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Sorption, Diffusion, and Permeation Coefficients of Benzene, Substituted Benzenes, and Bis(2-methoxyethyl) Ether into Tetrafluoroethylene–Propylene Copolymeric Sheets in the Temperature Range from 298.15 to 343.15 K

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Diffusion, permeation, and sorption equilibrium coefficients were determined for benzene, substituted benzenes, and bis(2-methoxyethyl) ether into tetrafluoroethylene–propylene copolymeric sheets in the temperature range from 298.15 to 343.15 K. From a temperature dependence of the transport coefficients, the activation parameters have been estimated. It is observed that the values of the transport coefficients and the derived parameters depend on the nature of penetrant molecules rather than their sizes.

Introduction

In recent years, polymeric materials have found astonishing applications as barrier materials in many industrial and engineering areas and in tackling the environmental pollution problems (*1–3*). The synthesis of such materials with improved and tailor-made properties has been one of the main thrusts of research activities in this area. The criterion for reaching this goal is a detailed knowledge of the mechanism of solvent transport into the barrier materials. One of the important questions related to both the fundamental and applied research in the area of molecular transport of liquids into polymeric barrier materials is the influence of polymer structure and its interactions with the penetrant molecules (*4–6*).

The understanding of polymer–solvent interactions is necessary to predict the behavior of the barrier materials upon exposure to aggressive chemicals. Solvent diffusion into polymeric materials is one of the limiting factors in their intended applications. However, the solvent absorption and swelling of the polymers have been reported to affect the mechanical properties of the polymers (*7*). An investigation of the causes of such phenomena requires a detailed knowledge of solvent sorption and diffusion characteristics. Hence, diffusion coefficients, equilibrium sorption parameters, and permeation coefficients are required to assess the solvent resistivity of the barrier materials.

The recently developed tetrafluoroethylene–propylene copolymeric sheets (Aflas FA 100S TFE elastomers, manufactured by 3M) exhibit a unique combination of high-temperature and chemical resistivity. These elastomers were designed for use in molded goods and extruded shapes and profiles, and find applications as O-rings, seals used in hydraulic and brake systems, jet engines, cable clamps, electrical connectors, wire and cable insulation, hose, pipeline patches, etc. Their good property retention and moderate volume swell prompted us to investigate the molecular transport characteristics of these polymers in the presence of organic liquids.

Recent reports from our laboratory have addressed aspects of diffusion anomalies for a variety of polymer + solvent systems (*8–13*). The objective of the present study is to measure the sorption, *S*, diffusion, *D*, and permeation, *P*, coefficients for the tetrafluoroethylene–propylene copolymeric (TFE elastomers) sheets with benzene, chlorobenzene, 1,2-dichlorobenzene, bromobenzene, nitrobenzene, and bis(2-methoxyethyl) ether in the temperature interval of 298.15–343.15 K. The activation parameters for the different transport processes have been estimated from a temperature dependence of *S*, *P*, and *D*. From a knowledge of these parameters and from an analysis of the experimental and calculated results, the molecular transport phenomenon was found to follow the normal Fickian behavior. The transport results are discussed in terms of the penetrant shapes, polarity effects, and interacting abilities with the polymer chain segments.

Experimental Section

Materials and Specimen Preparation. FA 100S grade Aflas tetrafluoroethylene (TFE) polymer sheets in dimensions of 14.7 cm × 14.7 cm × 0.225 cm were supplied by 3M Industrial Chemical Products Division, St. Paul, MN (courtesy of Mr. Bobb Eggers). Aflas FA 100S are mixed with curatives, fillers, and other compounding ingredients by the conventional mill or internal mixing methods. In typical formulations, it is recommended that the peroxide curing agent and coagent be preblended with the dry powders prior to addition 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. However, the present polymers are prepared by the internal mixing method. Care should be taken to avoid mixing temperatures above 394.15 K. After mixing, the stock should be cooled rapidly by either an air or water cooling technique. The mixed catalyzed compound should be stored in a cool dry place prior to use. Elastomer compositions along with some of their typical physical/mechanical properties are given in Table 1.

The solvents benzene (Sisco Chemical Industries, Bombay, India), chlorobenzene (S.D. Fine Chemicals Ltd., India), 1,2-dichlorobenzene (Sisco Research Laboratories, Pvt. Ltd., Bombay, India), bromobenzene (Ranbaxy Laboratories, Ltd., Punjab, India), nitrobenzene (Thomas Baker Chemicals, Pvt. Ltd., Bombay, India) and bis(2-methoxyethyl) ether (BDH, Poole, England) were purified by the standard procedures before use (*14, 15*). Representative physical properties of these liquids are given in Table 2.

