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Mass Transfer Rate through Liquid Membranes: Interfacial Chemical Reactions and Diffusion as Simultaneous Permeability Controlling Factors

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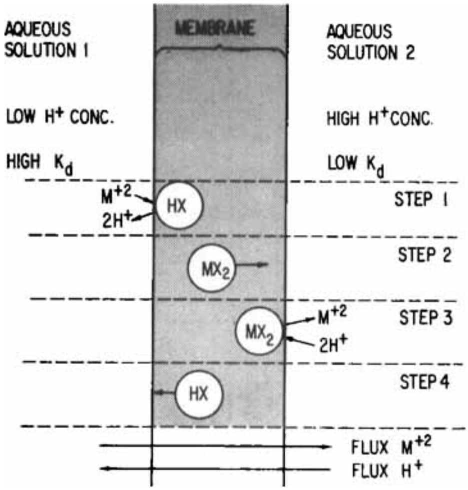
Abstract

Equations describing the permeability of a liquid membrane to metal cations have been derived taking into account aqueous diffusion, membrane diffusion, and interfacial chemical reactions as simultaneous permeability controlling factors. Diffusion and chemical reactions have been coupled by a simple model analogous to the one previously described by us to represent liquid–liquid extraction kinetics. The derived equations, which make use of experimentally determined interfacial reaction mechanisms, qualitatively fit unexplained literature data regarding Cu^{2+} transfer through liquid membranes. Their use to predict and optimize membrane permeability in practical separation processes by setting the appropriate concentration of the membrane carrier [LIX 64 (General Mills), a commercial β-hydroxy-oxime] and the pH of the aqueous copper feed solution is briefly discussed.

INTRODUCTION

Coupled transport through liquid membranes has been recently proposed as a new technology for the selective separation and concentration



RESULT: THE FLUX OF H^+ CAUSES A FLUX OF M^{+2} WHICH IS AGAINST THE CONCENTRATION DIFFERENCE OF M^{+2}.

$$M^{+2} + 2\overline{HX} \rightleftharpoons \overline{MX}_2 + 2H^+ \; ; \; K_d = \frac{[M]\ \text{MEMBRANE}}{[M]\ \text{WATER}}$$

FIG. 1. Schematic description of coupled transport of a divalent metal cation M^{2+} through a liquid membrane. HX represents the membrane carrier. *Step 1*: Carrier HX reacts with the solute being pumped, M^{2+}, releasing the energy-supplying solute H^+. *Step 2*: Carrier complex MX_2 diffuses across the membrane. *Step 3*: The energy-supplying solute H^+ reacts with the carrier complex releasing solute M^{2+}. *Step 4*: Carrier returns across the membrane. Uncomplexed solute M^{2+} cannot diffuse back across the membrane because of low solubility. (Adapted from Ref. 1.)

of metals from dilute aqueous solutions (*1*, *2*). The principle of liquid membrane coupled transport is schematically illustrated in Fig. 1.

Theoretical treatments of coupled transport phenomena have been generally restricted to the limiting case where the chemical reactions between the membrane carrier and the permeating solute are fast (*3–7*). In this instance the membrane permeability can be treated only in terms of diffusional processes inside the membrane layer. However, these treatments, which often contain difficultly measured parameters, all basically reduce to the simplified Fick's first diffusion law:

$$J_0 = \frac{D_{\overline{m}}}{\delta_0}(\overline{m}_1 - \overline{m}_2) \tag{1}$$

when two simplifying assumptions:

I. Steady state
II. Linear concentration gradient throughout the membrane

are introduced. In Eq. (1), J_0 represents the diffusional flux through the membrane, $\bar{m}_1$ and $\bar{m}_2$ are the concentrations of the diffusing species at the two extremes of the membrane, $D_{\bar{m}}$ is the membrane diffusion coefficient of the metal–carrier complex, and δ_0 is the membrane thickness. The situation is schematically illustrated in Fig. 2, when only the processes occurring inside the membrane are considered.

In spite of their simplicity, Assumptions I and II do hold well enough in those cases where coupled transport through liquid membranes has been measured with well-stirred aqueous solutions and with chemical systems characterized by fast chemical reactions (*1*, *6*, *8*).

