Molecular Transport of Organic Esters into Tetrafluoroethylene/Propylene Copolymer Membranes

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SYNOPSIS

Diffusion, permeation, and equilibrium sorption coefficients have been determined using a sorption gravimetric technique for methyl acetoacetate, ethyl acetoacetate, methyl benzoate, ethyl benzoate, methyl salicylate, isobutyl salicylate, and diethyl malonate into tetrafluoroethylene/propylene copolymer membranes in the temperature range 25–70°C. The sorption kinetics process has been characterized by first-order rate constants and penetration velocities. From a temperature dependence of the transport coefficients, the activation parameters have been estimated. It is observed that the values of the transport coefficients for the systems of this study depend on the nature of the penetrant molecules rather than on their molecular sizes. On the whole, the mechanism of solvent transport into the copolymer membranes used here follows nearly the Fickian trend. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The molecular transport of low molecular weight liquids into a polymeric membrane is of great practical significance in a variety of applications such as food packaging,[1] drug and pesticide release,[2-4] reverse osmosis,[5] and pervaporation.[6] Research activities in these areas have been quite active in the past decades.[7] The main thrust in these areas has been to achieve a better understanding of the factors influencing the transport process as well as the phenomenological description of the transport phenomenon.[8] A proper understanding of the molecular transport in polymers is vital to the quantitative analysis of the diffusion processes, as these have many practical implications. Diffusion of small molecules into the polymer matrix is therefore a complex problem with diverse applications. Several experimental techniques have been used to follow the solvent transport into polymers.[9-16] Of these, the sorption gravimetric method is simple and yields reliable diffusion data of polymer–solvent systems that follow the Fickian-type mechanism.[17,18]

The recently developed tetrafluoroethylene/propylene copolymer membranes (Aflas™ FA 100S TFE elastomers, manufactured by 3M) exhibit a unique combination of high-temperature, chemical, and electrical resistance properties. These elastomers were designed for use in molded goods and extruded shapes and profiles and find applications where compression-set resistance is important as well as gas (e.g., N_2 and CO_2) blistering and antiextrusion resistance. The TFE elastomers provide service-life advantages in acids, bases, steam/hot water, amines, oils, and hydraulic fluids. Other 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 investigate the molecular transport characteristics of these membranes in the presence of organic esters.

Previous reports from our laboratory have addressed different aspects of diffusion anomalies for a variety of polymer–solvent systems.[19-25] Our recent studies[24,25] dealt with the molecular-transport characteristics of a variety of engineering polymers with reference to organic esters. In continuation of these studies, the present study is undertaken as a part of

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the general program to measure the sorption, diffusion, and permeation characteristics of tetrafluoroethylene/propylene copolymer (TFE elastomers) membranes in the presence of esters such as methyl acetoacetate, ethyl acetoacetate, methyl benzoate, ethyl benzoate, methyl salicylate, isobutyl salicylate, and diethyl malonate in the temperature interval of 25–70°C. These esters were chosen particularly in view of their importance as plasticizing agents and their migration in polymer processing industries.

In the present study, the molecular transport parameters such as diffusion, D, permeation, P, and sorption, S, have been obtained in addition to activation parameters for these processes. The values of the sorption kinetics rate constants and penetration velocities have also been estimated. From a knowledge of these parameters and from an analysis of the experimental and calculated results, the molecular transport phenomenon of these liquids into the TFE elastomers was found to follow the regular Fickian mechanism. Furthermore, the transport results are discussed in terms of the penetrant shapes and their interacting abilities with the polymer-chain segments.

EXPERIMENTAL

Materials

FA 100S-grade Aflas™ TFE polymer sheets in dimensions of 14.7 × 14.7 × 0.225 cm were supplied by 3M Industrial Chemical Products Division, St. Paul, MN (courtesy of Mr. Bobb Eggers). Aflas™ FA 100S can be mixed with curatives, fillers, and other compounding ingredients by conventional mill or internal mixing methods. In typical formulations, it is recommended that the peroxide curing agent and co-agent be 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 the 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

The esters are particularly selected because of their industrial importance and in view of their applica-

Table I   Compound Formulations and Some Representative Physical/Mechanical Properties

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

Rheological Properties (at 177°C, 100 cpm, 3° Arc, Micro Die)	
Minimum torque, in-lbs. (N m)	24.0 (2.71)
Time to 50% cure (min)	3.0
Maximum torque at 12 min, in-lbs. (N m)	69.5 (7.85)

