling in the presence of organic solvent. This kind of limited swelling in semicrystalline polymers is due to sorption kinetics. Thus, by using the first-order kinetic equation, the first-order kinetic rate constant k can be calculated as¹⁴

$$dM/dt = k(M_{\infty} - M_t) \quad (12)$$

which upon integration gives

$$kt = \ln[M_{\infty}/(M_{\infty} - M_t)] \quad (13)$$

The calculated values of the rate constants in the temperature interval of 30–60°C are also included in Table V. The kinetic rate constants follow a regularly increasing trend with temperature and show a decrease with increasing size of the solvent molecules. The kinetic rate constants at 30°C vary in

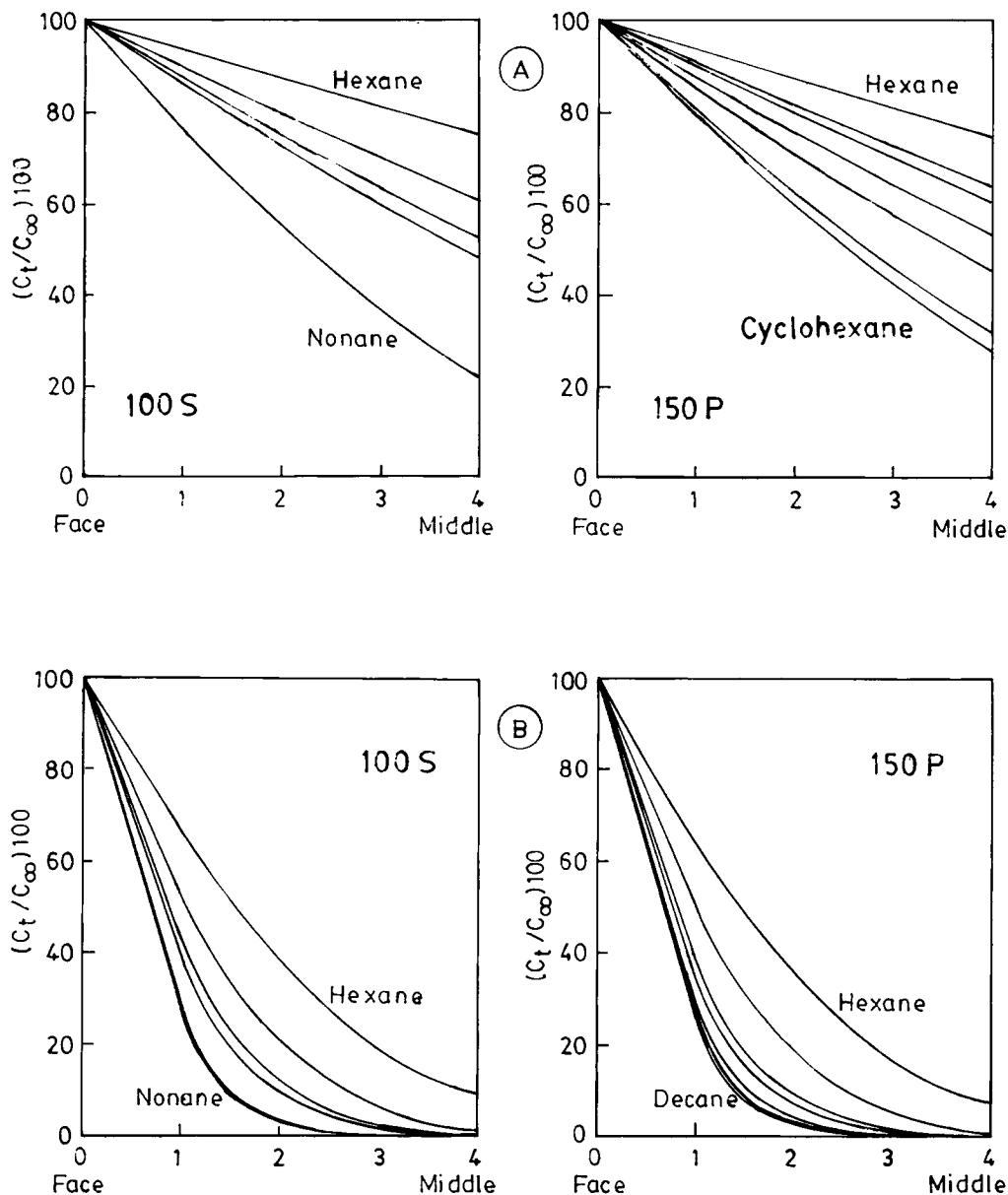


Figure 7 Comparison of concentration profiles for FA 100S and FA 150P with alkanes by the (A) analytical method, using eq. (6) and (B) numerical eq. (9) at 30°C.

the same order as those of D and P values in view of the fact that at long sorption times the term $n \geq 1$ as well as $\ln(8/\pi^2)$ may be ignored so that eqs. (7) and (11) simplify to give

$$\ln\left(\frac{M_\infty}{M_\infty - M_t}\right) \cong \frac{\pi^2 Dt}{h^2} \quad (14)$$

where

$$k = \frac{\pi^2 D}{h^2} \quad (15)$$

For extensive swelling, h^2 obviously does not remain constant and, hence, D increases due to the influx of the solvent into the polymer. However, the first-order kinetics seems to apply in the present polymer-solvent systems.

