

$$\partial[(2n+1)a_0 + na_1 + (n-1)a_2 + (n-2)a_3 + \dots + a_n]/\partial\tau = \partial^2[(2n+1)a_0 + na_1 + (n-1)a_2 + (n-2)a_3 + \dots + a_n]/\partial y^2$$

Therefore, at any time

$$\frac{1}{\pi^{1/2}} \int_0^\tau (n+1) \frac{i(\eta)}{FSC^0 D^{1/2}} d\eta = (2n+1) - [(2n+1)a_0 + na_1 + (n-1)a_2 + (n-2)a_3 + \dots + a_n]_{y=0}$$

Thus, during the anodic potential step, the current varies between two limits corresponding to complete reversibility ($[a_0]_{y=0} = 0$, $[a_1]_{y=0} = 1$, $a_{j=2..n} = 0$):

$$\frac{i(t)}{FSC^0 D^{1/2}} = \frac{1}{(\pi t)^{1/2}}$$

and complete irreversibility ($[a_0]_{y=0} = 0$, $[a_{j=1..n}]_{y=0} = 0$):

$$\frac{i(t)}{FSC^0 D^{1/2}} = \frac{2n+1}{n+1} \frac{1}{(\pi t)^{1/2}}$$

In other words, the number of electrons per monomer passes from 1 to $(2n+1)/(n+1)$, i.e., to 2 when n is large (not taking account of the additional charging of the polymer¹²). The same is true in cyclic voltammetry.

Two types of calculations were performed for each mechanism. We first set all λ 's equal to zero except λ_1 , then all λ 's were made equal to zero except λ_1 and λ_2 , λ_2 was made equal to λ_1 , finally all λ 's were made equal to zero except λ_1 , λ_2 , and λ_3 , and λ_2 and λ_3 were made equal to λ_1 . The resulting $R-k_{ap}C^0\theta$ curves are represented in parts Aa and Ba of Figure 4 for the CR-CR and CR-S-irr mechanisms, respectively, while the resulting $R-k_{ap}C^0\theta^2$ curves are represented in Figure 5a for the CR-S-rev mechanism. The calculations could have been pursued for $\lambda_1 = \lambda_2 = \lambda_3 = \lambda_4$ and $(\lambda_j)_{j>4} = 0$ and so forth, but we noticed that the R curves

cease to vary appreciably in between the last two calculations (Figures 4Aa, Ba and 5a).

In the second series of calculations we apply the condition $\lambda_1 \ll (\lambda_j)_{j=2..n}$ and considered the case where $n \rightarrow \infty$. That amounts to replacing the preceding sets of partial derivative equations, initial and boundary conditions, by the following ones.

CR-CR

$$\frac{\partial a_0}{\partial \tau} = \frac{\partial^2 a_0}{\partial y^2} + n\lambda_1 a_1^2$$

$$\frac{\partial a_1}{\partial \tau} = \frac{\partial^2 a_1}{\partial y^2} - 2n\lambda_1 a_1^2$$

CR-S-irr

$$\frac{\partial a_0}{\partial \tau} = \frac{\partial^2 a_0}{\partial y^2} + n\lambda_1 a_0 a_1$$

$$\frac{\partial a_1}{\partial \tau} = \frac{\partial^2 a_1}{\partial y^2} - 2n\lambda_1 a_0 a_1$$