Physical Properties		
Press cure 10 min at 177°C		
Tensile, psi (MPa)	ASTM D-412	2170 (14.9)
Elongation, %	ASTM D-412	325
Modulus at 100%, psi (MPa)	ASTM D-42	465 (3.2)
Hardness, Shore A	ASTM D-2240	68
Oven cure, 16 h at 200° C		
Tensile, psi (MPa)		2440 (17.3)
Elongation, %		285
Modulus at 100%, psi (MPa)		660 (4.6)
Hardness, Shore A		72
Brittle point, °C	ASTM D-2137	−40
Specific gravity		1.55
Color	Dark brown	

[a] phr, parts per hundred of polymer.

tions as solvent media in various polymerization processes. The esters, namely, methyl acetoacetate (S.D. Fine Chemicals, India), ethyl acetoacetate (Thomas Baker Chemicals, Bombay, India), methyl benzoate (Nardeen, Holland), ethyl benzoate (Sisco Chemical Industries, Bombay, India), methyl salicylate (Sisco), isobutyl salicylate (Kelkar, Bombay, India), and diethyl malonate (S.D. Fine Chemicals) were doubly distilled before use. The observed boil-

ing points of these solvents are listed in Table II along with their molar volumes.

Sorption Experiments

Circular disc-shaped samples (diameter = 1.94–1.97 cm) were cut from the polymer sheets using a sharp-edged carbon-tipped steel die and the cut samples were dried perfectly by placing them in a vacuum oven at 25°C overnight before use. Further, these samples were soaked in screw-tight bottles containing 15–20 mL of the respective solvents maintained at the desired temperature (±0.5°C) in a hot-air oven (Memmert, Germany). Samples were removed periodically, and the surface-adhered solvent drops were wiped off by using filter paper wraps and then weighed immediately on a digital Mettler balance, Model AE 240 (Switzerland), within a precision of ±0.01 mg. The other experimental details are the same as given in our earlier publications.[19-25]

When the samples attained equilibrium saturation, no more weight gain was observed, which did not change significantly over a further period of 1 or 2 days. The mol % weight gain, Q_t, during solvent sorption was calculated as

$$Q_t = \frac{W_t - W_0}{W_0} \times \frac{100}{M_S} \qquad (1)$$

where W_0 is the initial polymer sample weight; W_t, the weight of the polymer sample at time t; and M_S, molecular weight of the solvent used as the penetrant.

RESULTS AND DISCUSSION

Sorption, Diffusion, and Permeation Behavior

A comprehensive understanding about the molecular transport of penetrants into rubbery polymers has been achieved in terms of sorption, diffusion, and permeation phenomena. For a polymer–solvent system, the sorption results before the attainment of 50–55% equilibrium saturation have been fitted to an empirical relation of the type[26,27]

$$\frac{Q_t}{Q_\infty} = Kt^n \qquad (2)$$

to estimate the values of the parameters K and n by the method of least-squares. Here, Q_∞ represents the equilibrium value of sorption. The value of the exponent n indicates the type of transport mechanism. For a Fickian transport, the values of n are in the neighborhood of 0.50, whereas for the non-Fickian transport, n takes the values in the close proximity of unity. However, most generally, for rubbery polymer–solvent systems, well above the glass transition temperature of the polymer, the values of n generally vary from 0.50 to 1.0, suggesting the anomalous transport behavior. The estimated values of K and n are given in Table III.

The values of n in this study are found to be slightly affected by the temperature variations, but these effects are not very systematic. It is observed that the values of n vary in the close vicinity of 0.50, but rarely increases to 0.60; this suggests that the transport phenomenon is very close to the Fickian type. This is further supported by the fact that the plots of Q_t vs. $t^{1/2}$ at 25 and 70°C shown in Figure 1 for all the penetrants are initially linear (i.e., no sigmoidal shapes) before completion of 50–55% of equilibrium sorption. The magnitude of K depends on the nature of the penetrant molecule. For instance, with isobutyl salicylate and diethyl malonate, the trends of K with temperature are different; the diethyl malonate is the unique case where K decreases at 70°C, and for isobutyl salicylate, only the value of $K = 0.63$ at 25°C is out of the general trend (values distributed in the 0.96–1.30 interval). The