Measurements. Circular disk 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 by placing them in a vacuum oven at 298.15 K overnight before use. Further, these samples were soaked in screw-tight bottles containing 15–20 mL of the respective solvents

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Table 1. Compound Formulations (Internal Mixing Method) and Representative Typical Physical/Mechanical Properties

compound		formulation (phr)[a]
Aflas FA 100S		100
MT black (N-990)		30
peroxide (Vul-Cup 40 KE)		4
coagent (100% active TAIC)		4
process aid (sodium stearate)		1
Rheological Properties (450.15 K, 100 cpm, 3° Arc, Micro Die)		
minimum torque (N·m)		2.71
time to 50% cure (min)		3.0
maximum torque at 12 min (N·m)		7.85
Physical Properties Press Cure 10 min at 450.15 K		
tensile (MPa)	ASTM D-412	14.9
elongation %	ASTM D-412	325
modulus at 100% (MPa)	ASTM D-42	3.2
hardness, Shore A	ASTM D-2240	68
Oven Cure 16 h at 473.15 K		
tensile (MPa)		17.3
elongation %		285
modulus at 100% (MPa)		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 rubber.

Table 2. Boiling Temperature, T_b, Molar Volume, V_m, Dipole Moment, μ, and Viscosity, η, of Solvents at 298.15 K

liquid	T_b (K)	V_m ($cm^3 \cdot mol^{-1}$)	μ	η (mPa·s) lit. (15)	η (mPa·s) obsd
benzene	353.15	89	0.00	0.603	0.604
chlorobenzene	405.15	102	1.62	0.718[a]	0.740
1,2-dichlorobenzene	453.15	113	2.14	1.324	1.312
bromobenzene	429.15	106	1.55	1.010[a]	1.003
nitrobenzene	484.15	103	4.00	1.619[a]	1.658
bis(2-methoxyethyl) ether	431.15	143	1.97	0.989	0.973

[a] Compared at 303.15 K.

maintained at the desired temperature (±0.5 K) in a hot air oven (Memmert, Germany). The samples were removed periodically, the surface-adhered solvent drops were wiped off by using filter paper wraps, and the mass was determined immediately on a digital Mettler balance, model AE 240 (Switzerland), within a precision of ±0.01 mg.

When the samples attained the equilibrium saturation, no more mass gain was observed which did not change significantly over a further period of one or two days. The gain, Q_t, expressed in mole percent units during solvent sorption, was calculated as

$$Q_t = \frac{w_t - w_0}{w_0}\frac{100}{M_S} \qquad (1)$$

where w_0 is the initial mass of the polymer sample, w_t is the mass of the polymer sample at time t, and M_S is the molecular weight of the solvent used as the penetrant.

Results and Discussion

Sorption, Diffusion, and Permeation Behavior. An understanding about the transport behavior of the penetrant molecules into the rubbery matrix materials can be achieved in terms of their sorption, diffusion, and permeation properties. The sorption results before the attainment of 55% equilibrium saturation have been fitted to the empirical relation (*16, 17*)

$$Q_t/Q_\infty = Kt^n \qquad (2)$$

to estimate the values of K and n by the method of least squares (Table 3). The results of n are accurate to ±0.005 unit, but are approximated to the second decimal place. However, the values of K are accurate to ±0.0004 unit. The value of the exponent n indicates the type of transport mechanism. For a Fickian transport, the values of n are around 0.50, while for the non-Fickian transport, n takes the values in the close proximity of unity. However, most generally, for the rubbery polymer + solvent systems, well above the glass transition temperature of the polymer, the values of n vary between 0.50 and 1.0, suggesting the anomalous transport behavior.

The values of n are insensitive over the temperature range of 298.15–343.15 K. The parameter K, which depends on the nature of the polymer–solvent interactions, shows a systematic increase with temperature, suggesting the increased molecular interactions. For the present systems the values of n vary from 0.50 to 0.56, suggesting the transport to be close to the simple Fickian type. However, the slight sigmoidal deviations observed for benzene and chlorobenzene at 298.15 K (Figure 1) before 55% equilibrium sorption are attributed to the polymer chain relaxation effects.

