Analysis of Transient Permeation in Composites with External Mass Transfer Resistance

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Introduction

Fitting membrane transport parameters to experimental permeation data (Fig. 1) often relies on solutions to "Fick's 2nd Law," i.e.:

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

Thus, Daynes (1920) solved Eq. 1 subject to:

$C(x,0)=0\ (0\le x\le L);\ C(0,t)=C_0;\ C(L,t)=0$

via *Separation of Variables, obtaining:*

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

Insertion of Eq. 2 into the expression for the mass permeated,

$$M(t)\equiv -D\int_0^t\frac{\partial C}{\partial x}(L,t)dt \text{ yielding the following result:} \qquad (3)$$

$$m=\tau-\frac{1}{6}-\frac{2}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n e^{-n^2\pi^2\tau}}{n^2} \quad (4) \quad \left[m\equiv\frac{M}{C_0L}=-\int_0^{\tau}\frac{\partial c}{\partial y}(1,\tau)d\tau \quad (5)\right]$$

It follows from Eq. 4 that a permeant's diffusion coefficient (D) may be deduced from the "time lag" (t_{Lag}) – which is formally defined as the t-axis intercept of the steady-state asymptote in a plot of mass permeated (M) vs. time (Fig. 2).

$$\text{Since } \lim_{t\to\infty} M=C_0L\left(\frac{Dt}{L^2}-\frac{1}{6}\right);\ \text{it follows that:}\quad D=\frac{L^2}{6t_{lag}} \qquad (6)$$

Needless to say, the theoretical analysis can be considerably more challenging, e.g., when there are significant external mass transfer effects or the membrane is a composite of different material laminates.

In such cases, as shown below, Laplace transformation (Churchill, 1944) is often a more straightforward and practical approach than *Separation of Variables.* *The lead terms in infinite series solutions obtained via Laplace transformation, often suffice to accurately model, not only the initial transient region, but even into the steady-state .*

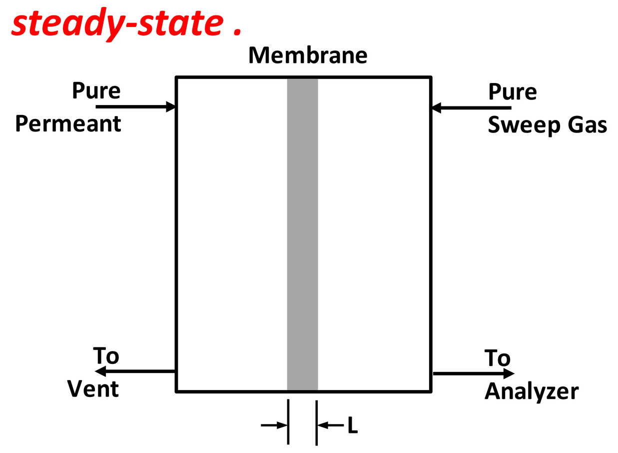

Fig. 1: Schematic diagram of the gas permeation apparatus. When the sweep gas flow is sufficiently high, the concentration gradient in the boundary layer at the downstream membrane surface will be negligible – i.e., *for mathematical modeling purposes*, the concentration at the surface may be set equal to zero.

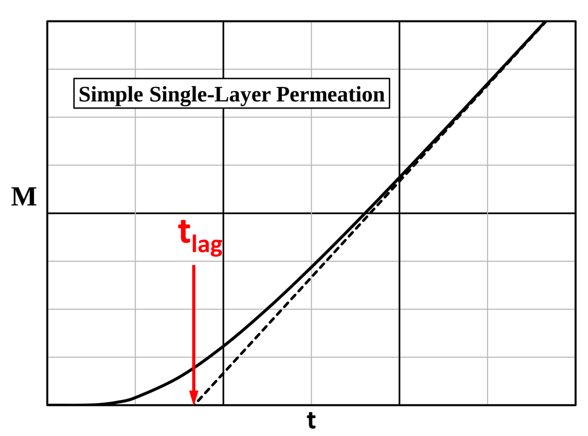

Fig. 2: Solid line: Cumulative mass permeated (M) vs. time (t). Broken line: Steady-state asymptote.

