

Numerical Examination of the Dual-Mode Model for Permeation, Sorption, and Desorption Rate Curves

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SYNOPSIS

Numerical solutions were applied to the dual-mode sorption and transport model for gas permeation, sorption, and desorption rate curves allowing for mobility of the Langmuir component. Satisfactory agreement is obtained between integral diffusion coefficient from sorption and desorption rate curves and apparent diffusion coefficient from permeation rate curves (time lag method). These rate curves were also compared to the curves predicted by Fickian-type diffusion equations. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

In former work,¹ we applied the dual sorption mechanism to analysis of the time lag diffusion (permeation) under the constraint that the penetrant fraction attributed as the Langmuir component is completely immobilized, but in local equilibrium with the Henry's law dissolution component. We yielded a mathematical description of transient permeation, consisting of a nonlinear partial differential equation. This equation was then solved by a finite-difference technique, for the case of permeation through a film to a gas reservoir of limited volume. Recently, the concentration dependence of apparent diffusion coefficients obtained in permeation rate experiments has been mainly analyzed to yield diffusion coefficients for dual-mode sorption and transport model. Numerical methods were used to examine the dual-mobility systems applied to sorption rate experiments with plane slab absorbers for mobilized Langmuir component systems.^{2,3} But no attempt appears to have been made to predict the numerical solution of the permeation, sorption, and desorption rate curves collectively, incorporating the dual-mode sorption and transport model with an immobilized Langmuir component. The objective of the present study was to provide this information

by comparing these predicted curves with the curves also predicted by the Fickian-type diffusion equations.

MATHEMATICAL MODEL

The equilibrium part of the theory is expressed simply by the following for the isotherm:

$$C = C_D + C_H = k_D p + \frac{C'_H b p}{1 + b p} \\ = C_D \left(1 + \frac{K}{1 + (b/k_D) C_D} \right) \quad (1)$$

where C is the total penetrant concentration, C_D is the concentration due to the Henry's law contribution, C_H is the concentration of penetrant held in microvoid or the Langmuir contribution, p is the upstream pressure, K is composite parameter ($K = C'_H b / k_D$) and k_D , b and C'_H are dual sorption parameters.

According to the model of Paul and Koros,⁴ the total diffusive flux N is given by

$$N = -D_D \frac{\partial C_D}{\partial x} - D_H \frac{\partial C_H}{\partial x} \quad (2)$$

where D_D and D_H are diffusion coefficients for the dissolved and Langmuir modes, respectively. All the

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gas previously associated with D_D as well as a fraction F ($F = D_H/D_D$) of that associated with C_H has a mobility with a diffusion coefficient D while the remaining fraction, $1 - F$, of C_H has zero mobility, so Fick's law must be written as

$$D \frac{\partial^2 C}{\partial x^2} = \frac{\partial C_D}{\partial t} g(C_D) \tag{3}$$

where $G(C_D)$ represents the function

$$g(C_D) = \frac{[1 + FK/(1 + (b/k_D)C_D)^2]}{[1 + K(1 + (b/k_D)C_D)^2]} \tag{4}$$

Concentration distribution of a gas in the membrane was calculated at regular time intervals by the finite-difference technique.⁵

Calculation of Permeation Rate Curve

In applying Eq. (3) to the permeation experiments, the following coordinates were used: the polymer membrane, of thickness l , is assumed to be of infinite extent in the y and z directions. The concentration of gas in the membrane is initially zero. Upstream pressure p is assumed to hold constant, but the downstream pressure p_t increases from the initial value 0 to the final value $p_{t\alpha}$. This is illustrated in Figure 1(a). The boundary and initial conditions on Eq. (3) are as follows:

$$\begin{aligned} t = 0 \quad l > x > 0 \quad C_D &= 0 \\ t > 0 \quad x = 0 \quad C_D &= k_D p \\ t > 0 \quad x = l \quad C_D &= k_D p_t \end{aligned} \tag{5}$$

In this case an additional boundary condition must

be applied. In gas flows through a membrane area A (cm^2) into a volume V (cm^3), the flow of gas is given by

$$V \left(\frac{\partial C_t}{\partial t} \right) = AD \left(\frac{\partial C}{\partial x} \right)_{x=l} \tag{6}$$

The quantity $(\partial C/\partial x)_{x=l}$ is obtained by the finite-difference technique with respect to x and setting $x = l$, where C_t is gas concentration of the downstream volume at time t ; then p_t can be represented as

$$p_t = \frac{RTL}{22,400} \frac{AD}{V} \int_0^t \left(\frac{\partial C}{\partial x} \right)_{x=l} dt \tag{7}$$

It is difficult to solve Eq. (3) analytically since the equation is nonlinear and the surface boundary at $x = l$ condition is transient. Then, a numerical solution using a computer seems to be convenient.

