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Kinetic Efficiency Factors for Facilitated Transport Membranes

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Abstract

A kinetic efficiency factor (η) is defined for facilitated transport membranes. η is defined as the actual facilitated flux divided by the facilitated flux under reaction equilibrium conditions. η is correlated with an inverse Damkohler number ε. A dimensionless equilibrium constant K and mobility ratio α also affect the value of η. η is shown to be useful in determining the operating regime of the system, comparing actual performance to maximum attainable, and providing a qualitative measure of the time to reach steady-state conditions.

INTRODUCTION

Facilitated transport through liquid membranes is a promising separation technique. This process uses a nonvolatile carrier in a liquid film. The carrier can react reversibly with the solute of interest. This reversible reaction allows for an increased flux of solute across the liquid film and increased selectivity. There are several recent review articles which describe facilitated transport in more detail (*2-4, 6-10, 12*).

The most common reaction mechanism postulated (*1-12*) is

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

where A = solute to be transported
B = nonvolatile carrier
AB = carrier-solute complex

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To fully utilize the concept of reversible chemical complexation for separation, it is important to have a measure of the effectiveness of the reaction in increasing the solute flux, and therefore increasing the selectivity. The objective of this work is to define a kinetic efficiency factor for facilitated transport through liquid membranes. This factor (η) provides a measure of the actual solute flux attained to the maximum possible. For mixtures, η would also correspond to a measure of the actual selectivity attained to the maximum possible. η is correlated with an inverse Damkohler number ε which is a ratio of diffusion to reaction times. The other dimensionless variables which affect system performance are a dimensionless equilibrium constant K and a mobility ratio α which is proportional to carrier concentration.

THEORY

For a planar membrane of thickness L, the one-dimensional steady-state differential mass balances are

$$0 = D_{\mathrm{A}} \frac{d^2C_{\mathrm{A}}}{dx^2} - k_1 C_{\mathrm{A}} C_{\mathrm{B}} + k_2 C_{\mathrm{AB}} \tag{2}$$

$$0 = D_{\mathrm{B}} \frac{d^2C_{\mathrm{B}}}{dx^2} - k_1 C_{\mathrm{A}} C_{\mathrm{B}} + k_2 C_{\mathrm{AB}} \tag{3}$$

$$0 = D_{\mathrm{AB}} \frac{d^2C_{\mathrm{AB}}}{dx^2} + k_1 C_{\mathrm{A}} C_{\mathrm{B}} - k_2 C_{\mathrm{AB}} \tag{4}$$

Equations (2)–(4) assume the reaction mechanism described in Eq. (1). It is also assumed that each diffusion coefficient is a constant. The solute is often much smaller than the carrier, and so the carrier and the carrier-solute complex are roughly equivalent in size. This allows one to assume $D_{\mathrm{B}} = D_{\mathrm{AB}}$. Based on this assumption, one can state

$$C_T = C_{\mathrm{B}} + C_{\mathrm{AB}} \tag{5}$$

where C_T is the amount of carrier initially present in the system.

The boundary conditions are:

$$\text{At } \chi = 0, \qquad C_{\mathrm{A}} = C_{\mathrm{A}_0}, \qquad dC_{\mathrm{B}}/dx = dC_{\mathrm{AB}}/dx = 0 \tag{6}$$

$$\text{At } x = L, \qquad C_{\mathrm{A}} = C_{\mathrm{A}_L}, \qquad dC_{\mathrm{B}}/dx = dC_{\mathrm{AB}}/dx = 0 \tag{7}$$

The boundary conditions on B and AB arise because the carrier and the carrier–solute complex are constrained to remain within the system. The boundary conditions on A indicate that there is a constant source of A at one boundary, and that A is removed from the opposite boundary so that the concentration at that point is a constant.

