Time Lag in Diffusion

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Synopsis

Adsorption and desorption diffusion time lags are given for some homogeneous hollow cylinder and spherical shell membrane systems. The treatment relates to a constant diffusion coefficient with solution or sorption obeying Henry's law. Time lags for both "forward" and "reverse" flow have been determined and identities between them derived. For the hollow cylinder and spherical shell membrane systems considered here, there are only three distinguishable time lags.

INTRODUCTION

Since 1920, when the concept of a time lag was first introduced by Daynes,[1] the greater part of time lag theory has been concerned with slab membranes. Relatively few studies have dealt with hollow cylindrical membranes and still fewer with spherical shell membranes. An equation for what would now be termed the "outgoing adsorption time lag"[2-5] was first derived for a hollow cylindrical membrane by Barrer,[6] who later made the corresponding calculation for a spherical shell membrane.[7] A simplified form of Barrer's result for the hollow cylinder was given later by Jaeger.[8] More recently, the corresponding time lags for laminated hollow cylindrical systems have been the subject of two investigations in these laboratories.[9,10] To the best of our knowledge, expressions for "adsorption" and "desorption" time lags for hollow cylindrical and spherical shell systems are not available in the literature. They form the subject matter of this paper.

FORMULATION OF THE PROBLEMS

We consider isothermal radial diffusion in a ν-dimensional membrane[9,11,12] where $\nu = 1$ corresponds to a slab of unit area, $\nu = 2$ to a hollow cylinder of unit length, and $\nu = 3$ to a spherical shell.

The membrane is bounded by $r = R_1$ and $r = R_2$ with $R_2 > R_1$. Transport in the direction of increasing r is taken as positive, and the diffusion coefficient D of diffusant in the membrane is assumed to be constant (i.e., independent of concentration C, time t, and positional coordinate r). Solution or sorption within the membrane follows Henry's law, $C = kc'_g$, where C denotes the concentration of diffusant within the membrane in equilibrium with gas-phase concentration c'_g and k is the solubility or adsorption coefficient. Allowance is made for an initial arbitrary distribution of diffusant $f_\nu(r)$ within the membrane. At time $t = 0$, diffusant is admitted to $r = R_1$, $r = R_2$, the differing gas-phase concentrations c'_{g1}, c'_{g2} (and hence $C_1 = kc'_{g1}$, $C_2 = kc'_{g2}$ with $C_1 \neq C_2$) at these boundaries being maintained

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constant for all $t > 0$. The differential equation of transport and boundary conditions are then

$$\frac{\partial C}{\partial t} = \frac{1}{r^{\nu-1}} \frac{\partial}{\partial r}\left(r^{\nu-1} D \frac{\partial C}{\partial r}\right) \tag{1}$$

$$C(R_1, \nu, t) = C_1 \qquad t > 0$$

$$C(R_2, \nu, t) = C_2 \qquad t > 0 \tag{2}$$

$$C(r, \nu, 0) = f_\nu(r) \qquad R_1 < r < R_2$$

CALCULATION OF THE TIME LAG AT $r = R$

We derive the time lag $L(R, \nu)$ at $r = R$ ($R_1 \leqslant R \leqslant R_2$) using the procedure originally due to Frisch.[11,13] Steady-state results required in the derivation have been given elsewhere[12] and will be quoted.

From eq. (1), subject to the boundary conditions of eq. (2), we obtain

$$\frac{\omega_\nu}{D} \int_{R_1}^{R_2} \frac{1}{r^{\nu-1}} \int_r^R r^{\nu-1} \frac{\partial C}{\partial t}\, dr\, dr = (-)\frac{\Phi(R, \nu, t)}{D} I_\nu(R_1, R_2) + \omega_\nu(C_1 - C_2) \tag{3}$$

where[9,12]

$$\Phi(R, \nu, t) \equiv \left|(-)\, \omega_\nu r^{\nu-1} D \frac{\partial C}{\partial r}\right|_{r=R}$$