Table II   Some Properties of Esters at 25°C

Esters	Formula	bp (°C)	Molar Volume (cm³mol⁻¹)
Methyl acetoacetate	$CH_3COCH_2COOCH_3$	172	108
Ethyl acetoacetate	$CH_3CH_2COCH_2COOCH_3$	181	127
Methyl benzoate	$C_6H_5COOCH_3$	200	126
Ethyl benzoate	$C_6H_5COOCH_2CH_3$	212	145
Methyl salicylate	$o\text{-HO} - C_6H_4 - COOCH_3$	233	129
Isobutyl salicylate	$o\text{-HO} - C_6H_4 - COOCH_2CH(CH_3)_2$	244	183
Diethyl malonate	$CH_2(COOC_2H_5)_2$	199	153

Table III Estimated Values of n, K of Eq. (2), Sorption Coefficient (S), Diffusivity (D), and Permeability (P) of Fluoropolymers with Esters at Different Temperatures

Esters	Temp (°C)	n	$K \times 10^2$ (g/g min^n)	$S \times 10$ (mol %)	$D \times 10^8$ (cm^2/s)	$P \times 10^8$ (cm^2/s)
Methyl acetoacetate	25	0.44	1.12	0.308	1.03	0.04
	40	0.47	1.09	0.422	1.50	0.07
	55	0.53	1.51	0.520	5.00	0.30
	70	0.55	2.18	0.662	10.72	0.82
Ethyl acetoacetate	25	0.44	1.17	0.278	0.95	0.03
	40	0.45	1.38	0.328	1.83	0.08
	55	0.54	1.39	0.485	4.37	0.28
	70	0.56	2.09	0.583	10.35	0.79
Methyl benzoate	25	0.51	1.29	1.055	2.70	0.39
	40	0.51	1.73	1.164	6.70	1.06
	55	0.56	2.26	1.493	14.21	2.89
	70	0.54	3.11	1.812	21.38	5.28
Ethyl benzoate	25	0.51	1.06	0.980	1.95	0.29
	40	0.53	1.48	1.132	5.13	0.87
	55	0.55	1.75	1.464	8.43	1.85
	70	0.55	2.39	1.611	17.70	4.28
Methyl salicylate	25	0.49	1.04	1.050	1.63	0.26
	40	0.53	1.28	1.240	3.86	0.73
	55	0.54	1.77	1.604	7.66	1.87
	70	0.53	2.42	1.803	14.41	3.96
Isobutyl salicylate	25	0.49	0.63	1.023	0.57	0.11
	40	0.53	0.77	1.266	1.55	0.38
	55	0.56	0.86	1.814	2.60	0.92
	70	0.60	1.03	1.818	6.38	2.25
Diethyl malonate	25	0.47	0.96	0.429	1.02	0.07
	40	0.47	1.41	0.535	2.71	0.23
	55	0.53	1.69	0.701	6.09	0.68
	70	0.61	1.30	0.848	9.83	1.34

values of K generally increase with temperature, suggesting the increased molecular interactions between the solvent molecules and the polymer-chain segments. In reality, the magnitude of K indicates the movement of the solvent front, but the solvent transport is restricted if the interacting solvent possesses bulky groups, suggesting its sluggish movement into the polymer matrix.

The values of sorption coefficients, S (which are equivalent to Q_∞ values), have been obtained from the equilibrium sorption results of the plots of Q_t vs. $t^{1/2}$ (Fig. 1). The values of these coefficients are included in Table III. It is noteworthy to mention that the shapes of the sorption curves and the equilibrium time requirement vary depending upon the nature of the solvent. For instance, aromatic esters like methyl benzoate, ethyl benzoate, methyl salicylate, and isobutyl salicylate at 25°C transport more quickly into the available free-volume spaces within the polymer matrix, thereby giving the higher sorp-

tion values (Fig. 1). On the other hand, penetrants like diethyl malonate, methyl acetoacetate, and ethyl acetoacetate require longer times to achieve equilibrium sorption; also, the equilibrium values for these penetrants are smaller than those of the other esters. However, at 70°C as seen in Figure 1, the equilibrium time is reduced dramatically with higher equilibrium sorption values.

