Capillary Mass Transfer

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Makiya (1970) has derived the following equations for capillary mass transfer of a nonelectrolyte based on irreversible thermodynamics:
Solute

$$\frac{d}{dz} Q_W C_A = -\pi R_{lm} [(L_P - L_{PD})(P - P_s)(C_A + C_s) + (L_D - L_{PD}) RT (C_A^2 - C_s^2)] \quad (1)$$

Solvent (water)

$$\frac{d}{dz} Q_W = -2\pi R_{lm} [L_P (P - P_s) + L_{PD}(C_s - C_A) RT] \quad (2)$$

Momentum

$$\frac{dP}{dz} + A_2 Q_W \frac{dQ_W}{dz} + A_1 Q_W = 0 \quad (3)$$

Specifying the initial conditions of concentration, volumetric flow rate, and pressure, he solved these equations for selected membrane parameters using the IBM-CSMP program (1969). In this note simplifications of the above equations are made which permit analytical solutions in dimensionless form for ideal semipermeable membranes and for pure water transport.

An ideal semipermeable membrane transfers no solute. This condition requires that the phenomenological coefficients be equal

$$L_P = L_{PD} = L_D \quad (4)$$

as shown by Katchalsky and Curran (1965). Equation (1) is consistent with this definition since it shows that $Q_W C_A$ is constant ($= Q_{W0} C_{A0}$) down the capillary indicating no solute mass transfer in the radial direction.

Since the kinetic energy of a fluid flowing in a capillary is small (low Reynolds number) compared to frictional effects, Equation (3) can be simplified to

$$P = P_0 - \int_0^z A_1 Q_W dz \quad (5)$$

Upon substitution of Equation (5) for P and $C_A = (Q_{W0} C_{A0})/Q_W$ into Equation (2) one gets

$$\frac{dQ_W}{dz} - 2\pi R_{lm} L_P \left[\int_0^z A_1 Q_W dz + \left(\frac{Q_{W0} C_{A0}}{Q_W} - C_s \right) RT \right] = -2\pi R_{lm} L_P (P_0 - P_s) \quad (6)$$

The term $1/Q_W$ is nonlinear, and no solutions were found. Therefore $1/Q_W$ was expanded in a Taylor series, and the first two terms were taken to give the following equation:

$$\frac{dQ_W}{dz} - 2\pi R_{lm} L_P \left[\int_0^z A_1 Q_W dz - \left(\frac{Q_W C_{A0}}{Q_{W0}} \right) RT \right] = -2\pi R_{lm} L_P [(P_0 - P_s) - (2C_{A0} - C_s) RT] \quad (7)$$

Solution of this equation with the initial condition at $z = 0$, $Q_W = Q_{W0}$, by the Laplace transform method gives

$$Q_W = \frac{Q_{W0}}{B_1 - B_2} (B_1 e^{B_1 z} - B_2 e^{B_2 z}) - 2\pi R_{lm} L_P (P_0 - P_s + R C_s T - 2R C_{A0} T) \left(\frac{e^{B_1 z} - e^{B_2 z}}{B_1 - B_2} \right) \quad (8)$$

where

$$B_1 = \frac{-\pi R_{lm} L_P R T C_{A0}}{Q_{W0}} + \left[\left(\frac{\pi R_{lm} L_P R T C_{A0}}{Q_{W0}} \right)^2 + 2\pi R_{lm} L_P A_1 \right]^{1/2} \quad (9)$$

and

$$B_2 = \frac{-\pi R_{lm} L_P R T C_{A0}}{Q_{W0}} - \left[\left(\frac{\pi R_{lm} L_P R T C_{A0}}{Q_{W0}} \right)^2 + 2\pi R_{lm} L_P A_1 \right]^{1/2} \quad (10)$$

Earlier, the pressure was defined by Equation (5); upon substitution of Equation (8) for Q_W the pressure is given by

$$P = P_0 + (e^{B_2 z} - e^{B_1 z}) \frac{Q_{W0} A_1}{B_1 - B_2} - \frac{2\pi R_{lm} L_P A_1 (P_0 - P_s + R C_s T - 2R C_{A0} T)}{B_1 - B_2} \left(\frac{e^{B_2 z}}{B_2} - \frac{e^{B_1 z}}{B_1} + \frac{1}{B_1} - \frac{1}{B_2} \right) \quad (11)$$

