Transient Sorption by Two-Component Laminate Slabs in a Semiinfinite Bath

INTRODUCTION

Equations describing transient diffusion of permeate across a binary laminate slab separating finite and semiinfinite baths and the transient sorption by a two-component laminate slab in a finite bath have been reported.[1-3] Equations have also been reported describing transient sorption in two-component laminate slabs with constant surface concentrations under certain restricted initial conditions, e.g., a semiinfinite lamina, and finite laminae with an infinite diffusion coefficient in the inner lamina or with a constant concentration gradient in the outer lamina.[4,5] In this paper sorption equations for four systems with potential for modeling membrane applications and describing experiments used for evaluating membranes are presented and their characteristics discussed. Simple equations obtained at large t are used to compare transient sorption behavior in this extensive time interval occurring in laminates having laminae with different diffusion and distribution coefficients.

PROCEDURE, EQUATIONS, AND SYSTEMS

The systems are plane-sheet membranes composed of two laminae, lamina A of thickness a and lamina B of thickness b, with lamina B attached to an impermeable substrate. The permeate concentration in the semiinfinite bath is c^0, a constant. The concentrations in each lamina prior to exposure to c^0 are uniform; C_A^i in lamina A and C_B^i in lamina B. Equilibrium is maintained at the phase interfaces unless otherwise specified; $K_A = C_A/c$ at $x = -a$ and $K = C_A/C_B$ at $x = 0$. The diffusion coefficients in the laminae, D_A and D_B, are constant.

Differential equations describing the transport are

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

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

Application of the Laplace transform method[6] provides solutions for the systems N = I, II, III, IV:

$$C_A^N(x,t) = C_A^0 + (C_A^i - C_A^0)\sum_{n=1}^{\infty} A_n^N(x)\exp[-D_B(R_n^N)^2(t/b^2)] \tag{2}$$

$$C_B^N(x,t) = C_B^0 + (C_B^i - C_B^0)\sum_{n=1}^{\infty} B_n^N(x)\exp[-D_B(R_n^N)^2(t/b^2)] \tag{3}$$

where the R^N are roots of an auxiliary equation determined by the boundary conditions.

The reduced change of permeate mass in the membrane $F^N(t) = [(M(t) - M^0)/(M^i - M^0)]_N$ is given by

$$F^N(t) = \sum_{n=1}^{\infty} Z_n^N \exp[-D_B(R_n^N)^2(t/b^2)] \tag{4}$$

where $M^0 = C_A^0 a + C_B^0 b$, $M^i = C_A^i a + M_B^i b$, and $M(t)$ is the mass of permeate in the slab at time t. At large t only the first term in eq. (4) is significant and the equation becomes simple exponential, such that

$$\ln (F^N)_e = \ln Z_1^N - D_B(R_1^N)^2(t/b^2) \tag{5}$$

or

$$\ln(F^N)_e = [-D_B(R_1^N)^2/b^2](t - \theta^N) \tag{6}$$

when θ^N is the time lag defined by

$$\theta^N = \frac{b^2 \ln (Z_1^N)}{D_B\,(R_1^N)^2} \tag{7}$$

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the intercept of the limiting line of a graph of ln $(F^N)_e$ versus t on the t axis.

The systems examined are (I) two laminae initially in equilibrium with permeate at a concentration differing from that in the bath, $C_A^i \neq C_A^0$ and $C_B^i \neq C_B^0$; (II) lamina A initially in equilibrium with the bath, $C_A^i = C_A^0$, and lamina B initially in equilibrium with permeate at a concentration differing from that in the bath, $C_B^i \neq C_B^0$; (III) system I with a contact barrier between the two laminae; and (IV) system I with the impermeable substrate removed so permeate crosses the interfaces at $x = -a$ and $x = b$. Systems composed of free symmetrical ABA laminate slabs with identical boundary conditions are equivalent to systems I–III.

System I

The boundary conditions for I are

$$C_A^I(-a,t) = C_A^0,\ t \geq 0;\ C_A^I(x,0) = C_A^i,\ -a < x \leq 0 \tag{8}$$

$$\left(\frac{\partial C_B^I}{\partial x}\right)_{x=b} = 0,\ t \geq 0;\ C_B^I(x,0) = C_B^i,\ 0 \leq x \leq b \tag{9}$$

$$K = \frac{K_A}{K_B} = \frac{C_A}{C_B}, \qquad D_A \frac{\partial C_A}{\partial x} = D_B \frac{\partial C_B}{\partial x}, \qquad x = 0, t \geq 0 \tag{10}$$

