

# Permeation of Methyl Chloride and Benzene through FEP Teflon\*

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## Synopsis

Permeabilities and diffusivities of methyl chloride and benzene vapors at low activities in FEP Teflon membranes were measured in a continuous-flow permeation cell, at temperatures ranging from 47°C to 150°C. In all cases investigated, the permeabilities and diffusivities were independent of the penetrant partial pressure, and the permeation process was well described by a Henry's law sorption-Fickian diffusion model. The activation energies for permeation and diffusion and the sorption enthalpy were respectively 34.8 kJ/mol, 50.1 kJ/mol, and -15.3 kJ/mol for methyl chloride and 49.5 kJ/mol, 69.1 kJ/mol, and -19.6 kJ/mol for benzene. The diffusional activation energies for these two substances and other low molecular weight hydrocarbons correlate reasonably well with the Lennard-Jones collision diameters of the penetrant molecules. The solubilities correlate approximately with the penetrant boiling points, but the highly polar nature of methyl chloride and the aromaticity of benzene lead to deviations between the solubilities of these substances and those of nonpolar aliphatics with the same tendency to condense from the vapor phase.

## INTRODUCTION

A permeable, nonporous polymer membrane placed as an interface between a pollutant-containing gas stream and a secondary carrier gas stream can provide reproducible gas samples for continuous emissions monitoring.<sup>1</sup> The quantities of particulates, corrosive species, and water in the final sample gas are negligible, and the interface tends to remain relatively free from particulate adhesion.<sup>1-3</sup>

An ongoing research study at North Carolina State University involves determining transport and sorption characteristics of candidate sampling interface materials. The permeation of methyl chloride and benzene vapors in FEP Teflon was investigated in a recent phase of this study. This paper reports the results of these experiments.

## EXPERIMENTAL

### Continuous Permeation Measurements

In a continuous permeation experiment, one surface of a flat membrane is exposed to a penetrant at a constant partial pressure while the other surface is exposed to a flowing penetrant-free carrier gas stream. The penetrant diffuses through the membrane into the carrier gas, which passes out of the membrane chamber to an analyzer. The rate of permeation of the penetrant is obtained

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as the product of the carrier gas flow rate and the measured penetrant concentration downstream of the membrane chamber.<sup>1-6</sup>

Since the downstream membrane surface is continuously swept clean, the concentration of dissolved penetrant at this surface is usually negligible relative to that at the upstream surface. The permeability of the penetrant in the membrane in this circumstance is defined as

$$P = F_{ss}h/p \quad (1)$$

where  $F_{ss}$  is the steady-state flux of penetrant through a membrane of thickness  $h$  when the upstream penetrant partial pressure is  $p$ . If sorption of the penetrant in the membrane is described by Henry's law with solubility coefficient  $S$ , and diffusion of the dissolved penetrant is described by Fick's law with diffusion coefficient  $D$ , then the permeability is given by<sup>4</sup>

$$P = SD \quad (2)$$

While the permeability can be obtained from the steady-state flux through the membrane, the diffusion coefficient must be determined from the transient response of the system to a step change in penetrant concentration at the upstream membrane surface. If  $F(t)$  is the flux of penetrant into the downstream carrier gas at a time  $t$  after the imposition of the step change and  $M_0$ , the zeroth moment of the response, is calculated as

$$M_0 = \int_0^{\infty} [1 - F(t)/F_{ss}] dt \quad (3)$$

then the diffusion coefficient may be determined as<sup>4</sup>

$$D = h^2/6M_0 \quad (4)$$

A difficulty with the implementation of eq. (4) is that the given relationship involves the transient response of the membrane alone, and does not include contributions to the response from components of the system such as feed and exit lines, the upstream and downstream membrane chambers, and the analyzer. Suppose  $R(t)$  is the measured step response of the entire system, and that  $M'_0$  is the zeroth moment of this response:

$$M'_0 = \int_0^{\infty} [1 - R(t)/R_{ss}] dt \quad (5)$$

Felder et al.<sup>6</sup> have shown that the value of  $M_0$  which should be substituted into eq. (4) is

