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Abstract

Facilitated transport is a process whereby the diffusion of a solute across a membrane is chemically enhanced. In this report an analysis is given of a facilitated transport system involving a volatile species A which reacts with a nonvolatile carrier species B to form the nonvolatile product AB. The species A is transported across the membrane by ordinary diffusion, as well as by the diffusion of the product AB. It is assumed that the reaction rates are large, so the reactions are confined mostly to thin boundary layers near the surfaces of the membrane. The method of matched asymptotic expansions is used to derive the asymptotic solution of the nonlinear boundary value problem governing equilibrium. The effect of various parameters on the facilitation factor is analyzed in detail.

1. Introduction

Facilitated transport is a process whereby the diffusion of a solute across a membrane is chemically enhanced. The phenomenon of facilitated transport is observed, for example, when a volatile species A diffuses across a membrane and the membrane contains a nonvolatile carrier species B which reacts reversibly with A to form the nonvolatile complex AB. In addition to the ordinary diffusion of A, we have the diffusion of the complex AB across the membrane. The carrier B cannot leak out of the membrane, so the total amount of B is conserved and, to balance the diffusion of AB, the carrier B diffuses in a direction opposite to that of A and AB. This circulation of B enhances the transport of A across the membrane. Near the surface of higher concentration of A the reaction of A and B is such that the complex AB is formed, while near the opposite surface the complex AB dissociates into its components A and B. After the dissociation, A leaves the membrane and B diffuses back through the membrane to form additional products AB. The flux of A is thus facilitated by the presence of the carrier species B. This mechanism of facilitated transport is, in fact, used in separation and purification processes -- for example, to separate hexene from heptane (cf.

Matulevicius and Li [1]). It is also assumed to play an important role in transport phenomena in biological membranes, cf. Murray [2].

The phenomenon of facilitated transport was first observed in 1959 by Scholander [3] and Wittenberg [4]. It was studied by Ward [5] who formulated a mathematical model and compared the results of numerical calculations with experimental data for the facilitated transport of nitric oxide in a ferrous chloride solution. Ward also gave an expression for the facilitation factor in the case of equal diffusion coefficients and infinite reaction rates. The expression was derived by selectively applying boundary conditions to the resulting algebraic equations, in an ad hoc manner. Smith, Meldon and Colton [6] considered the same mathematical model and found asymptotic solutions corresponding to membranes that are either very thin or very thick. They recognized that the latter case leads to a singularly perturbed boundary value problem. Assuming equal diffusion coefficients for the nonvolatile species they used the method of matched asymptotic expansions to construct an approximate solution valid for large membrane thicknesses and carrier-dominated diffusion. Goddard, Schultz and Bassett [7] also employed the method of matched asymptotic expansions to consider the facilitated transport problem with large reaction rates and equal diffusion coefficients. This work is reviewed in the article by Goddard, Schultz and Suchdeo [8], and in the monograph by Aris [9], where an excellent description of facilitated transport can be found.

In this report we discuss the carrier facilitated transport problem described earlier. As in [6]-[9], we assume a fast reaction mechanism, so the reactions are confined mostly to thin boundary layers near the surfaces of the membrane and chemical equilibrium pertains throughout most of the interior of the membrane. We make no assumptions about the diffusivities or any of the other parameters that enter the model, except that they are constant -- but not necessarily equal -- throughout the membrane. Our results are asymptotically complete to lowest order for large reaction rates. In the case of equal diffusion coefficients for the nonvolatile species our solution reduces to the solution found by Goddard, Schultz and Bassett [7] which was also given by Ward [5]. In the final section we give a general appraisal of the effect of the various parameters of the problem upon the facilitation factor.

2. Mathematical Model

We consider the steady molecular diffusion of a chemical species A through a membrane. The membrane has the form of a plane slab of finite thickness L. Inside the membrane the species A undergoes a reversible chemical reaction with a second species B to form a complex species AB, say,

$$A+B \rightleftharpoons AB \ . \tag{1}$$

The carrier B and the complex AB diffuse freely inside the membrane, but cannot leak out of it. Thus, only the species A is transferred through the membrane, either by ordinary diffusion or by carrier-mediated transport.

