# Transient Sorption by Two-Component Laminate Slabs in a Finite Bath

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## Synopsis

Diffusion equations are presented describing the transient sorption of diffusant from a finite constant volume bath through plane-sheet symmetric ternary-laminate membranes and their equivalent binary-laminate coatings attached to an impermeable substrate. The equations are used to analyze the sorption-desorption results obtained for propane diffusant in symmetric ternary-laminate membranes prepared from two block copolymer membranes of bisphenol-*A* carbonate and dimethyl siloxane. The sorption properties of two-component laminates are discussed and compared with properties of homogeneous membranes.

## INTRODUCTION

Membranes and coatings often occur as laminates. Some are prepared as such to obtain desired properties and others, initially homogeneous, are effectively laminated by surface reactions.[1-3]

Sorption equations have been obtained for two-component slabs, spheres and cylinders with a constant concentration of diffusant at the outer surface.[4,5] A finite difference procedure has been used to evaluate the transient-sorption behavior of a binary-laminate cylinder in a finite bath.[6] Kubin and Spacek[7] provided equations for the transient permeation across symmetric *ABA* membranes in contact with one or two finite baths. The diffusion equations were derived using the simplification of a constant diffusant concentration gradient in the outer laminae. The same simplifying procedure has been applied for plane sheets and cylinders in infinite or semi-infinite media.[5,8]

This paper presents diffusion equations for analysis of sorption-desorption by plane-sheet *ABA*-laminate membranes with constant diffusion coefficients in a finite, constant-volume bath, and reports their application in an experimental measurement.

## DIFFUSION EQUATIONS

Consider a plane-sheet binary-laminate coating of cross section $F$, with lamina $A$ of thickness $a$ in contact with a well-stirred bath of volume $V$, and lamina $B$ of thickness $b$. This system is designated $(AB/$, where the parenthesis represents the finite volume and the solidus denotes the impermeable substrate. It is equivalent to a symmetric $ABA$ ternary-laminate free membrane with lamina thicknesses $a$ and $2b$, respectively, designated $(ABA)$. The concentrations at $t = 0$ are uniform in each phase; $c^0$ in the bath, and $C_A^i$ and $C_B^i$ in the respective

membrane laminae. Equilibrium is maintained at the phase interfaces $x = 0$ and $x = -a$ and the constant partition coefficients defined for the system are: $K_A = C_A/c$, $K_B = C_B/c$, and $K = C_A/C_B = K_A/K_B$. The diffusion constants in the laminae are $D_A$ and $D_B$, respectively.

The differential equations and boundary conditions are for $C_A(x,t)$,

$$\frac{\partial^2 C_A}{\partial x^2} = \frac{1}{D_A} \frac{\partial C_A}{\partial t}, \qquad -a < x < 0 \tag{1}$$

$$C_A(-a,0) = C_A^0; \qquad C_A(x,0) = C_A^i, \qquad -a < x \le 0 \tag{2}$$

$$\frac{\partial C_A}{\partial x} = \frac{1}{D_A h_A} \frac{\partial C_A}{\partial t}, \qquad x = -a, \qquad t \ge 0 \tag{3}$$

for $C_B(x,t)$

$$\frac{\partial^2 C_B}{\partial x^2} = \frac{1}{D_B} \frac{\partial C_B}{\partial t}, \qquad 0 < x < b \tag{4}$$

$$C_B(x,0) = C_B^i, \qquad 0 \le x < b \tag{5}$$

$$\frac{\partial C_B}{\partial x} = 0, \qquad x = b, \qquad t \ge 0 \tag{6}$$

and

$$K = \frac{K_A}{K_B} = \frac{C_A}{C_B}; \qquad D_A \frac{\partial C_A}{\partial x} = D_B \frac{\partial C_B}{\partial x}, \qquad x = 0, \qquad t \ge 0 \tag{7}$$

where $h_A = K_A F/V$, $K_A = C_A/c$, $K_B = C_B/c$, and $c$ is the diffusant concentration in $V$.

