Sorption and Diffusion of Organic Esters into Fluoropolymer Membranes

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SYNOPSIS

A sorption gravimetric technique has been used to estimate the diffusion and thermodynamic parameters of four different VITON fluoropolymers in the presence of five ester molecules. Diffusion parameters have been obtained by assuming the Fickian transport and their concentration dependencies are studied. Fluorine contents of the fluoropolymers have significant effects on the membrane transport characteristics. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Molecular transport of organic chemicals into elastomers has been studied extensively in the past two decades in view of their importance in a number of areas such as chemical pond lining, polymer processing, and membrane science phenomena.[1,2] When polymer products are brought in contact with organic chemicals, a reduction in polymer property often occurs due to swelling and relaxation of the chain segments, sometimes leading to chemical degradation of the products. Previous papers[3-5] from this laboratory reported on the use of a gravimetric method as a rapid and convenient means of studying polymer–solvent interactions, wherein a group of organic solvents were studied with a number of structurally different polymer membranes.

The DuPont VITON fluoropolymer series is one of the toughest and most versatile polymers ever developed to seal hot and corrosive fluids that quickly destroy ordinary rubber. Generally, VITON has excellent resistance to oils, fuels, lubricants, most mineral acids, and hydraulic fluids and resists aliphatic and aromatic hydrocarbons such as carbon tetrachloride, benzene, toluene, and xylene that act as solvents for other rubbers. Furthermore, VITON remains tough and elastic even after long-term exposure to 150°C in oil. However, VITON is not recommended for certain amines, hot anhydrous hydrofluoric or chlorosulfonic acids, and alkylphosphate esters; the resistivity of VITON polymers in the presence of esters is not known. This prompted us to undertake a detailed investigation of the interaction of these membranes with esters such as methyl acetate, ethyl acetate, isopropyl acetate, isobutyl acetate, and isoamyl acetate in the temperature interval of 25–60°C. Diffusion and sorption parameters of four different fluoropolymers with the esters were evaluated from the Fickian model. Efforts were also made to estimate the activation parameters from the temperature-dependent diffusion parameters. Furthermore, the first-order kinetic equation was used to analyze the sorption data. The experimental and computed results were explained in terms of the nature of polymer–solvent interactions.

EXPERIMENTAL

Materials

Molded polymer sheets in dimensions of (1/16) × 6 × 6 in. were fabricated in DuPont's R & D plant. Polymers of VITON slabs were classified into three types as A, B, and F. The A type is based on VITON A201C with a fluorine content of 66% and the sample is designated as 1430, which contains dipolymers of hexafluoropropylene (HFP) and vinyledene fluoride (VF$_2$). The B type is based on VITON B600 with a fluorine content of 68% and the sample is designated as 1141, which contains terpolymers of HFP, VF$_2$, and tetrafluoroethylene (TFE). The two F-type samples are VITON GF (with 70% fluorine) and VITON GFLT (with 67% fluorine) and are designated, respectively, as samples 1433 and 1144. The prefix "G" in F-type families of samples designates polymers that are peroxide-curable. Because of comparable fluorine levels, polymers within families have similar heat and fluid resistance in addition to similar low-temperature properties. The elastomer compositions and their representative properties are given in Table I.

VITON fluoropolymers and products based on them present no health hazards. However, certain hazards may arise during the compounding and processing of the raw polymers into finished products or during service at temperatures above 200°C. For example, toxic vapors including hydrogen fluoride are possible at temperatures above 200°C.

Reagents

Reagent-grade solvents, namely, methyl acetate, ethyl acetate, isopropyl acetate, isobutyl acetate, and isoamyl acetate, were double-distilled before use. The polymer samples were cut circularly (diameter