$$M_0 = M'_0 - (\tau_1 + \tau_2 + \tau_3 + \tau_a) \quad (6)$$

where  $\tau_1$ ,  $\tau_2$ , and  $\tau_3$  are the mean residence times of the gases in the feed line to the chamber, the chamber itself, and the carrier gas exit line leading to the analyzer, and  $\tau_a$  is the time lag of the analyzer response. In the present study,  $\tau_1$ ,  $\tau_2$ , and  $\tau_3$  were determined from the known volumes of the system components and the throughput rates of the gas streams. The sum ( $\tau_1 + \tau_2 + \tau_3$ ) had a value in the range of 40-70 s. The conditions of the experiments were such that  $\tau_a$  could be neglected. The value of  $M_0$  varied from 25 s to 2500 s, so that for all but the highest temperatures and thinnest films studied (and hence the shortest

response times) the lags due to nonmembrane dynamics were relatively insignificant.

The temperature dependences of the permeability and diffusion coefficient of gases in rubbery polymers are given by Arrhenius relations<sup>4</sup>:

$$P = P_0 \exp(-E_p/RT) \quad (7)$$

$$D = D_0 \exp(-E_d/RT) \quad (8)$$

where  $E_p$  and  $E_d$  are the apparent activation energies for permeation and diffusion, respectively. The Henry's law solubility coefficient, which equals  $P/D$ , is expressible in terms of a van 't Hoff relation:

$$S = S_0 \exp(-\Delta H_s/RT) \quad (9)$$

where  $\Delta H_s$  is the apparent enthalpy of sorption of the penetrant in the polymer.

### Materials

The methyl chloride used as a source gas was a primary standard containing 0.535 mol % methyl chloride in nitrogen, supplied by Air Products, Inc. The benzene was a certified standard containing 1000 ppm in nitrogen, supplied by Scott Specialty Gases. The UPC-grade nitrogen used throughout the system was also supplied by Air Products, Inc.

The FEP Teflon® membranes used were of 0.0508 mm (2-mil) and 0.127 mm (5-mil) thicknesses, and were supplied by the Livingstone Coating Corp. of Charlotte, N.C. All membranes were annealed in nitrogen at 200°C for 24 h to relieve any residual stresses from the fabrication process.

### Apparatus

The continuous-flow permeation chamber used in this study consisted of two hollowed-out cylindrical sections of 304 stainless steel, which when clamped together formed two matching chambers separated by the polymer membrane being studied. Each chamber had tangential gas inlet and outlet ports. The upstream chamber was also equipped with thermocouple and manometer sensing ports for monitoring the chamber temperature and pressure during runs. 0.125-in. mesh stainless steel screens were used as membrane supports. The chamber was situated in a thermostatically controlled oven (Fisher Isotemp Model 350), and was attached to all external lines by 0.25-in. 304 stainless steel tubing. Additional details of the apparatus and its operation are given by Yi-Yan et al.<sup>7</sup>

The gas analyzer was a Shimadzu Model GC-6AM Gas Chromatograph, equipped with dual-flame ionization detectors. The chromatograph was modified to sample a gas stream either continuously or in 10 cm<sup>3</sup> pulses. Signals produced in the continuous mode were traced by a Shimadzu bench-type automatic balancing recorder and analyzed by hand. Signals produced in the pulse mode were analyzed by a Shimadzu C-R1A Chromatopac Electronic Integrator.

The carrier gas used in all chromatograph lines was UPC-grade nitrogen. The

analyzer was calibrated by passing nitrogen over a gravimetrically calibrated permeation tube containing the desired penetrant (methyl chloride or benzene).

### Experimental Procedures

At the outset of a run, a gas stream containing a known partial pressure of the penetrant,  $p$ , was routed to the upstream permeation chamber. The downstream carrier gas flow rate was set at a level low enough to provide a detectable penetrant concentration, but high enough to preclude concentration polarization at the downstream membrane surface. Attainment of steady state was presumed when the measured penetrant concentration in the downstream gas showed no apparent variation over a period of at least 30 min.

The absolute calibration of the gas chromatograph was much more reliable for the pulse mode of analysis than for the continuous mode. Steady-state permeabilities were therefore determined with the gas chromatograph in the pulse mode. The average of five measured steady-state concentration values was multiplied by the carrier gas flow rate and divided by the exposed membrane surface area to obtain the steady-state flux  $F_{ss}$ . This process was repeated for several upstream partial pressures, and the results were plotted as  $F_{ss}$  vs.  $p/h$ . The permeability of the penetrant in the polymer at the run temperature was taken to be the slope of a least-squares line fitted to the plotted points [see eq. (1)].