The values of the sorption coefficients, S, are obtained from the plateau regions of the plots of Q_t versus $t^{1/2}$. These results are included in Table 3. It may be noted that the shapes of the sorption curves and the time to attain equilibrium saturation depend on the type of the penetrant molecule. For instance, benzene having a symmetrical structure transports quickly into the free voids of the polymer and thus gives a high sorption of 0.358–0.627 mol %. On the other hand, chlorobenzene exhibits lower values of S, i.e., 0.265–0.441 mol %; also, the time to attain equilibrium saturation is longer for chlorobenzene than benzene, probably due to its slightly larger size. The S values of 1,2-dichlorobenzene, bromobenzene, and nitrobenzene are generally smaller than those of benzene or chlorobenzene and decrease in the respective order. The time to attain equilibrium saturation is longer for nitrobenzene (383 h at 298.15 K) than for bromo- and 1,2-dichlorobenzenes (~110 h). At higher temperatures, the attainment of equilibrium saturation is very quick (~46 h). The sorption of nitrobenzene is smaller than those of all the penetrants, and this may be attributed to its sluggish movement (due to the presence of the bulky $-NO_2$ group) into the barrier polymer. The sorption of bis(2-methoxyethyl) ether is in between those of bromobenzene and nitrobenzene (Figure 1). On the whole, the sorption in the studied temperature interval follows the trend

benzene > chlorobenzene > bromobenzene >
1,2-dichlorobenzene > bis(2-methoxyethyl) ether >
nitrobenzene

It is observed that the S values increase with an increase in temperature, suggesting 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, respectively, in Figures 2–4 for benzene, bromobenzene, and nitrobenzene. In all cases, the initial slopes of such plots change with increasing temperature.

The diffusion coefficients, D, of the polymer + solvent systems have been calculated as (*18*)

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

Table 3. Coefficients of Sorption, *S*, Diffusion, *D*, and Permeation, *P*, of Polymer + Solvents at Different Temperatures

liquid	T(K)	n	10^2K (g/(g min^n))	S (mol %)	10^7D (cm^2·s^{-1})	10^7P (cm^2·s^{-1})
benzene	298.15	0.52	3.14	0.358	2.36	0.66
	313.15	0.54	3.94	0.427	4.29	1.43
	328.15	0.53	4.90	0.516	5.56	2.24
	343.15	0.52	5.74	0.627	7.38	3.62
chlorobenzene	298.15	0.51	3.11	0.265	2.13	0.64
	313.15	0.53	3.68	0.303	3.43	1.17
	328.15	0.54	4.14	0.368	4.66	1.93
	343.15	0.51	4.65	0.441	5.35	2.65
1,2-dichlorobenzene	298.15	0.54	1.69	0.147	0.71	0.15
	313.15	0.51	2.35	0.179	1.25	0.33
	328.15	0.54	2.94	0.201	1.92	0.57
	343.15	0.50	3.64	0.242	2.80	0.99
bromobenzene	298.15	0.52	1.77	0.119	0.68	0.13
	313.15	0.50	2.57	0.135	1.31	0.28
	328.15	0.52	3.55	0.162	2.54	0.65
	343.15	0.50	4.93	0.194	3.23	0.98
nitrobenzene	298.15	0.50	1.28	0.080	0.27	0.03
	313.15	0.50	1.74	0.096	0.56	0.07
	328.15	0.53	2.11	0.118	0.91	0.13
	343.15	0.53	2.47	0.141	1.43	0.25
bis(2-methoxyethyl) ether	298.15	0.50	2.01	0.088	0.72	0.09
	313.15	0.50	2.73	0.110	1.40	0.21
	328.15	0.50	3.95	0.128	2.48	0.43
	343.15	0.56	3.08	0.146	2.66	0.52

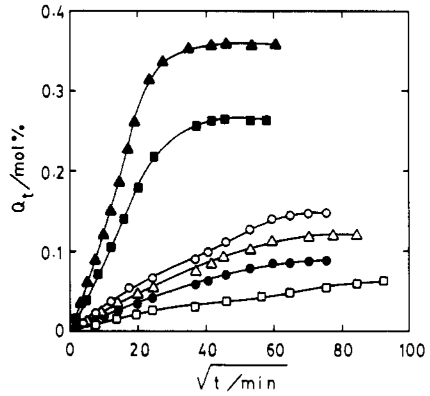

Figure 1. Mole percent sorption versus the square root of time for the polymer with (▲) benzene, (■) chlorobenzene, (○) 1,2-dichlorobenzene, (△) bromobenzene, (□) nitrobenzene, and (●) bis(2-methoxyethyl) ether at 298.15 K.

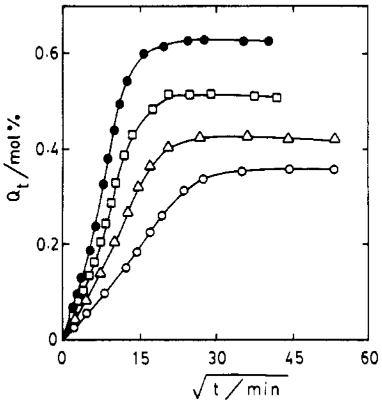

Figure 2. Mole percent sorption versus the square root of time for the polymer with benzene at (○) 298.15 K, (△) 313.15 K (□) 328.15 K, and (●) 343.15 K.