We assume that the temperature is uniform throughout the membrane, and that the diffusion processes are governed by Fick's law with constant (but not necessarily equal) diffusion coefficients. If we choose the x*-axis perpendicular to the membrane, with the membrane surfaces at x* = 0 and x* = L, then the molar concentrations C satisfy the differential equations

$$D_A \frac{d^2C_A}{dx^{*2}} = k_1 C_A C_B - k_2 C_{AB} \ , \tag{2a}$$

$$D_B \frac{d^2C_B}{dx^{*2}} = k_1 C_A C_B - k_2 C_{AB} \ , \tag{2b}$$

$$D_{AB} \frac{d^2C_{AB}}{dx^{*2}} = -k_1 C_A C_B + k_2 C_{AB} \ , \tag{2c}$$

for $0 < x^* < L$, and the boundary conditions

$$C_A(0) = C_A^0 \ , \quad C_A(L) = C_A^L \ , \tag{3a}$$

$$\frac{dC_B}{dx^*}(0) = \frac{dC_B}{dx^*}(L) = 0 \ , \tag{3b}$$

$$\frac{dC_{AB}}{dx^*}(0) = \frac{dC_{AB}}{dx^*}(L) = 0 \ . \tag{3c}$$

Here, the D's denote the diffusion coefficients of the various species; k_1 and k_2 are the reaction rates associated with the forward ($\rightarrow$) and backward ($\leftarrow$) reaction (1), respectively; C_A^0 and C_A^L are the specified molar concentrations of species A at the faces x* = 0 and x* = L of the membrane. The boundary

value problem (2),(3) is to be solved subject to the stoichiometric constraint

$$\frac{1}{L}\int_0^L (C_B+C_{AB})dx^* = C \ , \tag{4}$$

where C is a specified molar concentration. This constraint fixes the total amount of the nontransferable species B and AB present in the membrane.

The quantity of interest is the net molar flux of species A across the membrane, which is given by

$$N_A(x^*) = -\left(D_A \frac{dC_A}{dx^*} + D_{AB} \frac{dC_{AB}}{dx^*}\right) , \qquad 0 \leq x^* \leq L \ .$$

It follows from (2a) and (2c) that the quantity $D_AC_A+D_{AB}C_{AB}$ varies linearly across the membrane. Hence, N_A is constant; its value can be expressed in terms of the concentration differences of the species A and AB at the surfaces of the membrane,

$$N_A = \frac{D_A}{L}\left(C_A^0-C_A^L\right) + \frac{D_{AB}}{L}\left(C_{AB}(0)-C_{AB}(L)\right) \ . \tag{5}$$

The first term in this expression represents the contribution due to ordinary diffusion of the species A, whereas the second term represents the contribution due to carrier-mediated transport of A in the form of the complex AB. It follows from (5) that we are interested in finding the quantity $C_{AB}(0)-C_{AB}(L)$.

We introduce dimensionless variables,

$$x = x^*/L \ ,$$

$$u(x) = C_A(x^*)/C \ ,$$

$$v(x) = C_{AB}(x^*)/C \ ,$$

$$w(x) = C_B(x^*)/C \ ,$$

$$\gamma_0 = C_A^0/C \ , \qquad \gamma_1 = C_A^L/C \ ,$$

$$\kappa_1 = k_1CL^2/D_A \ , \qquad \kappa_2 = k_2L^2/D_A \ ,$$

$$\delta = D_{AB}/D_A \ , \qquad d = D_{AB}/D_B \ .$$

Then we have the following boundary value problem for the functions u, v, and w,

$$u'' = \kappa_1 uw - \kappa_2 v \ , \tag{6a}$$

$$\delta v'' = -\kappa_1 uw + \kappa_2 v \ , \tag{6b}$$

$$(\delta/d)w'' = \kappa_1 uw - \kappa_2 v \ , \tag{6c}$$

for $0 < x < 1$, and

$$u(0) = \gamma_0 \ , \quad u(1) = \gamma_1 \ , \tag{7a}$$

$$v'(0) = v'(1) = 0 \ , \tag{7b}$$

$$w'(0) = w'(1) = 0 \ , \tag{7c}$$

subject to the constraint

$$\int_0^1 (v+w)dx = 1 \ . \tag{8}$$

In terms of the dimensionless variables the quantity of interest, N_A, is given by

$$N_A = \frac{D_A C}{L} \{\gamma_0 - \gamma_1 + \delta[v(0)-v(1)]\} \ . \tag{9}$$

We recall that u, v, and w, representing dimensionless concentrations, are nonnegative functions on their entire domain of definition, $0 \leq x \leq 1$.

