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Effect of Convective Flow across a Film on Facilitated Transport

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Abstract

An analytical expression is derived for the facilitation factor in facilitated transport across a liquid film. This solution is an extension of previous results in that it accounts for convective flow across the film. In addition, the expression accounts for external mass-transfer resistances as well as diffusion and reaction within the liquid film. A solution procedure to evaluate the important system parameters is described.

INTRODUCTION

Facilitated transport is a process whereby a nonvolatile chemical carrier facilitates or augments the transport of a solute across a liquid film (see Ref. *1* for a detailed discussion). A measure of this facilitation effect is the facilitation factor which is defined as the ratio of the total solute flux with facilitation to the solute diffusion flux. The most common reaction mechanism studied is $A + B \rightleftharpoons AB$. Here A is the solute, B is the carrier, and AB is the carrier-solute complex.

Previously, Noble et al. (*2*) derived an analytical expression for the facilitation factor. This expression included external mass-transfer resistances as well as diffusion and reaction within the film. They developed a graphical method based on their result to analyze experimental data.

The objective of this study is to include the effect of convective flow across the film. This is done through the introduction of a Peclet number (Pe). This effect can be important in two cases. For ceramic membranes, where surface diffusion in the pores is the facilitating effect, bulk convective flow can occur in larger pores. In ion-exchange film supports, incomplete saturation of the sweep gas can cause water to flow across the film.

PROBLEM DESCRIPTION

Referring to Fig. 1, the differential equations which describe the steady-state solute transport with convection are:

$$D_A \frac{d^2C_A}{dx^2} - v\frac{dC_A}{dx} - k_f C_B C_A + k_r C_{AB} = 0 \tag{1}$$

$$D_{AB} \frac{d^2C_{AB}}{dx^2} + k_f C_B C_A - k_r C_{AB} = 0 \tag{2}$$

The appropriate boundary conditions are:

$$x = 0: \bar{k}_0\left(\frac{C_{A0}}{m} - C_A\right) = -D_A\frac{dC_A}{dx} + vC_A; \frac{dC_{AB}}{dx} = 0 \tag{3}$$

$$x = L: \bar{k}_l(C_A - 0) = -D_A\frac{dC_A}{dx} + vC_A; \frac{dC_{AB}}{dx} = 0 \tag{4}$$

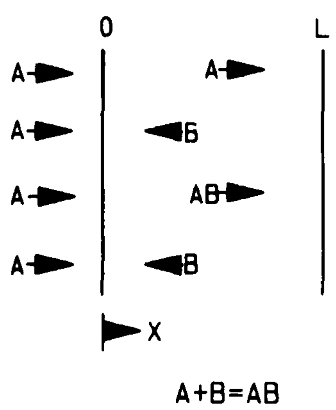

FIG. 1. Facilitated transport membrane.

Based on reaction equilibrium, Smith and Quinn (3) assumed that C_B is constant and is given by

$$C_B = \frac{C_T}{1 + K_{eq}\dfrac{C_{A0}}{m}} \tag{5}$$

Using Eq. (5), Eqs. (1) and (2) become linear, and an analytical solution is now possible. But before presenting the final solution, the above equations can be put in dimensionless form (2, 4, 5) where:

$$\varepsilon = \text{inverse Damkohler number} = D_{AB}/k_rL^2 \tag{6}$$

$$\alpha = \text{mobility ratio} = (D_{AB}C_Tm)/(D_AC_{A0}) \tag{7}$$

$$K = \text{dimensionless equilibrium constant} = k_fC_{A0}/k_rm \tag{8}$$

$$C_A^* = \text{dimensionless solute constant} = C_Am/C_{A0} \tag{9}$$

$$C_{AB}^* = \text{dimensionless complex concentration} = C_{AB}/C_T \tag{10}$$

$$\text{Sh} = \text{Sherwood number} = \bar{k}L/D_A \tag{11}$$

$$\text{Pe} = \text{Peclet nubmer} = (v/D_A)L \tag{12}$$

$$X = \text{dimensionless length} = x/L \tag{13}$$

The resulting equivalent dimensionless equations are

$$\frac{d^2C_A^*}{dX^2} - \text{Pe}\frac{dC_A^*}{dX} - \frac{\alpha K}{\varepsilon(1 + K)}C_A^* + \frac{\alpha}{\varepsilon}C_{AB}^* = 0 \tag{14}$$

$$\frac{d^2C_{AB}^*}{dX^2} + \frac{K}{\varepsilon(1 + K)}C_A^* - \frac{1}{\varepsilon}C_{AB}^* = 0 \tag{15}$$