with $\omega_1 = 1$, $\omega_2 = 2\pi$, $\omega_3 = 4\pi$, and

$$I_\nu(x, y) \equiv \int_x^y \frac{dr}{r^{\nu-1}} \tag{4}$$

so that $I_1 = (y - x)$, $I_2 = \ln(y/x)$, and $I_3 = (1/x) - (1/y)$. The steady-state flux $\Phi_\infty(\nu)$ through the membrane is given by[12]

$$\Phi_\infty(\nu) = \frac{\omega_\nu D(C_1 - C_2)}{I_\nu(R_1, R_2)} \tag{5}$$

Combining eqs. (3) and (5), we have

$$\Phi(R, \nu, t) = \Phi_\infty(\nu) - \frac{\omega_\nu}{I_\nu(R_1, R_2)} \int_{R_1}^{R_2} \frac{1}{r^{\nu-1}} \int_r^R r^{\nu-1} \frac{\partial C}{\partial t}\, dr\, dr$$

so that

$$Q(R, \nu, t) = \int_0^t \Phi(R, \nu, t)dt$$

$$= \Phi_\infty(\nu)t - \frac{\omega_\nu}{I_\nu(R_1, R_2)} \int_{R_1}^{R_2} \frac{1}{r^{\nu-1}} \tag{6}$$

$$\left[\int_r^R r^{\nu-1} [C(r, \nu, t) - f_\nu(r)]dr \right] dr$$

where $Q(R, \nu, t)$ is the quantity of diffusant that has crossed the surface at $r = R$ of area $\omega_\nu r^{\nu-1}$ up to time t. For large t, $Q(R, \nu, t) \to \Phi_\infty(\nu)(t - L(R, \nu))$, so that from eq. (6) with eq. (5) we obtain

$$L(R, \nu) = \frac{\int_{R_1}^{R_2} (1/r^{\nu-1}) \int_r^R r^{\nu-1} (C(r, \nu) - f_\nu(r))\, dr\, dr}{D(C_1 - C_2)} \tag{7}$$

where[12]

$$C(r, \nu) = C_1 \frac{I_\nu(r, R_2)}{I_\nu(R_1, R_2)} + C_2 \frac{I_\nu(R_1, r)}{I_\nu(R_1, R_2)} \tag{8}$$

Using eq. (8) and integration by parts, the double integral of eq. (7) is readily evaluated and after some rearrangement we obtain

$$L(R, \nu) = \Bigg\{ C_1 \Bigg[(4 - \nu)(R^2 + R_1^2) + 2(4 - \nu) R^\nu I_\nu(R, R_2) - \frac{2(R_2^{4-\nu} - R_1^{4-\nu})}{I_\nu(R_1, R_2)} \Bigg]$$

$$+ C_2 \Bigg[(-)(4 - \nu)(R^2 + R_2^2) + 2(4 - \nu) R^\nu I_\nu(R_1, R) + \frac{2(R_2^{4-\nu} - R_1^{4-\nu})}{I_\nu(R_1, R_2)} \Bigg] \tag{9}$$

$$+ 2\nu(4 - \nu) I_\nu(R_1, R_2) \left[\int_{R_1}^{R_2} \left(1 - \frac{I_\nu(R_1, r)}{I_\nu(R_1, R_2)} \right) r^{\nu-1} f_\nu(r)\, dr \right.$$

$$\left. - \int_{R_1}^{R} r^{\nu-1} f_\nu(r)\, dr \right] \Bigg\} / 2\nu(4 - \nu)\, D(C_1 - C_2)$$

