Gas Transport in Glassy Polymers

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Synopsis

Sorption kinetics and equilibria for CO_2 in polycarbonate were studied over a range of temperatures from 35° to 65°C and pressures from 3 to 22 atm. The dual mode sorption model of Vieth et al. was used to test the data, and a comparison was made with previous work on glassy polystyrene. Further evidence of the validity of generality of the model in providing a consistent picture of small-molecule diffusion in glassy polymers was thereby provided. The technical feasibility of membrane separation of H_2 from a H_2/CO_2 mixture by selective permeation through polycarbonate was examined at 50°C.

INTRODUCTION

The continuing interest in membrane separations requires understanding of the diffusion mechanism in the solid polymer. Some of the potential polymers of choice are the typically glassy ones, e.g., members of the new family of engineering plastics such as polycarbonate. Vieth, Frangoulis, and Rionda[1] studied the sorption of methane in glassy polystyrene using the "dual mode" sorption model developed by Vieth and Sladek.[2] Here, isothermal sorption of gas molecules may be thought of as consisting of two components: one expressible by the linear Henry's law relationship and the second, by a nonlinear Langmuir equation,

$$C = C_D + C_H = k_D P + \frac{C_H' b P}{1 + bP} \tag{1}$$

C = solubility, in cc (S.T.P.)/cc total polymer; k_D = Henry's law dissolution constant, in cc (S.T.P.)/cc atm; P = pressure, in atm; C_H' = microvoid saturation constant, in cc (S.T.P.)/cc total polymer; and b = microvoid affinity constant, in atm^{-1}. Ordinary dissolution is represented by the first term, C_D, while the second term corresponds to the "microvoid filling" component of the sorption process.

Analysis of the sorption data allows the determination of all these parameters. The diffusion constant was obtained from the numerical solution of the general nonlinear partial differential equation for diffusion in a microheterogeneous medium containing a nonlinear sink:

$$D \frac{\partial^2 C_D}{\partial x^2} = \frac{\partial C_D}{\partial t} \left[1 + \frac{C_H'(b/k_D)}{\{1 + (b/k_D)C_D\}^2} \right] \tag{2}$$

with the boundary conditions

$$t = 0 \qquad C_D = 0 \qquad -l \le x \le l$$

$$t \ge 0 \qquad \frac{\partial C_D}{\partial x} = 0 \qquad x = 0$$

$$t > 0 \qquad C_D = k_D P \qquad x = \pm l$$

$$l = \text{half-thickness of membrane.}$$

Thus, the mathematics postulate that the gas trapped in the microvoids is immobilized and the driving force for diffusion is the concentration gradient of dissolved species. Local equilibrium of the two modes is a further postulation. The solution to the equation involves curve-matching plots of the parameters Φ versus $(\theta'/D)^{1/2}$ with a standard Φ versus $(\theta')^{1/2}$ curve[2]:

$$\Phi = \frac{P_0 - P}{P_0 - P_f} \tag{3}$$

$$\theta' = \frac{Dt}{l^2} \left[1 + \frac{C_H'b/k_D}{(1 + bP)^2} \right]^{-1} \tag{4}$$

where P_0 = initial pressure, in atm; P = pressure at time t, in atm; P_f = final pressure, in atm; t = time, in sec; and l = half-thickness of polymer sheet, in cm.

EXPERIMENTAL

The apparatus is shown in Figure 1. The system is evacuated to 0.02 mm Hg, then pressurized as rapidly as possible. The ensuing pressure
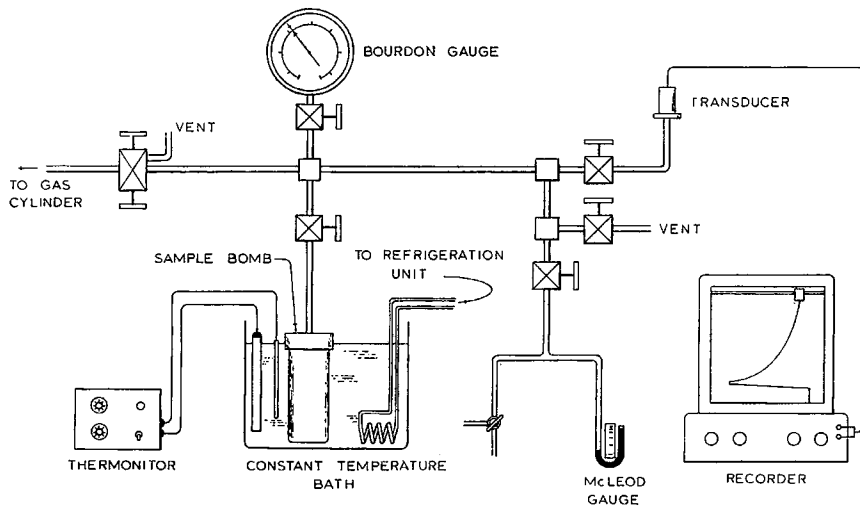