$$X = 0: \frac{dC_A^*}{dX} - (\text{Sh}_0 + \text{Pe})C_A^* = -\text{Sh}_0; \frac{dC_{AB}^*}{dX} = 0 \tag{16}$$

$$X = 1: \frac{dC_A^*}{dX} + (\text{Sh}_1 - \text{Pe})C_A^* = 0; \frac{dC_{AB}^*}{dX} = 0 \tag{17}$$

where

$$\frac{C_B}{C_T} = \frac{1}{1 + K} \tag{18}$$

The next step now is to transform Eqs. (14)–(17) to a fourth-order ordinary differential equation with four boundary conditions for Component A. We start by solving Eq. (14) for C^*_{AB} and then substituting it in Eqs. (15) through (17) to get

$$\frac{d^4C^*_A}{dX^4} - \mathrm{Pe}\frac{d^3C^*_A}{dX^3} - \left(\frac{\alpha K}{\varepsilon(1 + K)} + \frac{1}{\varepsilon}\right)\frac{d^2C^*_A}{dX^2} + \frac{\mathrm{Pe}}{\varepsilon}\frac{dC^*_A}{dX} = 0 \tag{19}$$

$X = 0$:

$$\frac{dC^*_A}{dX} - (\mathrm{Sh}_0 + \mathrm{Pe})C^*_A = -\mathrm{Sh}_0 \tag{20}$$

$$-\frac{\varepsilon}{\alpha}\frac{d^3C^*_A}{dX^3} + \frac{\varepsilon \mathrm{Pe}}{\alpha}\frac{d^2C^*_A}{dX^2} + \frac{K}{1 + K}\frac{dC^*_A}{dX} = 0 \tag{21}$$

$X = 1$:

$$\frac{dC^*_A}{dX} + (\mathrm{Sh}_1 - \mathrm{Pe})C^*_A = 0 \tag{22}$$

$$-\frac{\varepsilon}{\alpha}\frac{d^3C^*_A}{dX^3} + \frac{\varepsilon \mathrm{Pe}}{\alpha}\frac{d^2C^*_A}{dX^2} + \frac{K}{1 + K}\frac{dC^*_A}{dX} = 0 \tag{23}$$

The solution to the reduced equations above is

$$C^*_A = C_1 + C_2 \exp(m_2X) + C_3 \exp(m_3X) + C_4 \exp(m_4X) \tag{24}$$

where

$$m_2 = \frac{\mathrm{Pe}}{3} + 2\left(\frac{A}{3}\right)^{1/2} \sin\left(\frac{\theta}{3}\right) \tag{25}$$

$$m_3 = \frac{\mathrm{Pe}}{3} + 2\left(\frac{A}{3}\right)^{1/2} \sin\left(\frac{\pi}{3} - \frac{\theta}{3}\right) \tag{26}$$

$$m_4 = \frac{\text{Pe}}{3} - 2\left(\frac{A}{3}\right)^{1/2} \sin\left(\frac{\pi}{3} + \frac{\theta}{3}\right) \tag{27}$$

$$A = \frac{\text{Pe}^2}{3} + \frac{\alpha K}{\varepsilon(1 + K)} + \frac{1}{\varepsilon} \tag{28}$$

$$B = -\frac{2}{27}\text{Pe}^3 + \frac{2}{3}\frac{\text{Pe}}{\varepsilon} - \frac{\alpha K \text{Pe}}{3\varepsilon(1 + K)} \tag{29}$$

$$\theta = \sin^{-1}\left[\left(\frac{3B}{2A}\right)\left(\frac{3}{A}\right)^{1/2}\right] \tag{30}$$

The constant of integrations are then given by

$$C_1 = -\left[1 + \frac{m_2}{(\text{Sh}_1 - \text{Pe})}\right] \exp(m_2)C_2 - \left[1 + \frac{m_3}{(\text{Sh}_1 - \text{Pe})}\right] \exp(m_3)C_3 - \left[1 + \frac{m_4}{(\text{Sh}_1 - \text{Pe})}\right] \exp(m_4)C_4 \tag{31}$$

$$C_2 = \frac{(\text{Sh}_1 - \text{Pe})\text{Sh}_0[\exp(m_3) - \exp(m_4)]A_3A_4}{(\text{Sh}_0 + \text{Pe}) \det[A]} \tag{32}$$

$$C_3 = \frac{(\text{Sh}_1 - \text{Pe})\text{Sh}_0[\exp(m_4) - \exp(m_2)]A_2A_4}{(\text{Sh}_0 + \text{Pe}) \det[A]} \tag{33}$$

$$C_4 = \frac{(\text{Sh}_1 - \text{Pe})\text{Sh}_0[\exp(m_2) - \exp(m_3)]A_2A_3}{(\text{Sh}_0 + \text{Pe}) \det[A]} \tag{34}$$

$$\det[A] = A_2A_3B_4[\exp(m_3) - \exp(m_2)] + A_2A_4B_3[\exp(m_2) - \exp(m_4)] + A_3A_4B_2[\exp(m_4) - \exp(m_3)] \tag{35}$$