Equation (9) enables us to evaluate $L(R, \nu)$ for the particular C_1, C_2 and $f_\nu(r)$ of interest. Here, we restrict our considerations to two specific initial distributions of diffusant: (1) $f_\nu(r) = C_2$, for which

$$2\nu(4 - \nu)\, DL(R, \nu) = (4 - \nu)(R_1^2 + R^2) + 2(4 - \nu)R^\nu I_\nu(R, R_2) - \frac{2(R_2^{4-\nu} - R_1^{4-\nu})}{I_\nu(R_1, R_2)} \quad (10)$$

and (2) $f_\nu(r) = C_1$, for which

$$2\nu(4 - \nu)\, DL(R, \nu) = (4 - \nu)(R^2 + R_2^2) - 2(4 - \nu)R^\nu I_\nu(R_1, R) - \frac{2(R_2^{4-\nu} - R_1^{4-\nu})}{I_\nu(R_1, R_2)} \quad (11)$$

Equations (10) and (11) represent considerable simplifications of eq. (9) and, in particular, show that the $L(R, \nu)$ for these two specific initial distributions of diffusant within the membrane are independent of C_1 and C_2.

ADSORPTION AND DESORPTION TIME LAGS

The considerations of the previous two sections required $C_1 \neq C_2$ without specifying the relative magnitudes of C_1 and C_2. We now investigate the time lags for transport through the membrane with $C_1 > C_2$ and $C_2 > C_1$, respectively. For $C_1 > C_2$, transport of diffusant will occur in the direction of increasing r and will be termed "forward flow." "Reverse flow" (transport of diffusant in the direction of decreasing r) then corresponds to $C_2 > C_1$. In what follows, the subscripts a and d refer to adsorption and desorption conditions, respectively.[3] The four possible arrangements are illustrated in Figure 1. Taking forward flow first, $L_a(R, \nu)$ and $L_d(R, \nu)$ (Fig. 1) are given by eq. (10) and (11), respectively. In particular, we have

$$\nu(4 - \nu)DL_a(R_1, \nu) = (4 - \nu)R_1^2 + (4 - \nu)R_1^\nu I_\nu(R_1, R_2) - \frac{(R_2^{4-\nu} - R_1^{4-\nu})}{I_\nu(R_1, R_2)} \quad (12)$$

$$\nu(4 - \nu)DL_a(R_2, \nu) = (4 - \nu)\frac{(R_1^2 + R_2^2)}{2} - \frac{(R_2^{4-\nu} - R_1^{4-\nu})}{I_\nu(R_1, R_2)} \quad (13)$$

and

$$\nu(4 - \nu)DL_d(R_1, \nu) = (4 - \nu)\frac{(R_1^2 + R_2^2)}{2} - \frac{(R_2^{4-\nu} - R_1^{4-\nu})}{I_\nu(R_1, R_2)} \quad (14)$$

$$\nu(4 - \nu)DL_d(R_2, \nu) = (4 - \nu)R_2^2 - (4 - \nu)R_2^\nu I_\nu(R_1, R_2) - \frac{(R_2^{4-\nu} - R_1^{4-\nu})}{I_\nu(R_1, R_2)} \quad (15)$$

Two important results emerge from eqs. (12) through (15):

$$L_a(R_2, \nu) = L_d(R_1, \nu) \qquad \text{for all } \nu\ (\nu = 1, 2, 3) \tag{16}$$