Using the Laplace transform method,[5] the solution for the concentration of diffusant in each lamina can be expressed as

$$C_A(x,t) = C_A^i + \frac{(C_A^0 - C_A^i)}{1 + H_B + \lambda K H_B}$$

$$+ (C_A^0 - C_A^i) \sum_{n=1}^{\infty} A_{A,n}(x) \exp\left(\frac{-D_B R_n^2 t}{b^2}\right), \qquad -a < x < 0 \tag{8}$$

where

$$A_{A,n}(x) = \frac{2[\sin R_n \sin(\lambda R_n x/\delta) + \delta K \cos R_n \cos(\lambda R_n x/\delta)]}{L_n} \tag{9}$$

with

$$L_n = \delta \left\{ \left[ K(1 + H_B + \lambda K H_B) \cos\left(\frac{\lambda R_n}{\delta}\right) \right. \right.$$

$$- \left(\frac{R_n}{\delta}\right)(1 + \lambda K) \sin\left(\frac{\lambda R_n}{\delta}\right) \right] \cos R_n - \left[ R_n \left(K + \frac{\lambda}{\delta^2}\right) \cos\left(\frac{\lambda R_n}{\delta}\right) \right.$$

$$\left. \left. + \left(\delta K^2 H_B + \frac{\lambda K H_B}{\delta} + \frac{1}{\delta}\right) \sin\left(\frac{\lambda R_n}{\delta}\right) \right] \sin R_n \right\}$$

where $R_n$ are the nonzero positive roots of

$$\delta K = -\left(\frac{K H_B - (R/\delta)\tan(\lambda R/\delta)}{K H_B \tan(\lambda R/\delta) + (R/\delta)}\right) \tan R \tag{10}$$

and

$$\delta = (D_A/D_B)^{1/2}, \qquad \lambda = a/b = V_A/V_B, \qquad H_A = h_A a = K_A V_A/V = \lambda K H_B,$$
$$H_B = K_B V_B/V$$

Also,

$$C_B = (x,t) = C_B^i + \frac{C_B^0 - C_B^i}{1 + H_B + \lambda K H_B} + (C_B^0 - C_B^i)$$
$$\times \sum_{n=1}^{\infty} A_{B,n}(x) \exp\left(\frac{-D_B R_n^2 t}{b^2}\right), \qquad 0 < x < b \quad (11)$$

where

$$A_{B,n}(x) = \frac{2\delta K \cos[R_n(1 - x/b)]}{L_n} \tag{12}$$

Evaluation of $C_A(-a,t)$, eq. (8), using $K_A = C_A/c$, and rearrangement of the resulting equation directly yields an equation for a reduced change of the diffusant concentration in $V$,

$$F(t) \equiv \frac{c - c^f}{c^0 - c^i} = \sum_{n=1}^{\infty} Z_n \exp\left(\frac{-D_B R_n^2 t}{b^2}\right) \tag{13}$$

where

$$Z_n = \frac{2[-\sin R_n \sin(\lambda R_n/\delta) + \delta K \cos R_n \cos(\lambda R_n/\delta)]}{L_n} \tag{14}$$

$c^f$ is the final equilibrium concentration in $V$ and $c^i$ is the concentration in $V$ in equilibrium with the coating before initiating the sorption by changing the concentration to $c^0$.

Using the relationship

$$1 + H_B + \lambda K H_B = (c^0 - c^i)/(c^f - c^i) \tag{15}$$

other reduced concentration equations are derived: an equation avoiding the necessity of evaluating $c^0$;

$$G(t) = \frac{c - c^f}{c^f - c^i} = \sum_{n=1}^{\infty} Y_n \exp\left(\frac{-D_B R_n^2 t}{b^2}\right) \tag{16}$$

where

$$Y_n = (1 + H_B + \lambda K H_B) Z_n \tag{17}$$

and the fractional change of the diffusant concentration remaining in $V$,

$$M(t) \equiv \frac{c - c^f}{c^0 - c^f} = \sum_{n=1}^{\infty} X_n \exp\left(\frac{-D_B R_n^2 t}{b^2}\right) \tag{18}$$