The increase in equilibrium sorption with an increase in temperature suggests the increased molecular mobility of the polymer-chain segments. Some typical plots of the temperature dependence of Q_t vs. $t^{1/2}$ are shown in Figure 2 for methyl benzoate and diethyl malonate. The initial shapes of the Q_t vs. $t^{1/2}$ plots change considerably by increasing the temperature. Thus, the molecular transport phenomenon is greatly affected by the experimental temperature. The sorption results at 25°C vary according to the trend: methyl benzoate > methyl salicylate > isobutyl salicylate > ethyl benzoate > di-
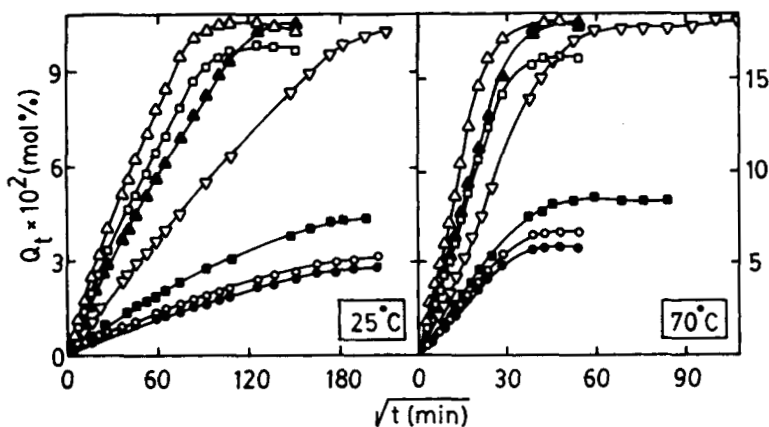
Figure 1   Mol % sorption vs. square root of time for TFE/propylene copolymer membranes with (○) methyl acetoacetate, (●) ethyl acetoacetate, (△) methyl benzoate, (□) ethyl benzoate, (▲) methyl salicylate, (▽) isobutyl salicylate, and (■) diethyl malonate.

ethyl malonate > methyl acetoacetate > ethyl acetoacetate.

Realizing the fact that sorption follows the Fickian kinetics, attempts have been made to calculate the diffusion coefficients, D, of the polymer–solvent systems by using the following relation[28]:

$$\frac{Q_t}{Q_\infty} = 1 - \left(\frac{8}{\pi^2}\right) \sum_{n=0}^{\infty} \left\{\left[\frac{1}{(2n+1)^2}\right]\right.$$
$$\left. \times \exp\left[\frac{-D(2n+1)^2\pi^2 t}{h^2}\right]\right\} \quad (3)$$

To compute D, an iterative procedure was used by considering the first 11 terms ($n = 0$–11) of eq. (3). The values of D thus obtained and given in Table III are accurate to ±0.005 units, but these are ap-

proximated to two decimal places. The permeability coefficients, P, have been calculated from the values of D and S using the empirical relation $P = D \cdot S$. These results over the investigated range of temperature are also included in Table III.

The mathematical relation for the determination of diffusivity of solvent molecules in the polymer matrix at long diffusion times is deduced from eq. (3) to give[29]

$$\ln(1 - Q_t/Q_\infty) = \ln\left(\frac{8}{\pi^2}\right) - \frac{D\pi^2 t}{h^2} \quad (4)$$

Thus, a plot of $\ln(1 - Q_t/Q_\infty)$ vs. t should be linear up to 55% of equilibrium sorption and the slope is directly proportional to D. Some of our data have
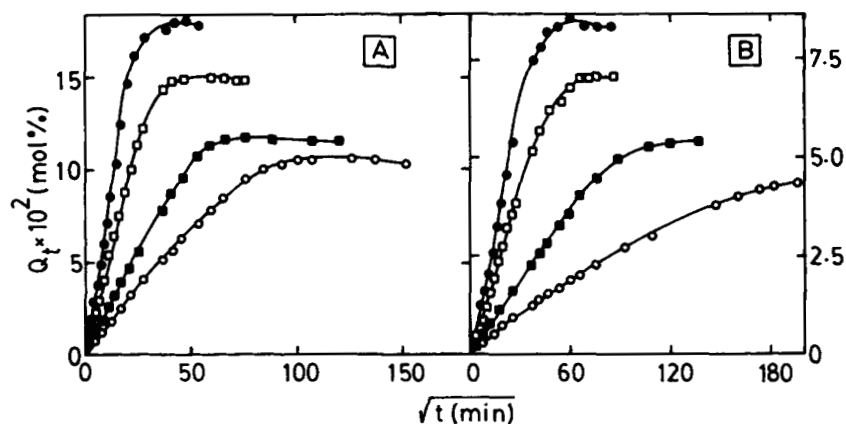

