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Optimal Equilibrium Constants for Interfacial Reactions Used in Liquid Membrane Transport

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Abstract

Two interfacial reactions which are used in liquid membrane transport are analyzed. They correspond to countertransport and cotransport across the membrane. A relationship is derived for the optimal equilibrium constant which will produce the highest flux across the membrane for a given set of physical properties and operating conditions. A comparison with experimental results is provided.

INTRODUCTION

One method to separate species which are insoluble in an organic liquid is to use a complexing agent in the organic phase. One example is ionic species. This complexing agent reacts with the species of interest at the aqueous-organic interface and solubilizes it in the organic phase as a complex.

This approach can be used to selectively transport one species across a liquid membrane. In this process the organic film containing the complexing agent is the liquid membrane, and there is an aqueous feed phase at one interface and a second aqueous receiving phase at the second interface.

Liquid membranes have two major configurations: emulsion liquid membranes (ELMs) and immobilized liquid membranes (ILMs) (*1*). Emulsion liquid membranes are actually double emulsions. An aqueous receiving phase is dispersed in the organic liquid membrane. This emulsion in then dispersed in a continuous aqueous feed phase. Immobilized liquid membranes use a porous polymer or ceramic material as a support for the liquid film. The liquid film is immobilized in the solid pore structure.

There are two main reaction mechanisms used for this separation. In countertransport the interfacial reaction is an ion-exchange. The solute of interest and the exchanged ion are transported in opposite directions. In cotransport the solute of interest and its counterion are transported together as a neutral species. A good reference for a description of the use of these reaction mechanisms in an ILM is Danesi (*2*).

Previously, Kemena et al. (*3*) and Kirkkopru-Dindi and Noble (*4*) developed a criteria for the optimal reaction equilibrium constant for facilitated transport across a liquid membrane. In facilitated transport the solute is soluble in the liquid membrane and the complexation reaction occurs throughout the liquid film. Noble (*5*) indicated that these results are useful for the determination of the optimal property set, to screen potential complexing agents, as a basis for structural modifications to the complexing agent, and to compare actual to optimal performance.

The purpose of this study is to extend the optimal analysis described above to liquid membrane transport involving interfacial reactions.

DERIVATION OF THE OPTIMAL CONDITION

The first reaction mechanism to be analyzed is

$$A + \bar{B} \underset{k_r}{\overset{k_f}{\leftrightarrow}} \bar{C} + D$$

Here A and D can be viewed as ionic species in aqueous solution and B and C are complexes in the organic phase (the overbar denotes the organic phase). This reaction occurs at the aqueous–organic interfaces as shown in Fig. 1. This reaction corresponds to a countertransport mechanism.

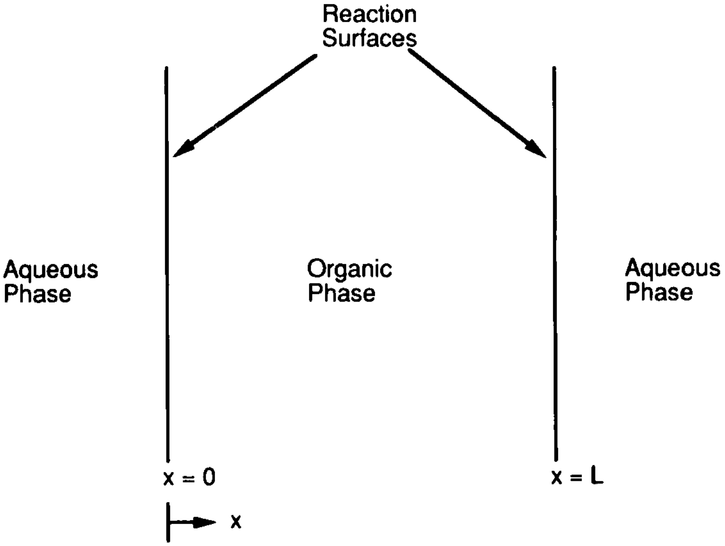

FIG. 1. System schematic.

A steady-state microscopic mass balance on Species B yields

$$0 = \frac{d^2C_B}{dx} \tag{1}$$

The boundary conditions are

$$X = 0 \qquad -D_B \frac{dC_B}{dx} = k_rC_CC_{D0} - k_fC_{A0}C_B \tag{2}$$

$$X = L \qquad = k_fC_{AL}C_B - k_rC_CC_{DL} \tag{3}$$

Assuming that the diffusion coefficients for both Species B and C are equal, the total concentration of complex (C_T) can be related to C_B and C_C at any point in the organic phase

$$C_T = C_B + C_C \tag{4}$$

Using Eq. (4), boundary conditions (2) and (3) can be rewritten as

$$X = 0 \qquad -D_B \frac{dC_B}{dx} = -(k_r C_{D0} + k_f C_{A0})C_B + k_r C_{D0} C_T \tag{5}$$

$$X = L \qquad = (k_r C_{DL} + k_f C_{AL})C_B - k_r C_{DL} C_T \tag{6}$$

The problem is now posed in terms of measurable quantities; the concentration of each ionic species at each interface (assumed equal to the bulk phase concentration) and the total concentration of the complexing agent in the organic phase.

