The Prediction of Facilitation Factors for Reaction Augmented Membrane Transport

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The flux of permeant across a thin, liquid film or membrane can be greatly enhanced by selective complexation with a mobile, membrane phase carrier component; the resulting transport process is referred to as being facilitated or carrier mediated. Such systems often involve the simple, reversible bimolecular reaction

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} AB$$

For reviews of carrier mediated transport systems, see Ward (1972), Schultz et al. (1974), Cussler (1975), Smith et al. (1977), and Matson et al. (1977). A general, closed form solution to the reaction/diffusion equations which describe these systems is not possible owing to nonlinear reaction rate terms. A number of numerical solutions for the permeant flux have been published, for example, Kutchai et al. (1970), Meldon (1973), and Ward (1970). In addition, asymptotic solutions for the regimes near the limits of reaction equilibrium and molecular diffusion are available (Goddard et al., 1970; Smith et al., 1973), although the former requires the solution of a series of implicit algebraic equations.

In this paper we present a simple approximate solution for prediction of the facilitation factor (the ratio of the facilitated permeant flux to that of simple molecular diffusion) for the entire range of reaction/diffusion times. The calculation of facilitation factors by the present method is straightforward, and predictions agree well with published numerical results. The principal utility of the analysis is in the interpretation of complex reaction schemes; because the solution is compact and explicit in the facilitation factor, it allows direct comparison with experimentally measured values. We demonstrate this by applying our solution to the facilitated transport of carbon dioxide in monoethanolamine (MEA) solutions, a system which we have investigated experimentally.

APPROXIMATE SOLUTION

For one-dimensional, steady state diffusion with reaction in a homogeneous medium, three mass balances can be written:

$$D_i \frac{d^2C_i}{dx^2} = R_i \quad i = A, B, AB \qquad (1) \text{ to } (3)$$

Note that R_i is a nonlinear function of the component concentrations; for example, $R_A = k_1C_AC_B - k_{-1}C_{AB}$. The permeant concentrations at the membrane boundaries are fixed by the adjoining bulk phase compositions. Additional constraints necessary to solve Equations (1) to (3) result from the fact that the carrier and its complex are confined to the membrane (Schultz et al., 1974). The usually reasonable assumption $D_B = D_{AB}$ is introduced to simplify the analysis.

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An analytical solution can be obtained by linearization of the reaction rate expression. Specifically, if C_B is assumed constant, the solution to Equations (1) to (3) in terms of the facilitation factor is

$$\frac{N_T}{N_o} = \frac{1 + F}{1 + \frac{F}{\phi}\tanh\phi} \qquad (4)$$

where

$$F = \frac{D_{AB}KC_B}{D_A}, \quad \phi = \frac{1}{2}\sqrt{\frac{k_1C_BL^2}{D_A}\left(\frac{1+F}{F}\right)}$$

[Equation (4) was introduced by Donaldson and Quinn (1975) for tracer diffusion through a reactive membrane solution equilibrated with a constant partial pressure of untagged gas; in the limit of vanishingly small tracer concentration, it is an exact solution for the facilitated tracer flux.] It is interesting to note that Equation (4) has the proper limiting forms for slow and for fast reactions or, more correctly, large and small Damköhler numbers (Smith et al., 1973). When facilitation is reaction rate limited ($\phi/\tanh\phi << F$), Equation (4) becomes

$$\frac{N_T}{N_o} = \frac{\phi}{\tanh\phi} \cong 1 + \frac{1}{12}\frac{k_1C_BL^2}{D_A} + \ldots \qquad (5)$$

Equation (5) is equivalent to the thin film asymptotic solution of Smith et al. (1973). Likewise, at reaction equilibrium, Equation (4) has the correct limiting form

$$\frac{N_T}{N_o} = 1 + F = 1 + \frac{D_{AB}KC_B}{D_A} \qquad (6)$$

The choice of an appropriate, constant value for C_B can be made by again considering the two limiting reaction regimes. At reaction equilibrium, C_B can be calculated from the local permeant concentration

$$C_B = \frac{C_T}{1 + KC_A} \qquad (7)$$

For the opposite regime of slow reaction rate, Smith et al. (1973) have shown that Equation (7) (with C_A equal to the arithmetic mean of the membrane boundary conditions) is also the proper first term in the power series expansion of C_B. We use Equation (7) to evaluate C_B for the entire range of reaction/diffusion times for two special cases.

