Early-Time Analysis of Membrane Transport

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Simple formulae are developed for modelling transient diffusion in membranes, including composite laminates. The formulae consist of the lead terms in "early-time" series solutions to the governing differential equations, which converge with fewer terms as time approaches zero. Because the truncated solutions are quite accurate over substantial ranges of time, they facilitate the determination of physical parameters from experimental data.

1. Introduction

When the diffusion coefficient, D, of a permeating species is essentially constant, it and the permeant's solubility may be determined by reconciling experimental data with a solution to the governing differential mass balance, i.e.:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$
(1)

The initial and boundary conditions, which depend on the nature of the experiment, typically conform to the following template:

a)
$$C(x,0) = f_i(x)$$
 $(0 \le x \le L)$
b) $\alpha_0 \frac{\partial C}{\partial x}(0,t) + C(0,t) = \beta_0$ $(t > 0)$
c) $\alpha_L \frac{\partial C}{\partial x}(L,t) + C(L,t) = \beta_L$ $(t > 0)$
(2)

Fitting of parameters to data is facilitated by closed-form solutions to Eq. 1. The latter are derivable when the boundary conditions are linear – i.e., when the α 's and β 's in Eqs. 2a and 2b are constants. In the case of *simple permeation* (α_0 , α_L , β_L , k, $f_i(x) = 0$; $\beta_0 = C_0$), the solution (Crank, 1975) is:

$$\frac{C}{C_0} = 1 - \frac{x}{L} - \frac{2}{\pi} \sum_{n=1}^{\infty} \sin\left(\frac{n\pi x}{L}\right) e^{-n^2 \pi^2 \tau} \qquad \left(\tau \equiv \frac{Dt}{L^2}\right)$$
(3)

It follows that the mass permeated per unit membrane area is:

$$M_{\rm P} = -D \int_0^t \left(\frac{\partial C}{\partial x}\right)_{x=L} dt = C_0 L \left[\tau - \frac{1}{6} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} e^{-n^2 \pi^2 \tau}\right]$$
(4)

Figure 1, in which the solid line is based on Eq. 4, illustrates the distinctive permeation "time lag": an asymptotically straight line relates M_P/C_0L to Dt/L^2 ; according to Eq. 4, the asymptote's intercept, Dt_{lag}/L^2 , is 1/6. Thus, D may be inferred from experimental data by plotting M_P vs. t, locating t_{lag} and equating D with $L^2/\delta t_{lag}$; C_0 follows from the asymptotic (steady-state) slope, DC_0/L .

The considerable convenience afforded by Eq. 4 is undercut when permeation is very slow, because determining t_{lag} then requires very long experiments. Furthermore, using Eq. 4 to acurately calculate M_P at earlier times requires increasing numbers of series terms; the number approaches infinity as time approaches zero. Thus, Eq. 4 may be deemed a "long-time solution" and an "early-time solution" is desirable.

2. Early-Time Permeation Analysis

A particularly useful tool for deriving series solutions that require *fewer* terms to converge as $t \rightarrow 0$ is Laplace transformation defined by the **L** operator as follows:

$$\mathbf{L}\left[f\left(x,t\right)\right] \equiv \int_{0}^{\infty} f\left(x,t\right) e^{-st} dt = \hat{F}\left(x,s\right)$$
(5)

It transforms Eq. 1 and the simple permeation boundary conditions to:



Figure 1: Dimensionless mass permeated *vs*. dimensionless time; simple permeation. Solid line: Eq. 4; broken line: steady-state asymptote; filled symbols: Eq. 4 truncated after lead term in series; unfilled symbols: lead in term in Eq. 10.

$$D\frac{d^{2}\hat{C}}{dx^{2}} = s\hat{C}; \quad \hat{C}(0) = \frac{C_{0}}{s}, \quad \hat{C}(1) = 0$$
(6)