The pulse mode of analysis had a maximum reliable sampling frequency of about one sample in 4 min, and was consequently not suitable for the transient step response measurement required to determine the diffusion coefficient. The continuous response mode of the gas chromatograph was therefore used for this purpose. The measured response was designated  $R(t)$ , and the long-time asymptotic value of the response was  $R_{ss}$  [see eq. (5)]. Since only relative and not absolute response values were required for the determination of  $D$  from eqs. (4)–(6), the lower accuracy obtainable in the continuous mode did not pose a problem.

The determination of  $D$  proceeded along the lines outlined previously. The zeroth moment of the system response,  $M_0$ , was first calculated from the measured response using eq. (5), and the moment of the membrane response,  $M_0$ , was determined from eq. (6). The diffusivity was then calculated from eq. (4). Once  $P$  and  $D$  had been determined at a given temperature, the solubility coefficient  $S$  was calculated as  $P/D$ .

## RESULTS AND DISCUSSION

### Methyl Chloride Permeation

Permeabilities and diffusion coefficients of methyl chloride in FEP Teflon were measured in 2-mil films for temperatures ranging from 48°C to 90°C, and in 5-mil films for temperatures in the range from 90°C to 120°C, at upstream partial pressures between 0.5 torr and 4.1 torr. No effects of partial pressure variations on measured transport properties were observed, although such effects would be expected at higher penetrant activities than were used in this study.

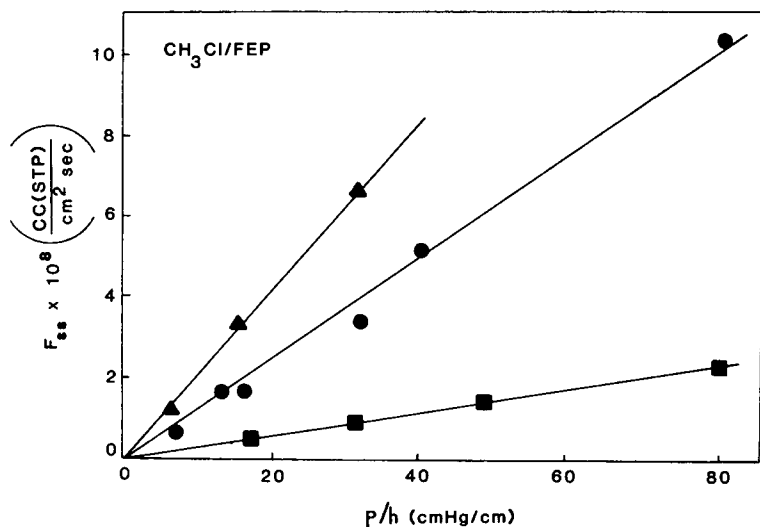


Fig. 1. Steady state methyl chloride permeation flux versus partial pressure gradient: (■) 2 mil, 48°C; (●) both 2 and 5 mil, 90°C; (▲) 5 mil, 110°C.

Figure 1 shows plots of  $F_{ss}$  vs.  $p/h$  at three representative temperatures. The linearity confirms the validity of the ideal solution-diffusion model for the existing experimental conditions. The slopes of the lines are the permeabilities at the respective run temperatures.

Figure 2 shows Arrhenius plots of the permeability and diffusivity of methyl chloride in FEP Teflon, and Figure 3 shows a van 't Hoff plot of the solubilities determined as  $P/D$ . The parameters associated with eqs. (7)–(9) which were determined from these plots are summarized in Table I.