Figure 2   Mol % sorption vs. square root of time for TFE/propylene copolymer membranes with (A) methyl benzoate and (B) diethyl malonate at (○) 25°C, (■) 40°C, (□) 55°C, and (●) 70°C.
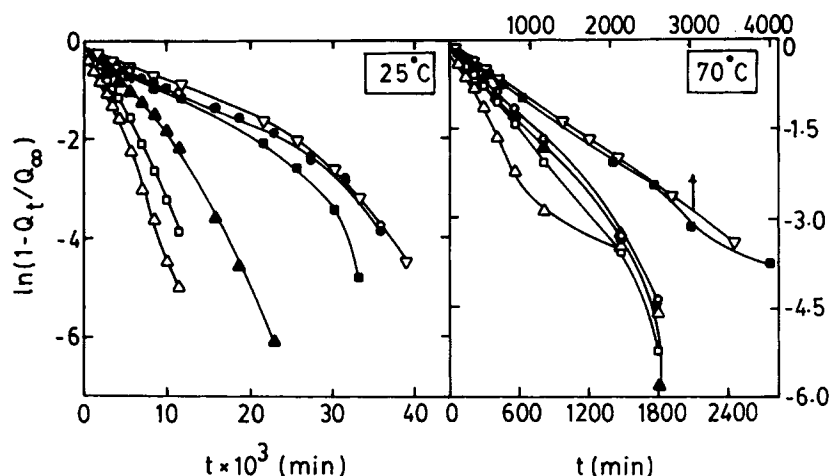
Figure 3 $\ln(1 - Q_t/Q_\infty)$ vs. t plots for polymer–solvent systems. Symbols are the same as in Figure 1.

been plotted in this format, which are in conformity with eq. (4) (see Fig. 3).

It is found that methyl benzoate exhibits the highest diffusion coefficients $(2.7–21) \times 10^{-8}$ cm^2 s^{-1}, whereas the smallest D is observed for isobutyl salicylate $(0.6–6) \times 10^{-8}$ cm^2 s^{-1}, and intermediate values are observed by the remaining esters. No systematic dependence of the diffusion coefficient on the size of the penetrant molecules is observed. Isobutyl salicylate, having the highest molar volume (183 cm^3 mol^{-1}) among the esters considered, shows the lowest D. However, in case of methyl benzoate, the highest D is observed though its molar volume is smallest among the selected esters. The smallest molecule such as methyl acetoacetate (molar volume 108 cm^3 mol^{-1}) exhibits a D value in the range of $(1–10.7) \times 10^{-8}$ cm^2 s^{-1}, which is higher than that observed for methyl benzoate. It may be noted that diffusion coefficients of ethyl benzoate are smaller than those of methyl benzoate. Similarly, D values of ethyl acetoacetate are smaller than those of methyl acetoacetate. Though the molecular sizes of ethyl acetoacetate, methyl benzoate, and methyl salicylate are more or less in the same range, these esters exhibit different diffusion trends. The diffusion data at 25°C follow the sequence: methyl benzoate > ethyl benzoate > methyl salicylate > methyl acetoacetate > diethyl malonate > ethyl acetoacetate > isobutyl salicylate. This clearly indicates that the diffusion results are not affected by the size of the penetrant molecules. However, polarity, molecular structure, and penetrant shape seem to influence the diffusion results in addition to their viscosity values and the polymer–solvent interactions. It may be noted that the values of D calculated from eq. (4) differ considerably at lower temperatures (25

and 40°C) when compared to the D values calculated from eq. (3), i.e., D from eq. (3) are lower than those calculated from eq. (4).

The results of permeability coefficients, P, in the investigated temperature range follow the sequence methyl benzoate > ethyl benzoate > methyl salicylate > isobutyl salicylate > diethyl malonate > methyl acetoacetate > ethyl acetoacetate. This trend is slightly different than that observed for diffusion coefficients, probably because of the fact that the permeability data are influenced by the sorption results.

