Analysis of Transient Permeation and Conduction in Composites with External Transport Resistance

Jerry H. Meldon [a,*], Phong A. Tran [b]

[a]Chemical and Biological Engineering Department, Tufts University, Medford, MA

[b]Chemical Engineering Department, Northeastern University, Boston, MA

Abstract—

Laplace transformation is applied to develop "short-time" solutions to the partial differential equations governing transient diffusive transport in single slabs and multi-layer composites, with and without external transport resistance. The solutions apply the well-known technique of manipulating a Laplace-domain solutions so that the infinite series which emerges in the time domain may be truncated after fewer terms as t → 0. In many cases, the lead terms in the short-time series and the conventional (separation-of-variables-based) "long-time" series together suffice to accurately characterize transport from t = 0 into the steady-state. This is illustrated here for the case of transient membrane permeation.

I. INTRODUCTION

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

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

Thus, Daynes (1920) solved Eq. 1 subject to [2]:

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

via separation of variables, obtaining:

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

Insertion of Eq. 2 into the mass permeated expression, i.e.:

$$M(t)\equiv -D\int_0^t \frac{\partial C}{\partial x}\left(L,\underline{t}\right)d\underline{t} \qquad (3)$$

$$\left[\, m\equiv\frac{M}{C_0L} = -\int_0^t \frac{\partial c}{\partial y}\left(1,\underline{\tau}\right)d\underline{\tau} \,\right] \qquad (4)$$

yields the following result:

$$m(\tau)=\tau-\frac{1}{6}-\frac{2}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n\,e^{-n^2\pi^2\tau}}{n^2} \qquad (5)$$

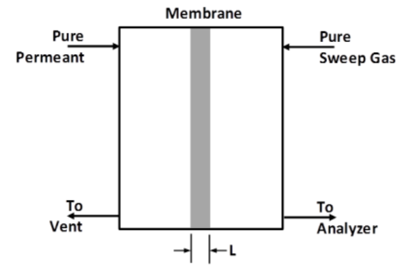

Fig. 1*: Schematic diagram of gas permeation apparatus. When the sweep gas flow is sufficiently high, the concentration gradient in the boundary layer at the downstream membrane surface will be negligible – i.e., for mathematical modeling purposes, the concentration at the downstream surface may be set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

It follows from Eq. 4 that the permeant's diffusion coefficient (D) can be deduced from the "time lag" (t_{Lag}), i.e. the t-axis intercept of the steady-state asymptote in a plot of mass permeated (M) vs. time (Fig. 2). Since $\lim_{\tau\to\infty} m = \tau - 1/6$, it follows that:

$$D = L^2/6t_{lag} \qquad (6)$$

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[3]. The lead terms in series solutions obtained via Laplace transformation, often suffice to accurately model, not only the initial transient period, but even into the steady-state.

* Corresponding Author: Science and Technology Center, Tufts University, 4 Colby Street, Medford, MA 02155; e-mail: Jerry.Meldon@tufts.edu

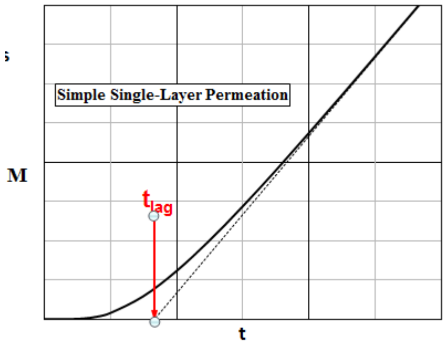

Fig. 2: Solid line: Cumulative mass permeated (M) vs. time (t). Broken line: Steady-state asymptote.

II. Methodology

The Laplace operator, L, is defined as follows:

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

Operation on non-dimensionalized Eq. 1 $\left(\partial c/\partial\tau = \partial^2 c/\partial y^2\right)$ and on the simple permeation boundary conditions yields:

$$\frac{d^2\hat{c}}{dy^2} = s\hat{c},\ \hat{c}(0) = \frac{1}{s},\ \hat{c}(1) = 0 \tag{8}$$

the solution to which is:

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

It follows that:

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

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

$$\hat{m} = \frac{1}{qs\cdot\sinh(q)} = \frac{2}{qs\left(e^{q}-e^{-q}\right)} = \frac{2e^{-q}}{qs\left(1-e^{-2q}\right)}$$
$$= \frac{2e^{-q}\left(1+e^{-2q}+e^{-4q}+\ldots\right)}{qs} = \frac{2\left(e^{-q}+e^{-3q}+e^{-5q}+\ldots\right)}{qs} \tag{11}$$

Widely available [ĝ(s),g(t)] tables (e.g., Myers, 1998) include the following entry[4]:

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

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

The solid curve in Fig. 3 is based on the exact solution, i.e., *either* series, Eq. 5 or 13. The symbols denote *m* values calculated from the lead terms, to which the respective infinite series reduce at long and short times (t →∞ and t→0), i.e.:

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

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

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

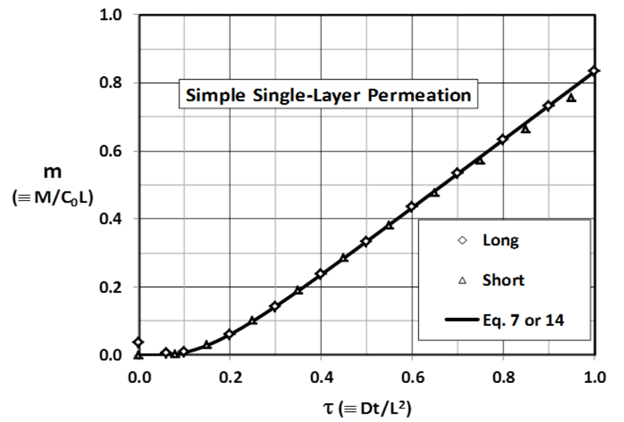

Fig. 3: Mass permeated vs. time (dimensionless terms). Solid curve: Eq. 5 or Eq. 13; diamonds: Eq. 15; triangles: Eq. 16.

III. Applications

A. *Permeation in a single layer 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:

$$\frac{\partial C}{\partial x}\bigg|_{x=L} = -\left(\frac{k}{D}\right)C_{x=L} \tag{16}$$

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

where *k* is the downstream gas-phase mass transfer coefficient and *B* is the mass transfer Biot number.

The separation of variables solution to Eq. 1 now gives:

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

where the eigenvalues, λ_n, are defined by:

$$\lambda_n + \mathrm{B}\tan\lambda_n = 0 \tag{19}$$

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

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

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

$$\hat{m} = \frac{\mathrm{B}}{qs\left[q\cosh(q) + \mathrm{B}\sinh(q)\right]} \tag{21}$$

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

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

The short-time solution, obtained by inverting the lead terms,

$$\hat{m} \approx \frac{2Be^{-q}}{qs(q+\mathrm{B})} \tag{23}$$

is:

$$m_{Short} = 2\left[2e^{-1/4\tau}\sqrt{\frac{\tau}{\pi}} - \frac{1+\mathrm{B}}{\mathrm{B}}erfc\left(\frac{0.5}{\sqrt{\tau}}\right) + \frac{e^{\mathrm{B}(1+\mathrm{B}\tau)}}{\mathrm{B}}erfc\left(\frac{0.5}{\sqrt{\tau}} + \mathrm{B}\sqrt{\tau}\right)\right] \tag{24}$$

Fig. 4 compares values of mass permeated vs. time (in dimensionless terms) for five different B values, based on Eqs. 18, 20 and 24.

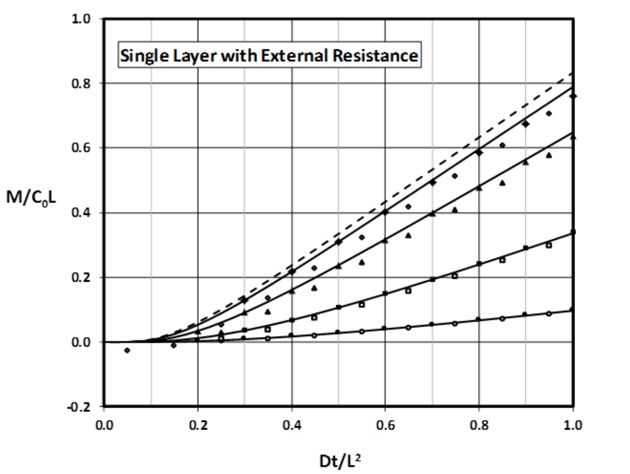

***Fig. 4**: Mass permeated vs. time (dimensionless terms); B =∞ (broken line), 25 (diamonds), 5 (triangles), 1 (squares), 0.2 (circles). Solid lines: exact solution (Eq. 18); unfilled symbols: Eq. 20; filled symbols: Eq. 24.*

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.