CR-S-rev

$$\frac{\partial a_0}{\partial \tau} = \frac{\partial^2 a_0}{\partial y^2} + n\lambda_1 a_0 a^2$$

$$\frac{\partial a_1}{\partial \tau} = \frac{\partial^2 a_1}{\partial y^2} - 2n\lambda_1 a_0 a_1^2$$

$$\tau = 0, y \geq 0: \quad a_0 = 1, \quad a_1 = 0$$

$$y = 0, \tau \geq 0: \quad \frac{\partial a_0}{\partial y} + \frac{\partial a_1}{\partial y} = 0$$

$$0 \leq \tau \leq \theta: \quad a_0 = 0 \quad \tau \geq \theta: \quad a_1 = 0$$

Calculation of Lag Time for Convective-Reactive Diffusion

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Closed form solutions for the steady-state permeability P and the lag time L of a linear diffusion system with concurrent convection and reaction were obtained by two methods. In the first method, we identify the singularity at $s = 0$ of the Laplace transform of the total amount of diffusant, $\hat{Q}(s)$, released into the receiver as representation of the asymptotic diffusion behavior. P and L are then obtained from the time-independent coefficients of an expansion of $\hat{Q}(s)$ about $s = 0$. In the second method, we transform the convective-reactive diffusion equation into a form that contains only first and second derivatives of the concentration distribution function. By comparison of the resulting equation with that for a heterogeneous diffusion system, relationships of the convection velocity and rate constant with the position-dependent partition coefficient in heterogeneous diffusion is found. Taking advantage of the known solutions for permeability and lag time in heterogeneous diffusion, the corresponding expressions for P and L in convective-reactive diffusion are then obtained by transcription. These methods have the advantage over earlier approaches in that solutions in an infinite form are avoided.

Introduction

Diffusion plays an important role in numerous processes, such as chemical reactions in condensed phases,¹ nucleation,^{2,3} nerve

impulse transmission,⁴ and colloid flocculation.⁵ In recent years some attention has been paid to the mathematical description of transient diffusion.⁶⁻⁸ This requires complete solutions to diffusion

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equations, which, however, apart from some simple cases, cannot be obtained in closed form. Therefore, one usually contents oneself with asymptotic solutions which provide information on the permeability and lag time, i.e., the steady-state rate of mass transport and time required for the attainment of steady state. With these two parameters, one is able to estimate the total amount of diffusant released into the receiver over long times. Such an estimate is adequate for most practical applications.

The lag time in simple homogeneous diffusion assumes a value of $h^2/6D$,⁹ where D is the diffusivity, and h the length of the diffusive path (thickness of membrane, etc.). Expressions for lag times have also been derived for more complex systems. For instance, Jaeger,¹⁰ by employing a Laplace transform, gave a routine (instead of an explicit expression) for the calculation of the lag time for thermal conduction across a multilayer slab. His procedure was followed by Barrie et al.¹¹ to calculate the lag time of mass diffusion in a three-layer slab. The pioneering work of Frisch¹² yielded an elegant method to obtain the lag time for a system with concentration-dependent diffusivity without solving diffusion equations. This strategy was also used by Paul¹³ to obtain the lag time for the dual absorption diffusion in polymer films. Later Frisch and collaborators¹⁴⁻¹⁷ and Chen and Fox¹⁸ formulated the lag time for a heterogeneous diffusion system characterized by a position-dependent diffusivity and partition coefficient. Chen and Rosenberger have recently extended the treatment to diffusion systems with serial and/or parallel paths¹⁹ and multiple and periodic laminates.²⁰ Earlier, employing Frisch's concept, Petropoulos and Roussis studied the lag time in diffusion systems with time- and position-dependent anomalies^{21,22} and the "directional diffusion lag time asymmetry".²³

The lag time in a diffusion system with a linear reaction and sorption process has been studied by Ludolph et al.²⁴ Their result is now superseded by that of Leypoldt and Gough,²⁵ obtained by employing a finite Fourier transform. Keister and Kasting²⁶ treated convective diffusion in a constant electrical field (electrodifusion) by a separation of variables method. They obtained solutions for the lag time in the form of infinite series, which require simplification based on the residue theorem in complex variable theory if compact forms for P and L are desired.