By eliminating the variable w we reformulate the problem (6),(7),(8) as a constrained boundary value problem for the functions u and v. From (6b) and (6c) it follows that w+dv is a linear function of x. According to (7b), the derivative of this function vanishes at the endpoints. Hence, w+dv is a constant, α say, so

$$w(x) = \alpha - dv(x) \ , \qquad 0 \leq x \leq 1 \ . \tag{10}$$

Substituting this expression in (8) we see that the constant α can be expressed in terms of v,

$$\alpha = 1 + (d-1)\bar{v} \ , \tag{11a}$$

where

$$\bar{v} = \int_0^1 v(x)dx \ . \tag{11b}$$

As $w(x)+dv(x) \geq 0$, it follows from (10) that the constant α is nonnegative. From (11) it follows that $\alpha \geq 1$ whenever $d \geq 1$. Of course, $\bar{v}$ depends implicitly on the parameter α, so eq. (11a) represents a (nonlinear) constraint which determines α.

Using (10) to eliminate w, we obtain a boundary value problem for the pair of functions (u,v),

$$u'' = \kappa_1 \alpha u - \kappa_2 v - \kappa_1 duv \ , \tag{12a}$$

$$\delta v'' = -\kappa_1 \alpha u + \kappa_2 v + \kappa_1 duv \ , \tag{12b}$$

for $0 < x < 1$, subject again to the boundary conditions (7a) and (7b), and the constraint (11). We will solve this problem assuming that the dimensionless reaction rates κ_1 and κ_2 are both large and of the same order of magnitude. That is, we assume that there exists a small positive parameter ε, $0 < \varepsilon << 1$, such that

$$\kappa_1 = \frac{\sigma_1}{\varepsilon^2} \ , \qquad \kappa_2 = \frac{\sigma_2}{\varepsilon^2} \ ,$$

where the ratio

$$\sigma = \sigma_2/\sigma_1$$

is a O(1)-quantity compared to ε. Thus, we consider the equations

$$\varepsilon^2 u'' = \sigma_1 \alpha u - \sigma_2 v - \sigma_1 duv \ , \tag{13a}$$

$$\varepsilon^2 \delta v'' = -\sigma_1 \alpha u + \sigma_2 v + \sigma_1 duv \ . \tag{13b}$$

Because the small parameter (ε^2) multiplies the derivatives u'' and v'', we are dealing with a singular perturbation problem. We will employ the method of matched asymptotic expansions to solve the equations (13) subject to the boundary conditions (7) and the constraint (11).

3. Solution of the Problem

3a. Interior Solution

To find the solution of eq. (13) for small ε we expand u and v,

$$u = u_0 + \varepsilon^2 u_1 + \ldots , \tag{14a}$$

$$v = v_0 + \varepsilon^2 v_1 + \ldots . \tag{14b}$$

Then, to lowest order in ε,

$$\sigma_1 \alpha u_0 - \sigma_2 v_0 - \sigma_1 d u_0 v_0 = 0 .$$

Thus, any nontrivial solution of the form (14) is such that

$$u_0(x) = \frac{\sigma v_0(x)}{\alpha - d v_0(x)} , \qquad 0 < x < 1 . \tag{15}$$

For the higher-order coefficients we obtain a set of linear algebraic equations

$$\sigma_1(\alpha - d v_0) u_i - (\sigma_2 + \sigma_1 d u_0) v_i = u''_{i-1} + \sigma_1 d \sum_{j=1}^{i-1} u_j v_{i-j} ,$$

$$-\sigma_1(\alpha - d v_0) u_i + (\sigma_2 + \sigma_1 d u_0) v_i = \delta v''_{i-1} - \sigma_1 d \sum_{j=1}^{i-1} u_j v_{i-j} ,$$

for $i=1,2,\ldots$. This set is solvable for (u_i, v_i) if the lower-order coefficients $(u_0,v_0),\ldots,(u_{i-1},v_{i-1})$ satisfy the solvability condition

$$u''_{i-1} + \delta v''_{i-1} = 0 .$$

In particular, for $i=1$,

$$u''_0 + \delta v''_0 = 0 . \tag{16}$$

From (15) we deduce an expression for u''_0 in terms of v_0 and its derivatives v'_0 and v''_0. When we use this expression, the solvability condition (16) becomes a second order nonlinear differential equation for v_0. In fact, the

