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Unsteady Mass Transfer in a Long Composite Cylinder with Interfacial Resistances

A solution is given for unsteady state concentration profiles in an infinitely long composite cylinder resulting from a step-change in concentration in a large reservoir surrounding the cylinder. The composite cylinder consists of an inner cylinder with diffusivity D_1 surrounded by a permeable tube with diffusivity D_2 and has interfacial mass transfer resistances at the cylinder-tube and tube-reservoir interfaces. Numerical values are given for the first eight roots and various coefficients of the solution for physical properties typical of tubular (hollow fiber) membranes. These results can be used in the analysis of data from unsteady state mass transfer experiments to determine the permeability of homogeneous tubular membranes. A simple, approximate method for data analysis is suggested for the rapid estimation of the permeability of both homogeneous and asymmetric (skinned) tubular membranes.

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SCOPE

Although permeability measurements are routinely made for flat membranes, no convenient and accurate method is available at present for making these measurements for small tubular (hollow fiber) membranes. In this paper a method based on an unsteady state diffusion experiment is proposed for measuring the permeability of tubular membranes. The objective of this paper is to present the mathematical analysis which is necessary for the interpretation of the experimental results. A detailed description of the experimental method and experimental data will be presented in a subsequent paper.

Small tubular membranes are finding increasing use in mass transfer devices such as the artificial kidney and are now being considered for novel applications such as reaction vessels for enzyme-catalyzed reactions. A convenient and accurate method for measuring the permeability of these membranes will be useful for modeling membrane behavior, evaluating candidate membranes for specific applications, optimizing membrane composition and processing conditions, and maintaining quality control during manufacturing. The analysis presented here can easily be applied to the analogous heat transfer problem

for cylindrical composite materials.

Solutions to unsteady state diffusion and heat conduction problems in infinitely long homogeneous cylinders for various boundary conditions can be found in books by Crank (1956) and Carslaw and Jaeger (1959). The problem of unsteady state heat conduction in a composite cylinder with no interfacial resistances has been solved by Jaeger (1941). Olcer (1968) has presented the solution to a very general three-dimensional time-dependent heat transfer problem in a two material hollow composite cylinder with interfacial resistances and internal heat sources. The solution given here can be obtained as a special case of Olcer's solution when a misprint in Olcer's paper is corrected. Equation (19) in Olcer (1968) is incorrect; the correct result can be obtained by evaluating Equations (10) and (18) in Olcer (1968).

CONCLUSIONS AND SIGNIFICANCE

An analytical solution is given to the boundary-initial value problem of diffusion in a composite cylinder with interfacial resistances.

Numerical values of the roots and various coefficients of the solution are reported for membrane constants typical of small tubular membranes.

An unsteady state diffusion experiment is proposed for the evaluation of membrane constants from which the permeability of homogeneous membranes can be calculated.

An approximate but rapid method of data analysis is presented for determining the permeability of both homogeneous and asymmetric (skinned) tubular membranes.

The conventional method for determining the permeability of tubular membranes involves construction of a small-scale dialyzer and the measurement of overall mass-transfer resistances. This method requires the production and potting of a large number of tubular membranes and the evaluation of the mass-transfer resistances at the fluid-membrane interfaces. The method proposed here for evaluating membrane permeability is more convenient and probably more accurate than the conventional method.

GOVERNING EQUATIONS

In this section the differential equations and boundary conditions are given for time-dependent concentration profiles in a permeable composite cylinder caused by a step-change in concentration (0 to C_∞ at time $t = 0$) in a solution external to the cylinder. We assume the composite cylinder consists of an inner cylinder of stagnant solution or gel (radius $= a$) surrounded by a permeable tube (outer radius $= b$). The concentration in the inner cylinder is designated C_1 (moles/liter of solution) and that in the permeable tube is C_2 (moles/liter of wet tube). When the concentrations in the tube and in the solutions are in equilibrium C_2 is related to C_1 and C_∞ by an equilibrium partition coefficient K ($= C_2/C_1 = C_2/C_\infty$ at equilibrium) which is assumed to be constant. A schematic concentration profile is illustrated in Figure 1.