where

$$X_n = (1 + H_B + \lambda K H_B) Z_n/(H_B + \lambda K H_B) \tag{19}$$

As $t$ becomes large the higher-order terms, $n \geq 2$, in the reduced concentration equations do not contribute significantly and the dependence of the reduced concentration on $t$ becomes simple exponential, e.g., at large $t$, eq. (18) reduces to

$$M(t) = X_1 \exp(-D_B R_1^2 t/b^2)$$

or

$$\ln M(t) = \ln X_1 - D_B R_1^2 t/b^2 \tag{20}$$

Equations (13) and (16) behave similarly. A time lag characterizing the establishment of the region of simple-exponential decay can be defined. Equation (20) is rewritten

$$\ln M(t) = \ln X_1 - (D_B R_1^2/b^2)(t - \theta) \tag{21}$$

where $\theta$, the time lag, is defined by

$$\theta = b^2 \ln (X_1)/D_B R_1^2 \tag{22}$$

Time lags can also be defined in a similar manner in terms of eqs. (13) and (16).

## COMPARISON OF A LAMINATE COATING (AB/ WITH A HOMOGENEOUS COATING (B/

Applications of the diffusion equation for a homogeneous coating of thickness $b$, (B/, designated System I, have been reported.[9,10] The diffusion equation corresponding to eq. (16) is[10]

$$G(t)^I = \frac{c - c^f}{c^f - c^i} = \sum_{n=1}^{\infty} Y_n^I \exp \left( \frac{-D_B Q_n^2 t}{(b^I)^2} \right) \tag{23}$$

where

$$Y_n^I = \frac{4Q_n \cos^2 Q_n - 2 \sin 2Q_n}{2Q_n - \sin 2Q_n} \tag{24}$$

where $Q_n$ are the nonzero positive roots of

$$H_B^I = -Q/\tan Q \tag{25}$$

with

$$H_B^I = K_B V_B^I/V^I = [(c^0 - c^f)/(c^f - c^i)]^I \tag{26}$$

The simple-exponential limiting equation is

$$\ln G(t)^I = \ln Y_1^I - D_B Q_1^2 t/(b^I)^2 \tag{27}$$

System II, the binary-laminate coating (AB/, is described, e.g., by eq. (16), where, by rearrangement of eq. (10),

$$H_B^{II} = \frac{-R}{\tan R} \left( \frac{1 - (1/\delta K)\tan(\lambda R/\delta)\tan R}{1 + \delta K \tan(\lambda R/\delta)/\tan R} \right) \tag{28}$$

with

$$H_B^{II} = K_B V_B^{II}/V^{II} \tag{29}$$

Assignment of $\lambda = 0$, $K = 1$, and $\delta = 1$ reduces the equations for system II to those for system I, e.g., eq. (10) becomes eq. (25), and eq. (17) becomes eq. (24).

Two comparisons between systems I and II are readily accomplished: the slopes $S$ of $\ln G(t)$ vs $t$ in the simple-exponential region, and the values of $Y_1$. The ratios of these values for systems I and II are, by eqs. (16) and (27),

$$(S_1^{II}/S_1^I) = (R_1/b^{II})^2(b^I/Q_1)^2 \tag{30}$$

and by eqs. (17) and (24),

$$(Y_1^{II}/Y_1^{I}) = \{2(1 + H_B^{II} + \lambda K H_B^{II})[-\sin R_1 \sin(\lambda R_1/\delta) + \delta K \cos R_1 \cos(\lambda R_1/\delta)]$$
$$\times [2Q_1 - \sin 2Q_1]\}/\{L_n[4Q_1 \cos^2 Q_1 - 2 \sin 2Q_1]\} \quad (31)$$

Table I presents the effects of $\delta$, $K$, and $H_B^{II}$ on the slope $S_1^{II}$ and intercept $\ln X_1^{II}$ for laminates with $\lambda = 1$. Increases in $\delta$ and $H_B^{II}$ increase the slope and intercept. An increase in $K$ increases the slope, but the dependence of the intercept is more complex.