equation is more succinctly formulated in terms of the function $w_0 = \alpha - dv_0$. Namely,

$$-(c^2+w_0^2)w_0w_0'' + 2c^2(w_0')^2 = 0 \ , \tag{17}$$

where we have introduced the abbreviation

$$c^2 = \alpha\sigma/\delta \ .$$

The equation (17) can be integrated exactly. Its general solution is

$$w_0(x) = ax + b \pm \sqrt{(ax+b)^2+c^2} \ , \qquad 0 < x < 1 \ ,$$

where a and b are arbitrary constants of integration. However, the lower sign must be rejected if w_0 is to be positive. Thus we find that, to lowest order in ε, the solution of (13) in the interior of the domain is given by

$$u_0(x) = \frac{\delta}{d}\left[\sqrt{(ax+b)^2+c^2} - (ax+b)\right] - \frac{\sigma}{d} \ , \tag{18a}$$

$$v_0(x) = \frac{\alpha}{d} - \frac{1}{d}\left[ax+b+\sqrt{(ax+b)^2+c^2}\right] \ . \tag{18b}$$

We observe that, in general, the functions u_0 and v_0 cannot be expected to satisfy the given boundary data (7a),(7b) for u and v. Therefore, the expansion (14) represents an asymptotic approximation to the solution in the interior of the domain. Near each of the boundaries it is necessary to construct boundary layer expansions that must be matched with the interior solution (18). For future reference we note from (18) that

$$u_0(x) \to u_0(0) = \frac{\delta}{d}\left[\sqrt{b^2+c^2} - b\right] - \frac{\sigma}{d} \ , \tag{19a}$$

$$v_0(x) \to v_0(0) = \frac{\alpha}{d} - \frac{1}{d}\left[b + \sqrt{b^2+c^2}\right] \ , \tag{19b}$$

as $x \to 0$, and

$$u_0(x) \to u_0(1) = \frac{\delta}{d}\left[\sqrt{(a+b)^2+c^2} - (a+b)\right] - \frac{\sigma}{d}\ , \tag{20a}$$

$$v_0(x) \to v_0(1) = \frac{\alpha}{d} - \frac{1}{d}\left[a+b + \sqrt{(a+b)^2+c^2}\right]\ , \tag{20b}$$

as $x \to 1$.

3b. Boundary Layer Solution near x=0

We introduce the stretched variable $z = x/\varepsilon$ and define the functions U^L and V^L by means of the relations

$$U^L(z) = u(\varepsilon z)\ , \quad V^L(z) = v(\varepsilon z)\ .$$

If u and v satisfy the equations (13), then U^L and V^L satisfy the equations

$$U'' = \sigma_1\alpha U - \sigma_2 V - \sigma_1 dUV\ , \tag{21a}$$

$$\delta V'' = -\sigma_1\alpha U + \sigma_2 V + \sigma_1 dUV\ , \tag{21b}$$

for $z > 0$. We will determine a solution (U^L,V^L) subject to the initial conditions

$$U(0) = \gamma_0\ , \quad V'(0) = 0, \tag{22}$$

cf. (7a)(7b), and the matching conditions

$$\lim_{z\to\infty} U(z) = u_0(0)\ , \quad \lim_{z\to\infty} V(z) = v_0(0)\ , \tag{23}$$

cf. (19a),(19b). (We drop the superscript L in the remainder of this subsection.)

First, we observe that $U+\delta V$ is a linear function of z. Since U and V both tend to finite limits as $z\to\infty$, we must have

$$U(z) + \delta V(z) = \beta\ , \qquad z > 0\ , \tag{24}$$

for some constant β. This relation allows us to eliminate U from (21) and

(22). The result is a nonlinear differential equation for V,

$$\delta V'' + \sigma_1 \left[d\delta V^2 - (\alpha\delta+\sigma+d\beta)V + \alpha\beta \right] = 0 , \tag{25}$$

which must be solved subject to the initial conditions

$$V(0) = (\beta-\gamma_0)/\delta , \quad V'(0) = 0 . \tag{26}$$

The equation (25) admits two solutions that do not depend on z, viz. $V(z) = V^+$ and $V(z) = V^-$, where

$$V^{\pm} = \frac{1}{2d\delta} \left[\alpha\delta + \sigma + d\beta \pm \sqrt{(\alpha\delta+\sigma+d\beta)^2 - 4\alpha\beta\delta d} \right] .$$