The skin on the surface of the tube at radius a has an infinitesimal thickness (zero mass capacity) and a finite mass-transfer coefficient k_a. A similar skin at the surface of radius b has a mass transfer coefficient k_{bs}. The mass transfer coefficient at the tube-reservoir interface is designated k_{bf}. The combined mass transfer coefficient at radius b, k_b, is given by $(k_b)^{-1} = (k_{bf})^{-1} + (k_{bs})^{-1}$. All mass transfer coefficients are defined in terms of concentrations in the solution which would be in equilibrium with the local concentrations in the skin. The term $C_1(a^-) - C_2(a^+)/K$ represents the concentration difference across a skin of infinitesimal thickness at the surface with radius a.

If we assume that (1) the density, equilibrium partition coefficient K, and the diffusivities D_1 (inner cylinder) and D_2 (permeable tube) are constant, (2) the mass-average velocity in the composite cylinder is zero, and (3) chemical reaction and adsorption are negligible, the unsteady state diffusion equation for an infinitely long composite cylinder can be written in dimensionless form as follows:

$$0 \leq \xi < \kappa^- \quad \tau > 0 \quad \frac{\partial \Theta_1}{\partial \tau} = \frac{1}{\xi}\frac{\partial}{\partial \xi}\left(\xi \frac{\partial \Theta_1}{\partial \xi}\right) \tag{1}$$

$$\kappa^+ < \xi < 1^- \quad \tau > 0 \quad \beta^2 \frac{\partial \Theta_2}{\partial \tau} = \frac{1}{\xi}\frac{\partial}{\partial \xi}\left(\xi \frac{\partial \Theta_2}{\partial \xi}\right) \tag{2}$$

The dimensionless initial and boundary conditions are

$$0 \leq \xi \leq 1^- \quad \tau = 0 \quad \Theta_1 = \Theta_2 = 0 \tag{3}$$

$$\xi = 0 \quad \tau > 0 \quad \frac{\partial \Theta_1}{\partial \xi} = 0 \tag{4}$$

$$\xi = \kappa \quad \tau > 0 \quad \frac{\beta^2}{K}\frac{\partial \Theta_1(\kappa^-)}{\partial \xi} = \frac{\partial \Theta_2(\kappa^+)}{\partial \xi} \tag{5}$$

$$\xi = \kappa \quad \tau > 0 \quad -\frac{\partial \Theta_1(\kappa^-)}{\partial \xi} = N_a(\Theta_1(\kappa^-) - \Theta_2(\kappa^+)) \tag{6}$$

$$\xi = 1 \quad \tau > 0 \quad -\frac{\partial \Theta_2(1^-)}{\partial \xi} = \frac{\beta^2}{K} N_b(\Theta_2(1^-) - 1) \tag{7}$$

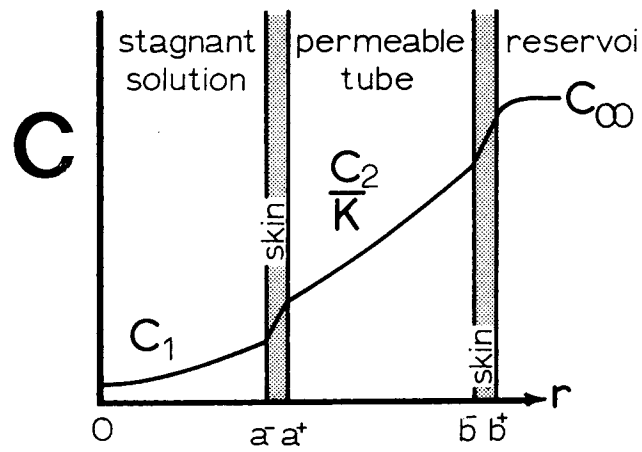

Fig. 1. Schematic unsteady state concentration profile in a composite cylinder with skins at the r = a and r = b surfaces.

Equations (1) to (7) can easily be reinterpreted to give a description of unsteady heat transfer in a composite cylinder.

The form of the solution to the preceding equations is greatly simplified by the use of the following cylinder functions:

$$D_{mn}(x, y) \equiv \frac{\partial^{m+n}}{\partial x^m \partial y^n}\left(I_0(x)K_0(y) - K_0(x)I_0(y)\right) \quad (8)$$

$$C_{mn}(x, y) \equiv \frac{\partial^{m+n}}{\partial x^m \partial y^n}\left(J_0(x)Y_0(y) - Y_0(x)J_0(y)\right) \quad (9)$$

When both m and n are zero, the subscripts are omitted.

