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Flux and Characteristic Parameters in Mediated Transport through Liquid Membranes. I. A Theoretical Model

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NOTE

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Abstract

A steady-state mathematical model with adjustable parameters is shown for mediated transport through liquid membranes. A study of the concentration change in the receiving (or source) phase allows determination of the equilibrium constant corresponding to the chemical reaction at the interfaces as well as the maximum initial flux through the membrane.

A liquid membrane is a liquid phase which separates two other liquid phases in which the membrane is immiscible. Chemical species may pass through the membrane if they have some solubility in the membrane; this transport may be accomplished by simple diffusion or by mediated transport. This process uses an active chemical carrier which can react reversibly with the solute of interest (permeate), transports the permeate

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through the membrane, and releases it at the other boundary. There are several review articles which describe this process in detail (*1–5*).

The most common mechanism proposed for the facilitated or mediated transport is

$$\mathrm{A} + \mathrm{B} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{AB} \tag{1}$$

where A = permeating solute
B = active chemical carrier
AB = carrier–solute complex

and can be summarized as follows (*6*) (Fig. 1a):

(1) Reaction which describes the uptake of Permeate A and the formation of the Complex AB at Interface 1.
(2) Diffusion of the complex across the membrane.
(3) Decomposition of the complex at Interface 2 and the release of A in the receiving phase.
(4) Backdiffusion of the carrier.

The reactive processes at the interfaces are characterized by the reaction rates (υ_1, υ_{-1}) and (υ_2, υ_{-2}) (see Fig. 1b) associated wtih the rate constants (k_1, k_{-1}) and (k_2, k_{-2}) by

$$\begin{aligned} \upsilon_1 &= k_1 C^s_{\mathrm{A}} C^s_{\mathrm{AB}}, & \upsilon_2 &= k_2 C^r_{\mathrm{AB}} \\ \upsilon_{-1} &= k_{-1} C^s_{\mathrm{AB}}, & \upsilon_{-2} &= k_{-2} C^r_{\mathrm{A}} C^r_{\mathrm{B}} \end{aligned} \tag{2}$$

where C_i (i = A, B, AB) represents the concentration of species i and superscripts s and r refer to the source and receiving phases, respectively ($C^s_{\mathrm{A}} > C^r_{\mathrm{A}}$). Since the chemical species involved in each interface are the same, we have

$$k_{-1} = k_1 \quad \text{and} \quad k_{-2} = k_2 \tag{3}$$

We will denote C_T as the total concentration of Carrier B in all its forms. In most of the cases treated in the literature, B and AB are of about the same size and the equal diffusivity assumption can be used with little error, and so (*7*)