B. ***Permeation in a 2-layer composite with downstream resistance***

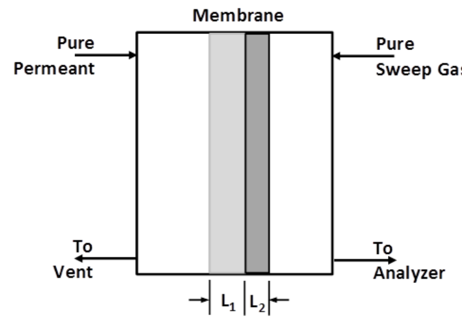

***Fig. 5**: Schematic diagram of gas permeation apparatus with two-layer composite membrane.*

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

$$\frac{\partial C_j}{\partial t} = D_j \frac{\partial^2 C_j}{\partial x_j^{\,2}} \quad (j = 1,2) \tag{25}$$

$$C_1(-L_1, t) = C_0, \; C_2(L_2, t) = 0$$

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

or, in dimensionless terms,

$$\frac{\partial^2 c_1}{\partial y_1^{\,2}} = \frac{\partial c_1}{\partial \tau}, \quad \frac{\partial^2 c_2}{\partial y_2^{\,2}} = \gamma^2\frac{\partial c_2}{\partial \tau} \tag{26}$$

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

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

$$\left[c_1 \equiv \frac{C_1}{C^*}, \; c_2 \equiv \frac{C_2}{KC^*}, \; \tau \equiv \frac{D_1 t}{L_1^{\,2}}, \; y_j \equiv \frac{x_j}{L_j}, \right.$$

$$\left. \gamma \equiv \frac{L_2}{L_1}\sqrt{\frac{D_1}{D_2}}, \; \beta \equiv \frac{K\,D_2\,L_1}{D_1\,L_2}, \; \mathrm{B} \equiv \frac{kL_2}{D_2}\right]$$

We first consider cases of negligible external transport resistance [B→∞, $c_2(1,\tau) = 0$]. For K = 1, solutions to the analogous heat conduction problem based on separation of variables, are applicable (Sakai, 1922)[5]. That of Carslaw and Jaeger (2011) yields the following result[6]:

$$m\left(\equiv \frac{M}{C^* L_1}\right) = \frac{\beta\tau}{\beta+1} - 2\beta\gamma\sum_{n=1}^{\infty} \frac{1 - e^{-\lambda_n^2\tau}}{\lambda_n^2\left[(1+\beta\gamma^2)\sin\lambda_n \sin(\gamma\lambda_n) - \gamma(\beta+1)\cos\lambda_n\cos(\gamma\lambda_n)\right]} \tag{27}$$

where the eigenvalues, λ_n, consist of:

$$\cot\lambda_n + \beta\gamma\cot(\gamma\lambda_n) = 0 \tag{28}$$

plus the common roots of:

$$\sin\lambda_n = 0 \;\; and \;\; \sin(\gamma\lambda_n) = 0 \tag{29}$$

The corresponding exact Laplace-domain expression is:

$$\hat{m} = \frac{2\gamma\beta}{qs\left\{(1+\beta\gamma)\sinh\left[q(\gamma+1)\right]+(1-\beta\gamma)\sinh\left[q(\gamma-1)\right]\right\}} \tag{30}$$

When Eq. 30 is manipulated as Eqs. 10 and 21 had been, the inverse of the truncated result is:

$$\begin{aligned} m_{Short} = \frac{4\gamma\beta}{(1+\beta\gamma)} \Bigg\{ & 2\sqrt{\frac{\tau}{\pi}}\left[e^{-\frac{(\gamma+1)^2}{4\tau}}+e^{-\frac{9(\gamma+1)^2}{4\tau}}\right] \\ & -(\gamma+1)\,erfc\left(\frac{\gamma+1}{2\sqrt{\tau}}\right)-3(\gamma+1)\,erfc\left[\frac{3(\gamma+1)}{2\sqrt{\tau}}\right] \\ & +\left[\frac{1-\beta\gamma}{1+\beta\gamma}\right]\cdot\Bigg[2\sqrt{\frac{\tau}{\pi}}\left(e^{-\frac{(3\gamma+1)^2}{4\tau}}-e^{-\frac{(\gamma+3)^2}{4\tau}}\right) \\ & +(\gamma+3)\,erfc\left(\frac{\gamma+3}{2\sqrt{\tau}}\right)-(3\gamma+1)\,erfc\left(\frac{3\gamma+1}{2\sqrt{\tau}}\right)\Bigg]\Bigg\} \end{aligned} \tag{31}$$

For the more general case of nonzero B (significant external mass transfer resistance), apparently no closed-form extension of Eq. 27 is available. The exact Laplace-domain expression for the mass permeated is:

$$\hat{m} = \frac{\kappa \mathrm{B} e^{-q}}{qs\left\{\begin{aligned}&\sinh\rho q+e^{-q}\sinh q\left(\kappa\cosh\rho q-\sinh\rho q\right)\\&+\omega q\left[\cosh\rho q\left(1-e^{-q}\sinh q\right)+\kappa e^{-q}\sinh\rho q\sinh q\right]\end{aligned}\right\}} \tag{32}$$

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

The corresponding manipulated expression is:

$$\begin{aligned}\hat{m}_{Short} = & \left[\frac{4\kappa\mathrm{B}e^{-q(1+\rho)}}{qs(\kappa+1)(1+\omega q)}\right]\cdot \\ & \left[1-\frac{(\kappa-1)(1-\omega q)e^{-2\rho q}}{(\kappa+1)(1+\omega q)}+\left(\frac{1-\omega q}{1+\omega q}\right)e^{-2(1+\rho)q}+\left(\frac{\kappa-1}{\kappa+1}\right)e^{-2q}\right]\end{aligned} \tag{33}$$

Inversion yields $m_{short}(\tau)$. The result is given in Appendix A.