SOLUTION OF EQUATIONS

The partial differential equations, Equations (1) and (2), can be reduced to ordinary differential equations (Bessel's modified equations) involving only spatial variables by use of the Laplace transform. The boundary conditions given by Equations (4) to (7) can be transformed in a similar manner and used in their dimensionless form to evaluate the constants in the dimensionless solutions to Bessel's modified equation. By this procedure we obtain

$$\overline{\Theta}_1(\xi, s) = \frac{I_0(\sqrt{s}\,\xi)}{\beta\kappa s W_1(s)} \quad (10)$$

$$\overline{\Theta}_2(\xi, s) = \frac{\sqrt{s}}{sW_1(s)}\left\{\frac{\beta}{K} I_1(\kappa\sqrt{s})\, D(\beta\sqrt{s}\,\xi, \beta\kappa\sqrt{s}) + \left[I_0(\kappa\sqrt{s}) + \frac{\sqrt{s}}{N_a} I_1(\kappa\sqrt{s})\right] D_{10}(\beta\kappa\sqrt{s}, \beta\sqrt{s}\,\xi)\right\} \quad (11)$$

where

$$W_1(s) = -\frac{\beta}{K} I_1(\kappa\sqrt{s}) \times \left[\frac{sK}{\beta N_b} D_{01}(\beta\kappa\sqrt{s}, \beta\sqrt{s}) + \sqrt{s}\, D(\beta\kappa\sqrt{s}, \beta\sqrt{s})\right] + \left[I_0(\kappa\sqrt{s}) + \frac{\sqrt{s}}{N_a} I_1(\kappa\sqrt{s})\right] \times \left[\frac{sK}{\beta N_b} D_{11}(\beta\kappa\sqrt{s}, \beta\sqrt{s}) + \sqrt{s}\, D_{10}(\beta\kappa\sqrt{s}, \beta\sqrt{s})\right] \quad (12)$$

Equations (10) and (11) can be inverted by using the inversion theorem for the Laplace transform and the residue theorem (Hildebrand, 1964; Carslaw and Jaeger, 1948, 1959).

The transformed dimensionless concentrations $\overline{\Theta}_1(\xi, s)$ and $\overline{\Theta}_2(\xi, s)$ are single-valued functions of s and have simple poles at $s = 0$ and $s = -\alpha_p^2$ where $\pm\alpha_p$, $p = 1, 2 \ldots$, are the roots of

$$\frac{\beta}{K} J_1(\kappa\alpha)\left[\frac{\alpha K}{\beta N_b} C_{01}(\beta\kappa\alpha, \beta\alpha) + C(\beta\kappa\alpha, \beta\alpha)\right] + \left[J_0(\kappa\alpha) - \frac{\alpha}{N_a} J_1(\kappa\alpha)\right] \times \left[\frac{\alpha K}{\beta N_b} C_{11}(\beta\kappa\alpha, \beta\alpha) + C_{10}(\beta\kappa\alpha, \beta\alpha)\right] = 0 \quad (13)$$

Procedures given by Carslaw and Jaeger (1940), Gray and Mathews (1922), and Jaeger (1942) have been used to prove that the roots of Equation (13) are all simple and not purely imaginary.

Evaluation of the residues of $e^{s\tau}\Theta(\xi, s)$ requires the calculation of $\beta\kappa s\, \partial W_1(s)/\partial s$ which is given by