The solution in *s*-space is:

$$\hat{C} = \frac{C_0 \sinh\left[q(L-x)\right]}{\sinh qL} \qquad \left(q \equiv \sqrt{\frac{s}{D}}\right) \tag{7}$$

and so:

$$\hat{\mathbf{M}}_{\mathbf{P}}\left(\mathbf{s}\right) = \frac{2}{qs\left(e^{qL} - e^{-qL}\right)} \tag{8}$$

Derivation of an *early-time* solution requires the following preliminary manipulation:

$$\hat{M}_{P}(s) = \frac{2}{qse^{qL}(1 - e^{-2qL})} = \frac{2e^{-qL}(1 + e^{-2qL} + e^{-4qL} + ...)}{qs}$$
(9)

Inversion now yields the following early-time solution:

$$\frac{M_{\rm P}}{C_0 L_{\rm A}} = 2 \sum_{n=0}^{\infty} \left[2 \sqrt{\frac{\tau}{\pi}} \, \mathrm{e}^{-\frac{(2n+1)^2}{4\tau}} - (2n+1) \mathrm{erfc}\left(\frac{2n+1}{2\sqrt{\tau}}\right) \right] \tag{10}$$

Figure 1 also compares results based on Eq. 4, Eq. 4 truncated after the lead term in its series, and Eq. 10 truncated after the lead term in *its* series. Together, the truncated early and long-time solutions accurately model all stages of permeation.

When external mass transfer resistance is significant, the x = L condition becomes:

$$-D\frac{\partial C}{\partial x}(L,t) = k_{M}C(L,t) \quad \left(\text{in Eq. 2b, } \alpha_{L} = -\frac{D}{k_{M}}, \ \beta_{L} = 0\right)$$
(11)

The long-time solution is then:

$$\frac{M_{\rm P}}{C_0 L} = \frac{B\tau}{1+B} + 2\sum_{m=1}^{\infty} \frac{\left(\lambda_m^2 + B^2\right)\cos\lambda_m}{\lambda_m^2 \left(B + \lambda_m^2 + B^2\right)} \left(1 - e^{-\lambda_m^2 \tau}\right) \left(B \equiv \frac{k_M L}{D}; \lambda_m + B\tan\lambda_m = 0\right) \quad (12)$$



Figure 2: Dimensionless mass permeated vs. dimensionless time; permeation with downstream mass transfer resistance. Solid lines: Eq. 12; darkened symbols: Eq. 13; unfilled symbols: Eq. 12 truncated after the lead term in series. Broken line: $B = \infty$ (Eq. 4); upper curve and symbols: B = 5; middle curve and symbols: B = 1; lower curve and symbols: B = 0.2.

The lead term of the early-time solution is:

$$\frac{M_{\rm P}}{C_0 L} \approx 2 \left\{ 2e^{-\frac{1}{4\tau}} \sqrt{\frac{\tau}{\pi}} - \frac{1+B}{B} \operatorname{erfc}\left(\frac{1}{2\sqrt{\tau}}\right) + \frac{e^{B(1+B\tau)}}{B} \operatorname{erfc}\left(\frac{1}{2\sqrt{\tau}} + B\sqrt{\tau}\right) \right\}$$
(13)

Figure 2 compares results based on Eq. 4, Eq. 12, Eq. 12 truncated after the lead term in its series, and Eq. 13. The truncated early-time series is quite accurate over substantial dimensionless times.

Modelling permeation in *composite* membranes (laminates) is complicated by the need to enforce Eq. 2 separately for each layer. Diffusion of a single species in a composite of membranes A and B, with negligible external mass transfer resistance and constant equilibrium distribution coefficient m, is governed by:

$$\frac{\partial C_{A}}{\partial t} = D_{A} \frac{\partial^{2} C_{A}}{\partial x_{A}^{2}}, \quad -L_{A} \le x_{A} \le 0; \qquad \frac{\partial C_{B}}{\partial t} = D_{B} \frac{\partial^{2} C_{B}}{\partial x_{B}^{2}}, \quad 0 \le x_{B} \le L_{B}$$
(14)

$$C_{A}(x_{A},0) = C_{B}(x_{B},0) = 0; C_{A}(-L_{A},t) = C_{0}; C_{B}(L_{B},t) = 0$$

$$C_{B}(0,t) = mC_{A}(0,t); D_{A}\frac{\partial C_{A}}{\partial x_{A}}(0,t) = D_{B}\frac{\partial C_{B}}{\partial x_{B}}(0,t)$$

$$(15)$$

The Laplace-domain solution is:



Figure 3: Dimensionless mass permeated *vs.* dimensionless time; composite permeation. $L_B/L_A=2$, $D_B/D_A=3.5$. Solids curves: numerical inversion of Eq. 16; squares: Eq. 17. Upper data sets: m = 2; lower data sets: m = 0.5.

$$\frac{\hat{M}_{\rm P}}{C_0 L_{\rm A}} = \frac{m \sqrt{\frac{D_{\rm B}}{D_{\rm A}}} e^{-2q}}{qs \left[\cosh q \sinh \left(\eta q\right) + \frac{m L_{\rm B}}{L_{\rm A}} \sinh q \cosh \left(\eta q\right)\right]} \qquad \left(\eta \equiv \frac{L_{\rm B}}{L_{\rm A}} \sqrt{\frac{D_{\rm A}}{D_{\rm B}}}\right) \tag{16}$$

The lead term in the *early*-time solution is:

$$\frac{M_{\rm P}}{C_0 L_{\rm A}} = \left(\frac{4\sqrt{\rho_{\rm D}}m}{1+\rho_{\rm L}m}\right) \left[2\sqrt{\frac{\tau}{\pi}} e^{-\frac{(1+\eta)^2}{4\tau}} - (1+\eta) \operatorname{erfc}\frac{1+\eta}{2\sqrt{\tau}}\right] \qquad \left(\tau \equiv \frac{D_{\rm A}t}{L_{\rm A}^2}\right) \tag{17}$$

Figure 3 compares results based on Eq. 17 and on exact *numerical* inversion of Eq. 16 (Scientist^R, Micromath). The early-time solution is again accurate up to large values of τ , this is particularly noteworthy because there is no simple long-time solution.

Early-Time Sorption Analysis

Finally, to illustrate the versatility of the early-time approach, we consider simple sorption governed by Eq. 1, subject to:

$$C(x,0) = 0; C(0,t) = C(L,t) = C_0 \quad (in \text{ Eqs. } 2, \alpha_0 = \alpha_L = 0, \ \beta_0 = \beta_L = C_0)$$
(17)



Figure 4: Dimensionless mass uptake *vs.* dimensionless time in simple sorption. Solid line: Eq. 18; shaded squares: first term in Eq. 19; blackened boxes: Eq. 18 truncated after the lead term in the series.

The long-time solution is:

$$\frac{M}{M_{\infty}} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{e^{-(2n+1)^2 \pi^2 \tau}}{(2n+1)^2} \qquad \left[M \equiv D \int_0^t \left(\frac{\partial C}{\partial x} \right)_{x=0} dt, \ M_{\infty} = \lim_{t \to \infty} M \right]$$
(18)

The early-time solution is:

$$\frac{M}{M_{\infty}} = \frac{2\sqrt{\tau}}{\Gamma(1.5)} + 4\sum_{n=1}^{\infty} (-1)^n \left(2\sqrt{\frac{\tau}{\pi}} e^{-\frac{n^2}{4\tau}} - n \operatorname{erfc}\frac{n}{2\sqrt{\tau}}\right) \quad (\Gamma = \text{the Gamma function}) \quad (19)$$

Figure 4 compares results based on Eq. 18, Eq. 18 truncated after the lead term in its series, and simply the first term in Eq. 19 (in light of that term, the abscissa was fixed as the square root of τ). As with permeation, the truncated early and long-time solutions suffice to accurately model all stages of sorption.

Reference

Crank, J., 1975, The Mathematics of Diffusion, Oxford University Press, Oxford.