The coefficients for $C(x,t)$ are

$$A_n^I(x) = \frac{2 \sin (2R_n^I) \sin [(R_n^I\lambda/\delta)(1 + x/a)]}{R_n^I[(\lambda/\delta) \sin (2R_n^I) + \sin (2R_n^I\lambda/\delta)]} \tag{11}$$

$$B_n^I(x) = \frac{4 \sin R_n^I \sin (R_n^I\lambda/\delta) \cos [R_n^I(1 - x/b)]}{R_n^I[(\lambda/\delta) \sin (2R_n^I) + \sin (2R_n^I\lambda/\delta)]} \tag{12}$$

where $\lambda = a/b$, $\delta^2 = D_A/D_B$, and the R_n^I are the positive roots of

$$\tan R \tan (R\lambda/\delta) - \delta K = 0 \tag{13}$$

The coefficients for the reduced mass equation $F^I(t)$ are

$$Z_n^I = \frac{2\delta K \sin (2R_n^I)}{(1 + \lambda K)(R_n^I)^2[(\lambda/\delta) \sin (2R_n^I) + \sin (2R_n^I\lambda/\delta)]} \tag{14}$$

System II

The boundary conditions for II are

$$C_A^{II}(-a,t) = C_A^0, \qquad t \geq 0; \qquad C_A^{II}(x,0) = C_A^0, \qquad -a \leq x < 0 \tag{15}$$

$$C_A^{II}(0,0) = C_A^i = KC_B^i \tag{16}$$

$$\left(\frac{\partial C_B^{II}}{\partial x}\right)_{x=b} = 0, \qquad t \geq 0; \qquad C_B^{II}(x,0) = C_B^i, \qquad 0 \leq x \leq b \tag{17}$$

$$K = \frac{C_A^{II}}{C_B^{II}}, \qquad D_A \frac{\partial C_A^{II}}{\partial x} = D_B \frac{\partial C_B^{II}}{\partial x}, \qquad x = 0, t \geq 0 \tag{18}$$

The coefficients for $C(x,t)$ are

$$A_n^{II}(x) = \cos (R_n^{II}\lambda/\delta)\, A_n^I(x) \tag{19}$$

$$B_n^{II}(x) = \cos (R_n^{II}\lambda/\delta)\, B_n^{II}(x) \tag{20}$$

where $R_n^I = R_n^{II}$. The coefficients for $F^{II}(t)$ are

$$Z_n^{II} = (1 + \lambda K) \cos (R_n^{II}\lambda/\delta) Z_n^I \tag{21}$$

At large t the slopes of ln $(F^N)_e$ versus t are identical for systems I and II but shifted by ln $[(1 + \lambda K) \cos (R_n^{II}\lambda/\delta)]$.

System III

The boundary conditions for III are

$$C_A^{III}(-a,t) = C_A^0, \quad t \geq 0; \quad C_A^{III}(x,0) = C_A^i, \quad -a < x \leq 0 \tag{22}$$

$$\left(\frac{\partial C_B^{III}}{\partial x}\right)_{x=b} = 0, \quad t \geq 0; \quad C_B^{III}(x,0) = C_B^i, \quad 0 \leq x \leq b \tag{23}$$

$$-\frac{\partial C_A^{III}}{\partial x} = h(C_A^{III} - KC_B^{III}), \quad D_A \frac{\partial C_A^{III}}{\partial x} = D_B \frac{\partial C_B^{III}}{\partial x}, \quad x = 0, t \geq 0 \tag{24}$$

where $h = H/D_A$ is a measure of the contact barrier. For $h \to \infty$ the barrier disappears and system III reduces to system I. Equilibrium exists at the interface $x = 0$ before the experiment, $K = C_A^i/C_B^i$, and at its completion $K = C_A^0/C_B^0$, but not during the transient phase of the sorption.

The coefficients for $C(x,t)$ are

$$A_n^{III}(x) = 2\{\sin R_n^{III} \sin (R_n^{III}\lambda x/\delta a) + [\delta K \cos R_n^{III} - (R_n^{III}/h\delta b) \sin R_n^{III}] \cos (R_n^{III}\lambda x/\delta a)\}/L_n \tag{25}$$

$$B_n^{III}(x) = 2\delta \cos [R_n^{III}(1 - x/b)]/L_n \tag{26}$$

where

$$L_n = R_n^{III}\{[(1/h\delta b) + (\lambda/\delta) + \delta K] \sin R_n^{III} \cos (R_n^{III}\lambda/\delta) + (1 + \lambda K) \cos R_n^{III} \sin (R_n^{III}\lambda/\delta) - (R_n^{III}\lambda/h\delta^2) \sin R_n^{III} \sin (R_n^{III}\lambda/\delta) + (R_n^{III}/h\delta) \cos R_n^{III} \cos (R_n^{III}\lambda/\delta)\} \tag{27}$$

where the R_n^{III} are the positive roots of

$$\tan R[(R/h\delta b) + \tan (R\lambda/\delta)] - \delta K = 0 \tag{28}$$

The coefficients for $F^{III}(t)$ are

$$Z_n^{III} = \frac{2\delta K \sin (2R_n^{III})}{(1 + \lambda K)\,(R_n^{III})^2\{(\lambda/\delta) \sin (2R_n) + \sin (2R_n\lambda/\delta) + (1/h\delta b) \cos^2 (R_n\lambda/\delta)[\sin (2R_n) + 2R_n]\}} \tag{29}$$