Fig. 1. Schematic diagram of the high-pressure sorption apparatus.

decay is followed with time. Preparation of materials and other details are found in ref. 3. The polycarbonate used is amorphous film of 0.02-in. thickness.

RESULTS AND DISCUSSION

In Figures 2a and 2b, the isotherms for sorption of methane in oriented polystyrene and carbon dioxide in polycarbonate are shown, respectively.

The slope of the high-pressure linear portion of the isotherm is set equal to k_D. Subtracting $k_D P$ from the total solubility C results in a determination of the microvoid-filling contribution to the solubility:

$$C_H = \frac{C_H' b P}{1 + bP} \tag{5}$$

$$\frac{P}{C_H} = \frac{1}{C_H' b} + \frac{P}{C_H'}. \tag{6}$$

A plot of P/C_H versus P enables determination of C_H' and b from the slope and intercept. The plots were fitted by the least-mean-squares technique. Figure 3 illustrates the microvoid-filling contribution in both polymers. Confidence limits on the solubilities are $\pm 6.5\%$ for CH_4 in polystyrene and $\pm 8.7\%$ for CO_2 in polycarbonate at the 95% level. Table I gives values of k_D, C_H, and b for the polymers.

TABLE I
Sorption Parameters

T, °C	k_D	C_H'	b
A. CH_4 in Oriented Polystyrene			
25	0.185	3.25	0.17
35	0.18	2.69	0.13
45	0.175	1.98	0.12
B. CO_2 in Polycarbonate			
35	0.765	9.53	1.50
45	0.708	7.20	1.16
65	0.346	7.09	0.94

The diffusion constants are calculated from plots of pressure decay Φ against

$$\left(\frac{\theta'}{D}\right)^{1/2} = \left(\frac{t}{l^2}\right)^{1/2} \left\{\left[1 + \frac{C_H' b/k_D}{(1 + bP)^2}\right]^{-1}\right\}^{1/2} \tag{7}$$