Temperature Effects and Arrhenius Parameters

The sorption and diffusion results show an increase with increasing temperature and, hence, attempts have been made to estimate the values of the Arrhenius activation energy, E_D , for diffusion as

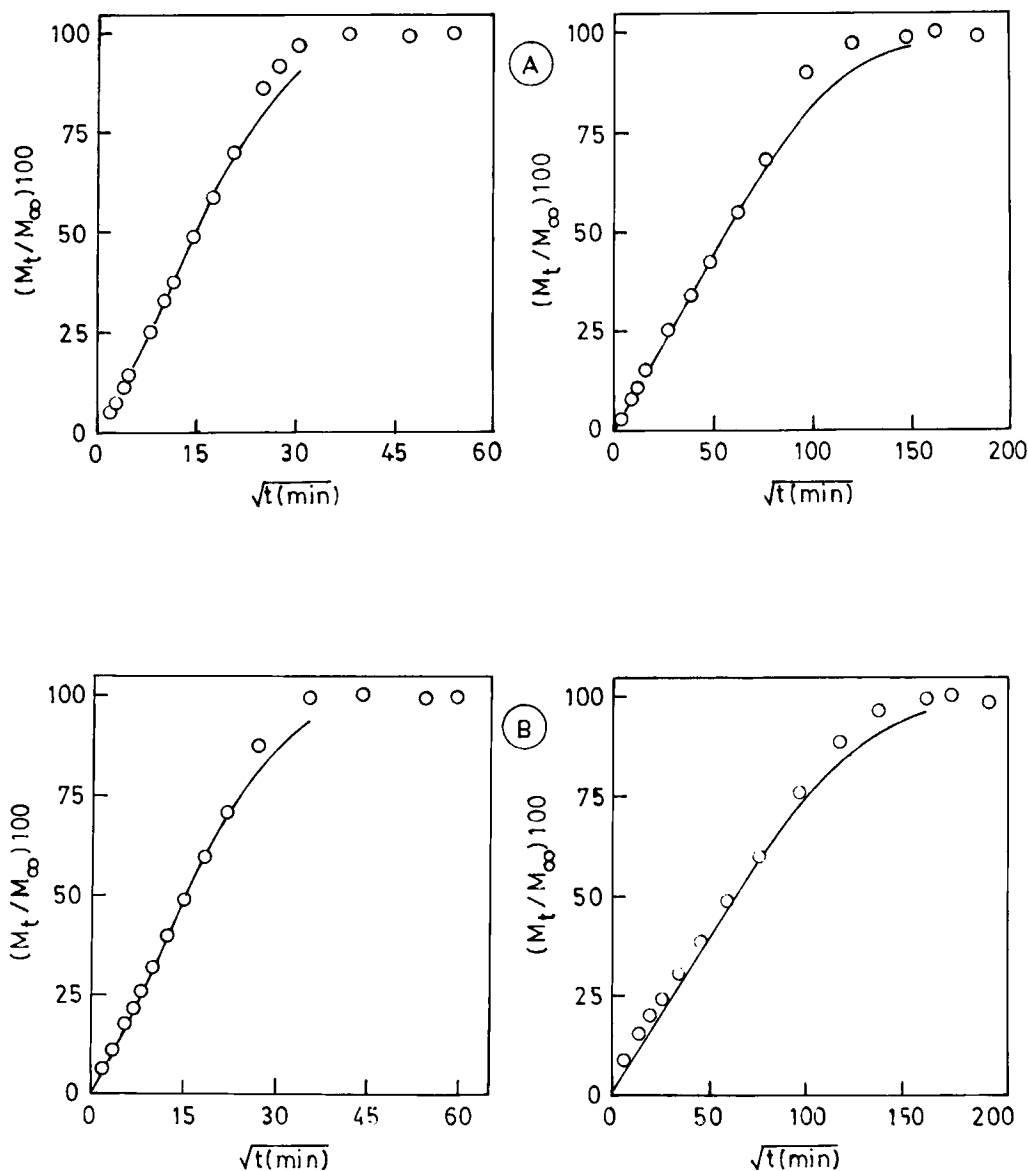


Figure 8 Comparison of theoretical (solid curves) and experimental sorption points for FA 100S and FA 150P samples with (A) hexane and (B) nonane at 30°C.

$$D = D_0 \exp(-E_D/RT) \quad (16)$$

$$S = S_0 \exp(-\Delta H_S/RT) \quad (17)$$

Here, E_D is a function of both intra- and interchain forces which must be overcome to create the space for a unit diffusional jump of the penetrant molecule. The D_0 is a preexponential factor and the energy term; RT has the usual meaning. Activation energy will be greater the larger the penetrant molecule, the stronger the polymer cohesive energy, and the more rigid the polymer chain segments.