Equation (8) can be expressed in terms of the dimensionless variables $Q^* = Q_W/Q_{W0}$ and $z^* = B_1 z$ as follows

$$Q^* = \left(\frac{1 - \phi_1}{1 - \phi_2} \right) e^{z^*} - \left(\frac{\phi_2 - \phi_1}{1 - \phi_2} \right) e^{\phi_2 z^*} \quad (12)$$

where

$$\phi_1 = \frac{2\pi R_{lm} L_P (P_0 - P_s + R C_s T - 2R C_{A0} T)}{Q_{W0} B_1} \quad (12a)$$

and

$$\phi_2 = B_2 / B_1 \quad (12b)$$

Equation (11) can be similarly put into dimensionless form

$$P^* = \frac{(P - P_0)(B_1 - B_2)}{Q_{W0}A_1} = \left(1 - \frac{\phi_1}{\phi_2}\right) e^{\phi_2 z^*} - (1 - \phi_1)e^{z^*} - \frac{\phi_1(\phi_2 - 1)}{\phi_2} \quad (13)$$

GRAPHICAL REPRESENTATION OF RESULTS

In Figures 1 and 2 the dimensionless flow rate Q^* is plotted versus the dimensionless distance z^* with ϕ_1 as a parameter. Figure 1 shows the results for $\phi_2 = -2.0$ while Figure 2 is for $\phi_2 = -10.0$. Figure 1 shows that as ϕ_1 increases from -2.0 to $+2.0$ three different transport regions are observed. First, only absorption takes place for the length of the capillary. Secondly, for the curves in the region $-0.5 \leq \phi_1 \leq 0.5$ filtration occurs initially followed by reabsorption. Finally, filtration is the only phenomenon occurring for the two remaining curves.

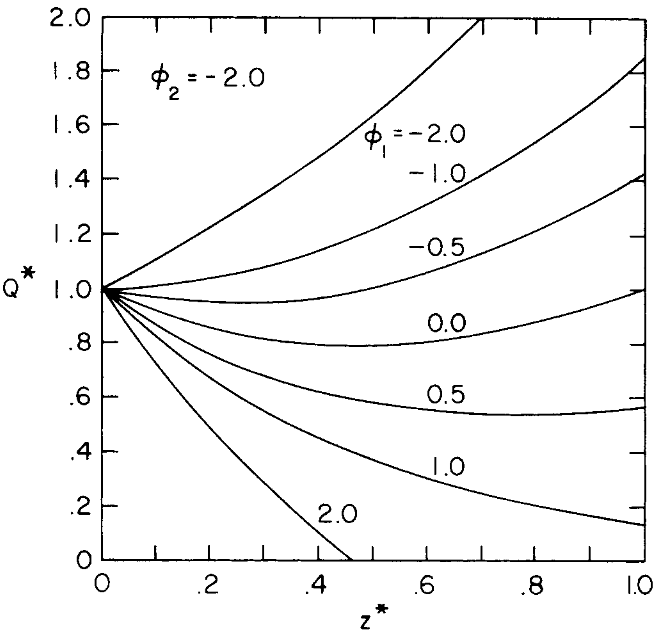

Fig. 1. Dimensionless axial flow for an ideal semipermeable membrane.

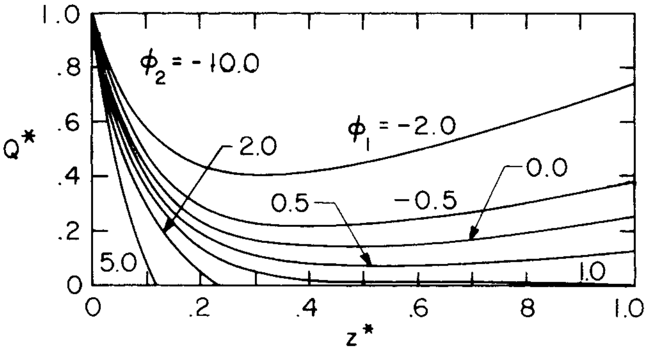

Fig. 2. Dimensionless axial flow for an ideal semipermeable membrane.