$$\beta\kappa s \frac{\partial W_1(s)}{\partial s} = \frac{\beta\kappa s}{2}\left\{\left[\frac{K\sqrt{s}}{\beta N_b} D_{11}(\beta\kappa\sqrt{s}, \beta\sqrt{s}) + D_{10}(\beta\kappa\sqrt{s}, \beta\sqrt{s})\right] \times \left[\kappa I_1(\kappa\sqrt{s}) + \frac{\kappa\sqrt{s}}{N_a} I_0(\kappa\sqrt{s})\right] + \left[I_0(\kappa\sqrt{s}) + \frac{\sqrt{s}}{N_a} I_1(\kappa\sqrt{s})\right] \times \left[\frac{K\sqrt{s}}{N_b} D_{10}(\beta\kappa\sqrt{s}, \beta\sqrt{s}) + \frac{\kappa K\sqrt{s}}{N_b} D_{01}(\beta\kappa\sqrt{s}, \beta\sqrt{s}) + \beta D_{11}(\beta\kappa\sqrt{s}, \beta\sqrt{s}) + \beta\kappa D(\beta\kappa\sqrt{s}, \beta\sqrt{s})\right] - \frac{\beta}{K}\left[\kappa I_0(\kappa\sqrt{s})\left(\frac{K\sqrt{s}}{\beta N_b} D_{01}(\beta\kappa\sqrt{s}, \beta\sqrt{s}) + D(\beta\kappa\sqrt{s}, \beta\sqrt{s})\right) + I_1(\beta\sqrt{s})\left(\frac{K\sqrt{s}}{N_b} D(\beta\kappa\sqrt{s}, \beta\sqrt{s}) + \frac{\kappa K\sqrt{s}}{N_b} D_{11}(\beta\kappa\sqrt{s}, \beta\sqrt{s})\right) + \beta D_{01}(\beta\kappa\sqrt{s}, \beta\sqrt{s}) + \beta\kappa D_{10}(\beta\kappa\sqrt{s}, \beta\sqrt{s})\right]\right\} \quad (14)$$

It is convenient to define a function $G(\alpha_p)$ as

$$\frac{1}{G(\alpha_p)} \equiv 2\left[\beta\kappa s \frac{\partial W_1(s)}{\partial s}\right]\left[I_0(\kappa\sqrt{s}) + \frac{\sqrt{s}}{N_a} I_1(\kappa\sqrt{s})\right] \times \left[\frac{K\sqrt{s}}{\beta N_b} D_{01}(\beta\kappa\sqrt{s}, \beta\sqrt{s}) + D(\beta\kappa\sqrt{s}, \beta\sqrt{s})\right]\Big|_{s=-\alpha_p^2} \quad (15)$$

By a rearrangement of Equation (14) which requires use of Equation (13) and the recurrence relation given by Equation (9.1.34) in Abramowitz and Stegun (1964), the following expression for $G(\alpha_p)$ can be obtained:

$$\frac{1}{G(\alpha_p)} = \left(\frac{\pi\beta\kappa\alpha_p}{2}\right)^2 \times \left\{\left[\left(\frac{K\alpha_p}{\beta N_b}\right) C_{01}(\beta\kappa\alpha_p, \beta\alpha_p) + C(\beta\kappa\alpha_p, \beta\alpha_p)\right]^2 \times \left[\frac{J_0^2(\kappa\alpha_p)}{K} - \left(J_0(\kappa\alpha_p) - \frac{\alpha_p}{N_a} J_1(\kappa\alpha_p)\right)^2 + \frac{1}{K}\left(1 - \frac{\beta^2}{K}\right) J_1^2(\kappa\alpha_p)\right]\right\} + \left[J_0(\kappa\alpha_p) - \frac{\alpha_p}{N_a} J_1(\kappa\alpha_p)\right]^2\left[1 + \left(\frac{K\alpha_p}{\beta N_b}\right)^2\right] \quad (16)$$

The time-dependent dimensionless concentration profiles are given by

$$\Theta_1(\xi, \tau) = 1 - \pi \sum_{p=1}^{\infty} e^{-\alpha_p^2\tau} J_0(\alpha_p\xi) \times \left[J_0(\kappa\alpha_p) - \frac{\alpha_p}{N_a} J_1(\kappa\alpha_p)\right] \times \left[\frac{K\alpha_p}{\beta N_b} C_{01}(\beta\kappa\alpha_p, \beta\alpha_p) + C(\beta\kappa\alpha_p, \beta\alpha_p)\right] G(\alpha_p) \quad (17)$$

and

$$\Theta_2(\xi,\tau) = 1 - \pi \sum_{p=1}^{\infty} e^{-\alpha_p^2\tau}\left[J_0(\kappa\alpha_p) - \frac{\alpha_p}{N_a} J_1(\kappa\alpha_p) \right]^2$$

$$\times \left[\frac{K\alpha_p}{\beta N_b} C_{01}(\beta\alpha_p\xi, \beta\alpha_p) + C(\beta\alpha_p\xi, \beta\alpha_p) \right] G(\alpha_p) \quad (18)$$

The derivation of Equation (18) requires the use of Equation (13) and the identities given by Equations (12) and (13) in Jaeger (1941). Additional details concerning the derivation of Equations (17) and (18) are given by Stevenson (1973).