A scaling factor defined by

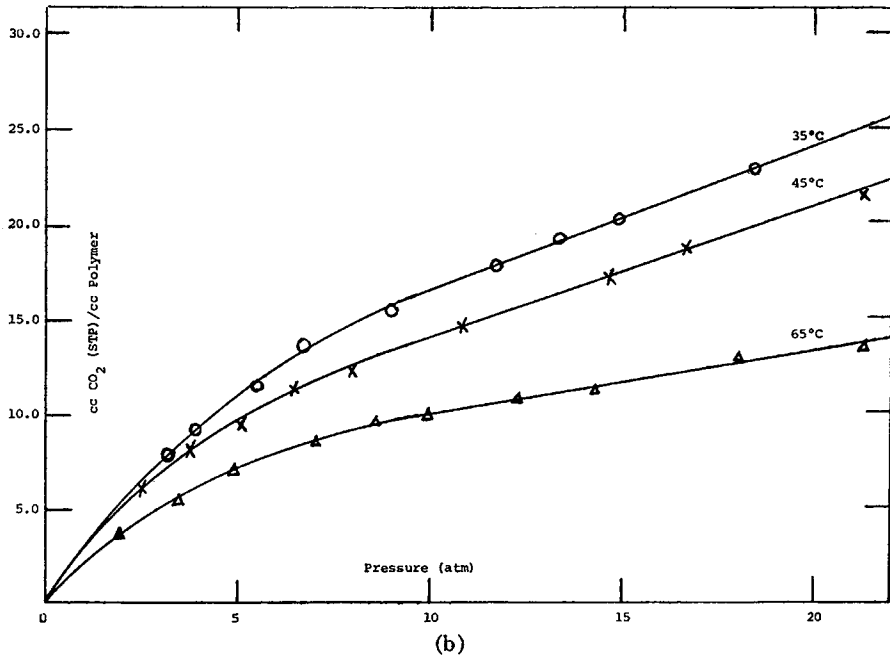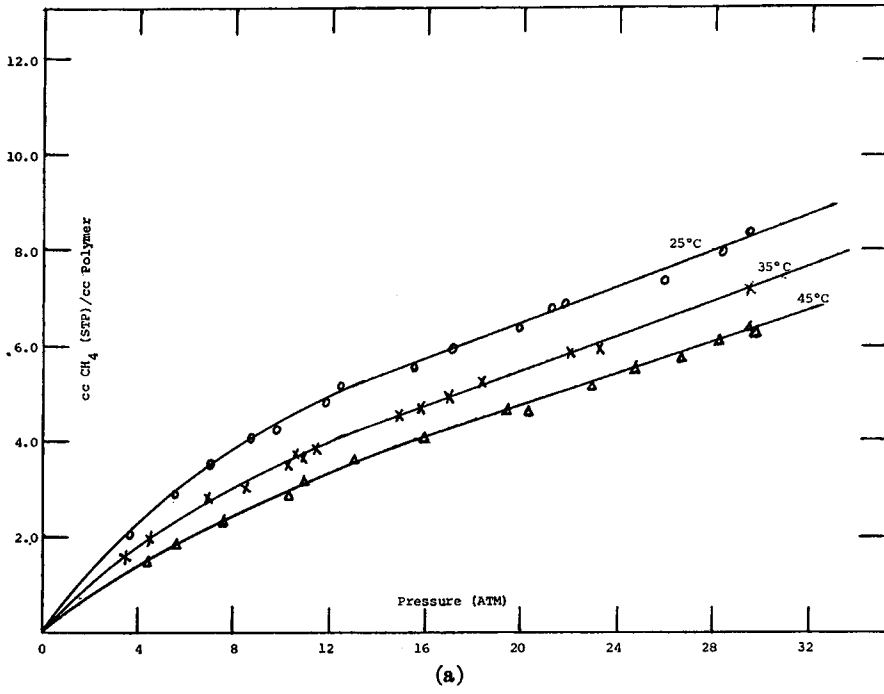$$D = \left[\frac{1}{\text{scaling factor}}\right]^2 \tag{8}$$

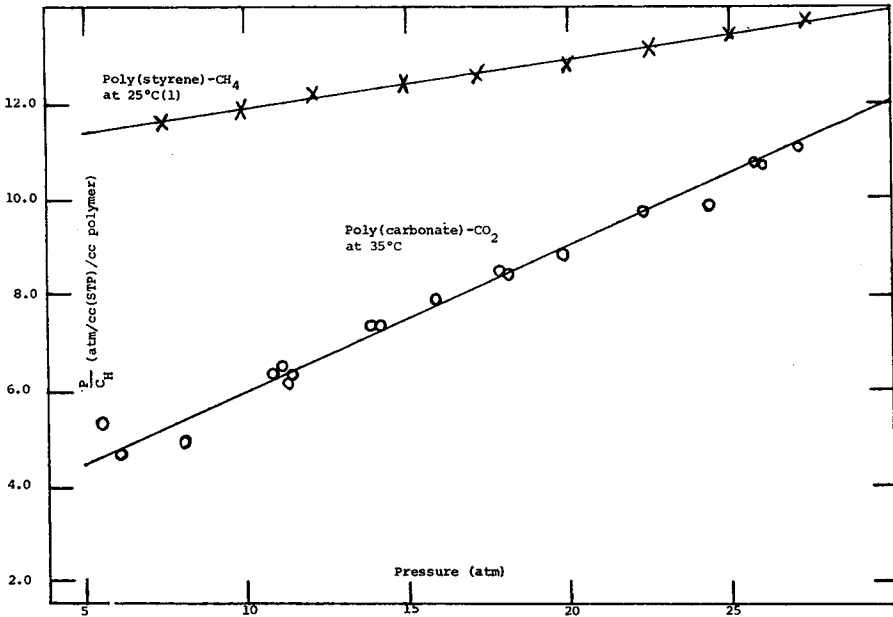Fig. 2. (a) Solubility of methane in oriented polystyrene (1); (b) solubility of CO₂ in polycarbonate.