For the range of ϕ_1 shown in Figure 2, a case of pure absorption is not shown. Filtration-reabsorption is seen to occur for the curves of $\phi_1 = -2.0, -0.5, 0, 0.5$. Filtration occurs for $\phi_1 = 1.0, 2.0$, and 5.0. The criterion for determining if filtration-reabsorption occurs is found by differentiating Equation (10) with respect to z^*, setting the derivative equal to zero, and solving for z^*. This gives

$$(z^*)_{Q^*\text{min}} = \frac{1}{1 - \phi_2} \ln \frac{\phi_2(\phi_2 - \phi_1)}{1 - \phi_1} \quad (14)$$

which shows that no minimum (filtration-reabsorption) occurs if $\phi_1 \gtrsim 1.0$. For only absorption to take place $\phi_1 = 1 + \phi_2$ or a larger negative number.

The value of Q^* at the point of reabsorption is

$$Q^*_{\text{min}} = \frac{(1 - \phi_1)}{(1 - \phi_2)} \left[\frac{\phi_2(\phi_2 - \phi_1)}{(1 - \phi_1)} \right]^{\frac{1}{1-\phi_2}} - \frac{(\phi_2 - \phi_1)}{(1 - \phi_2)} \left[\frac{\phi_2(\phi_2 - \phi_1)}{(1 - \phi_1)} \right]^{\frac{\phi_2}{1-\phi_2}} \quad (15)$$

PURE WATER TRANSPORT

For pure water transport several approaches can be used. First the starting Equations (1), (2), and (3) can be simplified. This results in elimination of Equation (1), and the solvent and momentum equations become

$$\frac{dQ_W}{dz} = -2\pi R_{lm} L_P (P - P_s) \quad (16)$$

and

$$\frac{dP}{dz} + A_1 Q_W = 0 \quad (17)$$

The solution of these equations gives

$$\frac{Q}{Q_{W0}} = \cosh(\alpha z) - [2\pi R_{lm} L_P (P_0 - P_s)/\alpha Q_{W0}] \sinh(\alpha z) \quad (18)$$

as shown by Makiya et al. (1971). Secondly, for pure water transport ($C_{A0} = 0$) Equations (9) and (10) simplify and $\phi_2 = -1$. With these conditions, Equation (12) becomes

$$Q^* = \frac{1}{2} [(1 - \phi_1)e^{z^*} + (1 + \phi_1)e^{-z^*}] \quad (19)$$

and the dimensionless pressure

$$P^* = (1 + \phi_1)e^{-z^*} - (1 - \phi_1)e^{z^*} - 2\phi_1 \quad (20)$$

It can be shown that Equation (19) is identical to Equation (18). A plot of Q^* versus z^* is shown in Figure 3 for various values of ϕ_1. Again a minimum is observed and its location can be found from

$$(z^*)_{Q^*\text{min}} = \frac{1}{2} \ln \frac{1 + \phi_1}{1 - \phi_1} \quad (21)$$

The dimensionless pressure as a function of the dimensionless distance is shown in Figure 4. All curves begin at zero from the definition of P^* given by Equation (13), and decrease. Depending on the value of ϕ_1 they continue to decrease or terminate when $Q^* = 0$. For negative values of ϕ_1, the pressure outside the capillary is greater than the inlet capillary pressure. This gives rise to absorption only and P^* decreases. For equal values of P_s and P_0, $\phi_1 = 0$ and the same results are obtained.

When P_0 is greater than P_s, ϕ_1 is positive and filtration continues until $Q^* = 0$. In a similar manner P^* decreases or goes through a minimum.

APPLICATIONS

Comparison of the theory developed above can be made with analytical results for porous tube flow and with experimental results for a capillary-type artificial kidney. Kozinski et al. (1970) presented solutions for low Reynolds number flow of an incompressible Newtonian fluid in tubes and slits with permeation through the walls. They assumed the radial velocity at the wall decreased exponentially with axial distance. For the case of limiting seepage rates they obtained a radial velocity profile which when integrated over the cross section yields

$$Q^* = 1 - \phi_1 + \phi_1 e^{-z^*} \tag{22}$$

This result agrees with Equation (19) if $\phi_1 = 1$ and becomes an exponential decrease. Comparison of these results also shows that the arbitrary decay constant α_{KSL} of Kozinski et al. (1970) can be expressed as

$$\alpha_{KSL} = (2\pi R_1 L_P A_1)^{1/2} \tag{23}$$

Here R_1 is used to replace R_{1m} for thin-walled tubes or the flux expressions used in this paper could have been based on the inner radius to give this result.

For pure water transport, Stewart et al. (1966) used a capillary bundle 6.0 cm. long with capillaries of I.D. = 90μ and O.D. = 110μ (prior to immersion in water). They found that the amount of filtered water $[Q_{W0} - (Q_W)_L]$ was a linear function of the hydrostatic pressure difference $(P_0 - P_s)$. Equation (19) shows Q^* is proportional to ϕ_1 which in turn is directly proportional to $(P_0 - P_s)$ in agreement with the experimental results.