The volume-average concentrations can be calculated as follows:

$$\langle\Theta_1\rangle \equiv \frac{\int_0^{\kappa} \Theta_1(\xi,\tau)\xi d\xi}{\int_0^{\kappa} \xi\alpha\xi} \equiv 1 - \sum_{p=1}^{\infty} A_p e^{-\alpha_p^2\tau}$$

$$= 1 - \frac{2\pi}{\kappa} \sum_{p=1}^{\infty} \frac{e^{-\alpha_p^2\tau}}{\alpha_p} J_1(\kappa\alpha_p)\left[J_0(\kappa\alpha_p) - \frac{\alpha_p}{N_a} J_1(\kappa\alpha_p) \right]$$

$$\left[\frac{K\alpha_p}{\beta N_b} C_{01}(\beta\kappa\alpha_p, \beta\alpha_p) + C(\beta\kappa\alpha_p, \beta\alpha_p) \right] G(\alpha_p) \quad (19)$$

$$\langle\Theta_2\rangle \equiv \frac{\int_{\kappa}^{1} \Theta_2(\xi,\tau)\xi d\xi}{\int_{\kappa}^{1} \xi\alpha\xi} \equiv 1 - \sum_{p=1}^{\infty} B_p e^{-\alpha_p^2\tau}$$

$$= 1 - \frac{2\pi}{1-\kappa^2} \sum_{p=1}^{\infty} \frac{e^{-\alpha_p^2\tau}}{\beta\alpha_p}\left[J_0(\kappa\alpha_p) - \frac{\alpha_p}{N_a} J_1(\kappa\alpha_p) \right]^2$$

$$\times \left[\frac{K\kappa\alpha_p}{N_b\beta} C_{11}(\beta\kappa\alpha_p, \beta\alpha_p) + \kappa C_{10}(\beta\kappa\alpha_p, \beta\alpha_p) + \frac{2}{\pi\beta\alpha_p} \right] G(\alpha_p) \quad (20)$$

The dimensionless concentration at the centerline can be obtained by evaluating Equation (17) at $\xi = 0$. For convenience this result can be written

$$\Theta_1(0,\tau) = 1 - \sum_{p=1}^{\infty} C_p e^{-\alpha_p^2\tau} \quad (21)$$

The coefficients A_p, B_p, and C_p defined in Equations (19) to (21) have been introduced to facilitate computation.

When N_a and N_b are set equal to infinity, Equations (13), (17), and (18) reduce to the results given previously by Jaeger (1941) for the case of no interfacial resistances. In the limits as $\kappa \to 0$ or as $\kappa \to 1$ these equations simplify to the solutions for unsteady state mass transfer in a homogeneous cylinder with an interfacial resistance (Carslaw and Jaeger, 1959 p. 202). With appropriate adaptions (Stevenson, 1973), the results given here can be related to the solution for unsteady state mass transfer in a composite cylinder in which (a) the inner cylinder is treated as a stirred tank (equivalent to $D_1 \to \infty$) and (b) the mass transfer coefficient at the inner radius is infinite but the coefficient at the outer radius is finite (Jaeger, 1940; Crank, 1956, p. 79). In these references Equation (29) (Jaeger, 1940) and Equation (5.75) (Crank, 1956) are in error; an exponent of 2 is missing on the $[A_n J_0(a\alpha_n) - k_2\alpha_n J_1(a\alpha_n)]$ term.

NUMERICAL EVALUATION

Equations (13), (19), and (20) were evaluated on an IBM 360-65 digital computer at Cornell University. The Bessel functions were calculated using Chebyshev polynomials and the roots of Equation (13) were located using Newton's method. Fifteen decimal place accuracy was retained for the coefficients in the Chebyshev series expansion (Clenshaw, 1962). No deviations greater than 2×10^{-15} between calculated and previously reported values (Aiken, 1947) of J_0 and J_1 were observed for arguments ranging from 0.1 to 80. Computed values for Bessel functions were routinely checked by substitution into the identities given by Equations (11) and (14) in Jaeger (1941). These identities were satisfied with deviations no greater than 5×10^{-15} for arguments ranging from 0.1 to 80. The first five roots of J_1 were computed and found to deviate from reported values (Gray and Mathews, 1922, Table IV) by no more than 3×10^{-15}. Computed roots and centerline concentrations ($\tau \geq 0.1$) for the conditions $\beta^2 = 1$, $K = 1$, $N_1 = \infty$ and N_2 ranging from 0.1 to ∞ were compared with available literature values (Abramowitz and Stegun, 1964, p. 414; Carslaw and Jaeger, 1959, p. 493; Olson and Schultz, 1942) and were found to deviate by no more than one unit in the last decimal place in the reported value.