Fig. 3. Langmuir plots for microvoid filling.

is used to fit the data of the general Vieth-Sladek correlation (Fig. 4).

An alternate approximate solution to the sorption (or desorption) from a sheet of polymer film without the nonlinear sink term is given in Crank and Park.[4] The final form for the diffusion coefficient is given by

$$D_{1/2} = 0.0492 \left(\frac{L^2}{t_{1/2}} \right) \qquad (9)$$

where L = total film thickness, in cm, and $t_{1/2}$ = time for half-saturation, and

$$Q_d(t_{1/2}) = \frac{S(t_{1/2}) - S(\infty)}{S(0) - S(\infty)} = \frac{1}{2} \qquad (10)$$

Q_d = fraction gas desorbed from film; $S(0)$ = gas sorbed at $t = 0$, cc (S.T.P.)/cc polymer; $S(\infty)$ = gas remaining at $t = \infty$; and $S(t_{1/2})$ = gas remaining at $t = t_{1/2}$. The overall expression for desorption at any time t is

$$Q_d(t) = \frac{8}{\pi^2} \sum_{n=0}^{\infty} (2n + 1)^{-2} \exp\left[-(2n + 1)^2 \ \pi^2 \ \frac{Dt}{L^2} \right]. \qquad (11)$$

Expanding the equation and truncating after the first term yields

$$Q_d(t) = \frac{8}{\pi^2} \left[\exp\left(-\pi^2 \ \frac{Dt}{L^2} \right) \right]. \qquad (12)$$

If, instead of determining the time at which one half of the gas remains in

the polymer, one chooses to calculate the diffusion constant when 75% of the gas remains, eq. (9) becomes

$$D_{3/4} = 0.00782 \left(\frac{L^2}{t_{3/4}} \right) \tag{13}$$

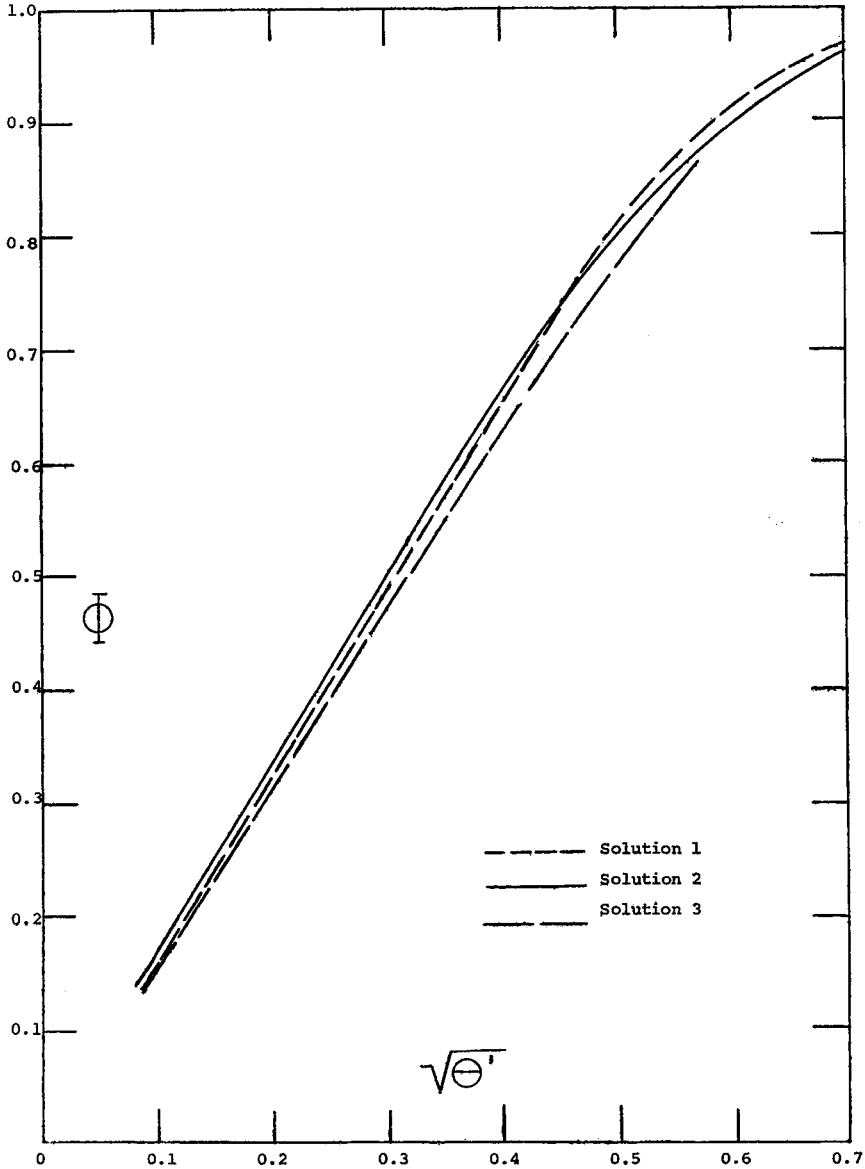$$D_{3/4} = 1.2 \times 10^{-8} \text{ cm}^2/\text{sec at } 35°C.$$