Now, the initial conditions (26) imply that there is no real value of β such that $V^+ = (\beta-\gamma_0)/\delta$, and that there is precisely one real value of β such that $V^- = (\beta-\gamma_0)/\delta$, namely

$$\beta = \gamma_0 + \frac{\alpha\delta\gamma_0}{\sigma+d\gamma_0} . \tag{27}$$

In that case,

$$U^L(z) = U_0 = \gamma_0 , \tag{28a}$$

$$V^L(z) = V_0 = \frac{\alpha\gamma_0}{\sigma+d\gamma_0} . \tag{28b}$$

Both matching conditions (23) are satisfied if we take

$$b = \frac{1}{2\delta} \left[-(\sigma+d\gamma_0) + \frac{c^2\delta^2}{\sigma+d\gamma_0} \right] . \tag{29}$$

The equation (25) admits other solutions besides the ones that are independent of z that we found above. Although they cannot be obtained explicitly, we can gain sufficient information about them to evaluate their relevance in the present context. If we multiply eq. (25) by V' and integrate, using the initial conditions (26), we obtain the following expression for V' in terms of V,

$$V' = \pm\left[\frac{2}{3}\, d\sigma_1 (V(0)-V)q(V)\right]^{1/2} , \tag{30}$$

where q is a quadratic function of V,

$$q(V) = V^2 + q_1 V + q_2 ;$$

with

$$q_1 = -\frac{1}{2d\delta}\,(2d\gamma_0+3\sigma+3\alpha\delta+d\beta) ,$$

$$q_2 = -\frac{1}{2\delta^2 d}\left[d\beta^2 + (d\gamma_0+3\sigma-3\alpha\delta)\beta - \gamma_0(2d\gamma_0+3\sigma+3\alpha\delta)\right] .$$

The existence of non-constant solutions V of the differential equation (30) is most easily studied in the phase plane (V,V'). Because of (26), we restrict our attention to trajectories that originate at (V(0),0). We observe that any trajectory emanating from the point (V(0),0) leaves the V-axis under a vertical tangent, cf. (30). Finally, we require that $\lim_{z\to\infty} V'(z) = 0$, so any trajectory of interest must end at some point of the V-axis. Now, if $q(V) > 0$ for all V, we must have $V \leq V(0)$ for V' to be real, so V is a decreasing function of z near $z = 0$. This rules out the upper (+) sign in (30). But then it is obvious that any trajectory, once it has left the V-axis at (V(0),0), stays in the lower half-plane to the left of the vertical line $V = V(0)$ for all $z > 0$ and will never return to the V-axis. Therefore, no trajectory originating at (V(0),0) meets the requirement that it end at some point of the V-axis. We conclude that (30) does not have a non-constant solution that meets all requirements. A similar conclusion holds if $q(V) < 0$ for all V.

Now, assume that q has two real zeros, V_+ and V_- say,

$$V_\pm = \frac{1}{4d\delta}\,(2d\gamma_0+3\sigma+3\alpha\delta+d\beta) \pm \frac{3}{4\delta}\sqrt{p(\beta)} ,$$

where

$$p(\beta) = \beta^2 + \frac{2}{3d}\,(2d\gamma_0+5\sigma-3\alpha\delta)\beta$$

$$+ \frac{1}{3d^2}\,(2d\gamma_0+3\sigma+3\alpha\delta)(-2d\gamma_0+\sigma+\alpha\delta) .$$

Then

$$V' = \pm\left[\frac{2}{3}\, d\sigma_1\, (V(0)-V)(V-V_-)(V-V_+)\right]^{1/2} . \tag{31}$$

We investigate whether it is possible that a trajectory which originates at $(V(0),0)$, terminates at either of the points $(V_-,0)$ or $(V_+,0)$.

First, we consider the case $V(0) < V_- < V_+$. Then, for V' to be real we must have $V < V(0)$ for z near 0, so V decreases, the upper (+) sign for V' is ruled out, and any trajectory leaving $(V(0),0)$ stays in the lower half-plane to the left of the vertical line $V = V(0)$. No trajectory can reach either of the points $(V_-,0)$, $(V_+,0)$ and, again, we conclude that there is no non-constant solution of (30) that meets all requirements.