Kinetics of Sorption and Penetration Velocity

Most cross-linked polymers exhibit swelling in the presence of interactive solvent media. Such a limited swelling in semicrystalline polymers may be attributed to sorption kinetics phenomenon. It has been shown that sorption in rubbery polymers can be treated by the use of the first-order kinetics.[16] In view of this, attempts have been made to calculate the first-order kinetics rate constants, k, by using the following relations:

$$dQ/dt = k(Q_\infty - Q_t) \tag{5}$$

which upon integration gives

$$kt = \ln[Q_\infty/(Q_\infty - Q_t)] \tag{6}$$

Representative plots of $\log(Q_\infty - Q_t)$ vs. t at 25 and 70°C are shown in Figure 4. The calculated values of rate constants in the temperature interval of 25–70°C are given in Table IV. The kinetics rate con-
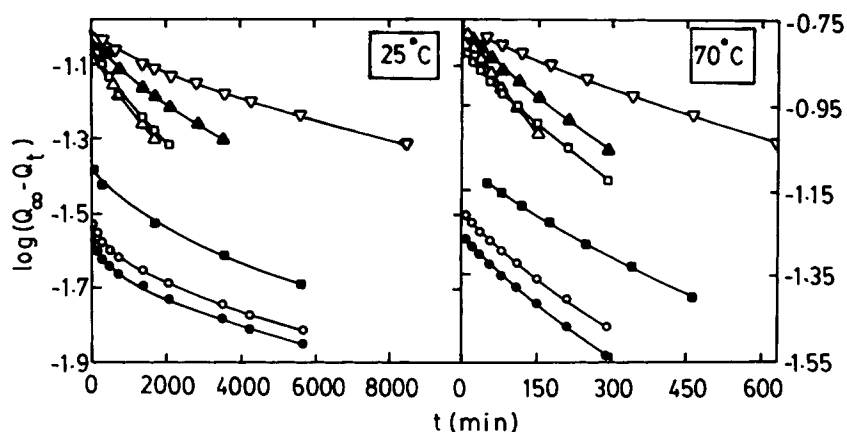
Figure 4 Kinetics plots for TFE/propylene copolymer membranes + esters at 25 and 70°C. Symbols are the same as in Figure 1.

stants follow a regularly increasing trend with temperature. These plots exhibit negative slopes and are slightly more curved at 25°C than at higher temperatures, viz., 70°C. The kinetics rate constant values at 25°C vary according to the sequence methyl benzoate > ethyl benzoate > methyl salicylate > diethyl malonate > methyl acetoacetate > ethyl acetoacetate > isobutyl salicylate.

Table IV Kinetics Rate Constants (k), Penetration Velocity (v), and Percent Volume Change ($\Delta V\%$) of Fluoropolymers with Esters at Different Temperatures

Esters	Temp (°C)	$k \times 10^4$ (min^{-1})	$v \times 10^5$ (cm/s)	ΔV (%)
Methyl acetoacetate	25	1.10	0.652	5.49
	40	2.02	1.184	8.56
	55	8.40	5.017	9.38
	70	21.11	12.514	9.83
Ethyl acetoacetate	25	1.00	0.567	7.40
	40	2.31	1.370	8.90
	55	8.22	4.934	9.91
	70	21.97	12.947	9.80
Methyl benzoate	25	4.27	2.462	21.11
	40	8.99	5.244	25.04
	55	24.09	13.328	26.47
	70	36.75	20.309	34.21
Ethyl benzoate	25	3.28	1.915	21.12
	40	8.48	5.050	28.36
	55	14.03	7.634	30.80
	70	23.98	12.368	36.14
Methyl salicylate	25	2.05	1.171	19.28
	40	5.23	2.915	26.91
	55	13.27	7.386	30.45
	70	22.03	11.780	35.15
Isobutyl salicylate	25	0.88	0.500	31.99
	40	2.34	1.326	36.25
	55	4.79	2.657	39.95
	70	9.76	4.973	50.12
Diethyl malonate	25	1.28	0.758	12.04
	40	3.18	1.815	13.96
	55	9.89	5.514	15.20
	70	14.72	7.751	20.10

For long sorption times, the term $n \geq 1$ as well as $\ln(8/\pi^2)$ can be ignored so that eq. (4) can be simplified to give

$$\ln\left(\frac{Q_\infty}{Q_\infty - Q_t}\right) \cong \frac{\pi^2 D t}{h^2} \tag{7}$$

when

$$k = \frac{\pi^2 D}{h^2} \tag{8}$$

For extensive swelling, h^2 obviously does not remain constant and, hence, D increases due to influx of the solvent into the polymer. As long as the increase in D matches h^2, the values of k in eq. (8) remain nearly constant, so that eq. (6) or eq. (7) is obeyed approximately and the first-order kinetics seems to apply to the present systems.