When, on the other hand, aqueous film diffusion, interfacial chemical reactions, and membrane diffusion simultaneously control the membrane permeability, explicit solutions for the membrane flux lead to not-easy-to-solve mathematical complexities. Further limitations to the development of theoretical treatments have been associated with the very scanty information which, until recently, was available on the rate and mechanisms of chemical reactions occurring at liquid membrane–water interfaces. These are the main reasons why no theoretical descriptions of liquid

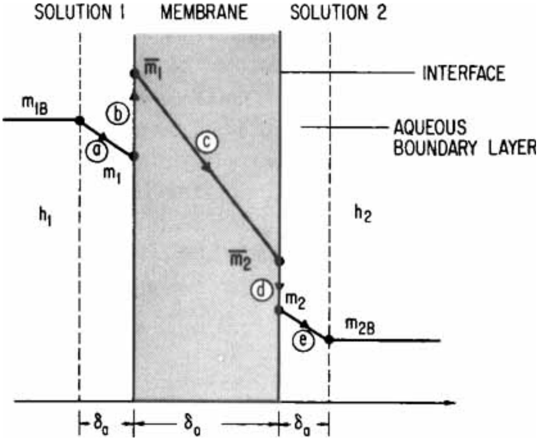


FIG. 2. Schematic representation of the processes controlling membrane permeability. *a* and *e* represent the diffusion through the aqueous boundary layers. *b* and *d* are the slow chemical reactions which control the crossing of the interface. *c* is the membrane diffusion of the carrier complex. h_1 and h_2 represent the hydrogen ion concentrations. The concentration gradient of h is assumed as negligible.

membrane permeabilities controlled by both diffusion processes and slow interfacial chemical reactions have until now appeared in the literature.

Lack of information on the mechanisms of the interfacial chemical reactions has indeed also prevented investigators from developing and applying simplified theoretical treatments, such as those based on Eq. (1), even when dealing with systems where slow interfacial reactions were known to occur. These considerations apply to the study of copper separation by solid supported liquid membranes, consisting of a commercial β-hydroxy-oxime (LIX 64N, General Mills) dissolved in kerosene absorbed on the polymeric membrane Celgard 2400 (Celanese Plastics Co.) described in Ref. *2*. In this work the kinetics of the interfacial reactions as well as the rate of diffusion through the aqueous boundary layers has not been taken into account to derive the flux equation describing the permeability of the membrane. Both the chemistry of the system and the experimental arrangement used to stir the aqueous phase at 60 rpm, on the other hand, do not allow one to neglect these two important contributions to the membrane permeability. The kinetics of interfacial copper mass transfer through water–LIX 64N organic solutions has been in fact repeatedly reported to be quite slow and controlled by the rate of the interfacial chemical reactions (*9–14*). Furthermore, previous liquid–liquid mass transfer kinetic studies performed by Lewis-type cells stirred at different rates have shown that at 60 rpm, diffusion through the aqueous boundary layers is a process as slow as the membrane diffusion itself, irrespective of possible different stirrer and cell geometries (*15–19*).

In the present work, previous information obtained by us on the rate and mechanisms of the interfacial reaction between copper(II) and a β-hydroxy-oxime dissolved in toluene (*14*), as well as a simplified model previously developed to couple experimentally identified interfacial chemical reactions with organic and aqueous film diffusion processes in liquid–liquid extraction kinetics studies through stirred flat interfaces (*15*, *16*), has been applied to derive membrane permeability equations where aqueous film diffusion, interfacial chemical reactions, and membrane diffusion are simultaneously considered. The derived equations are shown to describe well the data of Ref. *2*. Further, they allow one to predict membrane behaviors which are specific of partially chemically controlled permeabilities.

INTERFACIAL CHEMICAL REACTION. RATE AND MECHANISM

The kinetics of the heterogeneous complex formation reaction between Cu(II) and a β-hydroxy-oxime [2-hydroxy-5-t-octyl (acetophenone oxime)], HX, dissolved in toluene, has been described in Ref. *14*. The results reported in this reference have indicated that the foward reaction occurs according to the following rate law:

$$-\frac{d[\mathrm{Cu}]}{dt} = \vec{R}_0 = a_i k_1 [\mathrm{Cu}^{2+}][\overline{\mathrm{HX}}][\mathrm{H}^+]^{-1} \tag{2}$$

where $[\overline{\mathrm{HX}}]$ represents the monomer concentration in toluene and $k_1 = 2.86 \times 10^{-4}\ \mathrm{s}^{-1}\ \mathrm{cm}$. The bar indicates organic (membrane) phase species and a_i is the specific interfacial area. Rate (2) has been explained by the interfacial rate-determining step