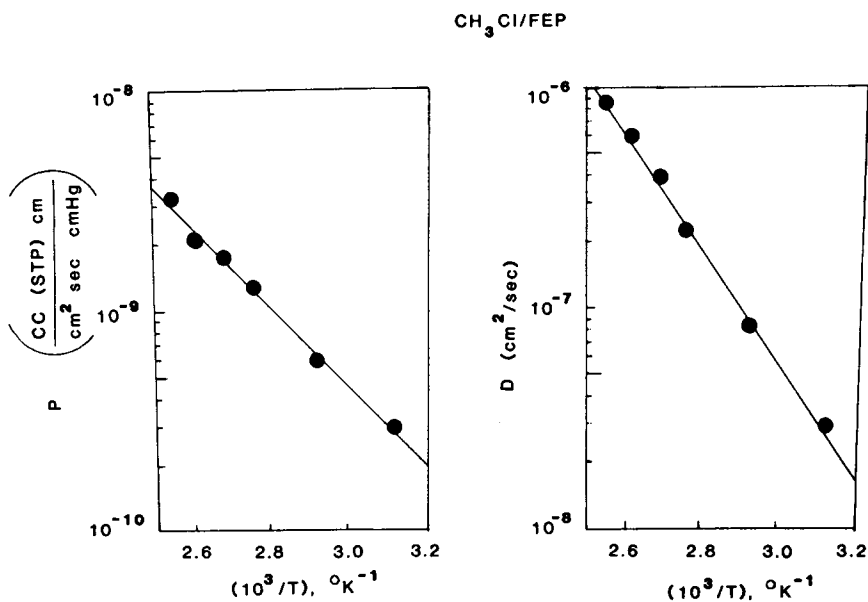


Fig. 2. Arrhenius plots of the permeability and diffusivity of methyl chloride in FEP Teflon.

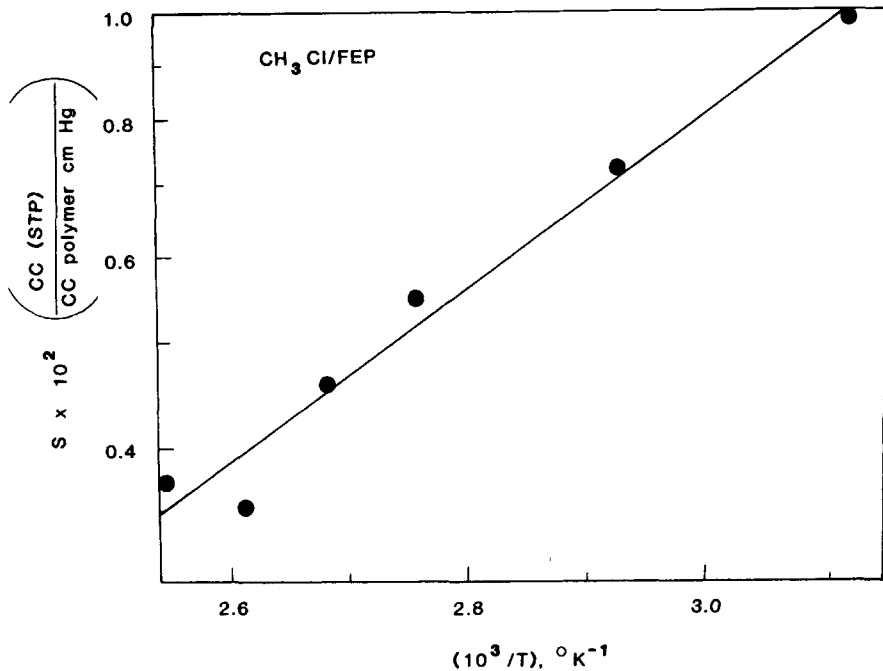


Fig. 3. Van 't Hoff plot of the solubility coefficient for methyl chloride in FEP Teflon.

### Benzene Permeation

Permeabilities and diffusion coefficients of benzene in FEP Teflon were measured in 2-mil films at a partial pressure of 0.76 torr and temperatures ranging from 47°C to 150°C. A separate series of experiments run at a single temperature of 98.8°C and partial pressures from 0.076 torr to 0.76 torr showed that partial pressure variations did not affect measured transport properties.

Figure 4 shows a plot of  $F_{ss}$  vs.  $p/h$  for the runs at 98.8°C. Again, the linearity of the plot confirms the validity of the assumptions underlying the calculation of  $P$  and  $D$  from the experimental data. The closeness of all points to the line suggests that the use of a single partial pressure for determination of permeability at all other temperatures should be a minimal source of error. Arrhenius and van 't Hoff plots of  $P$ ,  $D$ , and  $S$  for benzene are shown in Figures 5 and 6, and the parameter values determined from these plots are summarized in Table I.