In this article we present two other schemes to obtain closed form solutions for P and L . In the first method we utilize Laplace transforms as originally suggested by Carslaw and Jaeger²⁷ and solve the diffusion equation in the Laplace domain to obtain the total diffusant amount $\hat{Q}(s)$ released into the receiver. The asymptotic part of $\hat{Q}(s)$ is identified to correspond to the singularity at $s = 0$. The permeability and lag time are then obtained in closed forms from the expansion coefficients of $\hat{Q}(s)$ around $s = 0$. The second scheme makes use of the method of change of variables

to transform the original convective-reactive diffusion equation into the form which contains only terms of first and second derivatives of the concentration distribution function. By comparison of the resulting diffusion equation with that for a heterogeneous diffusion system,¹⁴⁻¹⁸ relationships of the convection velocity and rate constant with the position-dependent partition coefficient in heterogeneous diffusion is found. Taking advantage of the known solutions for permeability and lag time in heterogeneous diffusion, the corresponding expressions for P and L in convective-reactive diffusion are then obtained by transcription.

Laplace Transform Approach

Consider a convective-reactive diffusion process taking place in a membrane extending from $x = 0$ to $x = h$. The region $x < 0$ is designated as donor compartment, and the region $x > h$ as receiver compartment. During an experiment, the concentration of diffusant in the donor is kept at a constant level, ρ_0 , while that in the receiver is kept at zero. Thus, an "infinite constant supply and sink condition" is imposed. The membrane is void of diffusant at the onset of the experiment.

The mathematical description of the problem involves a diffusion equation of the form

$$\frac{\partial}{\partial t}\rho(x,t) = D\frac{\partial^2}{\partial x^2}\rho(x,t) - v\frac{\partial}{\partial x}\rho(x,t) - \kappa\rho(x,t) \quad (1)$$

supplemented with the initial and boundary conditions

$$\rho(x,0) = 0 \quad (2)$$

$$\rho(0,t) = K\rho_0 \quad (3)$$

$$\rho(h,t) = 0 \quad (4)$$

Here, $\rho(x,t)$ is the diffusant concentration at location x and time t ; D , v , and κ are the diffusivity, convective velocity, and rate constant of the first-order reaction, respectively. We assume that D , v , and κ are positive and constant. $K(0)$ in eq 3 represents the partition coefficient characterizing the distribution of diffusant on both sides of the interface at $x = 0$ and accounts for the continuity of the diffusant's chemical potential at this interface. The foregoing linear differential equation with constant coefficients can effectively be solved by a Laplace transform technique. In the Laplace domain, eqs 1-4 take on the forms

$$s\hat{\rho}(x,s) = D\frac{\partial^2}{\partial x^2}\hat{\rho}(x,s) - v\frac{\partial}{\partial x}\hat{\rho}(x,s) - \kappa\hat{\rho}(x,s) \quad (5)$$

$$\hat{\rho}(0,s) = \rho_0 K/s \quad (6)$$

$$\hat{\rho}(h,s) = 0 \quad (7)$$

Here, a circumflex over a function designates its Laplace transform on t , e.g.

$$\hat{\rho}(x,s) \equiv L(\rho(x,t)) \equiv \int_0^\infty \exp(-st)\rho(x,t) dt \quad (8)$$

where s is a Laplace variable. Note that the initial condition (2) has been incorporated into eq 5, and the partial differential equation has been transformed into an ordinary differential equation. The solution to eqs 5-7 is found to be

$$\hat{\rho}(x,s) = \frac{\rho_0 K}{s} \exp\left(\frac{vx}{2D}\right) \frac{\sinh q(h-x)}{\sinh qh} \quad (9)$$

with

$$q = \sqrt{(v/2D)^2 + (s + \kappa)/D} \quad (10)$$

An experimentally measurable quantity, $Q(t)$, the total amount of diffusant released into the receiver within time t , is defined as

$$Q(t) = \int_0^t J(h,\tau) d\tau = - \int_0^t \left[D \frac{\partial \rho(x,\tau)}{\partial x} - v\rho(x,\tau) \right]_{x=h} d\tau = - \int_0^t \left[D \frac{\partial \rho(x,\tau)}{\partial x} \right]_{x=h} d\tau \quad (11)$$