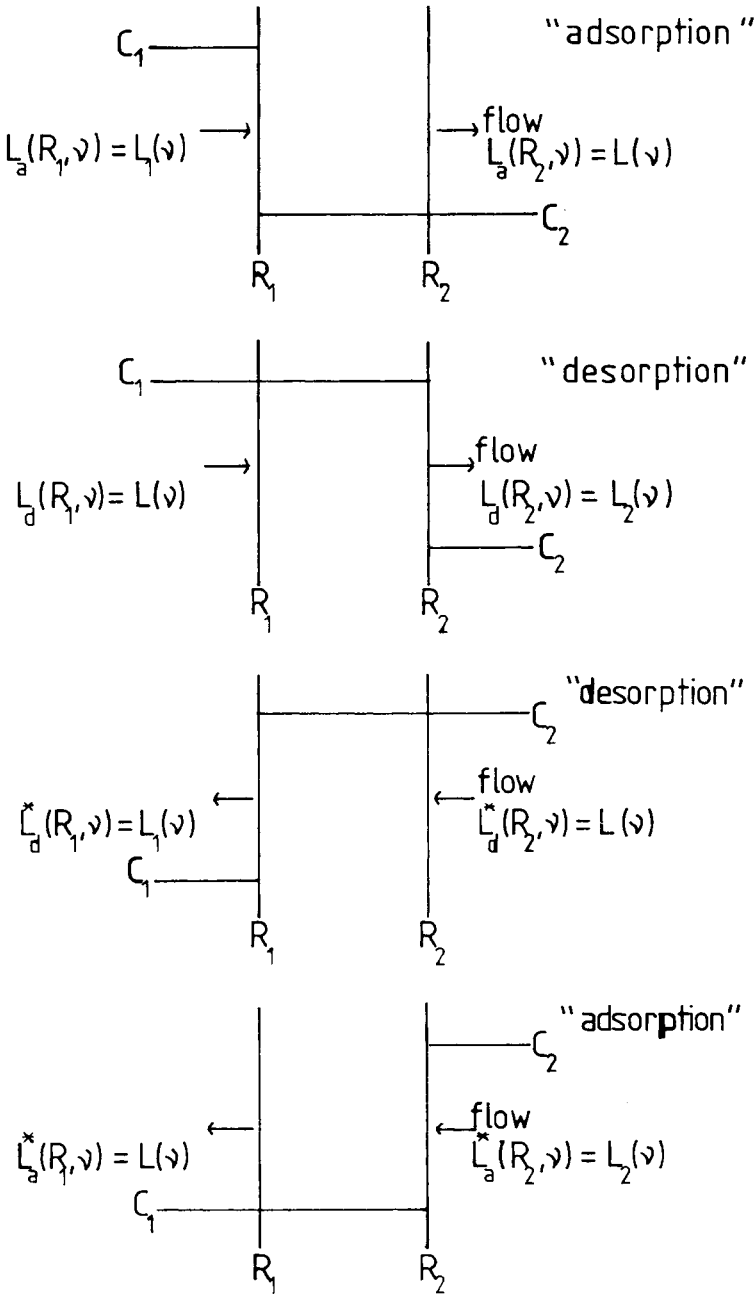

Fig. 1. Boundary conditions and time lags for the four flow systems.

and

$$L_a(R_1, \nu) = L_d(R_2, \nu) \qquad \text{for } \nu = 1$$

but

$$L_a(R_1, \nu) \neq L_d(R_2, \nu) \qquad \text{for } \nu = 2 \text{ and } \nu = 3 \tag{17}$$

For reverse flow, ($C_2 > C_1$, Fig. 1c and d), $L_a(R, \nu)$ and $L_d(R, \nu)$ are obtained from eqs. (11) and (10), respectively. In particular, we have

$$\nu(4 - \nu)DL_a^*(R_1, \nu) = (4 - \nu)\frac{(R_1^2 + R_2^2)}{2} - \frac{(R_2^{4-\nu} - R_1^{4-\nu})}{I_\nu(R_1, R_2)} \tag{18}$$

$$\nu(4 - \nu)DL_a^*(R_2, \nu) = (4 - \nu)R_2^2 - (4 - \nu)R_2{}^\nu I_\nu(R_1, R_2) - \frac{(R_2^{4-\nu} - R_1^{4-\nu})}{I_\nu(R_1, R_2)} \tag{19}$$

and

$$\nu(4 - \nu)DL_d^*(R_1, \nu) = (4 - \nu)R_1^2 + (4 - \nu)R_1{}^\nu I_\nu(R_1, R_2) - \frac{(R_2^{4-\nu} - R_1^{4-\nu})}{I_\nu(R_1, R_2)} \tag{20}$$

$$\nu(4 - \nu)DL_d^*(R_2, \nu) = (4 - \nu)\frac{(R_1^2 + R_2^2)}{2} - \frac{(R_2^{4-\nu} - R_1^{4-\nu})}{I_\nu(R_1, R_2)} \tag{21}$$