TABLE I  
Transport and Sorption Parameters for Methyl Chloride and Benzene

Parameter	Methyl chloride	Benzene
$P_0$ [ $\text{cm}^3$ (STP)/ $\text{cm}\cdot\text{s}\cdot\text{cm Hg}$ ]	$1.26 \times 10^{-4}$	$1.62 \times 10^{-2}$
$E_p$ (kJ/mol)	34.8	49.5
$D_0$ ( $\text{cm}^2/\text{s}$ )	3.941	307.5
$E_d$ (kJ/mol)	50.1	69.1
$S_0$ [ $\text{cm}^3$ (STP)/ $\text{cm}^3\cdot\text{cm Hg}$ ]	$3.209 \times 10^{-5}$	$5.265 \times 10^{-5}$
$\Delta H_s$ (kJ/mol)	-15.3	-19.6

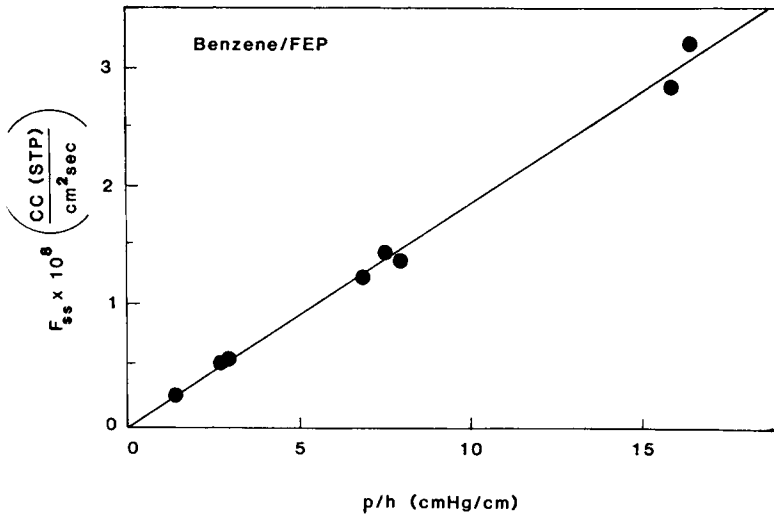


Fig. 4. Steady state benzene permeation flux versus partial pressure gradient, 2 mil, 98.8°C.

### Correlation of Transport and Sorption Parameters

The activation energy for diffusion,  $E_d$ , often exhibits a high level of correlation with the penetrant molecular diameter  $d$  or with some power of  $d$ .<sup>8</sup> Values of  $E_d$  and the Lennard-Jones collision diameter<sup>9</sup> for penetrants treated in the present study and a previous study<sup>7</sup> of permeation of FEP Teflon are listed in

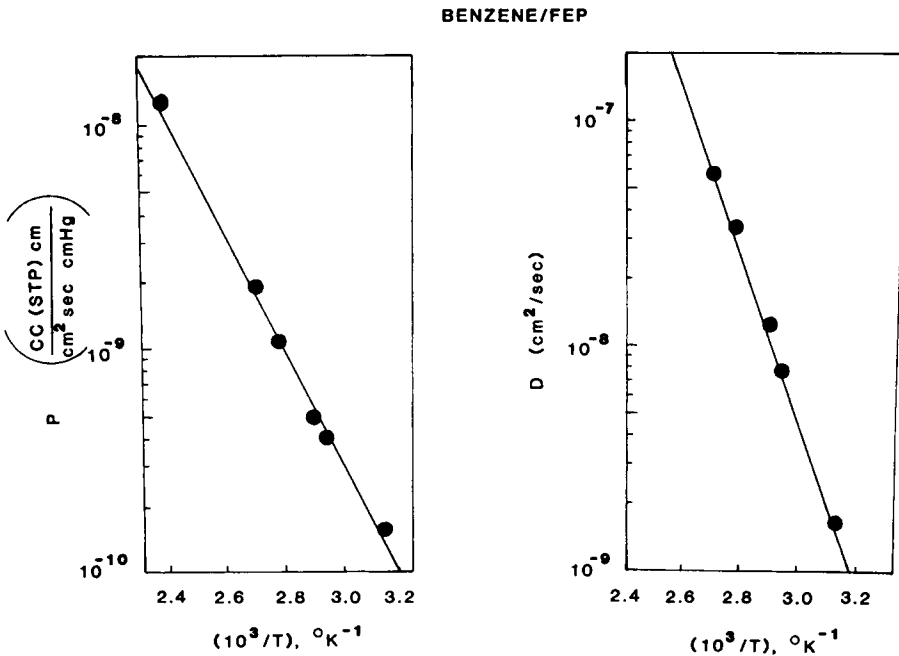


Fig. 5. Arrhenius plots of the permeability and diffusivity of benzene in FEP Teflon.