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where $J(h,t)$ is the diffusion flux into the receiver, and the boundary condition (4) has been used. The Laplace transform of $Q(t)$ in eq 11 acquires the form

$$\hat{Q}(s) = -\frac{D}{s} \left[\frac{\partial}{\partial x} \hat{\rho}(x,s) \right]_{x=h} \quad (12)$$

On substituting eq 9 into eq 12, one obtains

$$\hat{Q}(s) = \frac{\rho_0 DKq}{s^2} \exp\left(\frac{vh}{2D}\right) \operatorname{csch}(qh) \quad (13)$$

In general, the total release $Q(t)$ in a linear diffusion system subject to an infinite constant supply and sink condition consists of two parts: (1) The transient part, which decays with time eventually to zero, is a linear combination of terms in the form of $\exp(-\lambda_i t)$, where the λ_i 's are the eigenvalues of the Sturm-Liouville differential equation associated with the method of separation of variables.⁹ (2) The long-time asymptotic limit, which depends linearly on time, defines the permeability P and lag time L , respectively, as the slope of the asymptote and its intercept with the time axis. A combination of these two parts together gives $Q(t)$ in terms P and L as

$$Q(t) = \rho_0 P(t - L) + \sum_{i=1}^{\infty} c_i \exp(-\lambda_i t) \quad (14)$$

To obtain explicit expressions for P and L , we take the Laplace transformation of $Q(t)$ in eq 14:

$$\hat{Q}(s) = \frac{\rho_0 P}{s^2} - \frac{\rho_0 PL}{s} + \sum_{i=1}^{\infty} \frac{c_i}{s + \lambda_i} \quad (15)$$

Equations 13 and 15 are different expressions for the same entity. Equation 13 contains the parameters D , v , and κ to characterize the convective-reactive diffusion, while eq 15 contains P and L to characterize its asymptotic behavior. Thus one can deduce relations of P and L with D , v , and κ from the following consideration. Note that $\hat{Q}(s)$ possesses a pole at $s = 0$, and an infinite number of poles at $s = -\lambda_i$. The pole at $s = 0$ is of second order and accounts for the asymptotic part. The rest of the poles, on the other hand, account for the transient part. To obtain expressions for P and L , the singularity at $s = 0$ is removed by multiplying eq 18 by s^2 to obtain

$$s^2 \hat{Q}(s) = \rho_0 P - \rho_0 PLs + \sum_{i=1}^{\infty} \frac{s^2 c_i}{s + \lambda_i} \quad (16)$$

In the infinitesimal neighborhood around $s = 0$, where the asymptotic part dominates, $s^2 \hat{Q}(s)$ acquires the form of a Taylor series (instead of a Laurent expansion as in eq 15). Accordingly

$$\rho_0 P = \lim_{s \rightarrow 0} s^2 \hat{Q}(s) \quad (17)$$

$$\rho_0 PL = - \left[\frac{\partial}{\partial s} s^2 \hat{Q}(s) \right]_{s=0} \quad (18)$$

On substituting eq 13 into eqs 17 and 18, one obtains

$P =$

$$\frac{DK}{h} \exp\left(\frac{vh}{2D}\right) \left(\sqrt{\left(\frac{v}{2D}\right)^2 + \frac{\kappa}{D} h} \right) \operatorname{csch} \left(\sqrt{\left(\frac{v}{2D}\right)^2 + \frac{\kappa}{D} h} \right) \quad (19)$$

$$L = \frac{h^2}{6D} \left\{ 3 \left[\frac{\coth \left(\sqrt{\left(\frac{v}{2D}\right)^2 + \frac{\kappa}{D} h} \right)}{\sqrt{\left(\frac{v}{2D}\right)^2 + \frac{\kappa}{D} h}} - \frac{1}{\left(\left(\frac{v}{2D}\right)^2 + \frac{\kappa}{D}\right) h^2} \right] \right\} \quad (20)$$

Thus, we have derived expressions for P and L in convective-reactive diffusion without resorting to any solutions in forms of infinite series. All manipulations were performed in closed form. The advantage of using a Laplace transform in the formulation of P and L results from the fact that the asymptotic part corre-

sponding to the singularity of order 2 at $s = 0$ can be singled out from the transient part.