in which the asterisk denotes a quantity associated with reverse flow. Straightaway we see from eqs. (18) through (21) that

$$L_a^*(R_1, \nu) = L_d^*(R_2, \nu) \qquad \text{for all } \nu \text{ considered} \tag{22}$$

and

$$L_a^*(R_2, \nu) = L_d^*(R_1, \nu) \qquad \text{for } \nu = 1 \tag{23}$$

$$L_a^*(R_2, \nu) \neq L_d^*(R_1, \nu) \qquad \text{for } \nu = 2 \text{ and } \nu = 3$$

Comparison of the time lags for forward and reverse flow given in eqs. (12) through (15) and eqs. (16) through (19), respectively, reveals that

$$L_a(R_1, \nu) = L_d^*(R_1, \nu) \tag{24}$$

$$L_a(R_2, \nu) = L_d^*(R_2, \nu) = L_a^*(R_1, \nu) = L_d(R_1, \nu) \tag{25}$$

and

$$L_d(R_2, \nu) = L_a^*(R_2, \nu) \tag{26}$$

for all ν considered. For $\nu = 1$ only, we have

$$\begin{aligned} L_a(R_1, \nu) &= L_d^*(R_1, \nu) \\ &= L_a^*(R_2, \nu) \\ &= L_d(R_2, \nu) \end{aligned}$$

[see eqs. (17) through (23)].

Explicit expressions for $L_a(R_2, \nu)$, $L_a(R_1, \nu)$, and $L_d(R_2, \nu)$ for the hollow cylindrical ($\nu = 2$) and spherical shell ($\nu = 3$) membranes are given in Table I. For completeness, the corresponding time lags for the slab membrane ($\nu = 1$) are also tabulated. Expressions for the remaining (five) time lags are readily obtained via the equalities of eqs. (24) through (26).

DISCUSSION

For brevity we write $L_a(R_2, \nu) = L_d^*(R_2, \nu) = L_d(R_1, \nu) = L_a^*(R_1, \nu) \equiv L(\nu)$, $L_a(R_1, \nu) = L_d^*(R_1, \nu) \equiv L_1(\nu)$ and $L_d(R_2, \nu) = L_a^*(R_2, \nu) \equiv L_2(\nu)$. The time lags of the last section (and Table I) refer to situations in which, at time $t = 0$, the concentration of diffusant at one boundary is suddenly changed while the concentration at the other boundary remains undisturbed. Reference to Figure 1 shows that time lag $L(\nu)$ is associated in all four cases with the boundary undisturbed at $t = 0$, and the time lags $L_1(\nu)$ and $L_2(\nu)$ are associated with boundaries disturbed at $t = 0$. An interesting feature of the analysis is that $L_1(\nu)$ is specifically associated with the boundary at $r = R_1$ and $L_2(\nu)$ is specifically associated with the boundary at $r = R_2$. Thus, for the geometrically asymmetric homogeneous hollow cylindrical and spherical shell membrane systems considered here, there are only three distinguishable time lags. In order of magnitude, they are $L(\nu) > L_1(\nu) > L_2(\nu)$ with $L(\nu) > 0$, $L_1(\nu), L_2(\nu) < 0$.

Defining the time lag difference, $\Delta L(\nu)$ by

$$\Delta L(\nu) \equiv L(R_2, \nu) - L(R_1, \nu) \tag{27}$$

we see (from Fig. 1) that, for all ν,

$$\begin{aligned} \Delta L_a(\nu) &= L(\nu) - L_1(\nu) = \Delta L_d^*(\nu) > 0 \\ \Delta L_d(\nu) &= L_2(\nu) - L(\nu) = \Delta L_a^*(\nu) < 0 \end{aligned} \tag{28}$$

where

$$\begin{aligned} 2\nu D\, \Delta L_a(\nu) &= (R_2^2 - R_1^2) - 2R_1^{\nu} I_{\nu}(R_1, R_2) \\ 2\nu D\, \Delta L_d(\nu) &= (R_2^2 - R_1^2) - 2R_2^{\nu} I_{\nu}(R_1, R_2) \end{aligned} \tag{29}$$