Numerical values for the roots α_p of Equation (13) and the coefficients A_p, B_p, and C_p in Equations (19) to (21) are given in Table 1 for two sets of membrane constants. Similar results are available* for more than 60 combinations of membrane constants ranging from $1 \leq \beta^2 \leq 25$, $0.4 \leq \kappa \leq 0.95$, $0.40 \leq K \leq 1.0$, $0.1 \leq N_a \leq \infty$, and $0.1 \leq N_b \leq \infty$.

EXPERIMENTAL APPLICATIONS

Diffusive mass transfer in membranes is normally characterized by a steady state permeability which, in the absence of bulk flow, is defined as the steady state solute flux at a surface divided by the constant concentration difference (based on the external solution) across the membrane. Here it is useful to generalize the definition of permeability to include the unsteady state conditions described in this paper. To facilitate an approximate method of data analysis given below, the solute flux is defined as the solute flow rate (mole/s) at the inner radius of the permeable tube divided by the outer surface area of the tube. The dimensionless permeability Pb/D_1 defined in this manner is given by

$$\frac{Pb}{D_1} \equiv \frac{-\kappa \left.\frac{\partial\Theta_1}{\partial\xi}\right|_{\xi=\kappa^-}}{(\Theta_1(\kappa^-,\tau) - 1)} \quad (22)$$

The interfacial mass transfer resistances caused by the skins are included in the permeability and the mass transfer coefficient k_{bf} at the tube-reservoir interface is assumed to be infinite.

When the dimensionless concentration $\Theta_1(\kappa^-,\tau)$ is maintained at a constant value, Equation (22) is consistent with the conventional definition of a steady state membrane permeability. This dimensionless steady state permeability $P_s b/D_1$ is given in terms of membrane constants by

$$\frac{P_s b}{D_1} = \frac{1}{\frac{\beta^2 \ln(1/\kappa)}{K} + \frac{1}{\kappa N_a} + \frac{1}{N_b}} \quad (23)$$

The results given in this paper can be used to evaluate

* "Numerical Values for Roots, Coefficients, and Concentrations Describing Unsteady Mass Transfer in a Long Composite Cylinder with Interfacial Resistances" by J. F. Stevenson has been deposited as Document No. 02321 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 305 E. 46 St., N.Y., N.Y. 10017 and may be obtained for $1.50 for microfiche or $13.50 for photocopies.

TABLE 1. ROOTS OF EQUATION (13) AND COEFFICIENTS IN EQUATIONS (19) TO (21)

$\beta^2 = 3$	$K = 0.82$	$\kappa = 0.8$	$N_a = \infty$	$N_b = \infty$
p	α_p	A_p	B_p	C_p
1	1.6313574869	1.05910395	0.38816588	1.32110793
2	4.7810611174	−0.00082078	0.13987341	−0.56785974
3	7.8244089975	−0.03903731	0.19089346	0.55955842
4	10.0156707560	−0.03008394	0.14134993	−0.50983008
5	12.8834271401	−0.00223757	0.02474384	0.34978430
6	16.0563718254	0.00574398	0.00643706	−0.36013962
7	18.4119491490	0.01061718	0.00278618	0.38113476
8	20.9810275222	0.00210263	0.00443630	−0.29337378

$\beta^2 = 1$	$K = 1$	$\kappa = 0.6$	$N_a = 1$	$N_b = \infty$
p	α_p	A_p	B_p	C_p
1	1.4938384094	1.14121055	0.11111393	1.26395891
2	4.7439318030	−0.14056564	0.65454107	−0.50761823
3	6.6613107084	−0.00969712	0.01383160	0.29896416
4	11.7581319165	−0.00183733	0.01940992	−0.55127869
5	12.2063617323	0.01277076	0.07769499	0.52468001
6	17.0504530990	0.00017881	0.00004661	−0.06469885
7	19.8535984847	−0.00268112	0.04058699	0.06990791
8	22.2829832199	−0.00007129	0.00010059	−0.04744380