Change-of-Variables Approach

In this section we introduce a change of variables to transform eq 1 into a form containing only terms of first and second derivatives of the distribution function. The resulting equation is then compared with the governing equation for a heterogeneous diffusion system to obtain an expression for position-dependent partition coefficient in terms of D , v , k , and K in eqs 1-4. Such a relation will enable us to formulate permeability and lag time for convective-reactive diffusion system simply by transcription from their previously derived counterparts in heterogeneous diffusion. To this end, $\rho(x,t)$ is factored into a purely position-dependent part and position- and time-dependent part, namely

$$\rho(x,t) = g(x) f(x,t) \quad (21)$$

Substitution of eq 21 into eq 1 results in

$$\frac{\partial}{\partial t} f(x,t) = D \frac{\partial^2}{\partial x^2} f(x,t) + \left\{ 2D \frac{\partial}{\partial x} [\ln g(x)] - v \right\} \frac{\partial}{\partial x} f(x,t) + \left\{ D \frac{\partial^2}{\partial x^2} g(x) - v \frac{\partial}{\partial x} g(x) - \kappa g(x) \right\} \frac{f(x,t)}{g(x)} \quad (22)$$

Up to this point, the functional forms of $f(x,t)$ and $g(x)$ are unspecified. If $g(x)$ is set to satisfy the differential equation

$$D \frac{\partial^2}{\partial x^2} g(x) - v \frac{\partial}{\partial x} g(x) - \kappa g(x) = 0 \quad (23)$$

then eq 22 reduces to

$$\frac{\partial}{\partial t} f(x,t) = D \frac{\partial^2}{\partial x^2} f(x,t) + \left\{ 2D \frac{\partial}{\partial x} [\ln g(x)] - v \right\} \frac{\partial}{\partial x} f(x,t) \quad (24)$$

For conciseness, we refer henceforth to a diffusant whose distribution $f(x,t)$ obeys eq 24 as f diffusant, and, correspondingly, to one that follows eq 1 and eq 23, respectively, as ρ and g diffusants. Note that in view of eq 30 the diffusivity remains unchanged on transformation from ρ diffusant to f diffusant.

Now, imagine an f diffusant undergoing heterogeneous diffusion characterized by a constant diffusivity D and a position-dependent partition coefficient $K(x)$. The diffusion equation for such a heterogeneous diffusion system is^{14,15,18}

$$\frac{\partial}{\partial t} f(x,t) = D \frac{\partial}{\partial x} \left\{ K(x) \frac{\partial}{\partial x} \frac{f(x,t)}{K(x)} \right\} \quad (25)$$

or upon expansion

$$\frac{\partial}{\partial t} f(x,t) = D \frac{\partial^2}{\partial x^2} f(x,t) - D \left\{ \frac{\partial}{\partial x} K(x) \right\} \frac{\partial}{\partial x} f(x,t) - D \left\{ \frac{\partial^2}{\partial x^2} \ln K(x) \right\} f(x,t) \quad (26)$$