Equation (7) can be used to predict facilitation factors for systems with negligible downstream permeant concentration ($C_A{}^L = 0$) by setting $C_A = C_A{}^o$. The choice of $C_A{}^o$, as opposed to some mean concentration, is justified on the basis of giving the best overall agreement with numerical results (see below). Several authors have presented approximate solutions to Equations (1) to (3) based on linearized forms for the reaction rate term. Friedlander and Keller (1965) linearized about the limit of an

infinitesimally small driving force. Their solution is restricted to this limiting case and, therefore, does not approach the facilitation expected at reaction equilibrium for a finite driving force (Smith et al., 1973). The approximate solution of Yung and Probstein (1973), also for the case of $C_A^L = 0$, was obtained by effectively equating the constant carrier concentration C_B with C_T by assuming the product KC_A^o to be vanishingly small [see Equation (7)]; however, the use of Equation (4), with $C_A = C_A^o$ in Equation (7), gives generally better accuracy in predicting the facilitation factor. Finally, Hoofd and Kreuzer (1977) obtained a solution by postulating a functional form for the concentration profile. Their solution, however, requires a trial-and-error procedure.

The second case to which Equation (4) applies is that of the carrier concentration C_B being approximately equal to C_T. From Equation (7), $C_B = C_T$ when the product $KC_A^o << 1$. However, this situation of excess carrier (Cussler, 1975) is not commonly encountered among experimental systems of interest.

PREDICTED FACILITATION FACTORS

In Table 1, we compare facilitation factors predicted from Equation (4) (with $C_A^L = 0$) with results of two typical numerical techniques. Meldon (1973) derived a finite-difference solution to Equations (1) to (3); his calculations cover a wide range of parameters and are expressed in terms of appropriate dimensionless groups. Kutchai et al. (1970) used a quasilinearization technique to obtain a numerical solution for the particular case of oxygen diffusion through hemoglobin solutions. In both cases, values predicted from Equation (4) show close agreement with the numerical results.

Likewise, the experimental results of Ward (1970) for the nitric oxide/ferrous ion facilitated transport system

$$NO + Fe^{+2} \rightleftarrows Fe(NO)^{+2}$$

can be compared with those predicted by Equation (4). The facilitation factors calculated using the physical and system parameters of Ward (1970) are listed in Table 2, along with the experimentally measured facilitation factors. The comparison is very favorable.

Table 1. Comparison of Predicted Facilitation Factors
Finite-difference results as function of dimensionless ratios

$(k_{-1}L^2/D_B)^{1/2}$	Figure A3-1 (Meldon, 1973) N_T/N_o	Equation (4) N_T/N_o
$\left[\frac{D_BC_T}{D_AC_A^o}, \frac{k_1C_A^o}{k_{-1}}\right] = [1\,000, 10]$		
10^{-1}	2.2	1.7
10^0	16	14.9
10^1	140	129
10^2	500	568
10^3	840	858
$\left[\frac{D_BC_T}{D_AC_A^o}, \frac{k_1C_A^o}{k_{-1}}\right] = [10, 1]$		
10^0	1.3	1.35
10^1	4.2	4.3
10^2	5.8	5.8
10^3	6.0	6.0
$\left[\frac{D_BC_T}{D_AC_A^o}, \frac{k_1C_A^o}{k_{-1}}\right] = [10, 10]$		
10^0	1.6	1.6
10^1	5.5	6.4
10^2	9.0	9.5
10^3	10.0	10.0

Steady state oxygen diffusion through hemoglobin solution
[Parameters for Equation (4) taken from Kutchai et al, 1970]

$L(\mu m)$	Table IV (Kutchai et al., 1970) N_T/N_o	Equation (4) N_T/N_o
0.5	1.196	1.160
0.75	1.286	1.275
1.0	1.351	1.364
2.0	1.500	1.550
5.0	1.646	1.692
25.0	1.769	1.780
∞	1.803	1.803

Table 2. NO/Fe^{+2} Facilitated Transport System

$C_T(M)$	Experimental values (Ward, 1970) N_T/N_o	Equation (4) N_T/N_o
0.05	2.2	2.1
0.075	2.7	2.6
0.10	3.1	3.0
0.15	4.1	3.8
0.20	4.9	4.6

CARBON DIOXIDE/MONOETHANOLAMINE SYSTEM

A permeant carrier transport system involving more complex chemistry can also be analyzed by a modified form of Equation (4) (for the case of negligible downstream concentration) if the reaction term can be linearized by assuming a constant carrier concentration. The carrier concentration is set equal to the value which would result if the solution were equilibrated at the upstream permeant concentration [analogous to Equation (7)].