Calculation of Sorption and Desorption Rate Curves

In applying Eq. (3) to the sorption and desorption experiments, the following coordinates were used: The polymer membrane, of thickness $l = 2L$, is assumed to be of infinite extent in the y and z directions. These are illustrated in Figure 1(b) and 1(c). The concentration of gas in the membrane is initially zero for sorption and $k_D p$ for desorption, and the membrane surface is assumed to be always in equilibrium with the surrounding gas. To simplify the numerical solution, the condition of symmetry about $x = 0$ was used, and the solution was obtained for the half-membrane. Boundary conditions on Eq. (3) are then as follows:

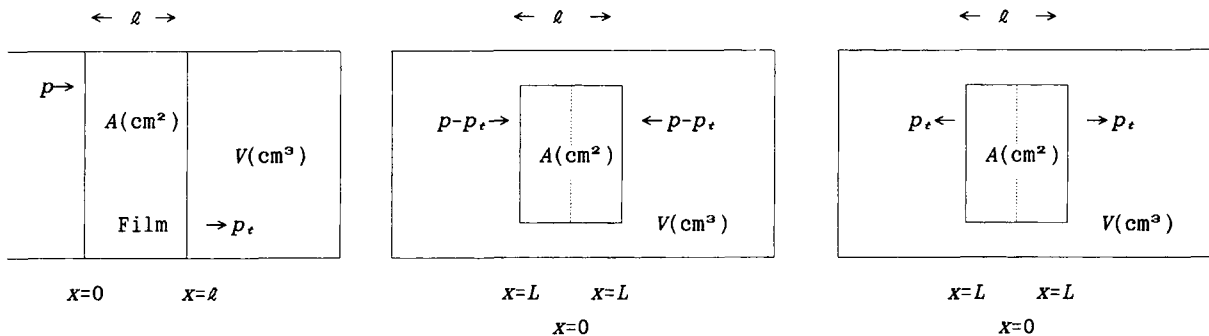


Fig. 1a

Fig. 1b

Fig. 1c

Figure 1 Coordinates for mathematical models: (a) permeation, (b) sorption, and (c) desorption.

For sorption,

$$\begin{aligned} t = 0 & \quad L > x > 0 & \quad C_D = 0 \\ t \geq 0 & \quad x = 0 & \quad \partial C_D / \partial x = 0 \\ t > 0 & \quad x = L & \quad C_D = k_D(p - p_t) \end{aligned} \quad (8)$$

The material balance that gives the values of p_t (pressure change of volume V at time t) is

$$p_t = p - \frac{RTl}{22,400} \frac{A}{V} \int_0^l (C_H + C_D) dx \quad (9)$$

For desorption,

$$\begin{aligned} t = 0 & \quad L > x > 0 & \quad C_D = k_D p \\ t \geq 0 & \quad x = 0 & \quad \partial C_D / \partial x = 0 \\ t > 0 & \quad x = L & \quad C_D = k_D p_t \end{aligned} \quad (10)$$

The material balance that gives the values of p_t (pressure change of volume V at time t) is

$$p_t = \frac{RTl}{22,400} \frac{A}{V} \int_0^l (C_H + C_D) dx \quad (11)$$

For the same reason as permeation, the numerical solutions using a computer seem to be convenient.

RESULTS AND DISCUSSION

The permeation, sorption, and desorption rate curves are calculated by the finite-difference technique using the parameters for CO₂ in a polyimide (PI2080) at 25°C, obtained by Toi et al.⁶ and polycarbonate at 35°C, obtained by Koros et al.;⁷ these

are listed in Table I as original parameters. It is confirmed that plots of the experimental data in both the studies fit well on the dual-mode model lines calculated using each set of the original parameters.

The calculations are carried out at pressures of 10, 25, 40, 60, and 76 cmHg for PI2080/CO₂ system and 10, 76, 380, 760, 1520 cmHg for polycarbonate/CO₂ system, respectively.