Finally:

$$A_i = -\frac{\varepsilon}{\alpha}m_i^3 + \frac{\varepsilon}{\alpha}(\text{Pe})m_i^2 + \frac{K}{1 + K}m_i \tag{36}$$

$$B_i = \frac{(\text{Sh}_1 - \text{Pe})}{(\text{Sh}_0 + \text{Pe})}m_i + (\text{Sh}_1 - \text{Pe})[\exp(m_i) - 1] + m_i \exp(m_i) \tag{37}$$

where $i = 2, 3, 4$. Note, the above solution is only valid when $(A^3/27) - (B^2/4) > 0$ (*6*). In this problem, however, it can be shown that the above restriction always holds for all possible A's and B's. The facilitation factor F is defined by

$$F = \frac{\left(\mathrm{Pe}C_A^* - \dfrac{dC_A^*}{dX}\right)\bigg|_{X=1,\alpha\neq 0}}{\left(\mathrm{Pe}C_A^* - \dfrac{dC_A^*}{dX}\right)\bigg|_{X=1,\alpha=0}} \tag{38}$$

The total flux for $\alpha = 0$ at $X = 1$ is found by referring back to the original equations (Eqs. 14 through 17) to get

$$\left(\mathrm{Pe}C_A^* - \frac{dC_A^*}{dX}\right)\bigg|_{X=1,\alpha=0} = \frac{\mathrm{Pe}\,\mathrm{Sh}_0\mathrm{Sh}_1 \exp(\mathrm{Pe})}{\mathrm{Sh}_1(\mathrm{Sh}_0 + \mathrm{Pe})\exp(\mathrm{Pe}) - \mathrm{Sh}_0(\mathrm{Sh}_1 - \mathrm{Pe})} \tag{39}$$

then the facilitation factor will be reduced to

$$F_1 = \frac{[\mathrm{Pe}C_1 + (\mathrm{Pe} - m_2)C_2 \exp(m_2) + (\mathrm{Pe} - m_3)C_3 \exp(m_3) + (\mathrm{Pe} - m_4)C_4 \exp(m_4)]}{\dfrac{\mathrm{Pe}\,\mathrm{Sh}_0\mathrm{Sh}_1 \exp(\mathrm{Pe})}{\mathrm{Sh}_1(\mathrm{Sh}_0 + \mathrm{Pe})\exp(\mathrm{Pe}) - \mathrm{Sh}_0(\mathrm{Sh}_1 - \mathrm{Pe})}} \tag{40}$$

After studying F for different input parameters, we have found that for all practical purposes Eq. (40) reduces to

$$F_2 = \frac{[\mathrm{Sh}_1(\mathrm{Sh}_0 + \mathrm{Pe})\exp(\mathrm{Pe}) - \mathrm{Sh}_0(\mathrm{Sh}_1 - \mathrm{Pe})]}{\mathrm{Sh}_0\mathrm{Sh}_1 \exp(\mathrm{Pe})} C_1 \tag{41}$$

where C_1 is given by Eq. (34). In Eq. (40) the term $(\mathrm{Pe} - m_4)C_4 \exp(m_4)$ is very small (10^{-127}) and the terms $(\mathrm{Pe} - m_2)C_2 \exp(m_2)$ and $(\mathrm{Pe} - m_3)C_3 \exp(m_3)$ cancel each other with a difference in the range of (10^{-4} to 10^{-8}). Hence, Eq. (41) is more practical to use without any loss of accuracy.

RESULTS

The facilitation factors calculated through Eqs. (40) and (41) agreed very well with respect to each other, and with respect to reported results by Noble et al. (*2*) for the case when Pe = 0 (see Table 1).

Table 2 shows that for a given Pe, F increases as Sh increases. This makes sense as increasing Sh reduces the external mass transfer resistance, which is nonselective. Again, this makes sense as the bulk flow through the membrane does not provide any selectivity.