Diffusion coefficients calculated from eq. (3) representing the solvent front movement into the polymeric materials are directly related to penetration velocities, v, of the moving solvent boundary and these can be calculated as[30,31]

$$v = \frac{dM_t/dt}{2\rho A M_\infty} \tag{9}$$

where M_t and M_∞ are the penetrant uptakes (g/g) at time t and at equilibrium time; dM_t/dt, the slope of the linear portion of the uptake curves; ρ, the density of the polymer; and A, the area of one face of the disc-shaped polymer sample, and factor 2 accounts for the solvent penetration through both the faces. The area of the circular side of the disc-shaped sample is also taken into consideration while computing the total area of the polymer sample exposed to the liquid. The results of v included in Table IV at 25°C show the trend methyl benzoate > ethyl benzoate > methyl salicylate > diethyl malonate > methyl acetoacetate > ethyl acetoacetate > isobutyl salicylate. The values of v, like any other transport property, shows a systematic increase with temperature. It may be noted that the results of vol % changes, ΔV, of the polymer–solvent systems presented in Table IV support the swelling tendencies of the polymers in relation to their transport coefficients.

Temperature Effects and Arrhenius Parameters

The transport coefficients, viz., D, P, and S, tend to increase with increase in temperature and, hence, attempts have been made to estimate the Arrhenius

parameters for these processes. According to the molecular models for the rubbery polymers well above their glass transition temperatures, the Arrhenius relation is generally observed experimentally, i.e.,

$$D = D_0 \exp(-E_D/RT) \tag{10}$$

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

Similarly, the sorption coefficient, S, can be expressed in terms of the van't Hoff relationship with a preexponential factor, S_0, as

$$S = S_0 \exp(-\Delta H_S/RT) \tag{11}$$

where ΔH_S is the heat of sorption and is a composite parameter. This involves contributions from (i) 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 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 more exothermic heats of sorption.

Because a sorption–diffusion process is involved, the permeability coefficient P ($= D \cdot S$) may also be expressed in a similar manner and the activation energy, E_P, for permeation is given as
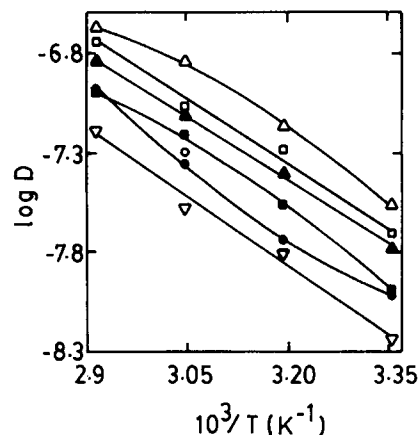

Figure 5 Arrhenius plots for the dependence of log D vs. $1/T$ for TFE/propylene membrane + esters. Symbols are the same as in Figure 1.

Table V   Activation Energy for Diffusion (E_D), Permeation (E_P), and Enthalpy of Sorption (ΔH_S) for TFE Elastomers with Esters

Esters	E_D (kJ/mol)	E_P (kJ/mol)	ΔH_S (kJ/mol)
Methyl acetoacetate	46.42	60.64	14.23
Ethyl acetoacetate	45.40	60.20	14.80
Methyl benzoate	39.66	50.21	10.55
Ethyl benzoate	40.40	50.33	9.92
Methyl salicylate	41.01	51.69	10.68
Isobutyl salicylate	43.96	55.87	11.91
Diethyl malonate	43.26	56.39	13.13

$$E_P = E_D + \Delta H_S \qquad (12)$$

Since in the present polymer–solvent systems the values of S, P, and D showed an increase with increase in temperature, hence, eqs. (10) and (11) were used to calculate E_D and ΔH_S values from the least-squares procedure. Figure 5 presents the plot of log D vs. $1/T$ results wherein the dependence follows a nonlinearity in the investigated range of temperature for ethyl acetoacetate, diethyl malonate, and methyl benzoate. Using eq. (12), the E_P values were calculated and these results are summarized in Table V. The results of E_D, E_P, and ΔH_S are higher for a smaller molecule such as methyl acetoacetate. However, due to a change in the rigidity and cohesive energy density of the polymer in the presence of a polar molecule such as methyl benzoate, somewhat lower values of activation parameters are observed (Table V). It may be noted that in all cases the values of ΔH_S are positive, suggesting that the sorption is dominated mainly by the Henry's law sorption mode, giving an endothermic contribution to the sorption process.

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