Table I Elastomer Compositions and Representative Properties

	Elastomer			
	1144	1433	1141	1430
VITON GFLT	100			
VITON GF		100		
VITON B600			100	
VITON A-201C				100
Fluorine Content (%)	67	70	68	66
Magnalite D[a]			3	
MT Black (N990)	30	30	30	25
Diac No. 7 (TAIC)[b]	3	3		
Luperco 101XL[c]	3	3		
Sublimed litharge[d]	3	3		
Calcium hydroxide			6	6
VPA No. 3[e]			1	
VPA No. 2[f]				0.5
100% modulus, MPa (Psi)	7.4	7.9	6.3	5
(ASTM D412-87, pulled)	(1075)	(1145)	(910)	(730)
Tensile strength, MPa (Psi)	14.5	19	13	14.5
(at 8.55 mm/s)	(2095)	(2750)	(1890)	(2120)
% Elongation at break	150	180	220	220
Hardness, Durometer A,				
points (ASTM D2240-87)	74	77	74	78
Specific gravity	1.89	1.91	1.85	1.82
Vulcanizate properties				
Press cure	10 m/177°C	10 m/177°C	10 m/177°C	5 m/180°C
Post cure	24 h/232°C	24 h/232°C	24 h/232°C	24 h/230°C

[a] High activity magnesium oxide.
[b] A curing agent (organic triazine).
[c] An organic peroxide [2,5-dimethyl-2,5-bis(t-butyl peroxyl)hexane].
[d] Lead oxide.
[e] A processing aid that is sulfone on the inert carrier.
[f] A processing aid that is natural vegetable wax.

= 1.96 cm) by a sharp-edged steel die. The thickness measurements were made at several points on the membranes using a micrometer screw gauge with an accuracy of ±0.001 cm.

Sorption Experiments

Sorption experiments were performed on cut polymer samples by immersing them in test bottles containing about 30–40 mL of the solvent maintained at the desired temperature in an electric oven (Memmert, Germany). The experimental details are the same as described earlier.[3–5] The output from a sorption experiment is the percent fractional weight gain vs. square root time, $t^{1/2}$ profile, for different values of the initial thickness, h, of the polymer samples. For the sake of convenience, these values were converted into mol % units expressed as moles of solvent sorbed by 100 g of the polymer sample.

For a Fickian mechanism, the sorption curves are generally independent of material thickness. If there is a negligible concentration-dependence of diffusivity over the concentration interval studied in a sorption experiment, a value of the mutual diffusion coefficient D can be calculated from the initial slope, θ, of the sorption curve as[6]

$$D = \pi(h\theta/4Q_\infty)^2 \qquad (1)$$

where Q_∞ is the maximum equilibrium sorption value for the polymer–solvent system. The slope θ, used in eq. (1), is calculated by using the least-squares technique to fit the linear part of the sorption curves before the attainment of 50% of equilibrium.

RESULTS AND DISCUSSION

The mol % uptake data, Q_t, as a function of square root of time, $t^{1/2}$, for the polymer + ester systems at 25°C are presented in Figures 1 and 2. In all cases, sorption is affected by the chemical constituent of the polymer membrane in addition to its fluorine content. The membrane 1430 contains 66% of fluorine, the lowest among the series of membranes tested. This membrane exhibits a higher sorption for all the esters as compared to other membranes.
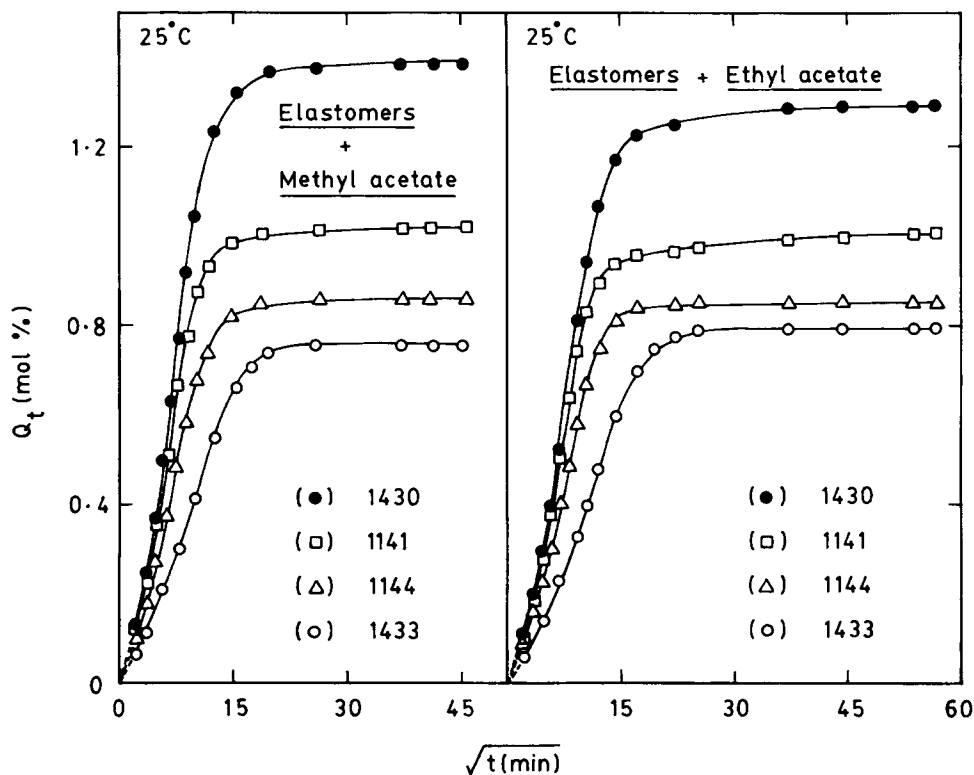