An example of this type that we have been studying in another context is the primary reaction of carbon dioxide in monoethanolamine (MEA) solution:

$$CO_2 + 2RNH_2 \rightleftarrows RNHCOO^- + RNH_3^+$$

$$(R = HOCH_2CH_2-)$$

The rate limiting step for this overall reaction is (Astarita et al., 1964; Danckwerts and McNeil, 1967)

$$CO_2 + RNH_2 \rightleftarrows RNHCOO^- + H^+ \qquad (a)$$

In addition, the amine carbamate product $RNHCOO^-$ can (more slowly) undergo hydrolysis to form a second product HCO_3-:

$$RNHCOO^- + H_2O \rightleftarrows RNH_2 + HCO_3- \qquad (b)$$

For this system, the facilitation factor for carbon dioxide transport is given by Equation (4), with F and K defined as

$$F = \frac{D_{RNHCOO-}}{D_{CO_2}} \frac{K(C_{RNH_2})}{(C_{H^+})},$$

$$K = \frac{(C_{H^+})(C_{RNHCOO-})}{(C_{CO_2})(C_{RNH_2})}$$

In applying Equation (4) to this system, we ignore the

possible influence of the hydrolysis reaction (*b*), which would increase the facilitation factor (Danckwerts and McNeil, 1967; Sada et al., 1976).

Unfortunately, a number of required physical and equilibrium parameters are not sufficiently well known for the carbon dioxide/MEA system to adequately test the model (Smith, 1978). However, the applicability of the constant carrier (that is, RNH_2) assumption can be tested by two complementary experiments. Using an experimental arrangement similar to that of Donaldson and Quinn (1975), we measured the tracer flux of $C^{14}O_2$ through membranes containing MEA solution, which had been equilibrated with a known partial pressure of carbon dioxide (in N_2) (Smith, 1978). Since the quantity of tracer was negligibly small, this arrangement represents exactly the uniform carrier condition. In addition, by flushing the downstream side with N_2, we measured the net carbon dioxide flux (by means of the parallel $C^{14}O_2$ flux) through these same membranes. The extent to which the facilitation factors for net transport approach those of the tracer flux indicates the adequacy of the assumption of uniform (equilibrium) carrier

Table 3. Tracer Flux and Net Transport Measurements for Monoethanolamine Solutions (Smith, 1978)

% CO_2*	$C_T(M)$	Case I: tracer flux N_T/N_W†	Case II: net transport N_T/N_W†
1	4.0	2.5	2.4
1	2.0	11.4	8.9
1	1.0	9.9	8.0
5	4.0	3.7	2.3
5	2.0	7.3	4.3
5	1.0	14.3	9.1
5	0.5	9.3	4.8
5	0.2	8.3	4.0

* For net transport, % CO_2 refers to the upstream CO_2 value.
† N_W is the flux through pure water; these are averaged values for N_T/N_W.

concentration. In Table 3, the experimental facilitation factors for the tracer flux of $C^{14}O_2$ (case I) and the net flux of carbon dioxide (case II) are listed for a number of MEA concentrations and carbon dioxide partial pressures; the agreement between the corresponding values is good.

The comparison would be even more favorable except for the influence of the second, consecutive reaction (*b*). For the tracer flux (case I), the RNH_2 concentration is higher than for the net transport trials, since both reactions (*a*) and (*b*) are at equilibrium with respect to the untagged species [reaction (*b*) forms additional RNH_2, the reactant species in (*a*)], while for the net transport of carbon dioxide (case II), the species in solution are generally not at equilibrium. Thus, the primary reaction (*a*) would occur to a greater extent in case I. As the partial pressure of carbon dioxide increases, and as the concentration of monoethanolamine decreases, the secondary reaction (*b*) becomes more important. As can be seen in Table 2, the values for the membrane facilitation factor for the two cases generally become more disparate.

The fact that the two cases agree as well as they do indicates that given the necessary physicochemical constants, Equation (4) can be used to predict approximate facilitation factors for carbon dioxide/MEA solutions. In the absence of any comparable predictive scheme, the constant carrier assumption may prove useful in evaluating other complex systems.

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NOTATION

A = permeant
B, AB = free and complex forms of carrier, respectively
C = concentration
C_T = overall carrier concentration based on the total amount of carrier added to the membrance divided by the membrane volume
D = diffusion coefficient
F = defined in Equation (4)
k_1 = forward reaction rate constant
k_{-1} = reverse reaction rate constant
K = equilibrium constant
L = membrane thickness
N_o = molecular diffusion flux
N_T = facilitated diffusion flux
R_i = local net rate of depletion of component i
x = distance
ϕ = defined in Equation (4)

Superscripts

o = upstream boundary
L = downstream boundary

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A Method of Estimating Self-Diffusion Coefficients in Liquids

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An empirical relationship has been developed which is useful for the estimation of the self-diffusion coefficient of liquids. The relationship is given by

$$D_{11} = \frac{4.5 \times 10^{-9}(V^* - v)T}{\eta V^{*4/3}} \qquad (1)$$

where D_{11} is the self-diffusion coefficient in the units of square centimeter per second, V^* and v are the molar volumes at the critical temperature and temperature T (in degrees Kelvin), respectively, and η is the viscosity at the temperature T expressed in poise.