Table 2 and Fig. 2 show that the facilitation factor is equal to 1 when the Sherwood and the Peclet numbers are equal and that F goes below 1 when the Peclet number becomes larger than the Sherwood number. This causes a sign change in the C_A^* term in Eq. (17) and also in Eq. (41). This sign change causes the concentration gradient to reverse sign. This implies that the diffusional flux at each boundary reverses direction. Of course, this has adverse effects on the magnitude of the solute flux and the membrane selectivity.

It is this finding that we believe is new and of great importance since it has been believed that the facilitation factor cannot go below 1. This finding then tells us that it is important in cases of high external mass-transfer (low Sherwood number) resistance to try to keep the convective mass-transfer as low as possible to maximize the facilitation factor. The

TABLE 1
Comparison of Facilitation Factor for
$\varepsilon = 0.001$, $K = 3$, $\alpha = 10.0$, Sh = 2

	F		
Pe	F_1	F_2	F_3
0.000	1.759	1.759	1.782
1.000	1.237	1.237	1.244
2.000	1.000	1.000	1.000
3.000	0.892	0.892	0.887
4.000	0.843	0.843	0.835
5.000	0.825	0.825	0.814
6.000	0.821	0.821	0.807
7.000	0.825	0.825	0.809
8.000	0.833	0.833	0.816
9.000	0.843	0.843	0.825
10.000	0.855	0.855	0.859

TABLE 2
Facilitation Factor Versus Sherwood Number for Different Peclet Numbers: $\varepsilon = 0.001$, $K = 3.0$, $\alpha = 10.0$

	Sh								
Pe	2	5	10	20	40	100	200	500	∞
0.000	1.759	2.608	3.563	4.645	5.621	6.505	6.881	7.131	7.310
1.000	1.237	1.803	2.441	3.163	3.815	4.406	4.657	4.824	4.944
2.000	1.000	1.398	1.846	2.355	2.815	3.232	3.409	3.528	3.613
3.000	0.892	1.184	1.514	1.890	2.230	2.540	2.672	2.760	2.823
4.000	0.843	1.067	1.319	1.608	1.871	2.110	2.212	2.281	2.330
5.000	0.825	1.000	1.200	1.429	1.638	1.829	1.911	1.966	2.005
6.000	0.821	0.962	1.123	1.309	1.480	1.637	1.704	1.750	1.782
7.000	0.825	0.940	1.073	1.226	1.368	1.500	1.556	1.595	1.622
8.000	0.833	0.928	1.039	1.167	1.287	1.399	1.447	1.480	1.503
9.000	0.843	0.923	1.016	1.125	1.227	1.323	1.364	1.393	1.413
10.000	0.855	0.922	1.000	1.093	1.181	1.264	1.300	1.325	1.342

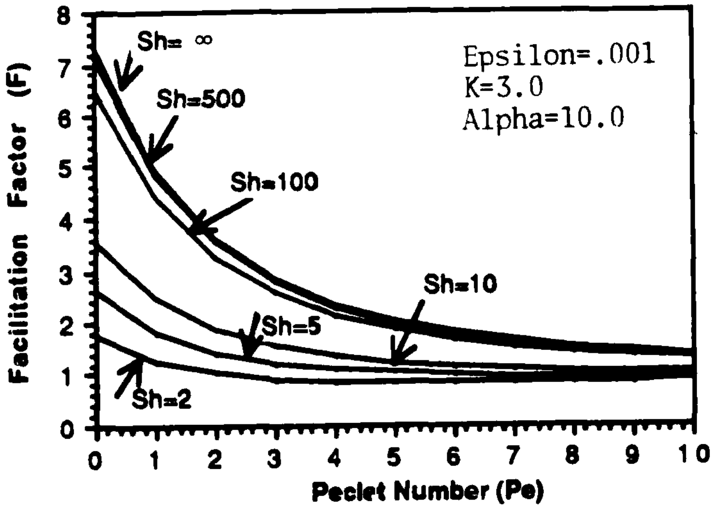

FIG. 2. Facilitated factor versus Peclet number for different Sherwood numbers.

no external resistance case corresponds to a Sherwood number equal to infinity, and since Pe is much less than that, the above finding has not been observed.

Table 2 and Fig. 2 also tell us that even for high Sherwood numbers, the Peclet number still has a considerable effect on the facilitation factor. For example, for Sh = ∞, as Pe goes from 0 to 10, the facilitation factor F goes from 7.3 to 1.3 (see Table 2). So even at high Sherwood numbers, the lower the Peclet number, the higher the facilitation factor would be.