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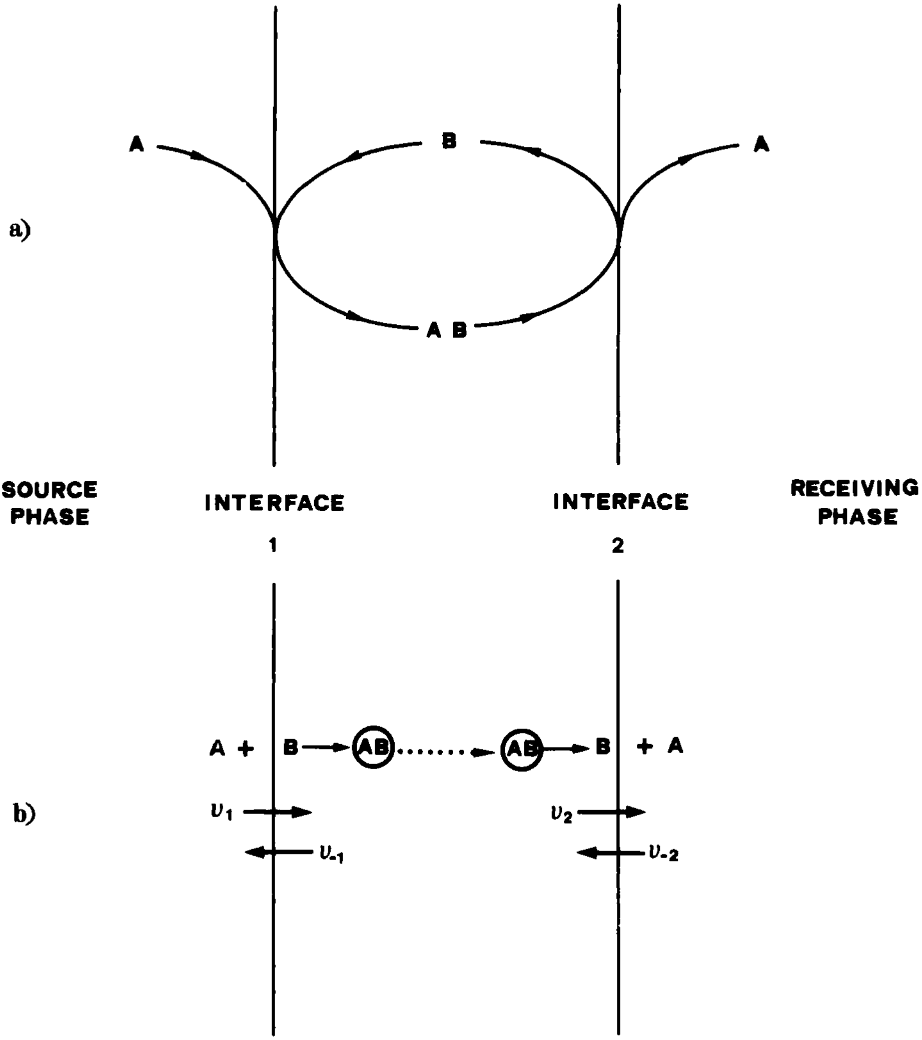

FIG. 1. Simplified representation of the mediated transport of Permeate A by the active Carrier B.

$$C_T = C_B + C_{AB} \tag{4}$$

In the steady state the concentrations of the different species in the membrane are constant at each point of the membrane. The steady-state assumption can be used when the concentration on each side of the membrane varies slowly with time. If a rapid chemical reaction converts the volatile Permeate A to a nonvolatile product at one boundary, then the concentration of A at that point is zero; this, combined with a constant source at the other boundary, would yield a steady-state flux condition. On the other hand, when the concentration of A at the source phase is large with respect to C_T, saturation of the carrier in the membrane is reached and a quasi-steady-state is established in the membrane. In steady-state conditions at both interphases, we have

$$\begin{aligned} \left.\frac{\partial C_{AB}}{\partial t}\right|_s &= k_1 C_A^s C_B^s - k_2 C_{AB}^s = 0 \\ \left.\frac{\partial C_{AB}}{\partial t}\right|_r &= k_1 C_A^r C_B^r - k_2 C_{AB}^r = 0 \end{aligned} \tag{5}$$

Equations (4) and (5) lead us to

$$\begin{aligned} C_{AB}^s &= \frac{k_e C_A^s C_T}{1 + k_e C_A^s} \\ C_{AB}^r &= \frac{k_e C_A^r C_T}{1 + k_e C_A^e} \end{aligned} \tag{6}$$

where $k_e = k_1/k_2$ is the equilibrium constant of Reaction (1) at the interfaces.

The facilitated flux, defined as the number of moles of Permeant A incorporated in the receiving phase/time, is due to the movement of Complex AB, and it is given by the first Ficks law. Therefore

$$J = P_{AB}(C_{AB}^s - C_{AB}^r) \tag{7}$$

where P_{AB} is the apparent permeability of AB through the membrane, being a factor containing interface areas, the thickness of the diffusion boundary layers, and the diffusion coefficient. Substitution of Eqs. (6) in Eq. (7) and rearrangement gives

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$$J = P_{\mathrm{AB}} k_e C_T \frac{(C^s_{\mathrm{A}} - C^r_{\mathrm{A}})}{(1 + k_e C^e_{\mathrm{A}})(1 + k_e C^r_{\mathrm{A}})} \tag{8}$$