Fig. 4.   Vieth-Sladek correlation.[2]

On the graph, labels visible:

Scaling Factor 10,250
$D=0.95 \times 10^{-8}$ cm^2/sec

Scaling Factor 8,750
$D=1.31 \times 10^{-8}$ cm^2/sec

Scaling Factor 9,400
$D=1.13 \times 10^{-8}$ cm^2/sec

$$\phi = \frac{P_i - P}{P_i - P_o}$$

△ Run 1 6.73→4.76 atm.
o Run 2 8.80→6.31 atm.
O Run 3 11.54→8.48 atm.
X Run 4 13.52→10.01 atm.
▯ Run 5 19.71→15.12 atm.

$$\left(\frac{\theta'}{D}\right)^{1/2} = \left\{\frac{t}{\ell^2}\left(1 + \frac{\frac{C_H'b/k}{D}}{(1+bP)^2}\right)^{-1}\right\}^{1/2} \times 10^{-3}$$
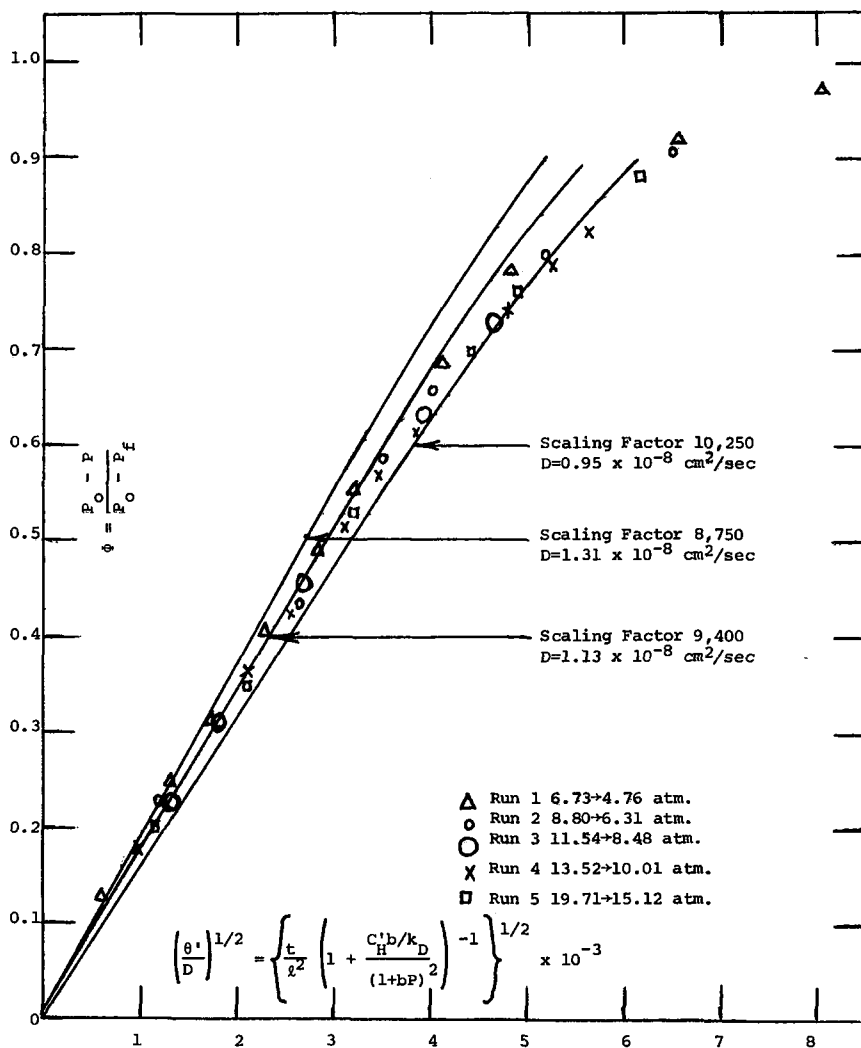
Fig. 5.   Determination of diffusion constants for methane in oriented polystyrene at 35°C.[1]