P_s from data obtained in unsteady mass transfer experiments. In a typical experiment a long sealed section of membrane tube is equilibrated with a solution containing a radioactive solute and then placed (at $\tau = 0$) in a large stirred or rotating tank containing no radioactive solute for a predetermined time. In a series of experiments with identical membrane tubes the amount of radioactive solute remaining in the sealed tubes is measured for various exposure times. The fraction of solute remaining in the sealed tube at dimensionless time τ is designated as R and can be calculated using the result

$$R(\tau, \beta^2, \kappa, K, N_a, N_b) = \frac{\kappa^2(1 - \langle\Theta_1\rangle) + (1 - \kappa^2)(1 - \langle\Theta_2\rangle)K}{\kappa^2 + (1 - \kappa^2)K} \quad (24)$$

Note that $1 - \langle\Theta\rangle$ is the appropriate volume-average concentration for the experiment described above.

A plot of ln (R) versus τ based on experimental data can then be compared with computed graphs which are parameterized by one of the unknown membrane constants β^2, K, κ, N_a or N_b. In experiments with homogeneous tubular membranes in a well-stirred bath, the constants N_a and N_b are infinite, κ is measured with a microscope, K is measured in an equilibrium sorption experiment, and β^2 is determined by matching experimental and computed curves of ln (R) versus τ. Once these membrane constants are known, the dimensionless steady state permeability given by Equation (23) is easily calculated. However, the equilibrium sorption experiment needed to measure K is rather difficult for small tubular membranes so a more convenient, approximate method of determining membrane permeability from experimental data is given below.

Examination of Equations (19) and (20) shows that at sufficiently large dimensionless times only the first term in each series will contribute. For large τ the slope of ln (R) versus τ can be measured to obtain an experimentally determined value of α_1.

$$\frac{d \ln (R)}{d\tau} = \text{slope} = -(\alpha_1)^2 \quad (\text{large } \tau) \quad (25)$$

An expression for a dimensionless unsteady state permeability can be obtained by substituting Equation (17) into Equation (22). As τ becomes large this dimensionless permeability approaches an asymptotic value $P_u b/D_1$ given by

$$\frac{P_u b}{D_1} = \frac{\kappa\alpha_1 J_1(\kappa\alpha_1)}{J_0(\kappa\alpha_1)} \quad (\text{large } \tau) \quad (26)$$

The approach of the unsteady state dimensionless permeability to an asymptotic value as the dimensionless time becomes large is analogous to the Nusselt number approaching an asymptotic value as the Graetz number becomes small. As noted by Friedly (1972), Equation (26) cannot be obtained by applying the final value theorem to the Laplace transform of the numerator and denominator of the right-hand side of Equation (22).

The dimensionless asymptotic permeability given by Equation (26) is somewhat lower than the dimensionless steady state permeability given by Equation (23), but in the limit as κ approaches 1, P_u approaches P_s. Computed values of the ratio P_u/P_s graphed as a function of κ for various values of the membrane constants β^2, K, N_a, and N_b are shown in Figure 2. As can be seen in this figure, P_u underestimates P_s by no more than 16% for the typical range of membrane constants $1 \geq \kappa \geq 0.75$, $K \leq 1$, $1 \leq \beta^2 \leq 25$, $0 < N_a \leq \infty$, and $N_b = \infty$. Note that P_u becomes a better approximation to P_s as β^2 decreases, K decreases, N_b increases, N_a decreases, or κ approaches 1. For all the curves shown in Figure 2, the value of $-d \ln (R)/d\tau$ is within 2% of $(\alpha_1)^2$ for $R \leq 0.25$. By the method outlined above a measurement of the dimensionless time-dependence of any quantity proportional to ln (R) at large τ (such as ln (counts per minute) from a scintillation counter) can be used to estimate the steady state permeability of either a homogeneous or asymmetric ($N_a < \infty$) tubular membrane.