$$\mathrm{Cu}^{2+} + \mathrm{X}^- \rightarrow \mathrm{CuX}^+ \tag{3}$$

Since the overall stoichiometry of the Cu^{2+} reaction is

$$\mathrm{Cu}^{2+} + 2\overline{\mathrm{HX}} \rightleftharpoons \overline{\mathrm{CuX}_2} + 2\mathrm{H}^+ \tag{4}$$

with

$$K_{\mathrm{eq}} = \frac{k_1}{k_{-1}} = \frac{[\overline{\mathrm{CuX}_2}][\mathrm{H}^+]^2}{[\mathrm{Cu}^{2+}][\overline{\mathrm{HX}}]^2} = 5.5 \times 10^{-1}$$

it follows from the principle of microscopic reversibility that

$$\overleftarrow{R}_0 = a_i k_{-1} [\overline{\mathrm{CuX}_2}][\overline{\mathrm{HX}}]^{-1}[\mathrm{H}^+] \tag{5}$$

with $k_{-1} = 5.2 \times 10^{-4}\ \mathrm{s}^{-1}\ \mathrm{cm}$. When $a_i = 1$, Eqs. (2) and (5) allow the derivation of the following equation for the interfacial flux J_i:

$$J_i = \vec{R}_0 - \overleftarrow{R}_0 = k_1[\mathrm{Cu}^{2+}][\overline{\mathrm{HX}}][\mathrm{H}^+]^{-1} - k_{-1}[\overline{\mathrm{CuX}_2}][\overline{\mathrm{HX}}]^{-1}[\mathrm{H}^+] \tag{6}$$

MEMBRANE PERMEABILITY EQUATIONS

When the experimental conditions are such that $\bar{m}_2 \ll \bar{m}_1$ and the membrane/aqueous distribution coefficient of the metal at the membrane–aqueous solution 1, $K_{\mathrm{d}1} = \bar{m}_1/m_{1\mathrm{B}}$, is substituted into Eq. (1), it follows that

$$P = J_0/m_{1\mathrm{B}} = \frac{D_{\bar{m}} K_{\mathrm{d}1}}{\delta_0} \tag{7}$$

$m_{1\mathrm{B}}$ is the metal concentration in the bulk aqueous solution 1, and P, which is often referred to as the membrane permeability coefficient (*8*), represents the permeation rate extrapolated to time zero.

Membrane permeability equations which also take into consideration diffusion through the aqueous boundary layer and the slow interfacial chemical reaction can be derived with the help of the scheme shown in Fig. 2. Here m_B represents bulk aqueous concentrations and m concentrations at the water–membrane interface. The permeability equations for the coupled transport of Cu^{2+} and H^+ through a β-hydroxy-oxime, HX, liquid membrane can now be obtained for the three cases:

A. Fast interfacial reactions, no aqueous diffusion layer
B. Slow interfacial reactions, no aqueous diffusion layer
C. Slow interfacial reactions, aqueous diffusion layer

The equations will be derived assuming that the metal concentration is much lower than that of the membrane carrier, HX, which is in turn assumed to behave ideally in the membrane phase. These two conditions, which can be easily removed by taking into account the stoichiometry of the reaction (Eq. 4) and the dimerization of the carrier molecule in the membrane phase (*11*, *14*), do not alter the general validity of the results obtained. Further, linear concentration gradients for the metal cations, a negligible concentration gradient for the hydrogen ion, and stationary state conditions will be assumed. For the sake of clarity the following symbols will be used: $m = [Cu^{2+}]$, $h = [H^+]$, $\overline{m} = [\overline{CuX_2}]$, δ_a = thickness of the aqueous diffusion layer, D_m and $D_{\overline{m}}$ = aqueous and organic diffusion coefficient of the metal species.

Case A. Fast Interfacial Reactions, No Aqueous Diffusion Layer ($\delta_a = 0$). By substituting the equilibrium constant of the heterogeneous reaction, $K_{eq} = \overline{m}h^2/m_B[\overline{HX}]^2$, into Eq. (7) it follows that

$$P = \frac{J}{m_{1B}} = \frac{D_{\overline{m}}}{\delta_0} K_{eq} \frac{[\overline{HX}]^2}{{h_1}^2} \tag{8}$$

In this case the overall flux, J, will be equal to the membrane diffusional flux, J_a. The logarithmic dependence of P on $[\overline{HX}]$ and h_1 is shown in Fig. 3(A).