Next, we consider the case $V_- < V(0) < V_+$. Then the condition that V' be real leads to $V > V(0)$ for z near 0, so V increases and the lower (-) sign is ruled out. This time, it is indeed possible that there exists a trajectory that originates at $(V(0),0)$ and ends at $(V_+,0)$, and that lies entirely in the upper half-plane between the vertical lines $V = V(0)$ and $V = V_+$. Such a trajectory is traversed in the direction of increasing V.

Similarly, if $V_- < V_+ < V(0)$ we find that there may exist a trajectory that originates at $(V(0),0)$ and ends at $(V_+,0)$, and that lies entirely in the lower half-plane between the vertical lines $V = V_+$ and $V = V(0)$. Such a trajectory is traversed in the direction of decreasing V.

Hence, we can restrict ourselves to the investigation of solutions V of (25) which are given implicitly by the formula (31), which satisfy the initial conditions (26), and which have the property that

$$\lim_{z\to\infty} V(z) = V_+ . \tag{32}$$

The corresponding functions U are found from (24). Of course, the parameter β is still to be determined at this point.

Next, we turn to the matching conditions (23). They become

$$\beta-\delta V_+ = \frac{\delta}{d}\left[\sqrt{b^2+c^2} - b\right] - \frac{\sigma}{d} ,$$

$$V_+ = \frac{\alpha}{d} - \frac{1}{d}\left[\sqrt{b^2+c^2} + b\right] ,$$

cf. (19). Multiplying the last equation by δ and adding the two equations we see that

$$b = \frac{1}{2}\left(\alpha - \frac{\sigma}{\delta} - \frac{d}{\delta}\beta\right) .$$

Then the second matching condition can be rewritten in the form

$$\sqrt{b^2+c^2} = \alpha - b - dV_+$$

$$= -\frac{1}{4}\left(\alpha - \frac{d}{\delta}(\beta-\gamma_0)\right) - \frac{1}{4}\frac{\sigma}{\delta} - \frac{1}{4}\frac{d\gamma_0}{\delta} - \frac{3}{4}\frac{d}{\delta}\sqrt{p(\beta)} .$$

However, because $W(0) = \alpha-dV(0) = \alpha-d(\beta-\gamma_0)/\delta \geq 0$, the expression in the right member is certainly negative, while the expression in the left member is positive. Hence, the matching conditions cannot possibly be satisfied for any choice of α and β. We conclude therefore, that a solution of the differential equation (25) of the form (31) cannot be made to match the interior solution (18) and must be ruled out. Hence, the only solution in the boundary layer near $x = 0$ that satisfies the initial conditions (26) and that can be matched with the interior solution (18) is the constant solution (28), with β given by (27).

3c. Boundary Layer Solution near x = 1

A similar analysis can be given for the boundary layer solution near $x = 1$. We introduce the stretched variable $z = (1-x)/\varepsilon$ and define the functions U^R and V^R by the relations

$$U^R(z) = u(1-\varepsilon z) , \quad V^R(z) = v(1-\varepsilon z) .$$

Then U^R and V^R satisfy the equations (21) for $z > 0$. Instead of (22) we have the initial conditions

$$U(0) = \gamma_1 , \quad V'(0) = 0 , \tag{33}$$

and the matching conditions

$$\lim_{\infty} U(z) = u_0(1) \ , \quad \lim_{z\to\infty} V(z) = v_0(1) \ . \tag{34}$$

As in the previous subsection we find that the only solution (U^R,V^R) is, in fact, independent of z and given by

$$U^R(z) = U_1 = \gamma_1 \ , \tag{35a}$$

$$V^R(z) = V_1 = \frac{\alpha\gamma_1}{\sigma+d\gamma_1} \ . \tag{35b}$$

The matching conditions (34) are satisfied if we take

$$a+b = \frac{1}{2\delta}\left[-(\sigma+d\gamma_1) + \frac{c^2\delta^2}{\sigma+d\gamma_1}\right] \ . \tag{36}$$

3d. Uniform Solution

Now that we have the interior solution to the boundary value problem (13), and the boundary layer solutions that are valid near x = 0 and x = 1 and that match the interior solution, we can combine the results to obtain a solution that is valid uniformly throughout the interval [0,1]. To lowerst order in ε we have

$$u(x) = \frac{\delta}{d}\left[\sqrt{(ax+b)^2+c^2} - (ax+b)\right] - \frac{\sigma}{d} \ , \tag{37a}$$

$$v(x) = \frac{\alpha}{d} - \frac{1}{d}\left[ax+b + \sqrt{(ax+b)^2+c^2}\right] \ , \tag{37b}$$

where a and b are given by the expressions (29) and (36). It remains to determine α from the constraint (11).