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NOTATION

a = inner radius of permeable tube, cm
A_p = coefficient defined by Equation (19)

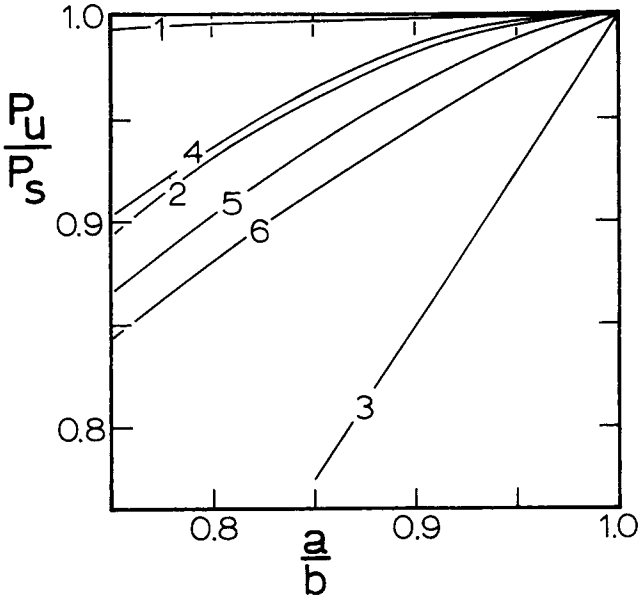

Fig. 2 Ratio of asymptotic unsteady state permeability P_u to steady state permeability P_s as a function a/b ($= \kappa$) for the following membrane constants. $\beta^2 = 1$, $K = 1$: (1) $N_a = 1$, $N_b = \infty$, (2) $N_a = N_b = \infty$, (3) $N_a = \infty$, $N_b = 1$; and $K = 0.82$, $N_a = N_b = \infty$: (4) $\beta^2 = 1$, (5) $\beta^2 = 3$, (6) $\beta^2 = 25$.

b = outer radius of permeable tube, cm
B_p = coefficient defined by Equation (20)
C_1 = concentration in inner cylinder, moles/liter of solution
C_2 = concentration in permeable tube, moles/liter of wet tube
C_∞ = concentration in external solution, moles/liter of solution
C_p = coefficient defined by Equation (21)
$C_{mn}(x, y)$ = cross-product of Bessel functions defined by Equation (9)
D_1 = diffusivity in solution, cm²/s
D_2 = diffusivity in permeable tube, cm²/s
$D_{mn}(x, y)$ = cross-product of Bessel functions defined by Equation (8)
$G(\alpha_p)$ = function defined by Equation (15)
$I_\nu(z)$ = modified Bessel function of first kind
$J_\nu(z)$ = Bessel function of the first kind
k_a = mass transfer coefficient for skin at inner radius of permeable tube, cm/s
k_b = $k_{bs}\, k_{bf}/(k_{bf} + k_{bs})$, mass transfer coefficient at outer radius of permeable tube, cm/s
k_{bf}, k_{bs} = mass transfer coefficient for membrane-fluid interface and skin, respectively, at outer radius of permeable tube, cm/s
K = C_2/C_1, equilibrium partition coefficient
$K_\nu(z)$ = modified Bessel function of the second kind
N_a = $k_a b/D_1$, dimensionless mass transfer coefficient at inner radius of permeable tube
N_b = $k_b b/D_1$, dimensionless mass transfer coefficient at outer radius of permeable tube
P = membrane permeability defined by Equation (22), cm/s
P_s, P_u = membrane permeability for steady state diffusion and asymptotic value for unsteady state diffusion, respectively, cm/s
r = radial coordinate, cm
R = fraction of solute remaining in sealed membrane tube, defined by Equation (24)
s = Laplace transform parameter
t = time, s
$Y_\nu(z)$ = Bessel function of the second kind
$W_1(s)$ = function defined by Equation (12)

Greek Letters

α_p = roots of Equation (13)
β^2 = D_1/D_2, ratio of diffusivities
Θ_1 = C_1/C_∞, dimensionless concentration in inner cylinder
Θ_2 = $C_2/(KC_\infty)$, dimensionless concentration in permeable tube
$\overline{\Theta}$ = Laplace transform of Θ
$\langle\Theta\rangle$ = volumetric average of Θ
κ = a/b, ratio of inner radius to outer radius
ξ = r/b, dimensionless radius
τ = $D_1 t/b^2$, dimensionless time

Subscripts

∞ = external solution
1 = inner cylinder of solution
2 = permeable tube

Superscripts

$+$ = outer surface of a skin
$-$ = inner surface of a skin

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