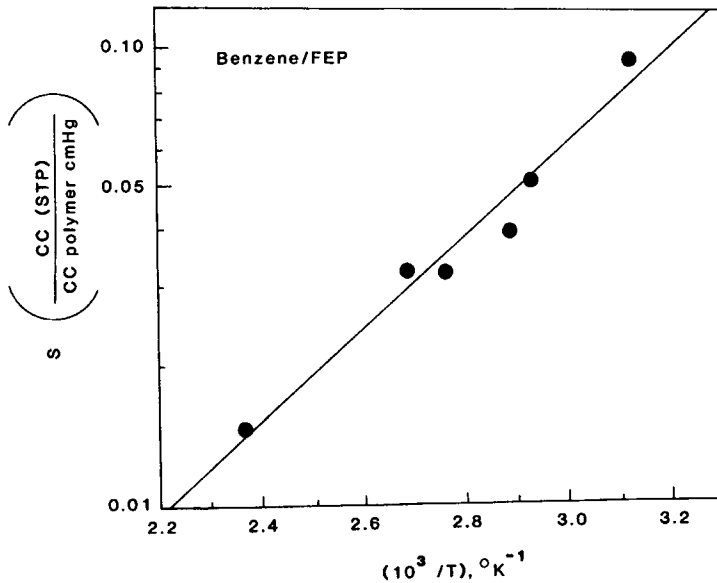


Fig. 6. Van't Hoff plot of the solubility coefficient for benzene in FEP Teflon.

Table II. Figure 7 shows a plot of  $E_d$  vs.  $d^2$ . The plot is clearly linear, with only the points for propane and benzene deviating from it. The line shown is given by the equation

$$E_d = 2.834d^2 \quad (10)$$

The diffusional activation energies of both benzene and propane clearly fall substantially below the correlation line that fits the rest of the species considered. In the case of propane, the unusually large value of  $d$  reported in Table II (larger than that of *n*-butane) appears to overestimate the characteristic dimension of this species as it moves through the polymer. The same argument might also apply in the case of benzene, since its planar configuration may permit orienta-

TABLE II  
Selected Properties of Various Penetrants in FEP Teflon®

Penetrant	Lennard-Jones diameter $d$ (Å)	Activation energy for diffusion $E_d$ (kJ/mol) <sup>a</sup>	Normal boiling point <sup>9</sup> $T_b$ (K)	Henry's law solubility coefficient at 90°C $S \times 10^3$ [cm <sup>3</sup> (STP)/cm <sup>3</sup> -cm Hg] <sup>a</sup>
Methane	3.758	41.3	112	2.86
Ethane	4.443	53.8	184	5.83
Propane	5.118	59.4	231	8.50
<i>n</i> -Butane	4.687	64.9	272	10.4
<i>i</i> -Butane	5.278	77.4	261	7.81
Methyl chloride	4.182	50.1	249	5.14
Benzene	5.348	69.1	353	34.7

<sup>a</sup>  $E_d$  and  $S$  for penetrants other than methyl chloride and benzene were determined in a previous study.<sup>7</sup>