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Laplace Transformation

The Laplace operator, L, is defined as follows:

$$L[g(t)]=\int_0^{\infty}e^{-st}g(t)dt=\hat{g}(s) \qquad (7)$$

Operation on non-dimensionalized Eq. 1 and the simple permeation boundary conditions yields

$$\frac{d^2\hat{c}}{dy^2}=s\hat{c}\qquad \hat{c}(0)=\frac{1}{s},\ \hat{c}(1)=0, \text{ the solution to which is:} \qquad (8)$$

$$\hat{c}=\frac{\sinh[q(1-y)]}{s\cdot\sinh(q)}\qquad (q\equiv\sqrt{s}) \qquad (9)$$

It follows that:

$$\hat{m}=\left(-\frac{1}{s}\frac{d\hat{c}}{dy}\bigg|_{y=1}\right)=\frac{1}{qs\cdot\sinh(q)} \qquad (10)$$

Rather than seek m(τ) via rigorous inverse transformation of Eq. 10, it pays to first manipulate it, as follows, into an equivalent expression whose inversion is straightforward:

$$\hat{m}=\frac{1}{qs\cdot\sinh(q)}=\frac{2}{qs(e^{q}-e^{-q})}=\frac{2}{qse^{q}(1-e^{-2q})}=\frac{2e^{-q}}{qs(1-e^{-2q})}$$
$$=\frac{2e^{-q}(1+e^{-2q}+e^{-4q}+...)}{qs}=\frac{2(e^{-q}+e^{-3q}+e^{-5q}+...)}{qs} \qquad (11)$$

Widely available [ĝ(s),g(τ)] tables (e.g., Myers, 1998) include the following entry:

$$L^{-1}\left(\frac{e^{-aq}}{qs}\right)=2\sqrt{\frac{\tau}{\pi}}e^{-a^2/4\tau}-a\cdot\operatorname{erfc}\left(\frac{a}{2\sqrt{\tau}}\right) \qquad (12)$$

$$\text{Thus, } m=2\sum_{n=0}^{\infty}\left[2\sqrt{\frac{\tau}{\pi}}e^{-(2n+1)^2/4\tau}-(2n+1)\operatorname{erfc}\left(\frac{2n+1}{2\sqrt{\tau}}\right)\right] \qquad (13)$$

The solid curve in Fig. 3 is based on the exact solution, i.e., either infinite series, Eq. 4 or 13. The symbols denote m values calculated from the lead terms, to which the respective infinite series reduce at *long* and *short* times (τ→∞ and τ→0), i.e.:

$$m_{Long}=\tau-\frac{1}{6}+\frac{2e^{-\pi^2\tau}}{\pi^2} \qquad (14)$$

$$m_{Short}=2\left[2\sqrt{\frac{\tau}{\pi}}e^{-1/4\tau}-\operatorname{erfc}\left(\frac{1}{2\sqrt{\tau}}\right)\right] \qquad (15)$$

Notably, the respective lead terms in the two infinite series solutions together suffice to accurately calculate the complete time dependence of the mass permeated.

This begs the question of whether this also applies to the analysis of more complex permeation scenarios.

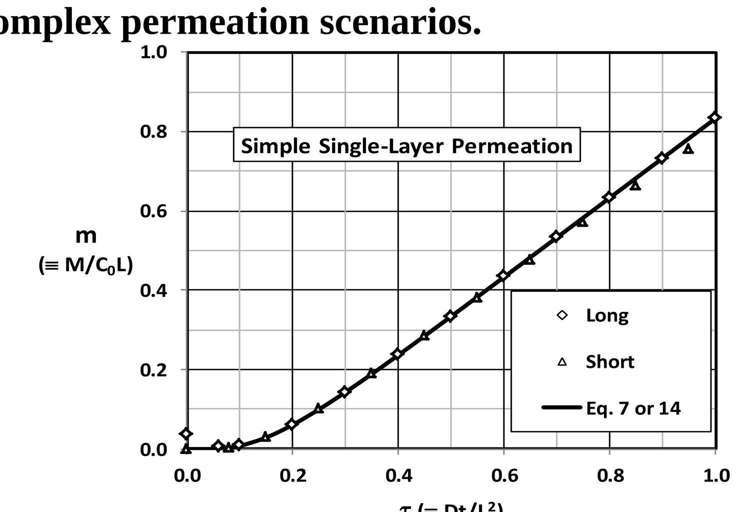

Fig. 3: Mass permeated *vs.* time (in dimensionless terms). Solid curve: either infinite series solution to Eq. 1; diamonds: Eq. 15; triangles: Eq. 16.