On comparing eq 24 with eq 26 term by term, one obtains

$$\frac{\partial}{\partial x} \ln K(x) = -2 \frac{\partial}{\partial x} \ln g(x) + \frac{v}{D} \quad (27)$$

$$\frac{\partial^2}{\partial x^2} \ln K(x) = 0 \quad (28)$$

The solution for $K(x)$ in eqs 27 and 28 is

$$K(x) = B \frac{\exp(vx/D)}{[g(x)]^2} \quad (29)$$

where B is a constant to be determined. A combination of eqs 27 and 28 gives

$$g(x) = A \exp\left(\frac{v - \sqrt{v^2 + 4\kappa D}}{2D} x\right) \quad (30)$$

The solution of both eqs 23 and 30 has the form

$$g(x) = A \exp\left(\frac{v - \sqrt{v^2 + 4\kappa D}}{2D}x\right) \quad (31)$$

where A is a constant to be determined. Without loss of generality, we set $A = 1$, which, in turn, implies that the boundary conditions for $g(x)$ in eq 23 are

$$g(0) = 1 \quad (32)$$

$$g(h) = \exp\left(\frac{v - \sqrt{v^2 + 4\kappa D}}{2D}h\right) \quad (33)$$

On substituting the boundary conditions (32) and (33) into eqs 2-4, one sees that $f(x,t)$ in eq 24 possesses the same initial and boundary conditions as $\rho(x,t)$. Specifically

$$f(x,0) = 0 \quad (34)$$

$$f(0,t) = K\rho_0 \quad (35)$$

$$f(h,t) = 0 \quad (36)$$

Substitution of $g(x)$ in eq 31 with $A = 1$ into eq 29 yields

$$K(x) = B \exp\left\{\frac{\sqrt{v^2 + 4\kappa D}}{D}x\right\} \quad (37)$$

At the interface $x = 0$, the partition coefficient K is given by eq 35 and, thus, from eq 37, $B = K$. As a result, the partition coefficient for the f diffusant in heterogeneous diffusion takes on the position-dependent form

$$K(x) = K \exp\left\{\frac{\sqrt{v^2 + 4\kappa D}}{D}x\right\} \quad (38)$$

To obtain relations for the permeability and lag time in convective-reactive diffusion, we compare the time development of the total diffusant released into the receiver in the long-time limit for a ρ diffusant, $Q^{(\rho)}(t)$, with that of an f diffusant, $Q^{(f)}(t)$. This yields

$$Q^{(\rho)}(t) = \int_0^t J^{(\rho)}(h,\tau) d\tau = \int_0^t \left\{-D \frac{\partial}{\partial x} \rho(x,\tau) + v\rho(x,\tau)\right\}_{x=h} d\tau = \int_0^t \left\{-D \frac{\partial}{\partial x} \rho(x,\tau)\right\}_{x=h} d\tau \quad (39)$$

where the boundary condition (4) is used and $J^{(\rho)}(x,t)$ denotes the diffusion flux (at location x and time t). Substitution of eq 21 into eq 39, with the help of eq 36, yields then

$$Q^{(\rho)}(t) = \int_0^t \left\{-g(x)D \frac{\partial}{\partial x} f(x,\tau)\right\}_{x=h} d\tau = \exp\left\{\frac{v - \sqrt{v^2 + 4\kappa D}}{2D}h\right\} \int_0^t \left\{-D \frac{\partial}{\partial x} f(x,\tau)\right\}_{x=h} d\tau = \exp\left\{\frac{v - \sqrt{v^2 + 4\kappa D}}{2D}h\right\} Q^{(f)} \quad (40)$$

This simple proportionality relationship between $Q^{(\rho)}(t)$ and $Q^{(f)}(t)$ holds for any $t > 0$. Specifically, in the long-time limit, we have

$$\lim_{t \rightarrow \infty} Q^{(\rho)}(t) = \rho_0 P^{(\rho)}(t - L^{(\rho)}) = \exp\left(\frac{v - \sqrt{v^2 + 4\kappa D}}{2D}h\right) \lim_{t \rightarrow \infty} Q^{(f)}(t) = \rho_0 \exp\left(\frac{v - \sqrt{v^2 + 4\kappa D}}{2D}h\right) P^{(f)}(t - L^{(f)}) \quad (41)$$