Fig. 6 and 7 show the overlap of results based on the exact and short-time solutions: Eqs. 27 and 31, without external mass transfer effects; Eqs. 32 (via numerical Laplace inversion) and 33, with such effects.

In the following section, Laplace transformation is applied to derive a short-time solution for permeation in a 3-layer composite.

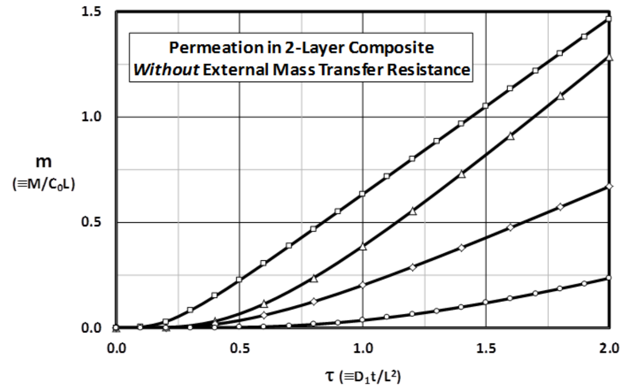

***Fig. 6**: Mass permeated vs. time (dimensionless terms), $B = \infty$, $K = 1$. Solid lines: Exact solution (Eq. 27). Symbols: Short-time solution (Eq. 31); circles: $\beta = 0.5$, $\gamma = 2$; diamonds: $\beta = 1$, $\gamma = 1$; triangles: $\beta = 25$, $\gamma = 1$; squares: $\beta = 5$, $\gamma = 0.2$.*

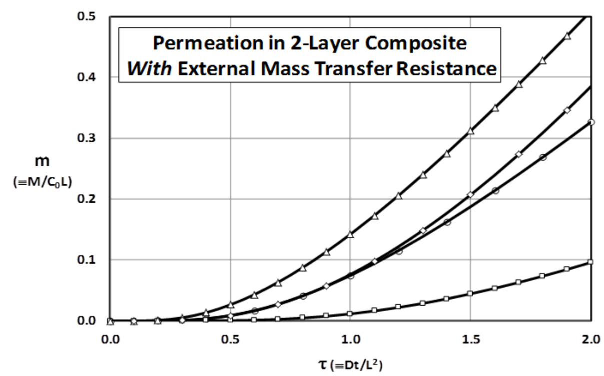

***Fig. 7**: Mass permeated vs. time, $B = 1$. Solid lines: numerical inversion of Eq. 32. Symbols: Short-time solution (Eq. 33); triangles: $\kappa = 2$, $\rho = 0.5$, $\omega = 2$; diamonds: $\kappa = 5$ $\rho = 1$, $\omega = 2$; circles: $\kappa = 1$ $\rho = 1$, $\omega = 1$; squares: $\kappa = 0.5$, $\rho = 2$, $\omega = 0.5$.*

C. *Permeation in a 3-layer composite*

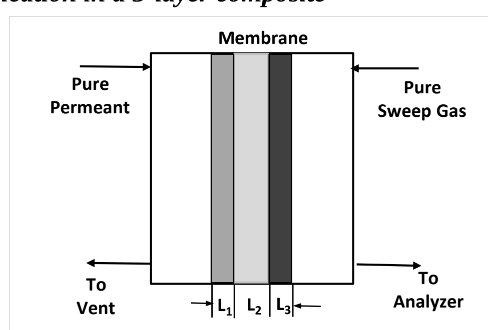

***Fig. 8**: Schematic diagram of gas permeation apparatus with three-layer composite membrane.*

$$\left.\begin{aligned} D_i \frac{\partial^2 C_i}{\partial x_i^2} &= \frac{\partial C_i}{\partial t} \\ C_i\left(x_i, 0\right) &= 0 \end{aligned}\right\} i = 1,2,3 \tag{34}$$

$$C_1\left(L_1, t\right) = \alpha_1 p = C_0,\ C_3\left(L_3, t\right) \approx 0$$

$$C_2\left(0,t\right) = K_{21} C_1\left(0,t\right),\quad C_3\left(0,t\right) = K_{32} C_2\left(L_2,t\right)$$