The term

$$\left(1 + \frac{m_4}{\mathrm{Sh}_l - \mathrm{Pe}}\right) \exp(m_4) C_4$$

in C_1 is very small compared to the other two terms, hence by neglecting it in Eq. (41) and taking the limit as $\varepsilon \to 0$, we obtain a useful equation for analyzing experimental reaction equilibrium data:

$$F_3 = \frac{A_2'\alpha + \mathrm{Sh}_l - \mathrm{Pe} + m_2'}{C_{10}[\mathrm{Sh}_l - \mathrm{Pe} + (\mathrm{Sh}_0 + \mathrm{Pe}) \exp(m_2')]A_2'\alpha + B_2'C_{10}(\mathrm{Sh}_0 + \mathrm{Pe})} \tag{42}$$

where

$$C_{10} = \frac{\mathrm{Sh}_1 \exp(\mathrm{Pe})}{\exp(m_2')[\mathrm{Sh}_1(\mathrm{Sh}_0 + \mathrm{Pe})\exp(\mathrm{Pe}) - \mathrm{Sh}_0(\mathrm{Sh}_1 - \mathrm{Pe})]} \tag{43}$$

$$m_2' = \frac{\mathrm{Pe}}{3}\left[1 + \frac{2(1+K) - \alpha K}{(1+K) + K\alpha}\right] \tag{44}$$

$$A_2' = \frac{K}{1+K} m_2' \tag{45}$$

$$B_2' = \frac{(\mathrm{Sh}_1 - \mathrm{Pe})}{(\mathrm{Sh}_0 + \mathrm{Pe})} m_2' + (\mathrm{Sh}_1 - \mathrm{Pe})[\exp(m_2') - 1] + m_2' \exp(m_2') \tag{46}$$

Table 1 shows the facilitation factor calculated via the three different equations presented here, and very little difference is noticeable.

Now, Eq. (42) can be put in a more practical form by just dividing the numerator and the denominator by α to get

$$F_3 = \frac{A_2' + (\mathrm{Sh}_1 - \mathrm{Pe} + m_2')\alpha^{-1}}{C_{10}[\mathrm{Sh}_1 - \mathrm{Pe} + (\mathrm{Sh}_0 + \mathrm{Pe})\exp(m_2')]A_2' + B_2' C_{10}(\mathrm{Sh}_0 + \mathrm{Pe})\alpha^{-1}} \tag{47}$$

or, to put it in a more compact and different form,

$$F_3 = \frac{a' + b' C_{A0}}{C' + d' C_{A0}} \tag{48}$$

since

$$\alpha = \frac{C_{A0} D_A}{D_{AB} C_T m}$$

where

$$a' = \frac{K}{1+K} m_2' \tag{49}$$

$$b' = (\mathrm{Sh}_1 - \mathrm{Pe} + m_2') \frac{D_A}{D_{AB} C_T m} \tag{50}$$

$$c' = C_{10}[\mathrm{Sh}_1 - \mathrm{Pe} + (\mathrm{Sh}_0 + \mathrm{Pe})\exp(m_2')]A_2' \tag{51}$$

$$d' = B_2'C_{10}(\mathrm{Sh}_0 + \mathrm{Pe})\frac{D_A}{D_{AB}C_T m} \tag{52}$$

So, if experimental data on F versus C_{A0} is available, a curve fit to Eq. (48) would give us a', b', c', and d', and then by using Eqs. (49) through (52) we can find Sh_0, Sh_1, Pe, and D_{AB}.

The procedure is as follows. Once a', b', c', and d' are known, Pe is calculated using Eq. (49), then plugging it in Eq. (50) and solving for Sh_1 in terms of D_{AB}. Substituting Sh_1 into Eqs. (51) and (52) results in having two equations and two unknowns (Sh_0 and D_{AB}).

Note that by putting Eq. (47) in the form of Eq. (48) made it easy to solve for Pe and then reduce the problem to just two algebraic equations instead of four.

It is important to point out that this solution (Eq. 24) is not valid when Pe equals zero. For this case, one can use the solution of Noble et al. (*2*).

In conclusion, the convective effect on the facilitation factor is important for high external mass-transfer resistance membranes. For low external resistance, the Peclet number should be minimized so as to maximize the facilitation factor. Finally, Eq. (48) is useful in experimental work to estimate the external mass-transfer resistance at the two membrane boundaries and to approximate the Peclet number and the effective diffusion coefficient for the carrier–solute complex.

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