The total flux of A across the membrane is

$$N_T = D_{\mathrm{A}} \frac{dC_{\mathrm{A}}}{dx} - D_{\mathrm{AB}} \frac{dC_{\mathrm{AB}}}{dx} \tag{8}$$

The above equations can be nondimensionalized as

$$0 = \frac{d^2C_{\mathrm{A}}^*}{d\chi^2} + \frac{\alpha K}{\varepsilon}\left(\frac{1}{K}C_{\mathrm{AB}}^* - C_{\mathrm{A}}^*C_{\mathrm{B}}^*\right) \tag{9}$$

$$0 = \frac{d^2C_{\mathrm{B}}}{d\chi^2} + \frac{K}{\varepsilon}\left(\frac{1}{K}C_{\mathrm{AB}}^* - C_{\mathrm{A}}^*C_{\mathrm{B}}^*\right) \tag{10}$$

$$0 = \frac{d^2C_{\mathrm{AB}}}{d\chi^2} + \frac{K}{\varepsilon}\left(C_{\mathrm{A}}^*C_{\mathrm{B}}^* - \frac{1}{K}C_{\mathrm{AB}}^*\right) \tag{11}$$

$$\text{At } \chi = 0, \qquad C_{\mathrm{A}}^* = 1, \qquad dC_{\mathrm{B}}^*/d\chi = dC_{\mathrm{AB}}^*/d\chi = 0 \tag{12}$$

$$\text{At } \chi = 1, \qquad C_{\mathrm{A}}^* = C_{\mathrm{A}_L}^*, \qquad dC_{\mathrm{B}}^*/d\chi = dC_{\mathrm{AB}}^*/d\chi = 0 \tag{13}$$

$$1 = C_{\mathrm{B}}^* + C_{\mathrm{AB}}^* \tag{14}$$

where the dimensionless variables are

$$\varepsilon = D_{\mathrm{AB}}/k_2L^2 = \text{inverse Damkohler number} \tag{15}$$

$$K = k_1C_{\mathrm{A}_0}/k_2 = \text{dimensionless equilibrium constant} \tag{16}$$

$$\alpha = D_{\mathrm{AB}}C_T/D_{\mathrm{A}}C_{\mathrm{A}_0} = \text{mobility ratio of carrier to solute} \tag{17}$$

$$\chi = x/L \tag{18}$$

$$C_{\mathrm{A}}^* = C_{\mathrm{A}}/C_{\mathrm{A}_0} \tag{19}$$

$$C_B^* = C_B/C_T \tag{20}$$

$$C_{AB}^* = C_{AB}/C_T \tag{21}$$

To measure the effect of the flux enhancement due to reversible chemical complexation, a facilitation factor F is defined:

$$F = N_T/N_0 \tag{22}$$

where N_0 is the diffusional flux of A. Therefore, F is a measure of the increased selectivity of the separation of A from a mixture. F is a ratio and should not be equated with capacity. A large value of F does not necessarily imply a larger total flux.

Equations (9), (10), and (11) can be solved using boundary conditions (12) and (13) to obtain the concentration gradients in the membrane. The facilitation factor can be defined in terms of the concentration gradients as

$$F = \frac{\left(-\dfrac{dC_A^*}{d\chi}\right)_{\chi=1,\alpha}}{\left(-\dfrac{dC_A^*}{d\chi}\right)_{\chi=1,\,\alpha=0}} \tag{23}$$

KINETIC EFFICIENCY

The effectiveness factor in catalysis is used as a measure of diffusion limitations on reaction kinetics. For catalysis, diffusion and reaction can be viewed as events in series. The reactant must diffuse to the catalyst site, react, and the product diffuse away from the site. Therefore, slow diffusion will limit the reaction rate and thereby reduce the "effectiveness" of the catalyst.

The kinetic efficiency factor for facilitated transport across liquid membranes is a different measure of "effectiveness." Since this process requires diffusion across the liquid film while the reaction is taking place, diffusion and reaction can be viewed as parallel events. A rapid reaction time will cause the process to be diffusion-limited (reaction equilibrium condition). This would correspond to the maximum "effectiveness" of the process since the carrier would have the maximum complexation with the solute. A slow reaction time relative to diffusion contributes to a slower reaction rate and a less effective separation.