Figure 1   Mol % sorption Q_t vs. square root of time, $t^{1/2}$ at 25°C for methyl acetate and ethyl acetate with elastomers. Symbols for elastomers: (●) 1430; (□) 1141; (△) 1144; (○) 1433.
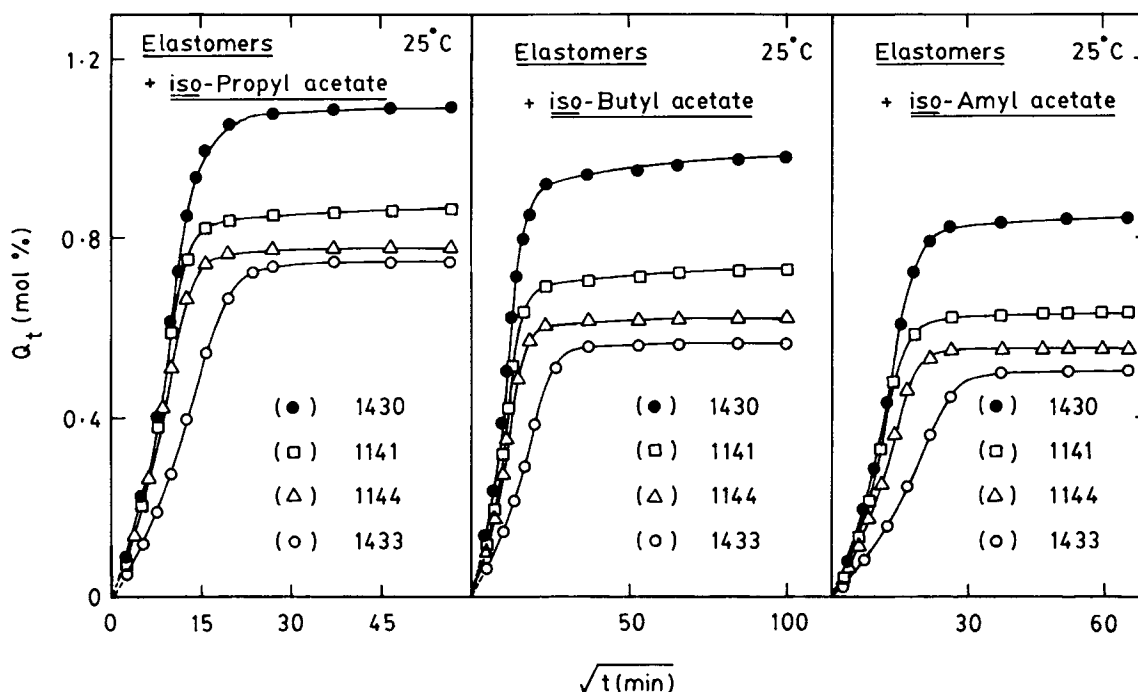
Figure 2   Mol % sorption Q_t vs. square root of time, $t^{1/2}$ at 25°C for isopropyl acetate, isobutyl acetate, and isoamyl acetate with elastomers. Symbols for elastomers have the same meaning as in Figure 1.