System IV

The boundary conditions for IV are

$$C_A^{IV}(-a,t) = C_A^0, \quad t \geq 0; \quad C_A^{IV}(x,0) = C_A^i, \quad -a < x \leq 0 \tag{30}$$

$$C_B^{IV}(b,t) = C_B^0, \quad t \geq 0; \quad C_B^{IV}(x,0) = C_B^i, \quad 0 \leq x < b \tag{31}$$

$$K = \frac{K_A}{K_B} = \frac{C_A}{C_B}, \quad D_A \frac{\partial C_A^{IV}}{\partial x} = D_B \frac{\partial C_B^{IV}}{\partial x}, \quad x = 0, t \geq 0 \tag{32}$$

The coefficients for $C(x,t)$ are

$$A_n^{IV}(x) = \frac{4 \sin R_n^{IV}[\cos (R_n^{IV}\lambda/\delta) - \cos R_n^{IV}] \sin [(R_n^{IV}\lambda/\delta)(1 + x/a)]}{R_n^{IV}[\sin (2R_n^{IV}\lambda/\delta) - (\lambda/\delta) \sin (2R_n^{IV})]} \tag{33}$$

$$B_n^{IV}(x) = \frac{4 \sin R_n^{IV}[\cos (R_n^{IV}\lambda/\delta) - \cos R_n^{IV}] \sin [(R_n^{IV}\lambda/\delta)(1 - x/b)]}{R_n^{IV}\,[\sin (2R_n^{IV}\lambda/\delta) - (\lambda/\delta) \sin (2R_n^{IV})]} \tag{34}$$

where the R_n^{IV} are the positive roots of

$$\delta K \tan R + \tan (R\lambda/\delta) = 0 \tag{35}$$

The coefficients for $F^{IV}(t)$ are

$$Z_n^{IV} = \frac{4 \tan (R_n^{IV}\lambda/\delta)[\cos (R_n^{IV}\lambda/\delta) - \cos R_n]^2}{(1 + \lambda K)(R_n^{IV})^2[\sin (2R_n^{IV}\lambda/\delta) - (\lambda/\delta) \sin (2R_n^{IV})]} \tag{36}$$

DISCUSSION

The value of these diffusion equations lies primarily in the interpretation or prediction of transient sorption behavior in a two-component laminate membrane in terms of the behavior of the each lamina. However, if the diffusion and partition coefficients for a permeate in one lamina are known,

TABLE I
Ratio of D to D_B for Systems I and II with $\lambda = 0.1$

δ	K	$R_1^{I,II}$	D/D_B eq. (38)	D/D_B eq. (39)
1.0	1.0	1.42800	1.000	0.826
1.0	0.2	1.07571	0.567	0.469
1.0	5.0	1.53976	1.163	0.961
0.2	1.0	0.58569	0.168	0.139
5.0	1.0	1.56454	1.200	0.992
5.0	0.2	1.54000	1.163	0.961
0.2	5.0	1.04720	0.538	0.444

these parameters can be determined for the second lamina from a sorption experiment using a laminate of the two. This procedure could be desirable if one lamina required the support of the second for mechanical integrity or if the outer lamina were established only in the presence of the inner one, e.g., a stagnant lamina of the medium in which a membrane consisting only of the inner lamina was immersed. This procedure is tedious. For example, if D_B and K_B are known for a sorption system of type I, D_A and K_B can be determined from a sorption experiment using a laminate. The slope of $\ln (F^I)_e$ versus t yields R_1^I by eq. (5). K_A is calculated by $M^0 = (K_A a + K_b b)c^0$. Then by eq. (13) δ can be determined by graphic or iterative procedures and D_A calculated.

A comparison of the limiting behavior at large t of $F^N(t)$ for the laminate systems N = I,II and $F(t)$ for a homogeneous membrane composed of B and of thickness l, where $l = a + b$ or $l = b$, is instructive. The experimental diffusion coefficient D obtained from a graph of $\ln F(t)$ versus t at large t for a homogeneous membrane with constant surface concentrations is calculated from the slope of the curve by[4]

$$D = -(\text{slope})(2l/\pi)^2 \tag{37}$$

For the laminate systems the D calculated in this manner is related to D_B by

$$D = D_B\,[2R_1^N(1+\lambda)/\pi]^2 \tag{38}$$

when $l = a + b$, and

$$D = D_B(2R_1^N/\pi)^2 \tag{39}$$

when $l = b$. Equation (38) shows that a surface reaction producing an outer lamina A with δ and K values far from unity can lead to poor values for D_B if the system is analyzed as if it were homogeneous. Equation (39) is most applicable in demonstrating the effect of a stagnant lamina. A few examples of the effect of an outer lamina with $\lambda = 0.1$ are presented in Table I. The effect of a stagnant lamina A on the sorption behavior of membrane B is small if δ and K are much greater than unity.

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