

Numerical Solution of the Time-lag Diffusion Incorporating the Dual Sorption Model

INTRODUCTION

Vieth and Sladek applied the dual sorption mechanism to analysis of the rate of gas sorption by assuming that the gas which exhibits normal solubility contributes to diffusion, whereas the gas trapped in microvoid does not diffuse.¹ These assumptions yielded a mathematical description of transient sorption, consisting of a nonlinear partial differential equation. This equation was then solved by a finite-difference technique, for the case of diffusion into a film from a gas reservoir of limited extent.

In this work, the same assumption was applied to analysis of the time-lag diffusion (permeation) and 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.

The solution was subsequently used in the analysis of experimental pressure increase data. The results showed how dual mode sorption mechanism indeed applies to the time-lag diffusion.

MATHEMATICAL MODEL

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

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

where C = solubility, p = pressure, and k_D , b , and C'_H are parameters. The first term C_D represents sorption of normally diffusible species while the second term C_H represents sorption in microvoids or cavities. The dissolved gas is free to diffuse, whereas the gas contained in the microvoid is apparently immobilized, so Fick's first law must be written as

$$J = -D \left(\frac{\partial C_D}{\partial x} \right) \quad (2)$$

At the same time the unsteady state transport equation for the gas is

$$\frac{\partial C}{\partial t} = \frac{\partial(C_D + C_H)}{\partial t} = \frac{-\partial J}{\partial x} \quad (3)$$

where J refers to the flux of dissolved gas.

It is assumed that adsorption occurs very rapidly and there is always local equilibrium between C_H and C_D . Using the isotherm to eliminate C_H yields the final equation

$$D \frac{\partial^2 C_D}{\partial x^2} = \frac{\partial C_D}{\partial t} \left[1 + \frac{C'_H (b/k_D)}{(1 + (b/k_D) C_D)^2} \right] \quad (4)$$

In applying this equation to the permeation experiments, the following coordinates were used: the polymer film, of thickness l , is assumed to be of infinite extent in the y - and z -directions. The concentration of gas in the film is initially zero. Upstream pressure p is assumed to hold constant, but the downstream pressure p_t increases from the initial value $p_0 = 0$, to the final value p_f .

The boundary conditions on eq. (4) are as follows:

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

In this case, an additional boundary condition must be applied. In gas flows through a film of area A (cm²) into a volume V (cm³), the flow of gas is given by

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

The quantity $(\partial C/\partial x)_{x=l}$ is obtained by differentiating 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

$$p_t = \frac{RT}{22,400} \frac{AD}{V} \left(\frac{\partial C}{\partial x} \right)_{x=l} dt \quad (7)$$

It is very difficult to solve eq. (4) analytically since the equation is nonlinear and the surface boundary at $x = l$ condition is transient. Then, a numerical solution using computer seems to be convenient.

The equation suggested by Douglas² had been applied to gas sorption in a glassy film by Vieth and Sladek¹; it was used to approximate the differential equation of the time-lag diffusion:

$$\frac{\partial C_D}{\partial x^2} = \frac{\partial C_D}{\partial t} g(C_D) \quad (8)$$

where $g(C_D)$ represents the function

$$g = 1 + \frac{C'_H b/k_D}{[1 + (b/k_D)C_D]^2} \quad (9)$$

A forward-differential equation was used to proceed from values of $C_{j,n}$ to values at the next time step $C_{j,n+1}$,

$$\Delta x^2 C_{j,n} = g(C_{j,n})(C_{j,n+1} - C_{j,n})/\Delta\theta \quad (10)$$

where $\Delta X = X/j$ (real distance $x = j\Delta X$), $\Delta\theta = r/j^2$ (real time $t = n\Delta\theta l^2/D$), and r is a parameter concerning the time step.

Equation (10) together with the boundary conditions discussed above was programmed for solution by BASIC language on a 8-bit microcomputer (pc-8001; NEC). The digital p_t values at finite times were stored in a disk file for later analysis or plotting by an xy-plotter to examine them in order to inspect their integrity of parameters. Although not as fast as comparable assembler programs would be, this system allows for easy modifications.