which indicates that

$$P^{(\rho)} = \exp\left(\frac{v - \sqrt{v^2 + 4\kappa D}}{2D}h\right) P^{(f)} \quad (42)$$

$$L^{(\rho)} = L^{(f)} \quad (43)$$

Expressions for the permeability and lag time in heterogeneous diffusion, in which both the diffusivity and partition coefficient are position dependent, have been derived previously.^{14,15,18} For constant diffusivity the expressions are

$$P = \left\{ \int_0^h \frac{1}{DK(x)} dx \right\}^{-1} \quad (44)$$

$$L = \left\{ \int_0^h \frac{1}{DK(x)} dx \right\}^{-1} \int_0^h K(x) \times \left\{ \int_0^x \frac{1}{DK(x')} dx' \int_x^h \frac{1}{DK(x')} dx \right\} dx \quad (45)$$

On substitution of eq 38 for $K(x)$ into eqs 44 and 45 one obtains for the permeability for the f diffusant and lag time for the f and ρ diffusants

$$P^{(f)} = K\sqrt{v^2 - 4\kappa D} \left\{ 1 - \exp\left(-\frac{\sqrt{v^2 - 4\kappa D}}{D}h\right) \right\}^{-1} \quad (46)$$

$$L^{(f)} = L^{(\rho)} = \frac{h^2}{6D} \left\{ 3 \left[\frac{\coth\left(\sqrt{\left(\frac{v}{2D}\right)^2 + \frac{\kappa}{D}h}\right)}{\left(\sqrt{\left(\frac{v}{2D}\right)^2 + \frac{\kappa}{D}h}\right)} - \frac{1}{\left(\sqrt{\left(\frac{v}{2D}\right)^2 + \frac{\kappa}{D}h}\right)^2} \right] \right\} \quad (47)$$

Substitution of eq 46 into eq 42 results then in

$$P^{(\rho)} = \exp\left(\frac{v - \sqrt{v^2 - 4\kappa D}}{2D}h\right) K\sqrt{v^2 - 4\kappa D} \times \left\{ 1 - \exp\left(-\frac{\sqrt{v^2 - 4\kappa D}}{D}h\right) \right\}^{-1} = \frac{DK}{h} \left\{ \exp\left(\frac{v}{2D}h\right) \left(\sqrt{\left(\frac{v}{2D}\right)^2 + \frac{\kappa}{D}h}\right) \operatorname{csch}\left(\sqrt{\left(\frac{v}{2D}\right)^2 + \frac{\kappa}{D}h}\right) \right\} \quad (48)$$

As expected, P and L obtained through the change of variables are identical to those resulting from Laplace transform, eq 20.

Discussion

The system dealt with above represents a prototype interplay between convection, reaction, and diffusion processes, of which convective diffusion, reactive diffusion, and simple diffusion systems are special cases. Hence, P and L for each subsystem should be derivable from our general expressions. For reactive diffusion, with $v = 0$ eqs 48 and 47 respectively give

$$P = \frac{DK}{h} \{\sqrt{\kappa/D}h \operatorname{csch}(\sqrt{\kappa/D}h)\} \quad (49)$$

$$L = \frac{h^2}{6D} \left\{ 3 \left[\frac{\coth(\sqrt{\kappa/D}h)}{(\sqrt{\kappa/D}h)} - \frac{1}{(\sqrt{\kappa/D}h)^2} \right] \right\} \quad (50)$$

Equation 50 was derived earlier by Leypoldt and Gough²⁵ using a finite Fourier transform.