Using (37b) we obtain the following expression for $\bar{v}$,

$$\bar{v} = \frac{\alpha}{d} - \frac{1}{2d}(a+2b)$$

$$- \frac{1}{2ad}\left[\left\{(a+b)\sqrt{(a+b)^2+c^2} - b\sqrt{b^2+c^2}\right\}\right.$$

$$\left. + c^2\left\{\ell n\left(a+b+\sqrt{(a+b)^2+c^2}\right) - \ell n\left(b+\sqrt{b^2+c^2}\right)\right\}\right] \ .$$

We substitute b and a+b from (29) and (36), and use the definition $c^2 = \alpha\sigma/\delta$. We then find

$$\bar{v} = \frac{\alpha}{d}\left[1 - \frac{\sigma}{\eta_0\eta_1+\alpha\sigma\delta}\,(\rho\sigma\delta\alpha+\eta_0\eta_1\omega)\right] ,$$

where η_0 , η_1, ρ and ω are given in terms of γ_0, γ_1, σ and d,

$$\eta_0 = \sigma + d\gamma_0 , \quad \eta_1 = \sigma + d\gamma_1 ,$$

$$\rho = \frac{1}{2}(\eta_0^{-1}+\eta_1^{-1}) ,$$

$$\omega = (\eta_0-\eta_1)^{-1}(\ell n\ \eta_0 - \ell n\ \eta_1) .$$

When we use the expression of $\bar{v}$ in the constraint (11) we obtain a quadratic equation for α,

$$p_0\alpha^2 + p_1\alpha + p_2 = 0 , \tag{38}$$

where the coefficients p_i are given in terms of the parameters of the problem,

$$p_0 = -\sigma\delta d\,\frac{\sigma^2 + \gamma_0\gamma_1 d + \frac{1}{2}(\gamma_0+\gamma_1)\sigma(1+d)}{(\sigma+\gamma_0 d)(\sigma+\gamma_i d)} ,$$

$$p_1 = \sigma\delta d - (1+(d-1)\sigma\omega)(\sigma+\gamma_0 d)(\sigma+\gamma_1 d) ,$$

$$p_2 = d(\sigma+\gamma_0 d)(\sigma+\gamma_1 d) .$$

It remains to investigate the roots of equation (38). Because p_0 is always negative and p_2 always positive, the roots are real and of opposite sign. Thus, there exists exactly one positive value of α such that the constraint (11) is satisfied, namely

$$\alpha = -\frac{1}{2p_0}\left[p_1 + \sqrt{p_1^2-4p_0p_2}\right] . \tag{39}$$

This completes the solution of the problem.

4. Facilitation Factor

We return to the expression (9) for the total flux of species A through the membrane. The extent to which the transport is enhanced is measured by the facilitation factor F,

$$F = \delta \frac{v(0) - v(1)}{\gamma_0 - \gamma_1} .$$

With the solution v given by (37b), where the constants a and b are given in (29) and (36) and the parameter α is determined according to (39), we have

$$F = \frac{\alpha\sigma\delta}{(\sigma+\gamma_0 d)(\sigma+\gamma_1 d)} . \tag{40}$$

We note the following special cases:

(i) $d = 1$ $(D_{AB}=D_B)$.

The quadratic equation (38) reduces to

$$(\alpha-1)(\sigma\delta\alpha + (\sigma+\gamma_0)(\sigma+\gamma_1)) = 0 ,$$

whence $\alpha = 1$, so

$$F = F_1 = \frac{\sigma\delta}{(\sigma+\gamma_0)(\sigma+\gamma_1)} . \tag{41a}$$

In terms of the original parameters we have

$$F_1 = \frac{D_{AB}}{D_A} \frac{k_1 k_2 C}{(k_2+k_1 C_A^0)(k_2+k_1 C_A^L)} . \tag{41b}$$

This expression agrees with the ones given by Ward [5, formula (12)], Smith, Meldon and Colton [6, formula (54)], and Goddard, Schultz and Bassett [7, formula (3.30)].

(ii) $d \approx 1$ $(D_{AB} \approx D_B)$.