Permeation with downstream mass transfer resistance

Referring again to Fig. 1, a finite sweep gas flowrate implies nonzero permeant concentrations at the downstream membrane surface; which require the following more generally applicable boundary condition:

$$\frac{\partial C}{\partial x}\bigg|_{x=L}=-\left(\frac{k}{D}\right)C_{x=L} \qquad (16) \qquad \text{or, in dimensionless terms:}$$

$$\frac{\partial c}{\partial y}\bigg|_{y=1}=-Bc_{y=1}\quad\left(B\equiv\frac{kL}{D}\right) \qquad (17)$$

(k is the downstream gas-phase mass transfer coefficient; B is the mass transfer Biot number)

The Separation of Variables-based solution to Eq. 1 now gives:

$$m=\frac{B\tau}{1+B}-2\sum_{n=1}^{\infty}\frac{B\sqrt{\lambda_n^2+B^2}\left(1-e^{-\lambda_n^2\tau}\right)}{\lambda_n^2\left(B+\lambda_n^2+B^2\right)} \qquad (18)$$

where the eigenvalues, λ_n, are defined by: $\lambda_n+B\tan\lambda_n=0$ (19)

The lead expression in Eq. 19, i.e., the long-time solution, is:

$$m_{Long}=\frac{B\tau}{1+B}-\frac{2B\sqrt{\lambda_1^2+B^2}\left(1-e^{-\lambda_1^2\tau}\right)}{\lambda_1^2\left(B+\lambda_1^2+B^2\right)} \qquad (20)$$

In the corresponding Laplace transformation-based solution, the transform of the dimensionless mass permeated becomes:

$$\hat{m}=\frac{B}{qs[q\cosh(q)+B\sinh(q)]} \qquad (21)$$

Manipulation analogous to what led from Eq. 10 to Eq. 11, leads Eq. 20 to assume the following more convenient form:

$$\hat{m}=\frac{2Be^{-q}\left[1-\left(\frac{q-B}{q+B}\right)e^{-2q}+\left(\frac{q-B}{q+B}\right)^2e^{-4q}-...+...\right]}{qs(q+B)} \qquad (22)$$

The truncated short-time solution, via inversion o f $\hat{m}\approx\frac{2Be^{-q}}{qs(q+B)}$:

$$m_{Short}=2\left[2e^{-1/4\tau}\sqrt{\frac{\tau}{\pi}}-\frac{1+B}{B}\operatorname{erfc}\left(\frac{0.5}{\sqrt{\tau}}\right)+\frac{e^{B(1+B\tau)}}{B}\operatorname{erfc}\left(\frac{0.5}{\sqrt{\tau}}+B\sqrt{\tau}\right)\right] \qquad (23)$$

Fig. 4 compares values of the mass permeated vs. time (in dimensionless terms, for five different B values), based on Eqs. 18, 20 and 23, respectively).

The long and short-time solutions closely approximate the exact solution. Notably, the high-accuracy range of the short-time approximation extends into the steady-state.

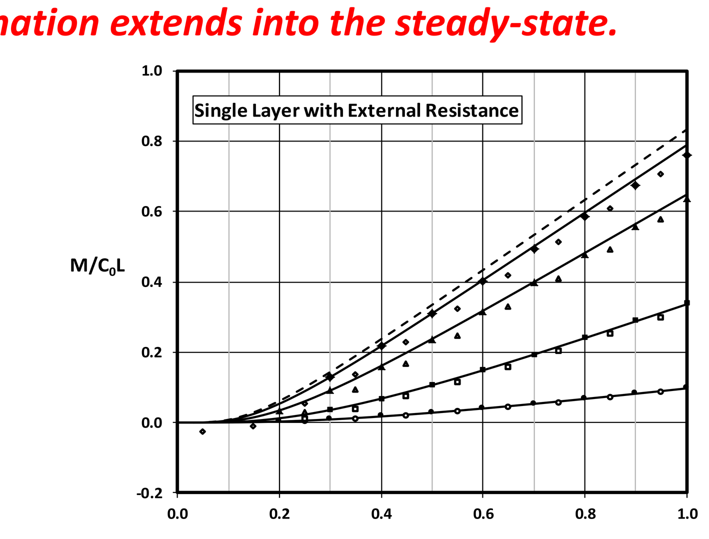

Fig. 4: Mass permeated vs. time (dimensionless terms); B = infinity (broken line), 25 (diamonds), 5 (triangles), 1 (squares), 0.2 (circles). Solid lines: exact solution (Eq. 18); unfilled symbols: Eq. 20; filled symbols: Eq. 23.