In a similar manner, S can be expressed by the van't Hoff equation with a preexponential factor, S_0 , as

where ΔH_S is the heat of sorption and is a composite parameter. This involves contributions from (i) the Henry's law mode which requires both the formation of a site and the dissolution of the species into that site (the formation of a site involves an endothermic contribution to this process), and (ii) Langmuir's (hole filling)-type sorption mechanisms, in which case the site already exists in the polymer matrix and sorption by hole filling gives exothermic heats of sorption.

The calculated values of E_D and ΔH_S from the least-squares procedure are given in Table VI. The results

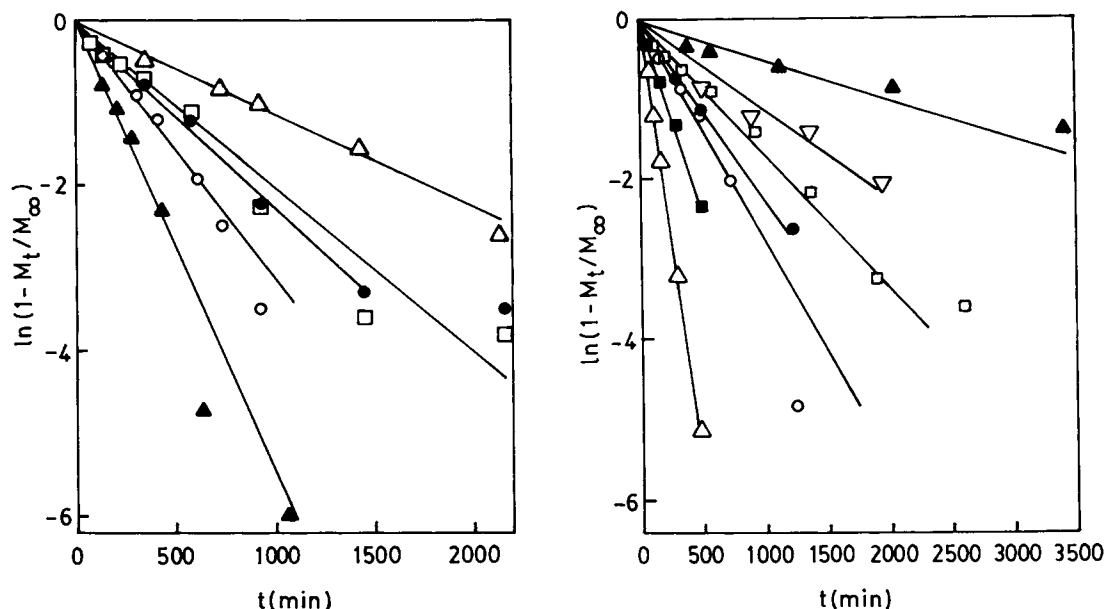


Figure 9 $\ln(1 - M_t/M_\infty)$ vs. t plots for the polymer-solvent systems given in Figures 1 and 2.

of E_D show an increase with increasing size of n -alkanes. The E_D for cyclohexane is quite higher than is hexane and the E_D of cyclohexane is almost equivalent to that of nonane. It may be noted that in all cases the values of ΔH_S are positive, suggesting that sorption is dominated mainly by the Henry's law of sorption mode giving an endothermic contribution. The results of percent increase in volume, $\Delta V\%$, are

also presented in Table VI, which indicate higher swelling for lower n -alkanes than for higher alkanes.

CONCLUSIONS

This article addresses the solvent transport (sorption and diffusion) of alkanes into two important

Table VI Activation Energy for Diffusion, Enthalpy of Sorption, and Percent Increase in Volume for Aflas Membranes with Alkanes

Liquid	E_D (kJ mol ⁻¹)	ΔH_S (kJ mol ⁻¹)	$\Delta V\%$
<u>Aflas FA 100S</u>			
Hexane	28.14	11.03 ± 0.31	32.3
Cyclohexane	63.73	14.18 ± 0.48	24.4
Heptane	31.83	11.68 ± 0.36	20.7
Octane	45.50	11.94 ± 0.19	17.9
2,2,4-Trimethylpentane	42.28	10.55 ± 1.52	36.7
Nonane	64.92	11.18 ± 0.42	14.1
<u>Aflas FA 150P</u>			
Hexane	19.77	11.68 ± 0.19	32.9
Cyclohexane	52.55	14.77 ± 0.81	21.7
Heptane	31.66	12.06 ± 0.21	21.1
Octane	51.91	11.98 ± 0.26	17.2
2,2,4-Trimethylpentane	39.94	10.67 ± 0.55	34.7
Nonane	63.56	11.70 ± 0.61	11.1
Decane	56.83	16.81 ± 0.81	10.9

copolymeric membranes made of tetrafluoroethylene and propylene monomers. These copolymers exhibit an anomalous transport behavior for the chosen solvent media. The transport parameters have shown a systematic dependence on the size of the solvent molecules and the experimental temperature. The Arrhenius diffusion parameters follow the conventional tradition laid by the Eyring's absolute reaction rate theory. The liquid concentration profiles generated for liquids within the polymer samples have been explained successfully on the basis of their diffusivity and permeability coefficients. For field applications, it becomes difficult to judge the quality of either FA 100S or FA 150P as both the polymers behave almost identically for the chosen solvent media.

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