This value is much smaller than the true constant of 2.14×10^{-8} cm^2/sec for CO$_2$ in polycarbonate at 35°C calculated by the method of Vieth and Sladek.   For D to equal $D_{3/4}$, $t_{3/4}$ would have to be equal to

$$t_{3/4} = \frac{0.00782}{0.0492}\, t_{1/2} = 0.159\, t_{1/2}. \tag{14}$$

The observed ratio of $t_{3/4}/t_{1/2}$ is 1656 sec/6008 sec, or 0.27, much larger than the value given by eq. (14).   This provides further evidence of the effect of immobilization of gas molecules in the microvoids during the initial time interval of desorption or sorption.   The full set of results of dif-
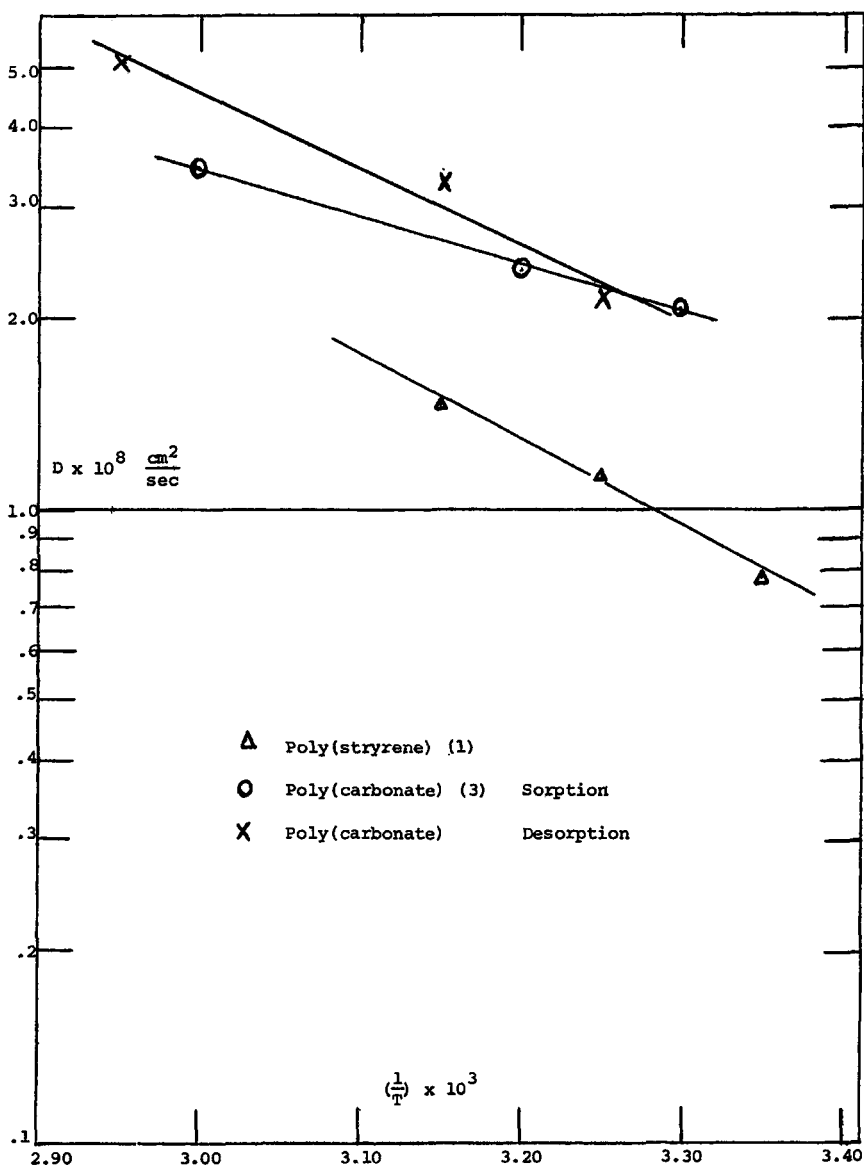
Fig. 6. Diffusion coefficients D vs. $1/T$ for CH_4 in polystyrene and CO_2 in polycarbonate.