RESULTS AND DISCUSSION

The calculated permeation curve was drawn in Figure 1 using an xy-plotter along with the experimental data points which were obtained by PVAc-CO₂ system at 40°C. Above T_g , diffusion

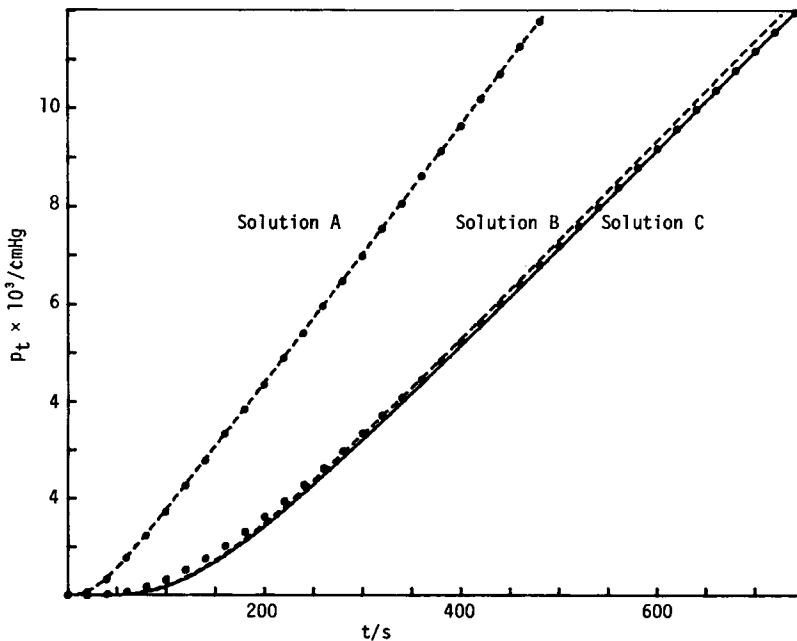


Fig. 1. Permeation curves for CO₂ in PVAc. The points are experimental data at 40°C (upper) and 22°C (lower). Three curves correspond to each solution of Table I.

TABLE I
Sets of Sorption Parameters and Diffusion Coefficient for Dual Sorption Diffusion Eq. (4)^a

Solution	Temp (°C)	p (atm)	b	C'_H	k_D	$D \times 10^{-9}$
A	40	0.511	0.0	0.0	2.58	7.386
B	22	0.980	0.525	6.45	0.889	8.494
C	22	0.980	2.65	0.778	2.60	2.945

^a Each solution was generated using the following numerical values: $j = 30$, $r = 0.4$, $A = 4.499$, $l = 1.35 \times 10^{-3}$, and $V = 110.5$.

is controlled only by dissolution; then b and C'_H are regarded as zero. Excellent agreement between the calculated curve and the experimental points provide strong support for the validity of this simulation method. Increasing repeat times of computation yield more accurate values. But the accuracy of the present method is equivalent to the experimental error allowed for the actual pressure-time curve.

Figure 1 also illustrates two calculated results together with actual data points for typical CO₂ permeation curves of PVAc at 22°C. For the PVAc below T_g (31°C), the apparent permeability coefficient P_a was regarded as independent of pressure below 1 atm as shown in Figure 2, so pressure dependence of the apparent diffusion coefficient D_a lends support to the total immobilization of the Langmuir component.³ Each solution corresponds to a given set of values for the dual sorption parameters and the diffusion coefficient, C'_H , b , k_D , and D . The values selected are in the range expected for CO₂ permeation in this polymer.⁴ Unlike above T_g , there are some differences between