If $C^r_{\mathrm{A}} = 0$, the Eq. (8) reduces to

$$J_0\!\uparrow = J_{\max} \frac{k_e C^s_{\mathrm{A}}}{1 + k_e C^s_{\mathrm{A}}} \tag{9}$$

which gives the initial flux from the source phase to the receiving phase in the considered conditions, and where

$$J_{\max} = P_{\mathrm{AB}} C_T \tag{10}$$

where $J_{\max}$ is the maximum initial flux which corresponds to $C_T = C^s_{\mathrm{AB}}$, i.e., $J_{\max}$ would be reached if all the molecules of Carrier B are in the form AB. When $C^s_{\mathrm{A}} = 0$, then

$$J_0\!\downarrow = -J_{\max} \frac{k_e C^r_{\mathrm{A}}}{1 + k_e C^r_{\mathrm{A}}} \tag{11}$$

The next objective is the integration of Eq. (8) to yield the permeant concentration in the receiving phase as a function of time, and from this result to determine the transport characteristic parameters, such as $J_{\max}$ and k_e. Let us assume that the initial concentrations at the extramembrane phases are $C^s_{\mathrm{A,0}}$ and $C^r_{\mathrm{A,0}}$, respectively ($C^s_{\mathrm{A,0}} > C^r_{\mathrm{A,0}}$ and both large with respect to C_T), and that at $t = 0$ the membrane does not include A.

If the system is closed, the total number of moles of permeate is constant, so that if initially in the extramembrane phases there are $N^s_{\mathrm{A,0}}$ and $N^r_{\mathrm{A,0}}$ moles of permeate, we can write

$$N^s_{\mathrm{A,0}} + N^r_{\mathrm{A,0}} = N^s_{\mathrm{A}} + N^r_{\mathrm{A}} + N^m_{\mathrm{A}} \tag{12}$$

where N^i_{A} ($i = s, r, m$) are the instantaneous values of moles of permeate in the source phase, the receiving phase, and the membrane, respectively, and so

$$C^s_{\mathrm{A,0}} V_s + C^r_{\mathrm{A,0}} V_r = C^s_{\mathrm{A}} V_s + C^r_{\mathrm{A}} V_r + \bar{C}_{\mathrm{AB}} V_m \tag{13}$$

where V_i ($i = s, r, m$) are the corresponding volumes. Dividing by V_s, it follows that

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$$C_0 = C^s_{\mathrm{A}} + C^r_{\mathrm{A}}\upsilon_r + \bar{C}_{\mathrm{AB}}\upsilon_m \tag{14}$$

with $\upsilon_r = V_r/V_s$, $\upsilon_m = V_m/V_s$, and $C_0 = C^s_{\mathrm{A,0}} + C^r_{\mathrm{A,0}}\upsilon_r$, and where $\bar{C}_{\mathrm{AB}}$ is the mean concentration of AB at the membrane, which in steady-state conditions has a constant value that can be very small in comparison with $C^s_{\mathrm{A,0}}$ and $C^r_{\mathrm{A,0}}$, and so, for similar volumes of different phases, $\bar{C}_{\mathrm{AB}}\upsilon_m$ may be suppressed in Eq. (14), and also in the case of thin membranes where $V_m \ll V_s$ and V_r. Assuming to a first approximation that this is so, then

$$C_0 = C^s_{\mathrm{A}} + C^r_{\mathrm{A}}\upsilon_r \tag{15}$$

In every case, J is given by

$$J = V_r\frac{dC^r_{\mathrm{A}}}{dt} = -V_s\frac{dC^s_{\mathrm{A}}}{dt} \tag{16}$$

From Eqs. (8), (10), (15), and (16), we get

$$V_r\frac{dC^r_{\mathrm{A}}}{dt} = J_{\max}k_e\frac{(C_0 - (1+\upsilon_r)C^r_{\mathrm{A}})}{(1+k_eC^r_{\mathrm{A}})(1+k_e(C_0-\upsilon_rC^r_{\mathrm{A}}))} \tag{17}$$