Case B. Slow Interfacial Reactions, No Aqueous Diffusion Layer ($\delta_0 = 0$). The interfacial flux, J_i, determined by the rate of the interfacial chemical reaction, will be represented by Eq. (6):

$$J_i = k_1 m_{1B}[\overline{HX}]{h_1}^{-1} - k_{-1}\overline{m}_1[\overline{HX}]^{-1}h_1 \tag{9}$$

From Eq. (9) it follows that

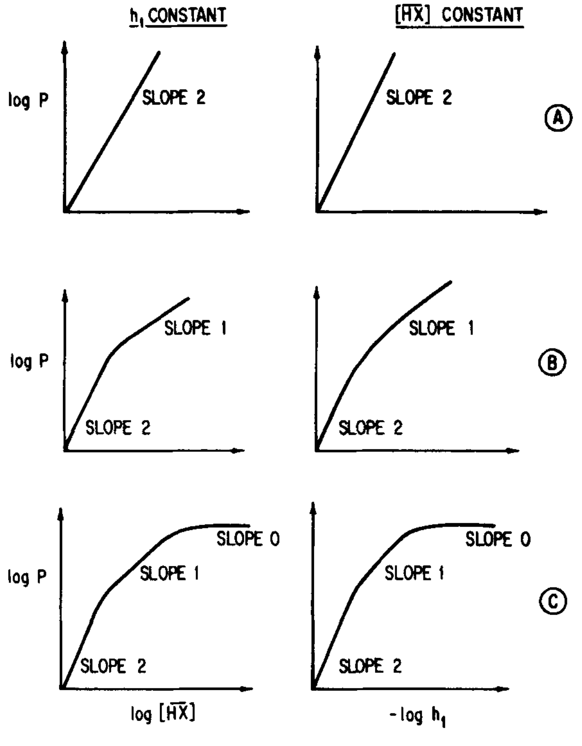


FIG. 3. Logarithmic plots of the membrane permeability, P, vs carrier concentration, $[\overline{HX}]$ or hydrogen ion concentration, h_1, in the aqueous feed solution 1. (A) Permeability controlled only by membrane diffusion. (B) Permeability controlled by membrane diffusion and interfacial chemical reactions. (C) Permeability controlled by membrane diffusion, interfacial chemical reactions, and aqueous boundary layers diffusion.

$$\bar{m}_1 = \frac{k_1 m_{1\mathrm{B}}[\overline{\mathrm{HX}}]h_1^{-1} - J_i}{k_{-1}[\overline{\mathrm{HX}}]^{-1}h_1} \tag{10}$$

Substituting Eq. (10) into Eq. (1) (with $\bar{m}_2 \ll \bar{m}_1$), considering that at the steady state $J_0 = J_i = J$, and solving for the flux, it follows that

$$P = \frac{J}{m_{1\mathrm{B}}} = \frac{k_1[\overline{\mathrm{HX}}]^2}{(\delta_0/D_{\bar{m}})k_{-1}h_1^2 + h_1[\overline{\mathrm{HX}}]} \tag{11}$$

The logarithmic dependence of P on $[\overline{\mathrm{HX}}]$ and h_1 is shown in Fig. 3(B). In this case there is a shift from a second-order to a first-order dependency of P on $[\overline{\mathrm{HX}}]$ and h^{-1}, respectively, when the membrane carrier concentration and the pH of the solution are increased. The change of slope from 2 to 1 in the plots of Fig. 3(B) indicates a transition from a region where the membrane permeability is only membrane diffusion controlled (slope 2) to a region where it is only kinetically controlled (slope 1).

Equation 11 shows that the region of slope 2 allows one to evaluate the membrane diffusional parameter $D_{\bar{m}}/\delta_0$, providing the equilibrium constant of the reaction, $K_{eq} = k_1/k_{-1}$, is known, since

$$\log P = \log (D_{\bar{m}}/\delta_0) + \log K_{eq} - 2 \log h_1 + 2 \log [\overline{\mathrm{HX}}] \qquad (12)$$