Various Fickian Diffusion Curves

The diffusion coefficients determined in the conventional manner were also substituted into the analytical solutions of the purely Fickian diffusion equations for permeation, sorption, and desorption into flat membranes.⁸

For permeation,

$$\begin{aligned} p_t = \frac{RTA}{22,400V} D_a (C_a - C_t) \frac{t}{l} \\ + \frac{2l}{\pi^2} \sum_{n=0}^{\infty} \frac{C_a \cos n\pi - C_t}{n^2} \left[1 - \exp\left(-\frac{D_a n^2 \pi^2 t}{l^2}\right) \right] \end{aligned} \quad (12)$$

where D_a is the apparent diffusion coefficient from the time lag method, C_a is apparent solubility, represented by $C_a = 76(P_a/D_a)p$ (where P_a is apparent permeation coefficient calculated from the slope of permeation curve), and C_t is a value of C_a at time t .

For sorption and desorption,

$$\begin{aligned} p_t = \frac{RTAlC_e}{22,400V} \\ \times \left(1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{\exp[-D_e(2n+1)2\pi^2 t/l^2]}{(2n+1)^2} \right) \end{aligned} \quad (13)$$

Table I Dual-Mode Sorption and Transport Parameters of CO₂ Diffusion in PI2080 Polyimide and Polycarbonate

	b (atm ⁻¹)	C'_H cm ³ (STP) cm ³	k_D cm ³ (STP) cm ³ atm	F —	D cm ² s
PI2080/CO ₂ system					
Original parameters ⁶	5.17	11.56	4.67	0.0174	1.73 × 10 ⁻⁹
①: From Eq. (14)	8.27	2.49	1.39	0.0114	1.78 × 10 ⁻⁹
②: From Eq. (15)	5.03	11.22	2.69	0.0021	1.67 × 10 ⁻⁹
PC/CO ₂ system					
Original parameters ⁷	0.338	15.3	0.938	0.101	4.67 × 10 ⁻⁸
③: From Eq. (14)	0.416	16.68	1.160	0.0886	4.62 × 10 ⁻⁸
④: From Eq. (15)	0.754	13.23	0.574	0.0146	3.74 × 10 ⁻⁸

where D_e is apparent diffusion coefficient calculated from the initial slope of sorption rate curve, C_e is apparent solubility from the equilibrium value of sorption/desorption rate curve. In this case, C_t is calculated from $22,400Vp_t/RTAIC_e$.

Representative permeation rate curves shown in Figure 2 are for the PI2080/CO₂ system at pressure 10 and 76 cmHg in the form of plots of p_t /cmHg versus p /atm. The points are calculated by the finite-difference technique using original parameters in Table I. The solid lines are calculated from Fickian permeation equation, Eq. (12), using apparent diffusion coefficient and solubility calculated from the points curves. As shown clearly, there is fairly good agreement between the points and the lines, except for a portion of non-steady state of the finite-difference curve at higher pressure (76 cmHg).

Figure 3 shows typical sorption and desorption cycles calculated from the dual-mode sorption and transport model as described previously using the above parameters for same polymer-gas system at the same pressures and temperatures. The points are calculated by the finite-difference technique using original parameters in Table I. The solid lines represent the predictions of the Fickian transport model, Eq. (13), with an apparent diffusion coefficient and solubility calculated from the points curves, respectively. As seen in this figure, the sorption curves lie above the corresponding desorption curves, indicating that the diffusion coefficient increase with increasing concentration. The Fickian model provides a fairly good description of initial portions of both the sorption and desorption curves.

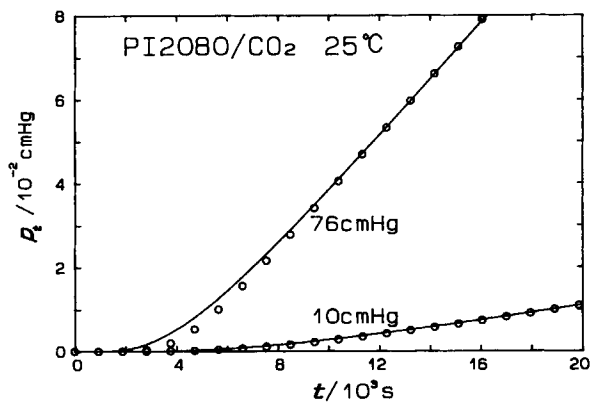


Figure 2 Permeation curves for CO₂ in PI2080 at 25°C, and 10 and 76 cmHg pressures. The points are calculated by the finite-difference technique using original parameters in Table I. The solid lines are calculated from Eq. (12) using apparent diffusion and solubility coefficients calculated from the points curves.