$$D_1 \frac{\partial C_1}{\partial x_1}\left(0,t\right) = D_2 \frac{\partial C_2}{\partial x_2}\left(0,t\right),\quad D_2 \frac{\partial C_2}{\partial x_2}\left(L_2,t\right) = D_3 \frac{\partial C_3}{\partial x_3}\left(0,t\right)$$

$$\mathrm{c}_1 \equiv \frac{C_1}{C_0},\quad \mathrm{c}_2 = \frac{C_2}{K_{21} C_0},\quad \mathrm{c}_3 = \frac{C_3}{K_{31} C_0},\ K_{21} \equiv \frac{\alpha_2}{\alpha_1},\ K_{32} \equiv \frac{\alpha_3}{\alpha_2}$$

$$\mathrm{y}_1 \equiv \frac{x_1}{L_1},\quad \mathrm{y}_2 \equiv \frac{x_2}{L_2},\ \mathrm{y}_3 \equiv \frac{x_3}{L_3},\ \tau \equiv \frac{D_1 t}{L_1^2}\quad \left(\mathrm{K}_{31} \equiv K_{21} K_{32}\right)$$

$$\frac{\partial^2 \mathrm{c}_1}{\partial y_1^2} = \frac{\partial \mathrm{c}_1}{d\tau},\quad \mathrm{c}_1\left(-1,\tau\right) = 1 \tag{35}$$

$$\frac{\partial^2 c_2}{\partial y_2^2} = \left(\frac{r_{12}}{\lambda_{12}^2}\right)\frac{\partial c_2}{\partial \tau},\quad \frac{\partial^2 c_3}{\partial y_3^2} = \left(\frac{r_{13}}{\lambda_{13}^2}\right)\frac{\partial c_3}{\partial \tau}$$

$$\mathrm{c}_3\left(1,\tau\right) = 0,\ \mathrm{c}_2\left(1,\tau\right) = K_{32}\mathrm{c}_3\left(0,\tau\right)$$

$$\mathrm{c}_1\left(0,\tau\right) = \mathrm{c}_2\left(0,\tau\right),\quad \frac{\partial c_1}{\partial y_1}\left(0,\tau\right) = K_{21}\left(\frac{\lambda_{12}}{r_{12}}\right)\frac{\partial c_2}{\partial y_2}\left(0,\tau\right)$$

$$\frac{\partial c_2}{\partial y_2}\left(1,\tau\right) = K_{32}\left(\frac{\lambda_{23}}{r_{23}}\right)\frac{\partial c_3}{\partial y_3}\left(0,\tau\right)$$

$$\mathrm{r}_{12} \equiv \frac{D_1}{D_2}, \lambda_{12} \equiv \frac{L_1}{L_2}, \mathrm{r}_{13} \equiv \frac{D_1}{D_3}, \lambda_{13} \equiv \frac{L_1}{L_3}, \mathrm{r}_{23} \equiv \frac{D_2}{D_3}, \lambda_{23} \equiv \frac{L_2}{L_3}$$

$$\hat{m} = \frac{\hat{M}}{L_1 C_o} = -\left(\frac{L_1}{D_1}\right)\frac{K_{31} D_3}{s L_3}\left(\frac{\partial c_3}{\partial y_3}\right)_{y_2 = 1} \tag{36}$$

$$\hat{m} = \frac{\alpha_3\sqrt{D_3}}{qs\left\{\begin{aligned} &\alpha_1\sqrt{D_1}\cosh[q]\left(\begin{aligned}&\cosh[\rho_{12}q]\sinh[\rho_{13}q]\\ &+\frac{\alpha_3}{\alpha_2}\frac{\sqrt{D_3}}{\sqrt{D_2}}\sinh[\rho_{12}q]\cosh[\rho_{13}q]\end{aligned}\right)\\ &+\alpha_2\sqrt{D_2}\sinh[q]\left(\begin{aligned}&\sinh[\rho_{12}q]\sinh[\rho_{13}q]\\ &+\frac{\alpha_3}{\alpha_2}\frac{\sqrt{D_3}}{\sqrt{D_2}}\cosh[\rho_{13}q]\cosh[\rho_{12}q]\end{aligned}\right)\end{aligned}\right\}} \tag{37}$$

which is equivalent to the Laplace-domain solution presented by Barrie *et al.* [7].

The manipulated transform and its time-domain inverse are listed in Appendix B.