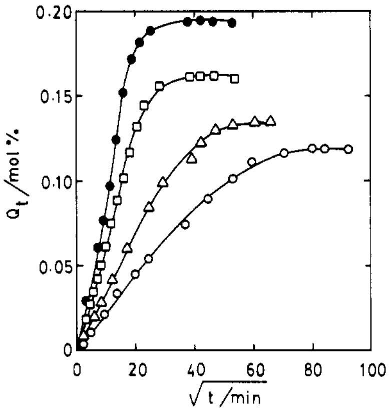

Figure 3. Mole percent sorption versus the square root of time for the polymer with bromobenzene at the same temperatures used in Figure 2.

The values of D were obtained by the iterative procedure considering the first 11 terms (n = 0–10) of eq 3. The calculated results of D, presented in Table 3, are accurate to ±0.005 unit, but are approximated to two decimal places. The permeability coefficients, P, have been calculated from the values of D and S using the relation $P = DS$. These results are also included in Table 3. The results of D and P in the investigated interval of temperature follow the sequence

D: benzene > chlorobenzene > bromobenzene > 1,2-dichlorobenzene > bis(2-methoxyethyl) ether > nitrobenzene

P: benzene > chlorobenzene > 1,2-dichlorobenzene > bromobenzene > bis(2-methoxyethyl) ether > nitrobenzene

It is found that benzene exhibits the highest diffusion coefficients (2–7) × 10^{-7} cm^2·s^{-1}, while the smallest D is observed for nitrobenzene (0.3–1.4) × 10^{-7} cm^2·s^{-1}, and the intermediary values are observed for the remaining liquids. However, no systematic dependence of D on the size of the penetrant molecules is observed. 1,2-Dichlorobenzene having a molar volume of 113 cm^3·mol^{-1} (the highest among the penetrants considered) exhibits D in the range (0.7–2.8) × 10^{-7} cm^2·s^{-1} which is slightly smaller than the value of (0.7–3.2) × 10^{-7} cm^2·s^{-1}, as observed for bromobenzene with a molar volume of 106 cm^3·mol^{-1}. On the other hand, bis(2-methoxyethyl) ether having a molar volume of 143 cm^3·mol^{-1} has

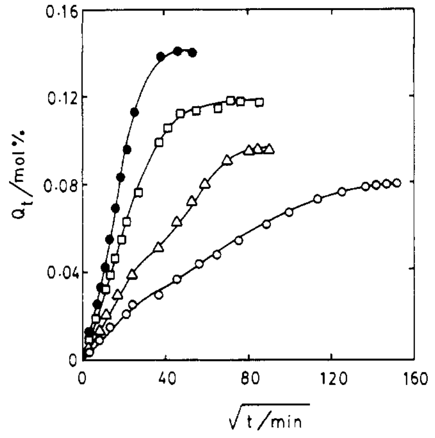

Figure 4. Mole percent sorption versus the square root of time for the polymer with nitrobenzene at the same temperatures used in Figure 2.

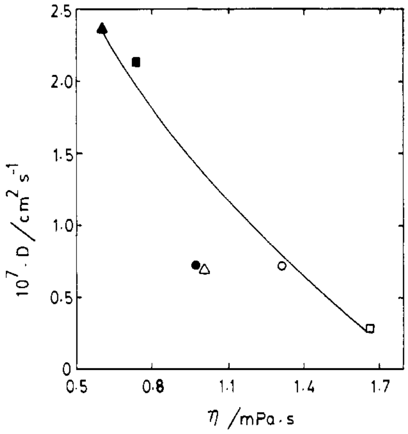

Figure 5. Diffusion coefficient versus viscosity for the polymer with the solvents given in Figure 1.

a D value in the range (0.7–2.7) × 10^{-7} cm^2·s^{-1}. This 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 data in addition to viscosity values.

For instance, the D, S, and P values of benzene are highest while these values are lowest for nitrobenzene. The above sequence follows the principle that the more polar nitrobenzene ($\mu = 4.0$) moves slower than the nonpolar benzene ($\mu = 0.0$). However, the intermediary values of D and S are exhibited by chlorobenzene, bromobenzene, 1,2-dichlorobenzene, and bis(2-methoxyethyl) ether. A close perusal of the data for these penetrants further suggests very little polarity effect on the transport parameters. For example, chlorobenzene is more polar than bromobenzene, but the S, D, and P values of the latter are smaller than those of the former, probably because of the large size of the bromine atom. On the other hand, bis(2-methoxyethyl) ether ($\mu = 1.97$) shows lower values of D, S, and P than all the aromatics except nitrobenzene, probably because of its aliphatic nature.