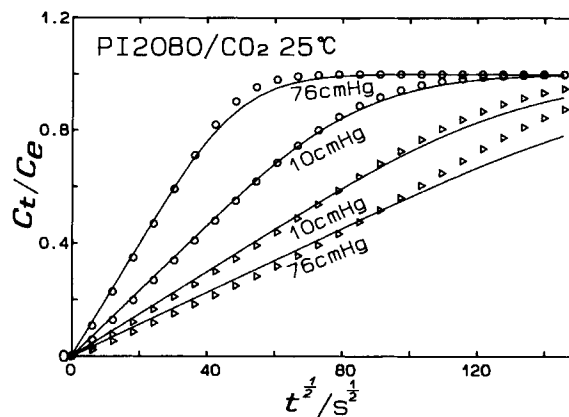


Figure 3 Sorption curves for CO₂ in PI2080 at 25°C, and 10 and 76 cmHg pressure. The points are calculated by the finite-difference technique using original parameters in Table I. The solid lines are calculated from Eq. (13) using apparent diffusion and solubility coefficients calculated from the points curves.

The deviations from the predictions of the model at longer times for the desorption cycles are presumably a consequence of the substantial concentration dependence of diffusion coefficient.⁴ In the same manner the sorption curve of higher pressure (76 cmHg) deviates at a portion before attainment of the sorption equilibrium.

These appearances are also found for PC/CO₂ systems as shown in Figures 4 and 5. A slight sigmoidal deviation from Fickian model lines was apparent in the desorption cycles. But in the permeation curves and sorption cycles, each run is almost entirely by pure Fickian diffusion. The results for both the systems implied that the sorption and permeation curves calculated using some combination of dual-mode parameters sometime show deviation

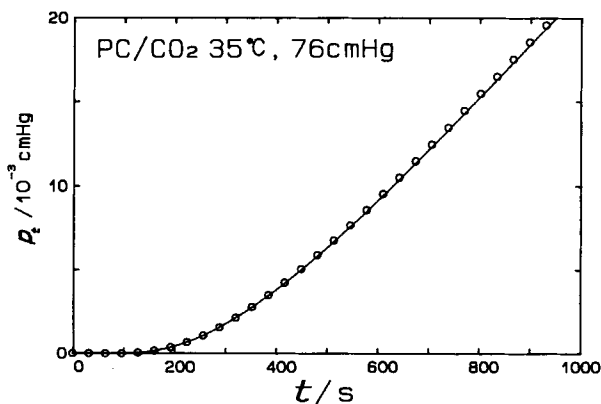


Figure 4 Permeation curves for CO₂ in PC at 25°C and 1 atm pressure. Symbols as in Fig. 2.

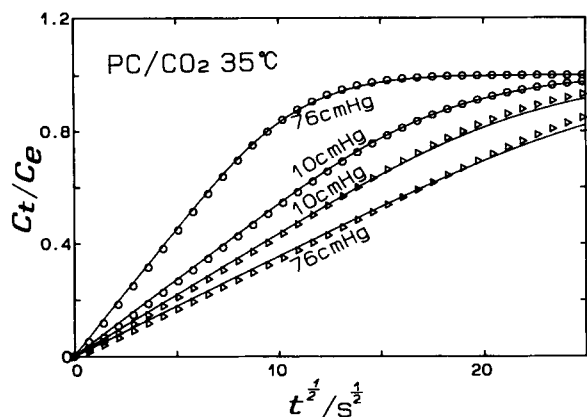


Figure 5 Sorption curves for CO₂ in PC at 25°C and 1 atm pressure. Symbols as in Fig. 3.

from the Fickian curve. But in the desorption cycle, a sigmoidal deviation from the Fickian curve is always apparent.

These methods are interested in studying the distinction between the pure dual-mode sorption-transport model curve and the actual sorption and permeation experiment curve that seems to contain the various unsolved appearances for diffusion and sorption of gases in glassy polymer.^{9,10} It becomes obvious that the deviations from the Fickian model in an experimental transport or sorption-desorption curve for a gas in a glassy polymer are not necessarily consistent with the onset of concomitant diffusion and relaxation,¹¹ but just owing the dual-mode model. That is to say, only the combinations of parameters of the dual mode model make the curve to be either fit with or deviation from the Fickian model curve.