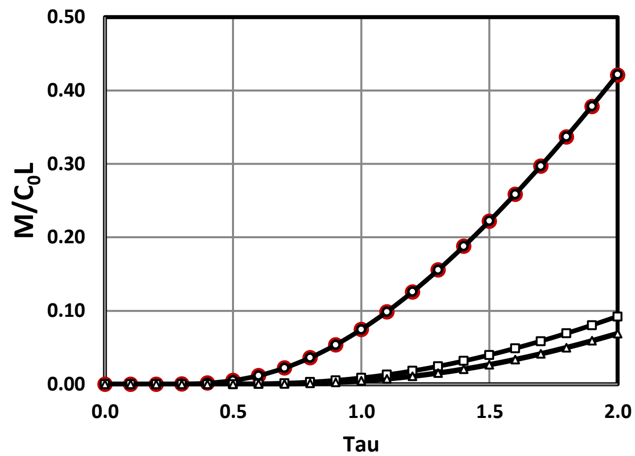

Fig. 9: *Mass permeated vs. time (dimensionless terms), B = 1. Solid lines: Exact solution (numerical inversion of Eq. 37). Symbols: Short-time solution (Appendix B); circles: α_1=1, α_2=α_3=2, D_1=1, D_2 =2, D_3 = 1, L_1 = L_2 =L_3 = 1; squares: α_1=2, α_2=α_3=1, D_1=D_2 =1, D_3 = 3, L_1 = 1, L_2 =2, L_3 = 1; triangles: α_1=2, α_2=α_3=1, D_1=D_2 =1, D_3 = 5, L_1 = 1, L_2 =2, L_3 = 2*

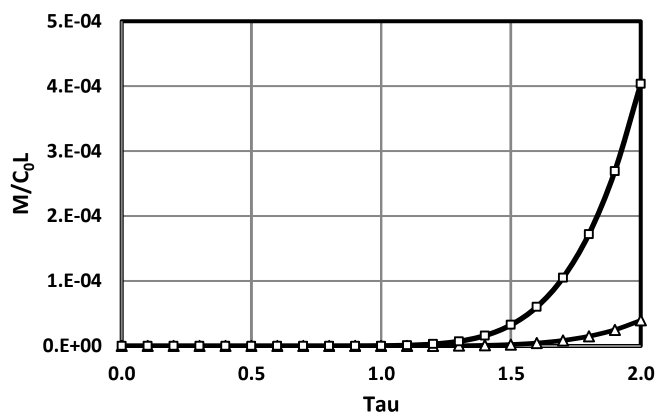

Fig. 10: *Mass permeated vs. time (dimensionless terms), B = 1. Solid lines: Exact solution (numerical inversion of Eq. 37). Symbols: Short-time solution (Appendix B); triangles: α_1=2, α_2=α_3=1, D_1=5, D_2 =D_3 = 1, L_1 =1, L_2 =2, L_3 = 1; squares: α_1=2, α_2=1, α_3=3, D_1=1, D_2 =3, D_3 = 1, L_1 = 1, L_2 =2, L_3 = 5.*

The short-time solution obtained via Laplace transformation again accurately predicts the early course of permeation.

REFERENCES

[1] Crank, J. The Mathematics of Diffusion. Oxford University press, 1979.

[2] Daynes, H. A. "The process of diffusion through a rubber membrane." Proc. Royal Society of London A 97, no. 685, pp. 286-307.(1920).

[3] Churchill, R. V.."Modern Operational Mathematics in Engineering." McGraw-Hill (1944).

[4] Myers, G. E. "Analytical Methods in Conduction Heat Transfer." (1971).

[5] Sakai, S. "Linear conduction of heat through a series of connected rods." Sci. Rep. Tohoku Univ 11 (1922): 351.

[6] Carslaw, H. S., and J. C. Jaeger. "Conduction of Heat in Solids." Oxford: Clarendon Press, 1959, 2nd ed. (1959)

[7] Barrie, J. A., J. D. Levine, A. S. Michaels, and P. Wong. "Diffusion and solution of gases in composite rubber membranes." Transactions of the Faraday Society 59 (1963): 869-878.