fusion coefficient calculations are shown in Figures 5 and 6 for the polymers under evaluation.   Rather good agreement of the polycarbonate data with earlier results[3] is obtained.

The activation energy for diffusion is shown (Fig. 6) to be 6.4 kcal/g-mole for methane in polystyrene and 5.5 kcal/g-mole for CO_2 in poly-carbonate.   For activated diffusion mechanisms, the normal energy re-quirement is about 10–12 kcal, while for slip flow, the activation energy

needed is of the order of 1–2 kcal. The observed values suggest that a combination of these mechanisms is present. Perhaps polymer micromotions are also significantly contributing to the diffusion process, but with a frequency and amplitude lower than in rubbery systems.[1]

From analysis of the data in Table I, it is clear that polycarbonate possesses an extremely high degree of free volume, manifested in the average C_H' value of about 8 cc (S.T.P.)/cc polymer, while this value is only 3.25 for polystyrene. The high impact strength of polycarbonate in particular, and perhaps of engineering plastics in general, may be owing to the relative ease of energy dissipation by viscous processes into this excess free volume.

APPLICATION

If polycarbonate could be formed into a geometry of high surface, such as the hollow fiber configuration of Permasep (du Pont registered trademark),[7] it might become technically feasible to use this glassy polymer in a membrane separation process. For a 0.5-mil wall thickness, the available permeation surface area is about 24,000 (ft²/ft³)/mil with Permasep.[7]

Consider the separation of H_2 from CO_2 in refinery off-gas,[6] using a diffusion cascade

$$\bar{P}_i = k_D D. \tag{15}$$

At 50°C from this work,

$$\bar{P}_{CO_2} = 0.660 \frac{cc\ (S.T.P.)}{cc\ atm} \times 4.02 \times 10^{-8} \frac{cm^2}{sec}$$

$$\bar{P}_{CO_2} = 2.65 \times 10^{-8} \frac{cc\ (S.T.P.)\ cm}{sec\ cm^2\ atm}$$

$$\bar{P}_{H_2} = 1.9 \times 10^{-7} \frac{cc\ (S.T.P.)\ cm}{sec\ cm^2\ atm} \quad \text{(ref. 5)}$$

$$\alpha = \frac{\bar{P}_{H_2}}{\bar{P}_{CO_2}} = 7.2.$$

Using cascade theory, the minimum number of stages at total reflux required for the refinery off-gas requirements of $x_f = 0.53$, $x_p = 0.992$, and $x_w = 0.05$ is close to unity. Thus, for an ideal or nearly ideal cascade, only a few stages would be required.

CONCLUSIONS

The "dual mode" sorption model provides a quite general method for describing sorption kinetics and equilibria for gases in glassy polymers. Of particular interest is the evaluation of free volume and diffusion parameters. The technical feasibility of a membrane separation process for re-

covery of H_2 from refinery off-gas by selective permeation through polycarbonate merits further evaluation. The calculated high level of free volume of polycarbonate may be mainly responsible for its observed high impact strength.

References

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