The region where the slope is equal to 1 allows one to evaluate the rate constants of the reaction since

$$\log P = \log k_1 + \log [\overline{\mathrm{HX}}] - \log h_1 \qquad (13)$$

Case C. Slow Interfacial Reactions, Aqueous Diffusion Layers ($\delta_a \neq 0$). If aqueous diffusion layers are present, a concentration gradient is also present between the bulk aqueous phase and the membrane interface. The Cu^{2+} concentration in Eq. (6) is no longer m_{1B} but is m_1 (see Fig. 2). The concentration at the interface, m_1, can be determined in terms of m_{1B} from the aqueous flux of the metal cation through the aqueous boundary layer, J_a, expressed by the simplified Fick's law

$$J_a = \frac{D_m}{\delta_a}(m_{1B} - m_1) \qquad (14)$$

and inserted into Eq. (11) instead of m_{1B}. Since, at the steady state, the aqueous diffusion flux J_a, the interfacial flux J_i, and the membrane diffusion flux J_0 must be equal, Eqs. (11) and (14) can be solved to yield

$$P = \frac{J}{m_{1B}} = \frac{k_1[\overline{\mathrm{HX}}]^2}{(\delta_0/D_{\bar{m}})k_{-1}h^2 + (\delta_a/D_m)k_1[\overline{\mathrm{HX}}]^2 + h_1[\overline{\mathrm{HX}}]} \qquad (15)$$

The logarithmic dependence of P on $[\overline{\mathrm{HX}}]$ and h_1 is shown in Fig. 3(C). While the change of slope from 2 to 1 has the same meaning as in Case B, the region of slope 0 indicates that the membrane permeability is entirely controlled by the diffusion process in the aqueous boundary layer. This region allows one to evaluate the aqueous diffusional parameter, D_m/δ_a, since

$$\log P = \log (D_m/\delta_a) \qquad (16)$$

COMPARISON WITH EXPERIMENTAL PERMEABILITY DATA

Equations (8), (11), and (15) and the corresponding graphic dependencies

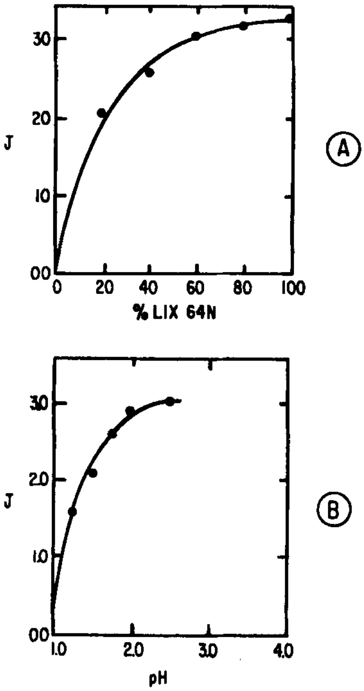


FIG. 4. Copper flux, J (μg/cm^2-min), vs carrier concentration (A) and vs pH of the aqueous feed solution 1. Data from Ref. *2*.

shown in Figs. 3(A), 3(B), and 3(C) can now be compared with the data of Ref. *2* where copper fluxes through supported liquid membranes consisting of the β-hydroxy-oxime, LIX 64N, dissolved in kerosene absorbed on the solid polymeric membrane, Celgard 2400, have been measured. Data from Ref. *2* are shown in Figs. 4(A) and 4(B). Since they refer to constant copper and H^+ concentrations (Fig. 4A) and constant copper and $[\overline{HX}]$ concentrations (Fig. 4B), a direct comparison can be made with the plots of Fig. 3. It appears that the sets of data of both Fig. 4(A) and 4(B) converge to a region of slope 0, indicating that they can be qualitatively well represented by Eq. (15). This result indicates that the copper fluxes are controlled by aqueous film diffusion, interfacial chemical reactions, and membrane diffusion, contrary to previous explanations (*2*) which had neglected both aqueous film diffusion and the interfacial chemical reactions. This conclusion is not unexpected in view of the slow interfacial chemical reactions which occur in the heterogeneous system and the low rate of stirring (60 rpm) of the two aqueous compartments separated by the liquid membrane.

As far as process applications are concerned, Eq. (15) can be a useful tool to guide the choice of the membrane carrier concentration and the pH of the aqueous copper feed solution. It can be seen that a limiting value exists for $[\overline{HX}]$, where the membrane permeability does not increase further. A further increase of $[\overline{HX}]$ beyond this limiting value not only does not improve the permeability of the membrane, but may even cause its decrease. This effect can be produced by the increased membrane viscosity which can in turn reflect in a lower value of the diffusion coefficient $D_{\overline{m}}$. Similarly, the use of copper feed solutions having very high pH's does not necessarily increase the membrane permeability. In fact, in spite of the increased gradient of the counter diffusing ion H^+, a limiting pH value is reached where the membrane permeability stays constant.

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