APPENDIX A: PERMEATION IN A TWO-LAYER COMPOSITE WITH EXTERNAL MASS TRANSFER RESISTANCE: SHORT-TIME SOLUTION

$$
m_{Short} \approx \frac{4\kappa\mathrm{B}}{[\kappa+1]}\left(\begin{array}{l}
2\sqrt{\frac{\tau}{\pi}}e^{-\frac{(1+\rho)^2}{4\tau}}-(1+\rho+\omega)erfc\left(\frac{1+\rho}{2\sqrt{\tau}}\right)+\omega e^{\frac{1+\rho}{\omega}+\frac{\tau}{\omega^2}}erfc\left(\frac{1+\rho}{2\sqrt{\tau}}+\frac{\sqrt{\tau}}{\omega}\right)\\
+\frac{[\kappa-1]}{[\kappa+1]}\left(2\sqrt{\frac{\tau}{\pi}}e^{-\frac{(3+\rho)^2}{4\tau}}-(3+\rho+\omega)erfc\left(\frac{3+\rho}{2\sqrt{\tau}}\right)+\omega e^{\frac{3+\rho}{\omega}+\frac{\tau}{\omega^2}}erfc\left(\frac{3+\rho}{2\sqrt{\tau}}+\frac{\sqrt{\tau}}{\omega}\right)\right)\\
-\frac{[\kappa-1]}{[\kappa+1]}\left(\begin{array}{l}
-5\omega^2\left(\sqrt{\frac{\tau}{\pi}}e^{-\frac{(3\rho+1)^2}{4\tau}}-\frac{e^{\frac{3\rho+1}{\omega}+\frac{\tau}{\omega^2}}}{\omega}erfc\left(\frac{3\rho+1}{2\sqrt{\tau}}+\frac{\sqrt{\tau}}{\omega}\right)\right)\\
-2\omega\left(-\frac{2}{\omega}\sqrt{\frac{\tau}{\pi}}e^{-\frac{(3\rho+1)^2}{4\tau}}+\left(1+\frac{3\rho+1}{\omega}+\frac{2\tau}{\omega^2}\right)e^{\frac{3\rho+1}{\omega}+\frac{\tau}{\omega^2}}erfc\left(\frac{3\rho+1}{2\sqrt{\tau}}+\frac{\sqrt{\tau}}{\omega}\right)\right)\\
+5\omega^2\sqrt{\frac{\tau}{\pi}}e^{-\frac{(3\rho+1)^2}{4\tau}}-3\omega erfc\left(\frac{3\rho+1}{2\sqrt{\tau}}\right)+2\sqrt{\frac{\tau}{\pi}e^{-\frac{(3\rho+1)^2}{4\tau}}}-(3\rho+1)erfc\left(\frac{3\rho+1}{2\sqrt{\tau}}\right)
\end{array}\right)\\
+\left(\begin{array}{l}
-5\omega^2\left(\sqrt{\frac{\tau}{\pi}}e^{-\frac{9(\rho+1)^2}{4\tau}}-\frac{e^{\frac{3(\rho+1)}{\omega}+\frac{\tau}{\omega^2}}}{\omega}erfc\left(\frac{3(\rho+1)}{2\sqrt{\tau}}+\frac{\sqrt{\tau}}{\omega}\right)\right)\\
-2\omega\left(-\frac{2}{\omega}\sqrt{\frac{\tau}{\pi}}e^{-\frac{9(\rho+1)^2}{4\tau}}+\left(1+\frac{3(\rho+1)}{\omega}+\frac{2\tau}{\omega^2}\right)e^{\frac{3\rho+1}{\omega}+\frac{\tau}{\omega^2}}erfc\left(\frac{3(\rho+1)}{2\sqrt{\tau}}+\frac{\sqrt{\tau}}{\omega}\right)\right)\\
+5\omega^2\sqrt{\frac{\tau}{\pi}}e^{-\frac{9(\rho+1)^2}{4\tau}}-3\omega erfc\left(\frac{3(\rho+1)}{2\sqrt{\tau}}\right)+2\sqrt{\frac{\tau}{\pi}e^{-\frac{9(\rho+1)^2}{4\tau}}}-3(\rho+1)erfc\left(\frac{3(\rho+1)}{2\sqrt{\tau}}\right)
\end{array}\right)
\end{array}\right)
$$

APPENDIX B: PERMEATION IN A 3-LAYER COMPOSITE: LAPLACE-DOMAIN SOLUTION AND SHORT-TIME TIME-DOMAIN SOLUTION

$$\hat{m}=\frac{8\alpha_3\sqrt{D_3}}{sq\left\{\begin{array}{l}\alpha_1\sqrt{D_1}\left(e^{q}+e^{-q}\right)\left(\left(e^{q(\rho_{12}+\rho_{13})}-e^{q(\rho_{12}-\rho_{13})}+e^{q(-\rho_{12}+\rho_{13})}-e^{q(-\rho_{12}-\rho_{13})}\right)+\dfrac{\alpha_3}{\alpha_2}\dfrac{\sqrt{D_3}}{\sqrt{D_2}}\left(e^{q(\rho_{12}+\rho_{13})}-e^{q(-\rho_{12}+\rho_{13})}+e^{q(\rho_{12}-\rho_{13})}-e^{q(-\rho_{12}-\rho_{13})}\right)\right)+\\ \alpha_2\sqrt{D_2}\left(e^{q}-e^{-q}\right)\left(\left(e^{q(\rho_{12}+\rho_{13})}-e^{q(-\rho_{12}+\rho_{13})}-e^{q(\rho_{12}-\rho_{13})}+e^{q(-\rho_{12}-\rho_{13})}\right)+\dfrac{\alpha_3}{\alpha_2}\dfrac{\sqrt{D_3}}{\sqrt{D_2}}\left(e^{q(\rho_{12}+\rho_{13})}+e^{q(-\rho_{12}+\rho_{13})}+e^{q(\rho_{12}-\rho_{13})}+e^{q(-\rho_{12}-\rho_{13})}\right)\right)\end{array}\right\}}$$