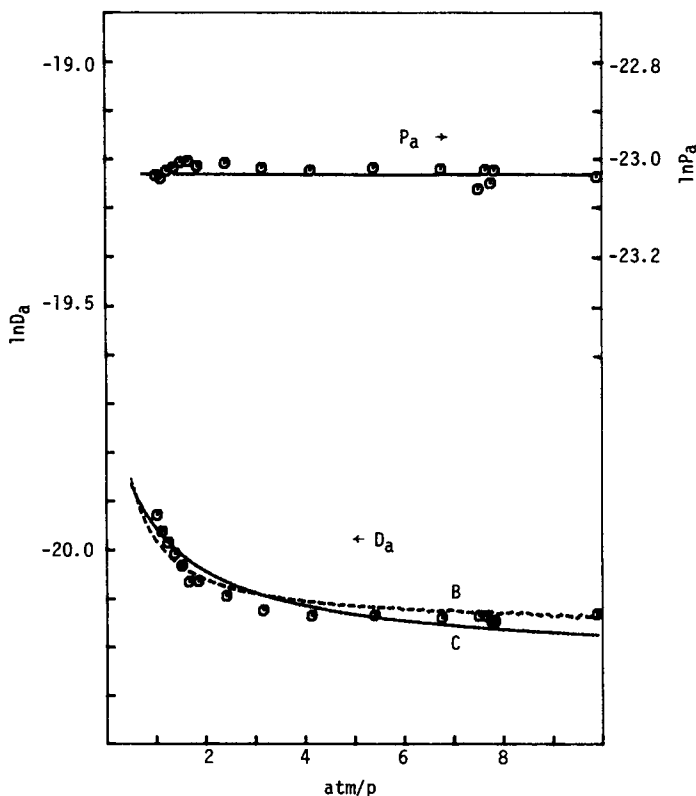


Fig. 2. Pressure dependence of diffusion coefficients and permeability coefficients (upper) for CO₂ in PVAc at 22°C. The points are observed values. The curves are calculated by total immobilization equation using the same parameters in Table I: (---) Solution B; (—) Solution C.

the calculated curves and experimental points at this temperature, especially in transient region, as shown in Figure 1.

The parameter sets examined correspond to the pressure dependence of apparent diffusion coefficients depicted in Figure 2 with experimental points for well annealed samples at this temperature. The fact that the calculated curves and the experimental plots are not quantitatively consistent with each other demonstrated that more exact and reliable parameters must be determined by the optimization process. If the concept of the total immobilization model alone cannot satisfactorily represent the experimental results, then it is necessary to compensate the effect of dual sorption in order to investigate another effect.

CONCLUSION

In summary, a convenient technique has been developed for the estimation of gas permeation in a polymer film obeying a nonlinear isotherm. The present study will establish a new experimental tool which can be used to examine how dual sorption mode mechanism applies to the time-lag diffusion and, moreover, to reveal the detailed mechanism of diffusion in glassy polymers.

The authors would be willing to supply copies of their computer program in BASIC language for those who wish to have a copy.

APPENDIX: NOMENCLATURE

A	film area (cm ²)
b	hole affinity constant [atm ⁻¹ (101,325 Pa) ⁻¹]
C	concentration [cm ³ (STP)/cm ³ (polymer) (44.613 mol/m ³)]
C'_H	hole saturation constant [cm ³ (STP)/cm ³ (polymer) (44.613 mol/m ³)]
D	diffusion coefficient for Henry's law species (cm ² /s)
D_a	apparent diffusion coefficient (cm ² /s)
j	distance step number
k_D	Henry's law constant [cm ³ (STP)/cm ³ (polymer)·atm (4.403 × 10 ⁻⁴ mol/m ³ ·Pa)]
l	film thickness (cm)
n	time step number
p	upstream pressure [atm (101,325 Pa)]
p_t	downstream pressure [cm Hg (1333.224 Pa)]
P_a	apparent permeability coefficient {cm ³ (STP)·cm/cm ³ ·s·cm Hg [(3.34625 × 10 ⁻⁶ mol)/m·s·Pa]}
r	parameter concerning time step
t	time (s)
V	downstream cell volume (cm ³)
x	real distance (cm)
δx	distance step (cm)
$\Delta\theta$	time step

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