With these ideas in mind, one can define a kinetic efficiency factor (η) as

$$\eta = \frac{\text{actual facilitated flux}}{\text{facilitated flux under reaction equilibrium conditions}}$$

$$= \frac{F_{\text{actual}}}{F_{\text{reaction equilibrium}}} = \frac{F_a}{F_{re}} \qquad (24)$$

η can be correlated with ε. ε is a measure of diffusion to reverse reaction. This variable is analogous to the Thiele modulus used in catalysis. Fixing the value of K and α corresponds to selecting a certain carrier and carrier concentration for a given solute.

F_a can be calculated using Eq. (23). An analytical expression is available for N_T under reaction equilibrium conditions (*11*). This allows one to calculate F_{re}:

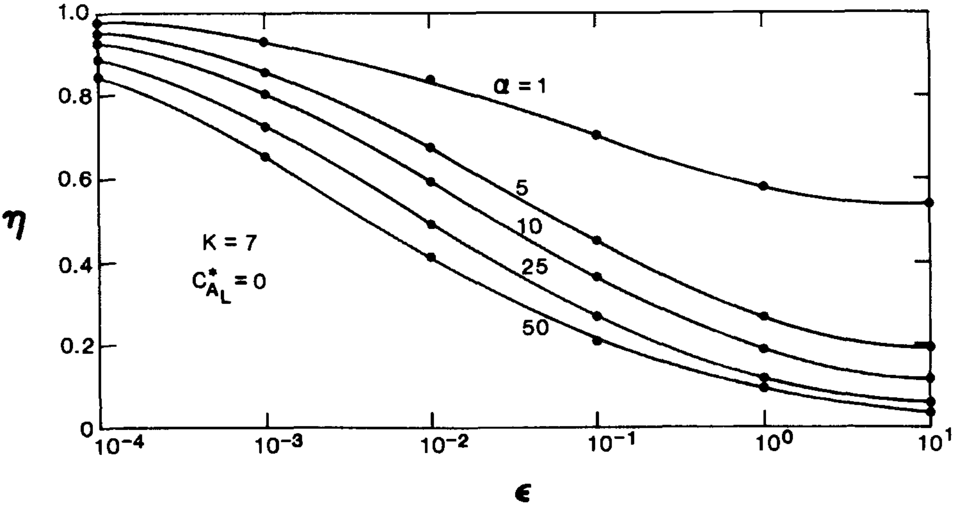

FIG. 1. Kinetic efficiency factor vs inverse Damkohler number.

$$F_{re} = 1 + \frac{\alpha K}{(1 + K)\left[1 + K\left(\frac{C_{A_L}}{C_{A_0}}\right)\right]} \tag{25}$$

Figures 1 and 2 show some plots of η vs ε for a typical facilitated transport system. The value of K was chosen based on optimal values given by Kemena et al. (5). As the carrier concentration (α) increases, η decreases. As seen from Eq. (25), tripling α would correspond to tripling the quantity ($F_{re} - 1$). Referring to Table 1, tripling α would correspond to an increase of less than three times in ($F_a - 1$). Thus, as you increase carrier concentration, F_{re} is increasing faster than the F_a in η. Physically, if you increase the carrier concentration under reaction equilibrium conditions, the carrier will be fully utilized. If you increase the carrier concentration under other conditions, the carrier is not fully utilized and will not increase the flux as much as it would under reaction equilibrium conditions.

The variation of η with ε reflects the operating regime of the system. In Fig. 1, the values of η for ε between 1 and 10 are fairly constant. This regime corresponds to the reaction-limited regime. It is apparent from the definition of η that this region would correspond to the lowest values of η.