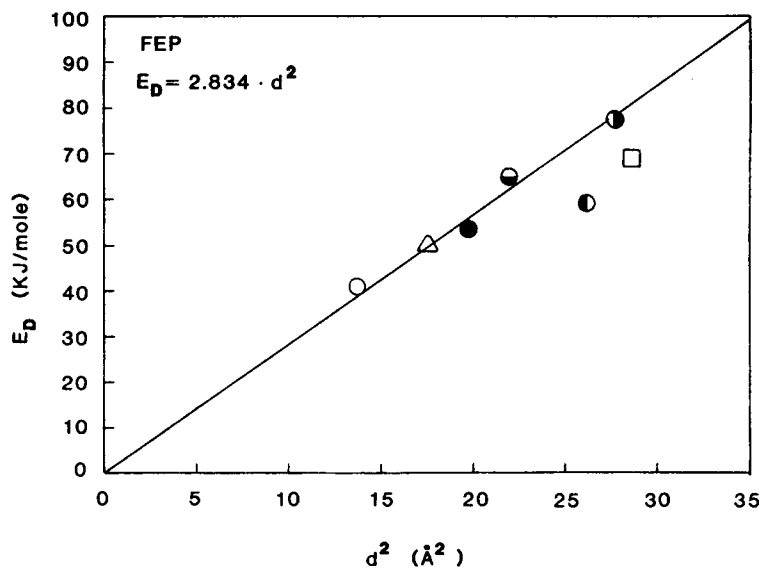


Fig. 7. Correlation of the activation energy for diffusion with the Lennard-Jones collision diameter of the penetrant. (O) Methane; (●) ethane; (◐) propane; (◑) butane; (◒) isobutane; (Δ) methylchloride; (□) benzene.

tion-specific diffusional jumps. Thus, both propane and benzene appear to require the existence of smaller openings to execute diffusional jumps than one might expect on the basis of their collision diameters determined from bulk phase properties.

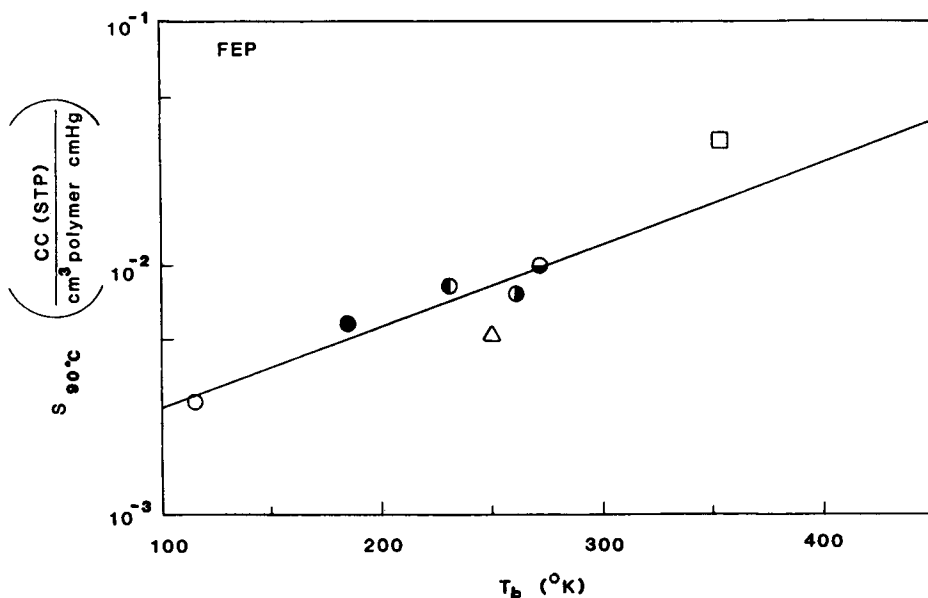


Fig. 8. Correlation of the solubility coefficient at 98°C with the normal boiling point of the penetrant. (O) Methane; (●) ethane; (◐) propane; (◑) butane; (◒) isobutane; (Δ) methylchloride; (□) benzene.

The solubility of a vapor in a polymer is related to its tendency to condense, as measured by its normal boiling point  $T_b$ . The logarithm of the solubility has frequently been found to correlate linearly with  $T_b$ .<sup>10</sup> Table II lists values of the solubility coefficients of various penetrants at 90°C, along with the boiling points of these penetrants, and a semilog plot of  $S$  vs.  $T_b$  is shown in Figure 8. The temperature 90°C was selected for convenience, since data at this temperature exist for all penetrants studied.

The line shown on Figure 8 represents a fit to all of the points except those for benzene and methyl chloride, and is given by the expression<sup>7</sup>

$$\ln S_{90^\circ\text{C}} = -6.69 + 7.74 \times 10^{-3} T_b \quad (11)$$

The points for methyl chloride and benzene clearly deviate from the correlation obtained for the other species in Figure 8, all of which are straight-chain hydrocarbons. The implication is that solubility correlations of this nature work best when limited to homologous species. The highly polar nature of methyl chloride and the aromaticity of benzene undoubtedly lead to differences between the solubilities of these substances in a polymer and those of nonpolar aliphatics with the same tendency to condense from the vapor phase.

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