The sorption of solvent molecules decreases systematically with an increase in the size of the penetrant molecules. However, this decrease in maximum sorption value is not so significant in the case of methyl acetate and ethyl acetate for the remaining membranes (see Fig. 1). The membrane 1433 with a fluorine content of 70% (the highest in the series considered) shows the lowest values of Q_∞ for all the penetrants. In case of 1433, sorption of ethyl acetate seems to be higher than that of methyl acetate. The remaining membranes, viz., 1141 and 1144, exhibit the intermediary sorption values between those of 1430 and 1433. In any case, a clearcut relationship exists between the fluorine content of the membranes with their solvent sorption capacities. With an increase in percent content of fluorine, there is a decrease in solvent sorptivity.

For branched esters like isopropyl acetate, isobutyl acetate, and isoamyl acetate, we observe a systematic decrease of sorption for all the polymer samples with an increase in the size of the ester molecules (see Fig. 2). However, in general, for all the esters, the sorption values of the membranes follow the sequence 1430 (66% fluorine) > 1141 (68% fluorine) > 1144 (67% fluorine) > 1433 (70% fluorine). Thus, it appears that the higher the fluorine content in the elastomer the lower is its sorption tendency. The shapes of the sorption curves are

more or less identical in all cases. However, the sorption curves are less sigmoidal. The initial portions of these curves are linear (i.e., before 50–55% completion of equilibrium) and from the slopes, θ, of the curves, the concentration-independent diffusion coefficients D have been calculated from eq. (1). These data together with the maximum sorption results are presented in Table II for all the polymer-solvent systems over the temperature interval of 25–60°C.

The decrease in sorption constant as a function of the molecular size of the penetrant can be attributed to the fact that smaller molecules occupy less volume and thereby transport more quickly than do the larger ones.[7,8] Additionally, the sorption seems to be governed not only by the differences in solubility parameters of solvents but also that of the polymer molecular structure (and its constituents) in addition to the size of the penetrant molecule. Furthermore, with all the penetrants, sorption might effectively take place only in the preexisting volume of the elastomer. The hole size decreases exponentially and, therefore, the available volume for sorption decreases when the penetrant size increases. Additionally, the polymer molecular structure and the shape of the penetrant molecule might also affect the equilibrium sorption data.

It may be noted that the solvent transport and

polymer chain extensions are intimately coupled when the polymer swells from the unperturbed to the solvated state. The increased chain mobility due to swelling stresses allows chain extension, resulting in additional free volume to facilitate the solvent transport. This is a dynamic relaxation phenomenon that affects the molecular transport of the solvent molecules into the polymer membrane. A rigorous mathematical analysis of the penetrant transport in swelling rubbery systems is an extremely difficult task and, thus, we shall attempt to analyze the data from the phenomenological viewpoints.

It would be also interesting to offer some comments on the times required to attain equilibrium for the penetrant–membrane systems. For the polymer 1430, the attainment of sorption equilibrium is much quicker with all the liquids as compared to other polymer membranes. However, the equilibrium attainment for 1433 is quite slow for all solvents. The membranes 1141 and 1144 have shown the intermediate values of equilibrium times. From the data given in Table II, it is observed that with a rise in temperature the values of D increase. With methyl acetate, due to its high volatility, the higher limit of temperature was restricted to 50°C. Moreover, the S values for this penetrant at 50°C are not systematic; in fact, sorption at 40°C was lower than at 25°C and the sorption data at 40 and 50°C are almost identical. Typical temperature-dependent sorption plots in the case of 1430 membrane with methyl ac-

etate, ethyl acetate, and isopropyl acetate are shown in Figure 3. From the sorption data given in Table II, it is observed that in all cases sorption decreases with a rise in temperature. Such anomalies have been discussed earlier.[3,5]