The diffusion results of the present study seem to bear a relationship with liquid viscosity as displayed in Figure 5. Such a dependence was also observed earlier by Vahdat (*19*) with elastomer + solvent systems. The trend in the variation of D versus liquid viscosity (Figure 5) is in accordance with the well-known Stokes–Einstein equation (*20*):

$$D = kT/6\pi\eta r \qquad (4)$$

where k is the Boltzmann constant, T is the absolute temperature, η is the liquid viscosity, and r is the hydrodynamic radius of the transporting molecule.

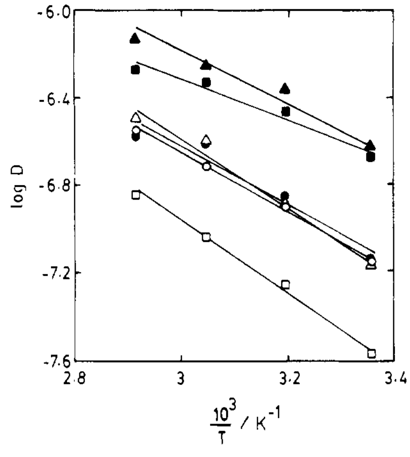

Figure 6. Arrhenius plots of log D versus $1/T$ for the polymer with the solvents given in Figure 1.

Temperature Effects and Arrhenius Parameters. Significant advances have been made over the past decades to develop a microscopic description of the diffusion phenomenon in polymers and to show that diffusion in rubbery polymers is very different from that in glassy polymers (*21*). According to the molecular models for the rubbery polymers well above their glass transition temperatures, the Arrhenius relation is generally valid experimentally; i.e.,

$$D = D_0 \exp(-E_D/RT) \qquad (5)$$

where E_D is the 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 conventional 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

$$S = S_0 \exp(-\Delta H_S/RT) \qquad (6)$$

where ΔH_S is the heat of sorption and is a composite parameter. This involves contributions from (i) Henry's law which requires both the formation of a site and the dissolution of the species into that site (the formation of a site involves the endothermic contribution to this process) and (ii) the Langmuir (hole filling) type sorption mechanism, 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 ($P \equiv DS$) may also be expressed in a similar manner and the activation energy, E_P, for the permeation is given as

$$E_P = E_D + \Delta H_S \qquad (7)$$

Since in the present polymer + solvent systems the values of S, P, and D have shown an increase with a rise in temperature, eqs 5 and 6 are used to calculate the E_D and ΔH_S values from the least-squares procedure. Figure 6 presents the Arrhenius plot of log D versus $1/T$. Using eq 7, the E_P values were calculated. The results of E_D, E_P, and ΔH_S summarized in Table 4 are higher for the polar nitrobenzene than for the other compounds. However, lower values of the activation

Table 4. Activation Parameters, E_D and E_P, and Enthalpy of Sorption, ΔH_S, for Polymer + Solvent Systems

liquid	E_D (kJ·mol^{-1})	E_P (kJ·mol^{-1})	ΔH_S (kJ·mol^{-1})
benzene	20.99	31.61	10.62
chlorobenzene	17.56	27.25	9.69
1,2-dichlorobenzene	25.92	34.99	9.07
bromobenzene	30.44	39.74	9.31
nitrobenzene	31.33	42.06	10.74
bis(2-methoxyethyl) ether	25.92	35.20	9.48

parameter are observed for chlorobenzene than for the other compounds. In all cases, the values of ΔH_S are positive, suggesting that the sorption is mainly dominated by Henry's mode, giving an endothermic contribution to the transport phenomenon.

Conclusions

The experimental transport results of benzene, substituted benzenes, and bis(2-methoxyethyl) ether into the tetrafluoroethylene–propylene copolymeric sheets are presented in the temperature interval from 298.15 to 343.15 K. The diffusion coefficients as estimated from the Fickian equation do not seem to bear any relationship to the size of the penetrant molecules. However, solvent polarity and the size of the substituent groups on the benzene ring seem to influence the transport results. The activation parameter values for the processes of diffusion and permeation fall in the range expected of those for the rubbery polymeric systems well above their glass transition temperatures. The heat of sorption results are indicative of the mild endothermic interactions (Henry-type sorption mode) between the polymer chain segments and the solvent molecules. Such results may be useful in intended field applications of the 3M Aflas polymers in the presence of the chosen solvents.

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