Integral Diffusion Coefficients

For sorption-desorption rate curves, a good estimation of integral diffusion coefficients can be obtained by taking the average of the diffusion coefficients calculated from first slope for the integral sorption (\bar{D}_s) and desorption (\bar{D}_d) cycle,⁸

$$\bar{D}_{av} = (\bar{D}_s + \bar{D}_d)/2$$

On the other hand, the apparent diffusion coefficient D_a is calculated from the time lag method of permeation rate curve.

$$D_a = l^2/6\theta$$

Both the diffusion coefficients should be coincident

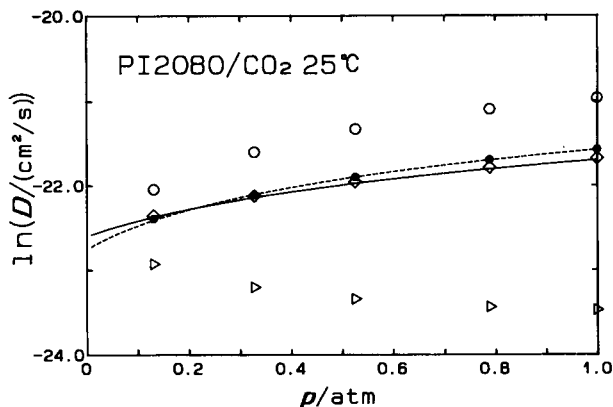


Figure 6 Pressure dependence of diffusion coefficients calculated from permeation (\diamond), sorption (\circ), and desorption (\triangle) rate curves for CO₂ in PI2080. \bullet is average value of diffusion coefficients from sorption and desorption rate curves at same pressure. The solid line is calculated from Eq. (14) using parameters ① in Table I. The dotted line is calculated from Eq. (15) using parameters ② in Table I.

at the same pressure and temperature. Strictly speaking, this comparison seems to be inapplicable to the PI2080/CO₂ system because the curves do not follow Fickian type, but applicable to the PC/CO₂ system.

Figure 6 shows the pressure dependence of diffusion coefficients calculated from permeation, sorption, and desorption rate curves for CO₂ in PI2080. The average values of diffusion coefficients from sorption and desorption rate curves \bar{D}_{av} are in fair agreement with that from permeation rate curve

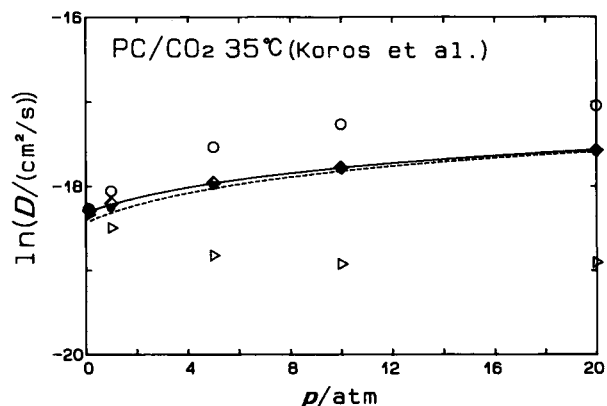


Figure 7 Pressure dependence of various diffusion coefficients for CO₂ in PC. The solid line is calculated from Eq. (14) using parameters ③ in Table I. The dotted line is calculated from Eq. (15) using parameters ④ in Table I. Other symbols as in Fig. 6.

D_a . The solid line in Figure 6 was computed from Eq. (14)

$$D_a = \frac{D[1 + FK/(1 + bp)]}{[1 + Kf(K, F, bp)]} \quad (14)$$

by using parameters ① in Table I. These parameters were generated by fitting the above relation to the D_a values by the "simplex" method and by nonlinear regression.^{4,11} The dotted line was also computed from Eq. (15)¹⁰

$$\bar{D}_{av} = \frac{D[1 + FK/(1 + bp)]}{[1 + K/(1 + bp)]} \quad (15)$$

by using parameters ② in Table I, which were generated in a similar manner as above.

As can be seen from Table I, there are poor agreements between the original parameters and the parameters determined from analysis of kinetic data for both the systems. The degree of the convergence depends on the method of calculation. More efforts and it would be made to improve the agreement. However, the agreements between the curves of the two diffusion coefficients are almost good as shown in Figures 6 and 7. For the PC/CO₂ system that is according to the Fickian-type curve, the agreement between D_a and D_{av} is somewhat better than for the PI2080/CO₂ system.

CONCLUSIONS

Numerical solutions were applied to the dual-mode sorption and transport model for gas permeation, sorption, and desorption rate curves allowing for mobility of the Langmuir component. These rate curves were almost consistent with the curves pre-

dicted by Fickian-type diffusion equation, except the desorption curve in which a slight sigmoidal deviation from the Fickian model line was apparent. The sorption and permeation curves calculated using some combination of dual-mode parameters sometime show deviation from the Fickian curve. Satisfactory agreements are also obtained between integral diffusion coefficient from sorption and desorption rate curves and apparent diffusion coefficient from permeation rate curves.

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