To investigate the type of diffusion mechanism, the sorption data of the polymer–solvent systems have been fitted to the following relation[9]:

$$\log(Q_t/Q_\infty) = \log K + n \log t \qquad (2)$$

where Q_t and Q_∞ represent the mol % increase in concentration at time, t, and at equilibrium time, t_∞. The value of n decides the type of transport mechanism. A value of $n = 0.5$ represents the Fickian mode and $n = 1$ indicates the non-Fickian transport. The intermediate values between 0.5 and 1.0 have been attributed to the anomalous transport mechanism.[9] However, the constant K of eq. (2) depends on the structural characteristics of the polymer network in addition to its interaction with the solvent. From a least-squares analysis, the values of n and K have been estimated and are listed in Table III. We could observe that in almost all cases the values of n vary between 0.6 and 0.75, suggesting the transport mechanism to be of an anomalous type. However, we could not observe any systematic dependence of n on temperature. On the other hand, K is found to increase steadily with an increase in temperature, suggesting increased polymer segmental

Table II Diffusion and Sorption Coefficients for Fluoropolymer + Ester Systems at Different Temperatures

| Ester	Temp (°C)	$D \times 10^7$ (cm²/s)				S (mol %)			
		1141	1144	1430	1433	1141	1144	1430	1433
Methyl acetate	25	9.69	8.85	11.05	7.64	1.02	0.86	1.39	0.76
	40	13.97	11.93	15.98	10.60	0.96	0.81	1.35	0.74
	50	14.67	14.43	17.79	10.95	0.98	0.84	1.29	0.75
Ethyl acetate	25	7.63	7.40	8.00	5.82	1.00	0.85	1.29	0.79
	44	11.59	10.31	13.58	9.03	0.92	0.8₁	1.21	0.76
	60	12.80	11.98	16.95	11.29	0.87	0.78	1.15	0.73
Isopropyl acetate	25	5.30	6.11	6.56	4.44	0.87	0.78	1.09	0.75
	44	8.22	7.82	9.34	6.44	0.80	0.72	1.01	0.69
	60	10.66	10.15	11.73	8.97	0.74	0.68	0.95	0.64
Isobutyl acetate	25	2.92	2.95	4.45	2.32	0.72	0.62	0.96	0.56
	44	5.10	5.23	6.12	3.75	0.65	0.57	0.86	0.52
	60	6.81	7.10	8.05	4.92	0.62	0.54	0.83	0.49
Isoamyl acetate	25	3.17	3.18	4.15	2.15	0.64	0.55	0.84	0.50
	44	5.26	4.90	5.85	3.44	0.58	0.50	0.77	0.46
	60	6.65	6.68	8.05	5.04	0.54	0.48	0.73	0.43
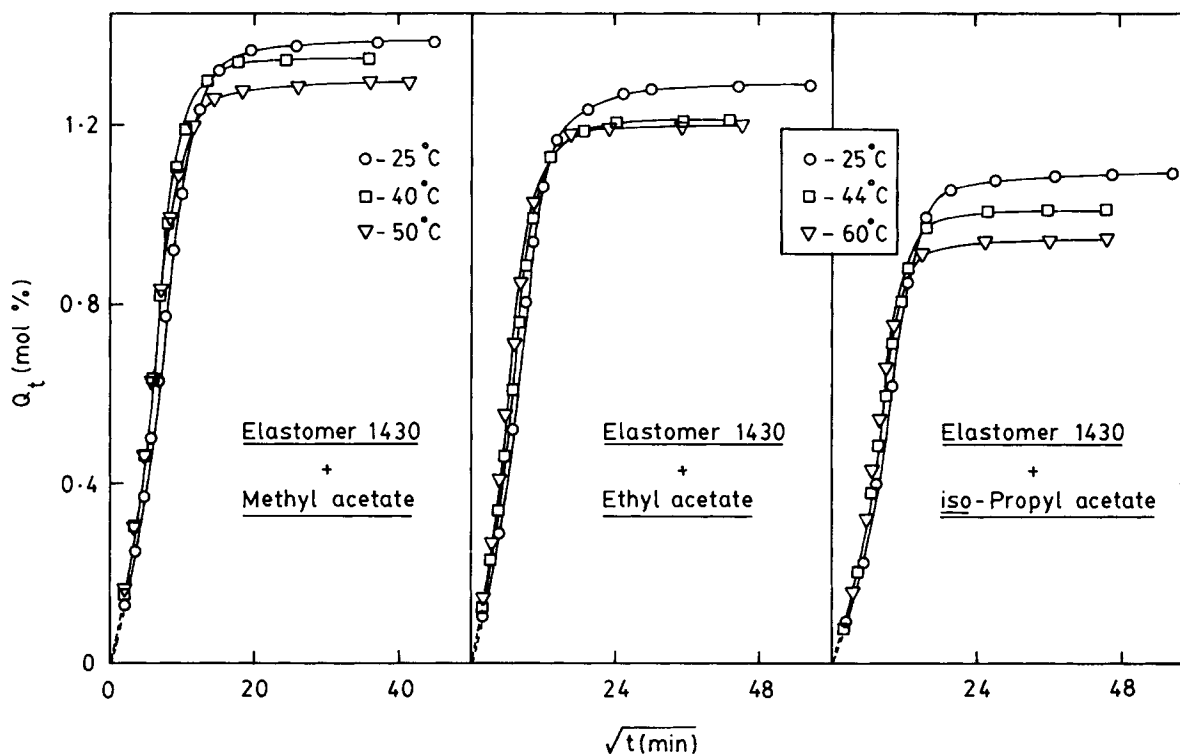
Figure 3 Temperature dependence of sorption for elastomer 1430 with methyl acetate, ethyl acetate, and isopropyl acetate at (O) 25°C, (□) 44°C, and (△) 60°C. For methyl acetate, experiments were carried out at 25, 40, and 50°C.