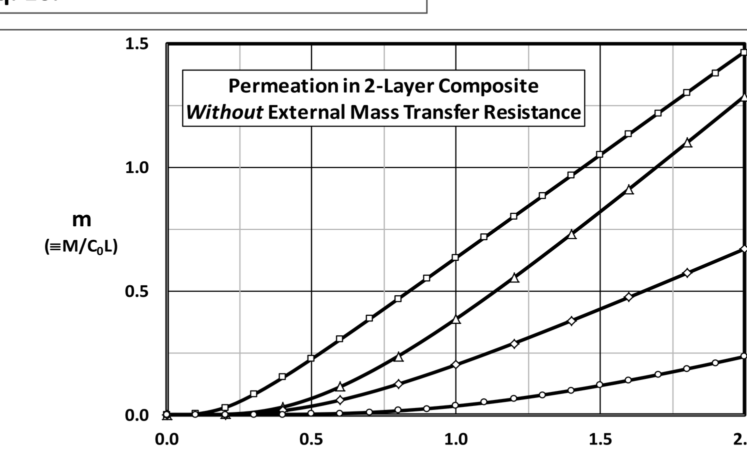

Fig. 6: Mass permeated vs. time (dimensionless terms); κ = 1, ρ = 1 ω = 1 (brown circles), κ = 0.5 ρ = 2 ω = 0.5 (green squares), κ = 2 ρ = 0.5 ω = 2 (red triangles), κ = 5 ρ = 1 ω = 2 (gray diamonds). (Solid lines: exact solution (Eq. 34); filled symbols: Eq. 35.

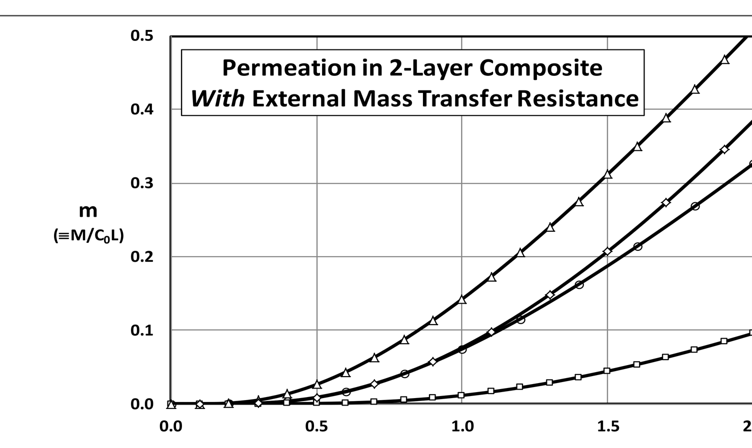

Fig. 7: Mass permeated vs. time (dimensionless terms); κ = 5 ρ = 0.2 ω = 0.2 (red triangles), κ = 5 ρ = 0.2 ω = 5 (gray diamonds). Solid lines: exact solution (Eq. 34); filled symbols: Eq. 35.

Permeation in Laminated Composite Membranes

Transient diffusion in the composite membrane in Fig. 5 is assumed to be governed by Eq. 1 as follows:

$$\frac{\partial C_j}{\partial t}=D_j\frac{\partial^2 C_j}{\partial x_j^2}\quad (j=1,2) \qquad (24)$$

$C_1(-L_1,t)=C^*,\ C_2(L_2,t)=0$

$C_2(0,t)=KC_1(0,t),\ D_1\frac{\partial C_1}{\partial x_1}(0,t)=D_2\frac{\partial C_2}{\partial x_2}(0,t)$

Or in dimensionless terms

$$\frac{\partial^2 c_1}{\partial y_1^2}=\frac{\partial c_1}{\partial \tau} \qquad (25)$$
$$\frac{\partial^2 c_2}{\partial y_2^2}=\gamma^2\frac{\partial c_2}{\partial \tau}$$

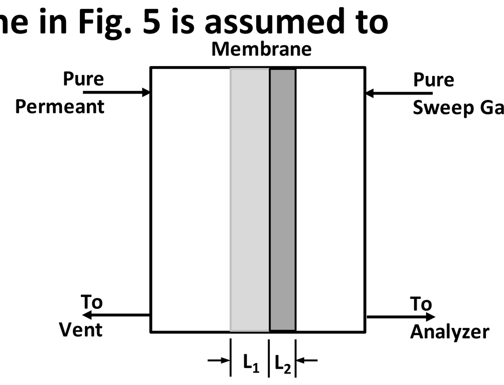

Fig. 5: Schematic diagram of gas permeation apparatus with two-layer composite membrane.