## EXPERIMENTAL

### Materials

Homogeneous and laminate membranes were prepared using two alternating random-block copolymers of dimethylsiloxane (DMS) and bisphenol-*A* carbonate (BPAC), generously supplied by the General Electric Research and Development Center, Schenectady, N.Y. The copolymer designated *A*, was 65% by weight DMS with average block lengths DMS/BPAC = 20/3.5. Copolymer *B* was 50% by weight DMS with average block lengths DMS/BPAC = 20/6. The preparation[11] and physical properties[12-14] of the copolymer have been reported. The membranes were cast on mercury from 10% methylene chloride solutions. After slow evaporation of the solvent to form the membranes, they were placed in a vacuum at 120°–125°C for at least 24 hr. The laminate was prepared from the two membranes by applying methylene chloride at the interfaces and holding the laminate in a clamp overnight. A firm clear seal was formed between the laminae.

The propane diffusant was Matheson, instrument purity, 99.5% minimum. It was further purified by freeze-thaw bulb-to-bulb distillation in the vacuum system.

### Apparatus and Procedure

A simple constant-volume sorption cell was attached to a conventional vacuum system. The pressure was measured with a pressure transducer (Bell and Howell, type 4-326, 0–15 psia) and the temperature of the cell and transducer

TABLE I
Effects of $\delta$, $K$, and $H_B^{II}$ on $\ln X_1^{II}$ and $S_1^{II}$

| $\delta$ | $K$ | $\lambda$ | $H_B^{II}$ | $S_1^{II} b^2/D_B$ | $X_1^{II}$ | $\ln X_1^{II}$ |
|---|---|---|---|---|---|---|
| 0.5 | 1.0 | 1.0 | 0.5 | −0.306 | 0.9589 | −0.0420 |
| 1.0 | 1.0 | 1.0 | 0.5 | −1.03 | 0.8620 | −0.1485 |
| 2.0 | 1.0 | 1.0 | 0.5 | −2.23 | 0.5650 | −0.5709 |
| 1.0 | 0.5 | 1.0 | 0.5 | −0.607 | 0.7995 | −0.2238 |
| 1.0 | 1.0 | 1.0 | 0.5 | −1.03 | 0.8620 | −0.1485 |
| 1.0 | 2.0 | 1.0 | 0.5 | −1.57 | 0.7465 | −0.2923 |
| 0.5 | 1.0 | 1.0 | 0.5 | −0.306 | 0.9584 | −0.0420 |
| 0.5 | 1.0 | 1.0 | 1.0 | −0.401 | 0.6156 | −0.4852 |
| 0.5 | 1.0 | 1.0 | 2.0 | −0.529 | 0.3675 | −1.0011 |

maintained at $\pm0.2°C$ in an air thermostat. Pressure readings were taken using a potentiometer and/or calibrated recorders, and were accurate to $\pm0.2$ Torr. The thickness of the membranes was measured with a micrometer caliper, and a microscope in the laminate case.

The ternary-laminate $ABA$ membrane was placed in the cell ($V \cong 12$ cm$^3$) and evacuated. Propane was then introduced by a rapid rotation of the stopcock separating the cell from the closed system containing propane and the pressure recorded until equilibrium was reached. The desorption run was initiated by a rapid rotation of the cell stopcock with the vacuum system evacuated. Again, the pressure was recorded until equilibrium was established. All experiments were carried out at $59.8°C$.

## Results and Discussion

A typical result of a sorption experiment is presented in Figure 1 in the form of a graph of $\ln G(t)$ vs $t$. The simple-exponential region is extensive enough to determine the intercept $\ln Y_1$ and the limiting slope $S_1$.

Experiments were carried out to examine the utility of the equations in describing transient sorption in the laminate $(ABA)$. Sorption-desorption experiments were first completed using the membranes $(A/$ and $(B/$. Then, the symmetric laminate $(ABA)$ was used. The results are provided in Table II. The results are the average values of two sorption and two desorption experiments for each membrane. Using the appropriate equations, the simple exponential intercept $\ln Y_1^{II}$ and the limiting slope $S_1^{II}$ were calculated from the results for the single-lamina membranes, with geometric considerations, and compared with the experimental results using the laminate. No correction for diffusion through the edges of the membranes was applied.