motion with temperature in the presence of the solvent.

As has been suggested earlier,[10–12] the solvent sorption mechanism into rubbery polymers can be studied in terms of the first-order kinetic model so that the change in sorption with respect to time, dQ/dt, is given as

$$dQ/dt = k(Q_\infty - Q_t) \qquad (3)$$

where k is the first-order rate constant. Integration of eq. (3) gives

$$kt = 2.303 \log[Q_\infty/(Q_\infty - Q_t)] \qquad (4)$$

The values of k have been estimated from the routine procedure employed earlier.[12] These data are reported in Table IV. Included in the same table are the values of the permeability coefficients as calculated from the simple $P = DS$ relation.

Additional support to justify the use of the first-order sorption kinetics comes from the other published reports. For instance, Smith and Fisher[13] related the solvent uptake to its diffusivity in the polymer structure; the effect of polymer porosity on sorption kinetics has been reported by Poinescu et

al.[14] Similarly, Blow[15] suggested that the mechanism of swelling is essentially a first-order phenomenon. For all the polymer–solvent systems, the rate constants increase with a rise in temperature and decrease according to the sequence 1433 < 1430 < 1144 < 1141 with a few exceptions. However, this trend is not observed for P values. The results of permeability coefficients follow the same trend as do the diffusion coefficients.

In the case of solvent transport into polymer matrix materials, the diffusion and permeation parameters depend most generally on the penetrant concentration. This prompted us to investigate the concentration dependence of diffusivity. The diffusivities were thus calculated at different intervals from the procedures suggested earlier[3] and some typical data are shown in Figures 4 and 5. In all cases, the polymer that shows maximum sorption also exhibits a pronounced maximum for the dependence of D on C. Thus, for polymer 1430, a sharp maximum in the D vs. C curve is observed exhibiting a pronounced dependence of D on C, but these maxima become broader for the 1433 sample, which has the least sorptivity. Such effects have also been observed earlier in the literature.[3,16]

Diffusion coefficients tend to increase with a rise

Table III Analysis of Sorption Data for Fluoropolymer + Ester Systems from Eq. (2)