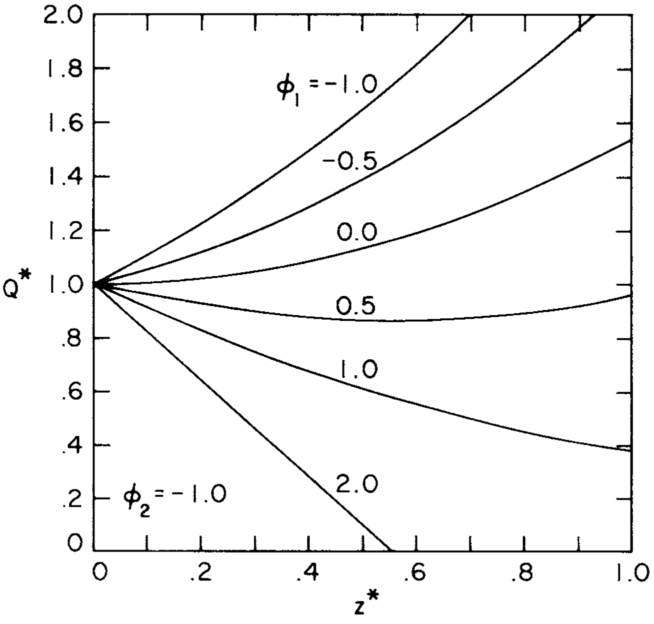

Fig. 3. Dimensionless axial flow for pure water transport in a capillary.

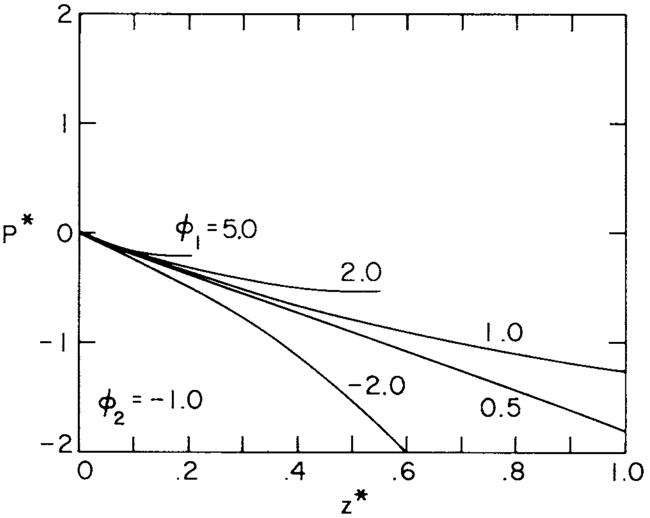

Fig. 4. Dimensionless pressure for pure water transport in a capillary.

The slope of a plot of Q^* versus ϕ_1 [or Q_W vs. $(P_0 - P_s)$] is

$$\frac{dQ^*}{d\phi_1} = \frac{e^{-z^*} - e^{z^*}}{2} \tag{24}$$

Stewart et al. (1966) found that changing the inlet flow rate did not result in a change of this slope but caused a change in the value of the intercept. Since z^* does not depend on the initial flow rate this finding agrees with Equation (24). The filtration coefficient L_P was calculated from this equation after correcting for the change in I.D. and O.D. by pressure drop data and volume increase data for deacetylated cellulose triacetate. The value found was 5×10^{-5} cm./(sec.)(atm) at 27°C. For a regenerated-cellulose, flat membrane, Kaufman and Leonard (1968) found that $L_P = 2.0 \times 10^{-5}$ cm./(sec.)(atm.). Correcting this value for the relative thicknesses, as shown by Makiya et al. (1971) brings the two values into agreement within 2%.

SUMMARY

A system of nonlinear differential equations describing capillary mass and momentum transfer processes has been solved by approximate analytical methods for the ideal semipermeable membrane and for pure water transport through a membrane. The solutions for Q^* and P^* as functions of z^* are characterized by two dimensionless parameters ϕ_1 and ϕ_2 which contain the system variables. Variation of these parameters shows the behavior of ideal semipermeable membranes with osmotic effects and the behavior of a membrane with pure water transport. The physiological phenomenon of filtration-reabsorption is described by the solutions and the necessary criterion for this phenomenon to occur is shown. In addition the solutions agree with previous theoretical and experimental results.