$$K_1=\alpha_1\sqrt{D_1},\ \ K_2=\alpha_1\sqrt{D_1}\frac{\alpha_3}{\alpha_2}\frac{\sqrt{D_3}}{\sqrt{D_2}},\ \ K_3=\alpha_2\sqrt{D_2},\ K_4=\alpha_3\sqrt{D_3},\ \ K_5=K_1+K_2+K_3+K_4$$

$$m_{Short}=\frac{8K_4}{sqK_5}\left\{\begin{array}{l}
2\left(\dfrac{\tau}{\pi}\right)^{\frac{1}{2}}e^{\frac{-(\rho_{12}+\rho_{13}+1)^2}{4\tau}}-(\rho_{12}+\rho_{13}+1)erfc\left(\dfrac{\rho_{12}+\rho_{13}+1}{2\sqrt{\tau}}\right)-\\
\left[2\left(\dfrac{\tau}{\pi}\right)^{\frac{1}{2}}e^{\frac{-(\rho_{12}+3\rho_{13}+1)^2}{4\tau}}-(\rho_{12}+3\rho_{13}+1)erfc\left(\dfrac{\rho_{12}+3\rho_{13}+1}{2\sqrt{\tau}}\right)\right]\left[\dfrac{-K_1+K_2-K_3+K_4}{K_5}\right]-\\
\left[2\left(\dfrac{\tau}{\pi}\right)^{\frac{1}{2}}e^{\frac{-(3\rho_{12}+\rho_{13}+1)^2}{4\tau}}-(3\rho_{12}+\rho_{13}+1)erfc\left(\dfrac{3\rho_{12}+\rho_{13}+1}{2\sqrt{\tau}}\right)\right]\left[\dfrac{K_1-K_2-K_3+K_4}{K_5}\right]-\\
\left[2\left(\dfrac{\tau}{\pi}\right)^{\frac{1}{2}}e^{\frac{-(3\rho_{12}+3\rho_{13}+1)^2}{4\tau}}-(3\rho_{12}+3\rho_{13}+1)erfc\left(\dfrac{3\rho_{12}+3\rho_{13}+1}{2\sqrt{\tau}}\right)\right]\left[\dfrac{-K_1-K_2+K_3+K_4}{K_5}\right]-\\
\left[2\left(\dfrac{\tau}{\pi}\right)^{\frac{1}{2}}e^{\frac{-(\rho_{12}+\rho_{13}+3)^2}{4\tau}}-(\rho_{12}+\rho_{13}+3)erfc\left(\dfrac{\rho_{12}+\rho_{13}+3}{2\sqrt{\tau}}\right)\right]\left[\dfrac{K_1+K_2-K_3-K_4}{K_5}\right]-\\
\left[2\left(\dfrac{\tau}{\pi}\right)^{\frac{1}{2}}e^{\frac{-(\rho_{12}+3\rho_{13}+3)^2}{4\tau}}-(\rho_{12}+3\rho_{13}+3)erfc\left(\dfrac{\rho_{12}+3\rho_{13}+3}{2\sqrt{\tau}}\right)\right]\left[\dfrac{-K_1+K_2+K_3-K_4}{K_5}\right]-\\
\left[2\left(\dfrac{\tau}{\pi}\right)^{\frac{1}{2}}e^{\frac{-(3\rho_{12}+\rho_{13}+3)^2}{4\tau}}-(3\rho_{12}+\rho_{13}+3)erfc\left(\dfrac{3\rho_{12}+\rho_{13}+3}{2\sqrt{\tau}}\right)\right]\left[\dfrac{K_1-K_2+K_3-K_4}{K_5}\right]-\\
\left[2\left(\dfrac{\tau}{\pi}\right)^{\frac{1}{2}}e^{\frac{-(3\rho_{12}+3\rho_{13}+3)^2}{4\tau}}-(3\rho_{12}+3\rho_{13}+3)erfc\left(\dfrac{3\rho_{12}+3\rho_{13}+3}{2\sqrt{\tau}}\right)\right]\left[\dfrac{-K_1-K_2-K_3-K_4}{K_5}\right]
\end{array}\right\}$$