Ester	Temp (°C)	$K \times 10^2$ (g/g min^n)				n			
		1141	1144	1430	1433	1141	1144	1430	1433
Methyl acetate	25	4.07	4.08	3.13	3.21	0.67	0.64	0.69	0.61
	40	3.75	5.35	3.63	4.03	0.75	0.63	0.72	0.60
	50	5.54	5.91	4.26	4.42	0.66	0.63	0.68	0.60
Ethyl acetate	25	3.26	3.64	2.82	2.57	0.69	0.64	0.67	0.62
	44	3.51	4.72	3.35	3.18	0.73	0.64	0.69	0.63
	60	5.31	5.82	4.16	3.13	0.66	0.62	0.68	0.67
Isopropyl acetate	25	2.19	2.60	2.16	1.94	0.73	0.69	0.69	0.64
	44	3.15	3.61	2.62	2.43	0.71	0.66	0.69	0.65
	60	3.83	4.30	3.15	2.95	0.70	0.66	0.68	0.65
Isobutyl acetate	25	2.29	2.42	1.71	1.64	0.63	0.63	0.68	0.60
	44	2.97	3.12	2.36	2.16	0.65	0.63	0.66	0.61
	60	3.49	3.67	2.73	2.55	0.66	0.64	0.67	0.61
Isoamyl acetate	25	2.11	2.20	1.65	1.59	0.66	0.63	0.67	0.60
	44	2.77	2.99	2.33	2.16	0.66	0.64	0.66	0.60
	60	3.30	3.61	2.74	2.57	0.67	0.63	0.67	0.61

Table IV Permeation Coefficient P and Kinetic Rate Constant k for Fluoropolymer + Ester Systems at Different Temperatures

| Temp (°C)	$P \times 10^7$ (cm^2/s)				$k \times 10^3$ (min^{-1})			
	1141	1144	1430	1433	1141	1144	1430	1433
Methyl acetate								
25	7.33	5.62	11.34	4.27	15.88	12.70	11.92	7.15
40	9.92	7.20	15.98	5.79	20.80	18.39	16.90	9.72
50	10.66	8.99	16.97	6.10	23.71	21.59	17.87	11.08
Ethyl acetate								
25	6.75	5.53	9.09	4.05	12.91	11.40	9.48	5.55
44	9.39	7.32	14.46	6.06	17.82	15.88	13.05	8.23
60	9.82	8.22	17.20	7.22	21.47	19.74	17.36	10.18
Isopropyl acetate								
25	4.68	4.85	7.31	3.38	9.03	9.13	7.19	4.22
44	6.69	5.76	9.65	4.51	13.72	12.47	9.34	6.23
60	8.03	7.06	11.33	5.89	16.97	15.92	11.63	8.56
Isobutyl acetate								
25	2.45	2.12	4.97	1.52	5.35	5.35	5.02	2.38
44	3.87	3.46	6.14	2.25	9.14	8.17	6.64	3.85
60	4.88	4.48	7.75	2.79	11.87	11.01	8.70	5.26
Isoamyl acetate								
25	2.62	2.29	4.54	1.40	5.82	4.79	4.47	2.19
44	3.94	3.22	5.86	2.05	8.35	8.12	6.50	3.66
60	4.67	4.18	7.65	2.82	11.61	10.66	8.66	5.14
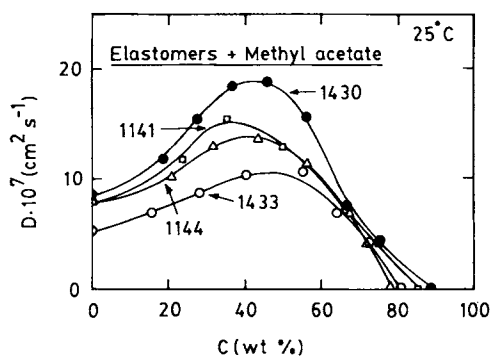
Figure 4 Concentration dependence of diffusion coefficient for elastomers with methyl acetate at 25°C. Symbols for elastomers have the same meaning as in Figure 1.
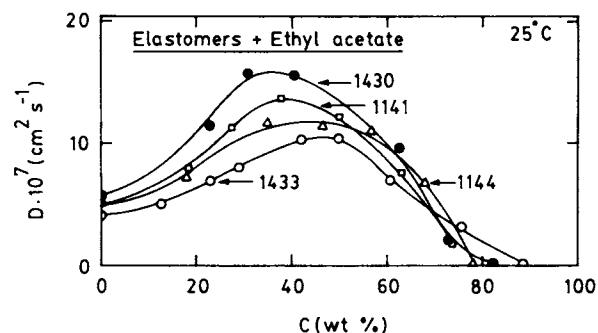
Figure 5 Concentration dependence of diffusion coefficient for elastomers with ethyl acetate at 25°C. Symbols for elastomers have the same meaning as in Figure 1.