A test of this equation is shown in Figure 1, where V^* on the ordinate is plotted against the quantity $D_{11}\eta/T(V^* - v)$ on the abscissa for a remarkably diverse set of liquids. It is noteworthy that V^* varies over five orders of magnitude, while the other variable covers a range of seven orders of magnitude (D_{11} varies by nine orders of magnitude and η varies by about eight orders of magnitude). The slope and intercept of the line depicted in the figure provide the value of the constant 4.5×10^{-9} and of the exponent 4/3 associated with V^* as given by Equation (1).

THE DATA

The filled points represent data which are directly identified in the figure, while the unfilled points represent data for low molecular weight organic liquids; requisite data, that is, D_{11}, η, V^*, and v, at various temperatures were obtained from Dullien (1972) and Reid et al. (1977).

The data on the liquid metals shown as the labeled filled points were obtained as follows. Values of D_{11} were taken from Nachtrieb (1967) and Breitling and Eyring (1972). Values of η and v were obtained from Miller (1952). Data for D_{11}, η, and v for thallium and η for indium were obtained from Cahill and Grosse (1965); V^* values for liquid metals were obtained from a compilation of McGongal (1962) or were estimated from liquid density measurements.

Data for the high molecular weight liquids also shown as the labeled filled points were obtained as follows. D_{11} data for polyethylene from McCall et al. (1959) and all other D_{11} values from Skewis (1966). v values were estimated from the reported polymer densities (Van Krevelen, 1976). The appropriate viscosity data for butyl rubber, SBR, and EPR were estimated using procedures detailed by Van Krevelen (1976) because data at the same temperatures at which D_{11} were measured could not be found in the literature. η for natural rubber was obtained from a plot of bulk viscosity vs. molecular weight given by Holden (1965). η for polyethylene was obtained from a plot of viscosity-molecular weight data given in Doolittle (1952) and in Mendelson et al. (1970).

For these high molecular weight liquids, we used the viscosity values which do not include the chain entanglement contribution (Van Krevelen, 1976). In general, the viscosity of a homologous family of liquids depends on the molecular weight M according to $\log \eta = a + \log M$, where a is a constant for a given series; at a particular value of M, the dependence changes to $\log \eta = A + 3.4 \log M$. This stronger dependence of η on M is attributed to mechanical entanglements between adjacent molecules which serve to reduce flow. For bulk flow of high molecular weight liquids, this entanglement phenomenon must be taken into account when viscosity is considered. However, for the very long time scales involved in diffusion phenomenon, entanglements should not play a role. Hence, the viscosity appropriate to diffusion was estimated for each polymer by extrapolating the bulk viscosity-molecular weight data for low molecular weight homologues whose entanglements are absent to higher molecular weight. This procedure provides values of η which are free of mechanical entanglement contributions.

Critical volumes for the polymers were obtained using an estimation method described by Fedors (1978). Estimates of V^* using alternative methods described in Reid et al. (1977) yielded similar numbers.

CONCLUSIONS

The data of Figure 1 demonstrate that Equation (1) is suitable for estimating self-diffusion coefficients for a very wide range of liquids. For organic liquids, the calculated and measured coefficients differ on the average by about 4%, with methanol and ethanol as two exceptions. However, if it is assumed that in these two liquids diffusion involves dimers, then these data also fall into their proper place. For the liquid metals, the average difference in calculated and measured diffusion coefficients is somewhat higher but well within the errors or spread in values associated with obtaining the experimental values. The high molecular weight liquids show the largest deviation from the prediction of Equation (1), and this is attributable to the uncertainties in the experimentally measured coefficients which are only of the order of 10^{-13} to 10^{-14} cm²/s. Such small coefficients are very difficult to measure precisely. However, even with this difficulty in mind, D_{11} values estimated via Equation (1) are within a factor of two or three of the experimentally measured values. It is also significant that the data for the long chain high molecular weight liquids follow the same relationship which obtains for low molecular weight liquids; the polymeric nature of a liquid does not confer special properties to the self-diffusion coefficient.

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