Equation (1) with boundary conditions (5) and (6) can be solved for the steady-state flux of B (= J). First, the following dimensionless variables are defined:

$$\Psi = \frac{J}{k_r C_T C_{DL}} = \frac{\text{steady-state flux of B}}{\text{maximum flux of D (assuming countertransport)}} \tag{7}$$

$$\phi = \frac{C_{DL}}{C_{D0}} = \text{concentration or dilution effect for Species D} \tag{8}$$

$$\varepsilon_1 = \frac{D_B}{k_r C_{D0} L} = \text{ratio of reverse reaction time to diffusion time} \tag{9}$$

$$K_1 = \frac{k_f}{k_r} = \text{equilibrium constant} \tag{10}$$

The solution is

$$\Psi = \frac{\phi^{-1}(C_{DL} + K_1 C_{AL}) - (C_{D0} + K_1 C_{A0})}{(C_{D0} + C_{DL}) + K_1(C_{A0} + C_{AL}) + (C_{D0} + K_1 C_{A0})(C_{DL} + K_l C_{AL})(\varepsilon_1 C_{D0})^{-1}} \tag{11}$$

The criteria for maximizing the flux of B across the organic film is

$$\frac{\partial \Psi}{\partial K_1} = 0 \tag{12}$$

The solution of Eq. (12) yields a quadratic equation for K_1. Only positive values of K_1 are physically realizable. The solution is

$$K_1 = \sqrt{\frac{\varepsilon_1 C_{\mathrm{D0}}^2(1 + \phi) + \phi C_{\mathrm{D0}}^2}{C_{\mathrm{A0}} C_{\mathrm{A}L}}} \tag{13}$$

Equation (13) the determines the value of the equilibrium constant which will produce the maximum flux of the complex across the liquid film for given physical properties and operating conditions. Note that K_1 in Eq. (13) is not a function of the total concentration of complex (C_T).

A second reaction mechanism is

$$\mathrm{A} + \bar{\mathrm{B}} \underset{k_r}{\overset{k_f}{\leftrightarrow}} \overline{\mathrm{AB}}$$

This mechanism corresponds to cotransport. Due to the stoichiometry, different dimensionless variables are defined as

$$K_2 = k_f C_{\mathrm{A0}}/k_r \tag{14}$$

$$\varepsilon_2 = D_{\mathrm{B}}/k_r L \tag{15}$$

The analysis is identical to that shown above, assuming $C_{\mathrm{DO}} = C_{\mathrm{D}L} = 1$. The result for the optimal equilibrium constant is

$$K_2 = \sqrt{\left(\frac{C_{\mathrm{A0}}}{C_{\mathrm{A}L}}\right)(1 + 2\varepsilon_2)} \tag{16}$$

COMPARISON WITH EXPERIMENTAL RESULTS

Yoshizuka et al. (*6*) state that the rate-determining step for copper extraction is

$$\mathrm{CuR^+} + \overline{\mathrm{HR}} \leftrightarrow \overline{\mathrm{CuR_2}} + \mathrm{H^+}$$

This mechanism is identical to the first reaction mechanism analyzed.

This reaction was studied by Jin et al. (*7*) and Tallarico et al. (*8*) with a rotating diffusion cell. They measured the kinetics of copper extraction with (*anti*)-2-hydroxy-5-nonylbenzophenone oxime (LIX65N) as the complexing agent. Typical operating conditions (*7*) and physical properties were

$$L = 1.5 \times 10^{-2}\ \mathrm{cm}$$

$$D_\mathrm{B} = 8 \times 10^{-6}\ \mathrm{cm^2/s}$$

$$C_{\mathrm{H^+O}} = 10^{-4}\ M$$

$$C_{\mathrm{H}+L} = 0.4\ M$$

$$c_{\mathrm{CuO}} = 1.574 \times 10^{-2}\ M$$

$$C_{\mathrm{Cu}L} = 3.15 \times 10^{-5}\ M$$

They determined the following values for the rate constants:

$$k_f' = 4.0 \times 10^{-8}\ \mathrm{m/s}$$

k_f' must be divided by $C_{\mathrm{H^+O}}$ to obtain k_f as defined in this paper. That result is

$$k_f = 4.0 \times 10^{-7} \frac{\mathrm{m^4}}{\mathrm{mol}} \cdot \mathrm{s}$$

The actual value of K_1 is

$$K_1 = \frac{k_f}{k_r} = 2.0 \times 10^4$$

Base on the above data, K_1 can be calculated from Eq. (12) by using $\varepsilon_1 = 2.67 \times 10^6$ and $\phi = 4.0 \times 10^3$.

$$K_1 = \left[\frac{(2.67 \times 10^6)(10^{-8}\,M^2)(4.0 \times 10^3) + (4.0 \times 10^3)(10^{-8}\,M^2)}{(1.574 \times 10^{-2}\,M)(3.15 \times 10^{-5}\,M)}\right]^{1/2} = 2.47 \times 10^4$$

This result shows that Jin et al. (*7*) were obtaining the largest copper flux through their membrane under the above conditions.

CONCLUSIONS

Equations relating the optimal equilibrium constant with the physical properties and operating conditions have been derived for both countertransport and cotransport mechanisms. A comparison with experimental data is shown. These results are useful for determining the optimal properties required for maximum flux, to screen potential complexing agents, as a basis for structural modifications to the complexing agent, and to compare actual to optimal performance.

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