For convective diffusion, we chose, for comparison, an iontophoresis (electrodifusion) system, in which a constant external

electrical field E is applied to enhance the permeability for ions. The convection velocity in this case is

$$v = DZFE/RT \quad (51)$$

where Z is the valence of the ions, F the Faraday constant, R the universal gas constant, and T the absolute temperature. Substitution of eq 51 into eqs 48 and 47 with $\kappa = 0$ results in the solution obtained by Keister and Kasting:²⁶

$$P = \frac{DK}{h} \left\{ \sqrt{\frac{ZFE}{2RT}} h \operatorname{csch} \left(\frac{ZFE}{2RT} h \right) \right\} \quad (52)$$

$$L = \frac{h^2}{6D} \left\{ 3 \left[\frac{\coth \left(\frac{ZFE}{2RT} h \right)}{\left(\frac{ZFE}{2RT} h \right)} - \frac{1}{\left(\frac{ZFE}{2RT} h \right)^2} \right] \right\} \quad (53)$$

With respect to simple diffusion, which corresponds to $v = 0$ and $\kappa = 0$, both eqs 47 and 48 yield indeterminate forms of $0/0$. This difficulty, however, can be removed by applying the following series expansion:²⁸

$$x \operatorname{csch} x = 1 - \frac{x}{6} + \frac{7x^3}{360} - \dots \quad (54)$$

$$x \coth x = 1 + \frac{x^2}{3} - \frac{x^4}{45} + \dots \quad (55)$$

with

$$x = \sqrt{\left(\frac{v}{2D} \right)^2 + \frac{\kappa}{D} h} \quad (56)$$

Substitution of eq 54 into eq 48 and eq 55 into eq 47, respectively, and taking the limit $x \rightarrow 0$, the well-known expressions $P = KD/h$ and $L = h^2/6D$ are recovered.

As revealed by eq 47, L is symmetric with respect to the direction (or the sign) of the convection velocity v and is independent of the partition coefficient K . The reciprocity of the lag time in a general convective-reactive diffusion has been proved mathematically in terms of the symmetry of the related Green's function with respect to the exchange of coordinate variables.²⁹ On the other hand, according to eq 48, P is proportional to K and dissymmetric with respect to the direction of v . Thus the permeabilities for forward and reverse direction, $P^{(+)}$ and $P^{(-)}$ can be related as

$$\ln (P^{(+)} / P^{(-)}) = v h / D \quad (57)$$

which results from eq 48 on altering the sign of v . In the iontophoresis experiment, eq 57 can be transformed with eq 51 to

$$h = \frac{RT}{ZFE} \ln \left(\frac{P^{(+)}}{P^{(-)}} \right) \quad (58)$$

This relation can be used to determine the thickness of the membrane from the measurement of $P^{(+)}$ and $P^{(-)}$.

Siegel³⁰ also used a Laplace transform, though in a different approach, to derive a lag time expression for a diffusion system governed by a linear equation with source terms. He obtained, written in our notation

$$L = - \frac{d}{ds} \left[\frac{s \hat{J}(s)}{J_s} \right]_{s=0} \quad (59)$$

where J_s is the steady-state diffusion flux. With $J_s = \rho_0 P$ and $\hat{J}(s) = s \hat{Q}(s)$, eq 59 is essentially identical to our eq 18.

The expression for lag time in eq 47 also reveals an interesting formal similarity between diffusion lag time and electric polarization. With eq 56, eq 47 can be rewritten to

$$L(y) = \frac{h^2}{6D} \left\{ \frac{3}{y} L(y) \right\} \quad (60)$$

where $L(y)$ is the Langevin function encountered in the theory of induced electric polarization. Though the connection between these two physical entities may be remote, eq 60 is still useful for mnemonic purposes.

In conclusion, we have obtained closed form solutions for the permeability and lag time of a diffusion system with convection and reaction. The Laplace transform and change-of-variables techniques have the advantage over earlier approaches that involve explicitly solving the relevant diffusion equation and manipulating the solution (usually in the form of infinite series) into a closed form. However, there is no guarantee that closed forms for lag time can be extracted from such infinite series solutions.²⁹

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