Integrating Eq. (17) over the time range $(0,t)$, we have

$$\begin{aligned} k_eJ_{\max}t = C_0V_r \Biggl[& \frac{k_e^2C_0\upsilon_r}{2(1+\upsilon_r)}[(\hat{C}^r_{\mathrm{A}})^2 - (\hat{C}^r_{\mathrm{A,0}})^2] + \biggl[\frac{(\upsilon_r-1)}{(1+\upsilon_r)}k_e \\ & - \frac{C_0k_e^2}{(1+\upsilon_r)^2}\biggr](\hat{C}^r_{\mathrm{A}} - \hat{C}^r_{\mathrm{A,0}}) + \frac{1}{1+\upsilon_r}\biggl[k_e + \frac{1}{C_0} + \frac{C_0k_e^2}{(1+\upsilon_r)^2} \\ & - \frac{\upsilon_r-1}{1-\upsilon_r}k_e\biggr] \ln \left[\frac{\hat{C}^r_{\mathrm{A}} - \dfrac{1}{1+\upsilon_r}}{\hat{C}^r_{\mathrm{A,0}} - \dfrac{1}{1+\upsilon_r}}\right]\Biggr] \end{aligned} \tag{18}$$

with $\hat{C}^r_{\mathrm{A}} = C^r_{\mathrm{A}}/C_0$.

If $\upsilon_r = 1$ (extramembrane phases with equal volume), Eq. (18) becomes

$$\frac{J_{\max}t}{k_e} = \frac{C_0V_r}{2}\left\{\frac{C_{\upsilon}}{2}\left[(C'_A)^2 - (C'_{A,0})^2 - (C'_A - C'_{A,0})\right] + \left[\frac{1}{k_e} + \frac{1}{C_0k_e^2} + \frac{C_0}{4}\right]\ln\left\{\frac{2C'_A - 1}{2C'_{A,0} - 1}\right\}\right\} \tag{19}$$

Equation (17) gives the instantaneous flux, $J(t)$. The transport rate, Q, which is the net amount of the permeant transferred through the membrane during a time interval t, is obtained from

$$Q = \int_0^t J(t)dt \tag{20}$$

When $\bar{C}_{AB}$ in Eq. (14) cannot be neglected, Eq. (18) remains valid by substituting $\hat{C}'_A$ by $\bar{C}'_A = C'_A/\hat{C}_0$ with $\hat{C}_0 = C_0 - \bar{C}_{AB}\upsilon_m$.

The characteristic parameters of the facilitated transport process are k_e and $J_{\max}$, and they may be determined from Eq. (19) (when $\upsilon_r = 1$), writing this equation in the form

$$\frac{J_{\max}}{k_e} - \frac{C_0\upsilon_r}{2k_e}\left[1 + \frac{1}{C_0k_e} + \frac{C_0k_e}{4}\right]\frac{1}{t}\ln\left\{\frac{2C'_A - 1}{2C'_{A,0} - 1}\right\} = \phi(t) \tag{21}$$

with

$$\phi(t) = \frac{C_0\upsilon_r}{4t}\left[(\hat{C}'_A)^2 - (\hat{C}'_{A,0})^2 - (\hat{C}'_A - \hat{C}'_{A,0})\right] \tag{22}$$

The plot of experimental points $[(1/t)\ln[(2\hat{C}'_A - 1)/(2\hat{C}'_{A,0} - 1)], \phi(t)]$ and the fit to them of an straight line gives k_e from the slope and $J_{\max}$ from the ordinate intercept.

Also, the characteristic parameters may be obtained by considering the initial flux equations. For example, with Eq. (9) we can accomplish an experiment where $C'_A = 0$ in spite of the flux through the membrane system, so that it is necessarily a rapid chemical reaction converting the Permeate A in a product insoluble in the membrane. In these conditions

$$J_0\uparrow = -V_s\frac{dC^s_A}{dt} \tag{23}$$

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whose integration over (0,*t*) leads to

$$\frac{J_{\max}}{V_s} = \frac{C^s_{A,0} - C^s_A}{t} + \frac{1}{k_e t} \ln \left[\frac{C^s_{A,0}}{C^s_A} \right] \tag{24}$$

Adjustment of a straight line to the points $[(C^s_{A,0} - C^s_A)/t, (1/t) \ln (C^s_{A,0}/C^s_A)]$ allows us to obtain k_e and $J_{\max}$ from the slope and ordinate intercept, respectively.

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