in temperature. As a further test of this, we have used the transport results (D, P, and S) to calculate the respective activation parameters (E_D, E_P, and ΔH_S) for diffusion, permeation, and sorption by considering the solvent transport to be an activated process:

$$\log X = \log X_0 - E_X/2.303RT \qquad (5)$$

Table V   Activation Parameters [E_A (kJ/mol), E_D (kJ/mol), E_P (kJ/mol), ΔH_S (kJ/mol), and ΔS (J/mol/deg)] for Fluoropolymer + Ester Systems

		Fluoropolymer			
Ester	Parameter	1141	1144	1430	1433
Methyl acetate	E_A	12.92	17.18	13.44	14.20
	E_D	13.82	15.63	15.61	12.06
	E_P	12.34	14.82	13.36	11.81
	$-\Delta H_S$	1.48	0.81	2.25	0.25
	$-\Delta S$	43.14	42.35	43.09	41.49
Ethyl acetate	E_A	12.08	13.01	14.24	14.45
	E_D	12.50	11.51	17.95	15.78
	E_P	9.09	9.50	15.29	13.81
	$-\Delta H_S$	3.41	2.01	2.66	1.98
	$-\Delta S$	49.68	46.42	45.11	46.88
Isopropyl acetate	E_A	15.03	13.12	11.33	16.67
	E_D	16.61	11.92	13.77	16.55
	E_P	12.84	8.80	10.39	13.04
	$-\Delta H_S$	3.77	3.11	3.37	3.50
	$-\Delta S$	52.12	50.82	48.86	52.47
Isobutyl acetate	E_A	18.69	16.97	12.31	18.58
	E_D	20.16	20.93	13.97	17.84
	E_P	16.40	17.75	10.38	14.43
	$-\Delta H_S$	3.76	3.18	3.59	3.41
	$-\Delta S$	53.61	52.95	50.70	54.49
Isoamyl acetate	E_A	16.25	19.04	15.61	20.25
	E_D	17.70	17.57	15.59	20.07
	E_P	13.82	14.14	12.22	16.41
	$-\Delta H_S$	3.88	3.43	3.37	3.67
	$-\Delta S$	55.07	54.74	51.04	56.32

where X represents D, P, or S and E_X is E_D, E_P, or ΔH_S. The values of E_D and E_P as estimated from Arrhenius plots of log D or log P vs. $1/T$ are compiled in Table V along with the results of activation energy, E_A, as estimated from the temperature dependence of rate constants. In all cases, the values of E_D are lower than those of E_A. Differences in the values of E_A are attributed to different polymer structures in addition to the nature of interacting groups of solvent molecules.

The maximum mol % sorption is nothing but the true equilibrium sorption constant, K_S (expressed as moles of solvent per 100 g of polymer).[17] These values, which are included in Table II, suggest the sequence for polymers as 1430 > 1141 > 1144 > 1433. This sequence is also true for diffusion coefficients. Using the data of K_S given in Table II, we have estimated the enthalpy, ΔH_S, and entropy, ΔS, of sorption by the use of the van't Hoff relation, i.e., log K_S vs. $1/T$:

$$\log K_S = (\Delta S/2.303R)$$

$$- (\Delta H_S/2.303R)(1/T) \quad (6)$$

The estimated values of ΔH_S and ΔS at the 95% confidence level are also included in Table V. For all the systems, ΔH_S is negative, implying the sorption to be exothermic. Similarly, the ΔS values are negative, suggesting the orderliness of the liquid structure even in the sorbed state within the polymer matrix.

CONCLUSIONS

The effects of different fluorine contents of the DuPont VITON fluoroelastomers have been studied in the presence of low molecular weight esters in the temperature interval of 25–60°C. The transport of the selected esters into the elastomer membranes tend to deviate slightly from the Fickian mechanism. The diffusion data have been calculated from the Fickian model. The dependence of transport coefficients on the penetrant size has been discussed. In all cases, at approximately 55–60 mol % uptake, the sorbed concentration tends to level off.

The present study suggests that the gravimetric method has good practical value in obtaining both kinetic and thermodynamic data from sorption experiments when there is a need to evaluate or screen liquids as to their aggressive interactions with a polymeric material. Research in this area on other membranes is in progress and these results will be reported in subsequent publications.

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