A straightforward perturbation procedure yields the result

$$F = F_1[1-\Phi(d-1)+O((d-1)^2)] \ , \tag{42}$$

where F_1 is the value of F for d = 1, which is given by (41), and

$$\Phi = \sigma \frac{\eta_0\eta_1\omega + \rho\sigma\delta}{\eta_0\eta_1 + \sigma\delta} + \frac{\gamma_0}{\eta_0} + \frac{\gamma_1}{\eta_1} - 1 \ . \tag{43}$$

Here, η_0, η_1, ρ and ω are given in terms of γ_0, γ_1 and σ,

$$\eta_0 = \sigma + \gamma_0 \ , \quad \eta_1 = \sigma + \gamma_1 \ ,$$

$$\rho = \frac{1}{2}(\eta_0^{-1}+\eta_1^{-1}) \ ,$$

$$\omega = (\eta_0-\eta_1)^{-1}(\ell n\ \eta_0 - \ell n\ \eta_1) \ .$$

We show that Φ is always positive.

Suppose $\gamma_0 \geq \gamma_1$. Then $\eta_0 \geq \eta_1$, so $\eta_0 = \eta_1(1+z)$ for some $z \geq 0$. Thus, $\omega = (\eta_1 z)^{-1}\ell n(1+z)$ and $\rho = \eta_1^{-1}(1 + \frac{1}{2}z)(1+z)^{-1}$. It follows from the inequality

$$\ell n(1+z) \leq z \frac{1 + \frac{1}{2}z}{1 + z} \ , \qquad z \geq -1 \ ,$$

that $\omega \leq \rho$. Hence,

$$\Phi \geq \sigma\omega + \frac{\gamma_0}{\eta_0} + \frac{\gamma_1}{\eta_1} - 1 \ .$$

Next, we use the inequality

$$\ell n(1+z) \geq \frac{z}{1+z} \ , \qquad z \geq -1 \ ,$$

to show that $\omega \geq \eta_1^{-1}(1+z)^{-1} = \eta_0^{-1}$, so

$$\Phi \geq \frac{\sigma}{\eta_0} + \frac{\gamma_0}{\eta_0} + \frac{\gamma_1}{\eta_1} - 1 = \frac{\gamma_1}{\eta_1} > 0 \ .$$

Similarly, one shows that $\Phi > 0$ if $\gamma_0 \leq \gamma_1$, so Φ is indeed always positive.

The coefficient Φ may be called the enhancement coefficient. It measures the effect of different diffusion coefficients for the nonvolatile species B

and AB on the facilitation factor F, relative to the situation where B and AB have equal diffusion coefficients. As can be seen from (42), the facilitation factor F is enhanced wher. $d < 1$ (i.e. $D_B > D_{AB}$), inhibited when $d > 1$ (i.e. $D_{AB} > D_B$).

Notation

A, B, AB	molecular species
D_A, D_B, D_{AB}	diffusion coefficients
C_A, C_B, C_{AB}	molar concentrations
x^*	coordinate perpendicular to the membrane surfaces
L	thickness of the membrane
k_1, k_2	forward (→) and backward (←) reaction rates in (1)
C_A^0, C_A^L	specified molar concentrations of A at $x^* = 0$ and $x^* = L$
C	specified total molar concentration of B and AB inside the membrane
N_A	total flux of species A
x	dimensionless coordinate
u,v,w	dimensionless molar concentrations
$\bar{v}$	integral of v over [0,1]
γ_0, γ_1	boundary values of u
κ_1, κ_2	dimensionless reaction rates
δ, d	ratios of diffusion coefficients
α, β, a, b	constants
ε	small parameter, $0 < \varepsilon \ll 1$
σ_1, σ_2	dimensionless reaction rates; $\sigma_i = \kappa_i/\varepsilon^2$
σ	ratio of reaction rates; $\sigma = \sigma_2/\sigma_1 = \kappa_2/\kappa_1$
c	parameter; $c^2 = \alpha\sigma/\delta$
u_0, u_1,...	coefficients of u in the interior solution
v_0, v_1,...	coefficients of v in the interior solution
U^L, V^L	boundary layer solution near x = 0
U^R, V^R	boundary layer solution near x = 1
η_0 , η_1	parameters
ρ, ω	parameters involving η_0 and η_1
p_0, p_1, p_2	parameters
q_1, q_2	parameters
F	facilitation factor
F_1	value of facilitation factor when $D_{AB} = D_B$
Φ	enhancement (inhibition) coefficient in the facilitation factor

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