TABLE I
Time Lags for the Three Types of Membrane

Time lag	Slab ($\nu = 1$)	Hollow cylinder ($\nu = 2$)	Spherical shell ($\nu = 3$)
$L_a(R_2,\nu)$	$\frac{(R_2 - R_1)^2}{6D}$	$\frac{(R_1^2 + R_2^2)\ln(R_2/R_1) - (R_2^2 - R_1^2)}{4D\ln(R_2/R_1)}$	$\frac{(R_2 - R_1)^2}{6D}$
$L_a(R_1, \nu)$	$(-)\frac{(R_2 - R_1)^2}{3D}$	$\frac{2R_1^2[1 + \ln(R_2/R_1)]\ln(R_2/R_1) - (R_2^2 - R_1^2)}{4D\ln(R_2/R_1)}$	$(-)\frac{(R_2 - R_1)^2}{3D(R_2/R_1)}$
$L_d(R_2, \nu)$	$(-)\frac{(R_2 - R_1)^2}{3D}$	$\frac{2R_2^2[1 - \ln(R_2/R_1)]\ln(R_2/R_1) - (R_2^2 - R_1^2)}{4D\ln(R_2/R_1)}$	$(-)\frac{(R_2 - R_1)^2}{3D(R_1/R_2)}$

[see eqs. (12) through (15) and (18) through (21)]. $\Delta L(\nu)$ is given by[3]

$$\Phi_\infty(\nu)\,\Delta L(\nu) = M_\infty(\nu) - M_i(\nu) \tag{30}$$

where $M_\infty(\nu)$ is the membrane diffusant content in the steady state and $M_i(\nu)$ is the initial value of this content. We can effect forward and reverse flow under comparable conditions by taking $C_1 = C_A$, $C_2 = C_B$ for forward flow and $C_1 = C_B$, $C_2 = C_A$ for reverse flow with (in both cases) $C_A > C_B$. Then, for the two adsorption systems of Figure 1, we have

$$\begin{aligned} \Phi_\infty(\nu)\,\Delta L_a(\nu) &= M_\infty(\nu) - M_{ia}(\nu) \\ \Phi^*_\infty(\nu)\,\Delta L^*_a(\nu) &= M^*_\infty(\nu) - M^*_{ia}(\nu) \end{aligned} \tag{31}$$

where

$$M_{ia}(\nu) = M^*_{ia}(\nu) = \frac{\omega_\nu}{\nu} C_B(R_2 - R_1)$$

and

$$\Phi^*_\infty(\nu) = (-)\Phi_\infty(\nu)$$

From eqs. (28), since $L_1(\nu) > L_2(\nu)$, we have $(-)\,\Delta L^*{}_a(\nu) > \Delta L_a(\nu)$. It then follows from eqs. (31) that $M^*_\infty(\nu) > M_\infty(\nu)$. (The same result follows from a consideration of the two desorption systems.) The difference in the steady-state diffusant contents $(M^*_\infty(\nu) - M_\infty(\nu))$, is readily evaluated from the combination of eqs. (5), (28), (29), and (31) and is given by

$$M^*_\infty(\nu) - M_\infty(\nu) = \frac{\omega_\nu(C_A - C_B)}{\nu\, I_\nu(R_1, R_2)} \left[(R_2^\nu + R_1^\nu)\, I_\nu(R_1, R_2) - (R_2^2 - R_1^2)\right] \tag{32}$$

For the slab membrane ($\nu = 1$), $M^*_\infty(\nu) = M_\infty(\nu)$, $L_1(\nu) = L_2(\nu)$ and there are only two distinguishable time lags for the geometrically symmetrical homogeneous membrane systems considered. These time lags are well known and need no further discussion here.

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