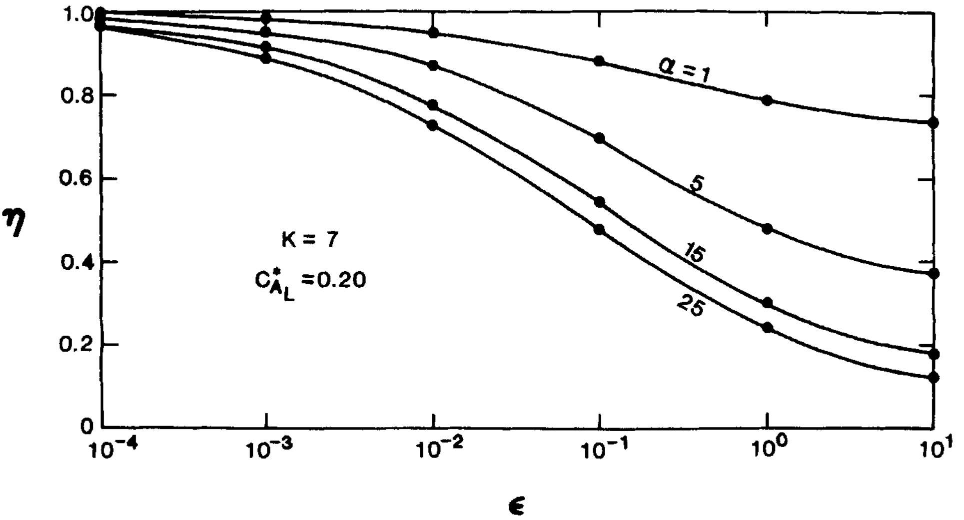

FIG. 2. Kinetic efficiency factor vs inverse Damkohler number.

TABLE 1
Values from Folkner and Noble (*1*) and Calculated Values of η for $K = 1$.

$F_a - 1$	ε	α	Time (dimensionless) to reach steady-state conditions	η
4.64	0.1	35	50	.305
3.63	0.1	25	40	.343
2.47	0.1	15	35	.408
0.99	0.1	5	25	.569
1.32	1.0	35	135	.125
1.00	1.0	25	120	.148
0.64	1.0	15	105	.193
0.23	1.0	5	75	.352
0.18	10.0	35	550	.064
0.13	10.0	25	550	.084
0.08	10.0	15	550	.127
0.03	10.0	5	500	.293

In the region of ε between 10^{-4} and 1, the value of η continuously changes with a change in ε. This corresponds to a region where both diffusion and reaction are rate-determining. In Fig. 2, the region of ε between 10^{-4} and 10^{-3} contains fairly constant values of η. This corresponds to the diffusion-limited regime. Physically, the variation of η with ε shows whether one will get a large increase in selectivity (η) with a change in membrane thickness L (contained in ε). Actual membrane performance can be compared (using η) to the maximum selectivity attainable to see if greater selectivity can be realized.

Figures 1 and 2 also demonstrate the limiting values of η. As ε approaches zero, η approaches 1. As ε becomes large, η approaches $(F_{re})^{-1}$.

Yung and Probstein (*13*) defined a parameter η which was related to the concentration of carrier (B in Eq. 1) in the membrane. This parameter had a value of 1 for reaction equilibrium and 0 for the reaction-limited condition. While the value of this parameter showed a departure from reaction equilibrium, a plot of their η vs ε does not show the three distinct regions: diffusion-limited, combined diffusion and reaction, and reaction-limited. Also, their η is related to concentration profiles, and the flux is the variable of importance in these studies.

Table 1 can be used to analyze the effect of η on the time to reach steady-state. One interesting observation is that the time to reach steady-state increases as η decreases. Physically, the diffusion-limited regime should have the minimum time to reach steady-state (high η). In the reaction-limited regime (low η), the diffusion time is fast compared to the reaction time, and the time required to reach steady-state increases. Therefore, 1/η is a qualitative measure of the time to reach steady-state conditions.

CONCLUSIONS

A kinetic efficiency factor (η) has been defined for facilitated transport membranes. Calculational procedures have been described. η provides a measure of the actual solute flux to the maximum attainable. For mixtures, η also provides a measure of actual selectivity to the maximum. η was correlated with an inverse Damkohler number ε for a given value of a dimensionless equilibrium constant K and mobility ratio α.

A plot of η vs ε can be useful in determining the operating regime of the system. Determining η can be used to compare actual system performance to the maximum attainable. Also 1/η is a qualitative measure of the time required to reach steady-state conditions.

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