Specifically, the values of $\delta$, $K$, and $H_B^I$ were calculated from the experiments with $(A/$ and $(B/$. $H_B^{II}$ was calculated from $H_B^I$ by

$$H_B^{II} = H_B^I(V_B^{II}/V^{II})(V^1/V_B^I)  \tag{32}$$

where $V_B^{II}$ is the volume of lamina $B$ in system II. $R_1$ was then determined using eq. (28), $S_1^{II}$ by eq. (30), and $\ln Y_1^{II}$ by eq. (17).
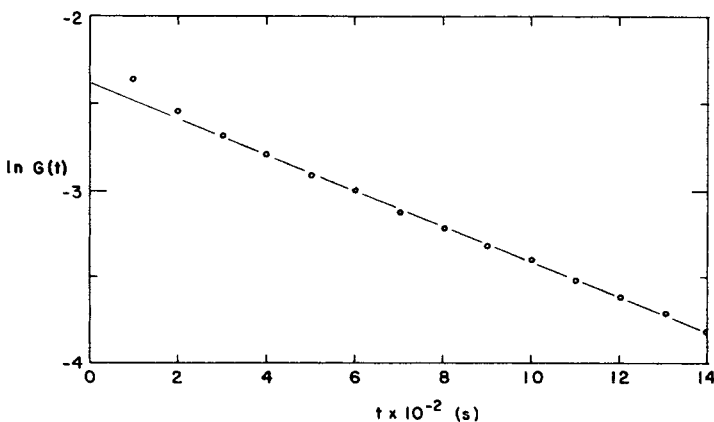


Fig. 1. $\ln G(t)$ vs $t$ for sorption of propane by an $ABA$ membrane: points are experimental, line represents simple-exponential behavior and extrapolates to $\ln Y_1$ at $t = 0$.

TABLE II
Properties of Membranes:  $A$, $B$, and $ABA$

| Membrane: Property | $A$ | $B$ | $ABA$ |
|---|---|---|---|
| 1) Experimental results | | | |
| Area $(F)$, cm$^2$ | 3.81 | 5.14 | 1.94 |
| Thickness/2, cm | (a) 0.066 | (b) 0.022 | (2a) 0.085 |
| | | | (b) 0.022 |
| $V$ membrane, cm$^3$ | 0.503 | 0.277 | 0.414 |
| $H^{\mathrm{I}}$ | 0.167 | 0.0631 | |
| $S_1$, sec$^{-1}$ | $-2.21 \times 10^{-3}$ | $-1.57 \times 10^{-2}$ | $-1.00\ 10^{-3}$ |
| $\ln Y_1$ | $-2.09$ | $-2.97$ | $-2.35$ |
| $D$, cm$^2$ sec$^{-1}$ | $3.47 \times 10^{-6}$ | $2.95 \times 10^{-6}$ | |
| $Q_1$ | 1.665 | 1.611 | |
| 2) Results calculated from experiments with $A$ and $B$ | | | |
| $\delta$ | | | 1.08 |
| $K$ | | | 1.21 |
| $\lambda$ | | | 3.83 |
| $H_B^{\mathrm{II}}$ | | | 0.0238 |
| $R_1$ | | | 0.3808 |
| $\ln Y_1^{\mathrm{II}}$ | | | $-2.22$ |
| $S_1^{\mathrm{II}}$ | | | $-0.88 \times 10^{-3}$ |

The agreement between the calculated and experimental values of $S_1^{\mathrm{II}}$ and $Y_1^{\mathrm{II}}$ is within 12%.

The simple-exponential limiting equations for the reduced concentrations provide a rather simple means for evaluating sorption-desorption properties of binary-laminate coatings in terms of the properties of each lamina.   Applications may occur in the determination of the sorption-desorption properties of a layer that developes on a homogeneous coating or membrane and in the characterization of diffusion-controlled solute-release systems that utilize laminates.

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