$c_1(y_1,0)=c_2(y_2,0)=0;\ c_1(0,\tau)=1,\ \frac{\partial c_2}{\partial y_2}(1,\tau)=-Bc_2(1,\tau)$

$c_1(0,\tau)=c_2(0,\tau),\ \frac{\partial c_1}{\partial y_1}(0,\tau)=\beta\frac{\partial c_2}{\partial y_2}(0,\tau)$

$$\left(c_1\equiv\frac{C_1}{C^*},\ c_2\equiv\frac{C_2}{KC^*},\ \tau\equiv\frac{D_1t}{L_1^2},\ y_j\equiv\frac{x_j}{L_j},\ \gamma\equiv\frac{L_2}{L_1}\sqrt{\frac{D_1}{D_2}},\ \beta\equiv\frac{KD_2L_1}{D_1L_2},\ B\equiv\frac{kL_2}{D_2}\right)$$

The physical behavior is characterized by four dimensionless groups: K, L_2/L_1, D_2/D_1 and B(≡kL_2/D_1). We first consider cases of negligible external transport resistance [B→∞, $c_2(1,\tau)=0$].

For K = 1, solutions based on Separation of Variables to the analogous heat conduction problem, are applicable (Sakai, 1922). That of Carslaw and Jaeger (2011) yields the following result:

$$m\left(\equiv\frac{M}{C^*L_1}\right)=\frac{\beta\tau}{\beta+1}-2\beta\gamma\sum_{n=1}^{\infty}\frac{1-e^{-\lambda_n^2\tau}}{\lambda_n^2\left[(1+\beta\gamma^2)\sin(\lambda_n)\sin(\gamma\lambda_n)-\gamma(\beta+1)\cos(\lambda_n)\cos(\gamma\lambda_n)\right]} \qquad (26)$$

where the eigenvalues, λ_n, consist of:

(a) the roots of: $\cot(\lambda_n)+\beta\gamma\cot(\gamma\lambda_n)=0$ (27)

and (b) the common roots of: $\sin(\lambda_n)=0$ and $\sin(\gamma\lambda_n)=0$ (28)

The corresponding exact Laplace-domain expression is:

$$\hat{m}=\frac{2\gamma\beta}{qs\{(1+\beta\gamma)\sinh[q(\gamma+1)]+(1-\beta\gamma)\sinh[q(\gamma-1)]\}} \qquad (29)$$

When Eq. 29 is manipulated as Eqs. 10 and 21 had been, the inverse of the resulting Laplace-domain approximation is as follows:

$$m_{Short}=\frac{4\gamma\beta}{(1+\beta\gamma)}\cdot\left\{2\sqrt{\frac{\tau}{\pi}}\left[e^{-\frac{(\gamma+1)^2}{4\tau}}+e^{-\frac{9(\gamma+1)^2}{4\tau}}\right]-(\gamma+1)\operatorname{erfc}\left(\frac{\gamma+1}{2\sqrt{\tau}}\right)\right.$$
$$-3(\gamma+1)\operatorname{erfc}\left[\frac{3(\gamma+1)}{2\sqrt{\tau}}\right]+\left[\frac{1-\beta\gamma}{1+\beta\gamma}\right]\cdot\left[2\sqrt{\frac{\tau}{\pi}}\left(e^{-\frac{(3\gamma+1)^2}{4\tau}}-e^{-\frac{(\gamma+3)^2}{4\tau}}\right)\right. \qquad (30)$$
$$\left.\left.+(\gamma+3)\operatorname{erfc}\left(\frac{\gamma+3}{2\sqrt{\tau}}\right)-(3\gamma+1)\operatorname{erfc}\left(\frac{3\gamma+1}{2\sqrt{\tau}}\right)\right]\right\}$$

For the more general case of nonzero B (significant external mass transfer resistance), apparently no closed-form extension of Eq. 26 is available. The exact Laplace-domain expression for the mass permeated is:

$$\hat{m}=\frac{\kappa Be^{-q}}{qs}\{\sinh\rho q+e^{-q}\sinh q(\kappa\cosh\rho q-\sinh\rho q)$$
$$\omega q[\cosh\rho q(1-e^{-q}\sinh q)+\kappa e^{-q}\sinh\rho q\sinh q]\}^{-1} \qquad (31)$$

$$\left(\kappa=K\sqrt{\frac{D_2}{D_1}},\ \rho=\sqrt{\frac{D_1}{D_2}}\frac{L_2}{L_1},\ \omega=\frac{\sqrt{D_1D_2}}{kL_1}\right)$$

The corresponding manipulated expression is:

$$\hat{m}_{Short}=\left[\frac{4\kappa Be^{-q(1+\rho)}}{qs(\kappa+1)(1+\omega q)}\right]\cdot\left[1-\frac{(\kappa-1)(1-\omega q)e^{-2\rho q}}{(\kappa+1)(1+\omega q)}+\left(\frac{1-\omega q}{1+\omega q}\right)e^{-2(1+\rho)q}+\left(\frac{\kappa-1}{\kappa+1}\right)e^{-2q}\right] \qquad (32)$$