ACKNOWLEDGMENT

The authors acknowledge the help of M. A. del Cid in obtaining the computer results used in this study.

NOTATION

A_1 = $(8\mu/\pi R_1^4)$ (9.87×10^{-7}), atm/cm.^{4} sec.
A_2 = $(\rho_W/\pi^2 R_1^4)$ (9.87×10^{-7}), atm-sec.^{2}/cm.^{6}

B_1 = constant defined by Equation (9), cm.$^{-1}$
B_2 = constant defined by Equation (10), cm.$^{-1}$
C_A = concentration of solute in capillary
C_{A0} = concentration of solute in capillary at $z = 0$
C_s = concentration of solute in surroundings
L = capillary length, cm.
$\left.\begin{array}{l}L_D, L_{DP}\\ L_P, L_{PD}\end{array}\right\}$ = phenomenological coefficients, cm./(sec.)(atm)
P = hydrostatic pressure inside capillary, atm
P^* = dimensionless pressure defined by Equation (13)
P_0 = hydrostatic pressure inside capillary at $z = 0$
P_s = hydrostatic pressure in the surroundings
Q^* = dimensionless axial flow rate, Q_W/Q_{W0}
Q_W = volumetric flow rate of solvent in capillary, cm.^{3}/sec.
Q_{W0} = volumetric flow rate of solvent in capillary at $z = 0$
R = gas law constant
R_1 = inside radius of capillary, cm.
R_2 = outside radius of capillary
R_{lm} = log mean radius of capillary, $(R_2 - R_1)/\ln(R_2/R_1)$
T = absolute temperature, °K
z = axial distance, cm.
z^* = dimensionless axial distance $B_1 z$
α = constant, $(2\pi R_{lm} L_P A_1)^{1/2}$, cm.$^{-1}$
μ = viscosity of solvent, poise
ϕ_1 = dimensionless parameter defined by Equation (12a)
ϕ_2 = dimensionless parameter defined by Equation (12b)
ρ_W = density of solvent (in dilute solutions density of solution), g/cm.^{3}

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Manuscript received March 15, 1972; communication accepted March 16, 1972.

Volume-Area Relationship in Capillarity

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If liquid which is in contact with a solid is increased in volume by the amount δV, the change in the surface area of the liquid-vapor interface δA and also in the liquid-solid interface δa is given by the equation

$$H\delta V = \delta A - \cos\theta\delta a \qquad (1)$$

Melrose pointed out the mathematical nature of this equation for any surface of minimum area at a given volume and proposed the problem of deriving it from mathematical rather than from physical principles (Melrose, 1966).

For the radially symmetric configuration shown in Figure 1, the areas and volume are given by

$$A = \int_{x_0}^{x_1} F\,dx \quad \text{where} \quad F = 2y(1 + y'^2)^{1/2} \qquad (2)$$

$$a = 2\int_{x_0}^{c_0} p(1 + p'^2)^{1/2}\,dx + 2\int_{c_1}^{x_1} q(1 + q'^2)^{1/2}\,dx \qquad (3)$$

$$V = \int_{x_0}^{x_1} G\,dx \quad \text{where} \quad \begin{array}{ll} G = y^2 - p^2 & \text{for} \quad x_0 \leqq x \leqq c_0 \\ G = y^2 & \text{for} \quad c_0 \leqq x \leqq c_1 \\ G = y^2 - q^2 & \text{for} \quad c_1 \leqq x \leqq x_1 \end{array} \qquad (4)$$

where the factor π has been deleted for simplicity. If y is a fixed function, then A and V are constants, but if the function y is considered to vary, then A are V are functionals. The differential of a functional is called a variation. Thus δA, δV, and δa are variations in A, V and a, corresponding to a small change from $y(x)$ to $y(x) + h(x)$ where, in addition, y represents a surface of least area corresponding to a fixed volume. Equation (1) can be derived from the calculus of variations.

The variation in area of the liquid-vapor interface having end points which are constrained to lie on $p(x)$ and $q(x)$ is (Gelfand, Fomin, 1963)

$$\delta A = \int_{x_0}^{x_1} \left(F_y - \frac{d}{dx} F_{y'} \right) h\,dx + [F + (q' - y')F_{y'}]_{x=x_1}\delta x_1 - [F + (p' - y')F_{y'}]_{x=x_0}\delta x_0 \qquad (5)$$