# Chemically Active Liquid Membranes in Inorganic Supports for Metal Ion Separations

**Jongheop Yi and Lawrence L. Tavlarides**
Dept. of Chemical Engineering and Materials Science, Syracuse University, Syracuse, NY 13244

*Ceramic membranes with pores filled with organic chelation acid show promise as the basis for inorganic membrane separator units for metal ion separations from dilute aqueous streams. The performance of such membranes in disk geometry is evaluated experimentally for a model system. The proposed model describes the metal ion flux through the membrane, and a batch or continuous operated separator using these membranes is analyzed. Copper ion fluxes through α-alumina/silica disks impregnated with 2-hydroxy-5-nonylacetophenone oxime were determined from a rotating diffusion cell apparatus for feed solution concentration of copper 0.03 mol/L, feed solution pH 3, strip solution pH of 0.3, and rotation speed of 130 rpm. Flux values range from $5.4\times10^{-6}$ to $2.2\times10^{-5}$ mol/cm$^2$·h and compare well with the reported values for metal ion transport through polymeric supporting membranes (Largman and Sifniades, 1978; Babcock et al., 1981; Teramoto and Tanimoto, 1983; Kojima and Miyauchi, 1981).*

*The proposed steady-state flux model describes the metal flux through chemically active liquid membranes in inorganic supports. The model includes film resistance to mass transfer in both liquid films, complexation and stripping reactions at the liquid-liquid interface in the membrane pores on both surfaces of the membrane, and metal ion/complex diffusion through the membrane. Separately designed experiments were executed using a precise pH-static technique to obtain the physical and chemical parameters of diffusivities, kinetic coefficients and equilibrium coefficients. Calculated fluxes compare well with experimentally determined values from batch experiments (average standard error, 11%).*

*The proposed lumped parameter linear kinetic rate model for the surface reaction rates interprets the kinetic data for the copper chelation reaction. The model is based on a multistep reaction mechanism and has the following form for the extraction reaction for the above mentioned conditions:*

$$R^F = 7.3\times10^{-4} C^{F*}_{Cu} - 7.1\times10^{-6}\, C^{F*}_{\overline{CuR_2}}$$

*A similar expression is presented for the strip reaction.*

*An analytical solution for the mathematical model predicts the performance of the chemically active liquid membrane reactor for the batch or continuous operation of the rotating diffusion cell. Calculated results describe expected trends and agree well with the experimental results.*

## Introduction

Supported liquid membranes have been recently recognized as a promising technology for the separation or purification of toxic or valuable metal ions from aqueous streams (Danesi et al., 1983a; Noble and Way, 1987; Noble, 1987; Tanigaki et al., 1988; Marchese et al., 1989; Sugiura et al., 1989; Teramoto et al., 1989; Drioli et al., 1989; Chaudry et al., 1990). In this

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Correspondence concerning this article should be addressed to L. L. Tavlarides.

J. Yi is currently at Rhône-Poulenc, 8410 Manchester Blvd., Houston, TX 77012.

process, solutions of liquid ion exchangers are impregnated into the pores of a solid matrix support, typically polymeric membranes. The forward extraction reaction occurs on the feed side and the reverse stripping reaction occurs on the receiving side. In the pores of the membrane, the chelated molecules are transported to the receiving side and regenerated ion exchange molecules diffuse in the opposite direction to renew the process.

Reviews of supported liquid membrane applications are presented elsewhere (Way et al., 1982; Schultz, 1983; Danesi, 1984; Noble et al., 1989) obviating the need to do so here. Suffice it to say that the relevant advantages of supported liquid membranes over the conventional separation technology (viz., liquid-liquid solvent extraction) include uphill transport against concentration gradients, high feed/strip volume ratios, and use of small amounts of extractants.

Despite promising performance, few processes using supported membrane technology have been commercialized for large-scale hydrometallurgical extraction (Noble and Way, 1987). The main disadvantages exhibited by the polymeric membranes being used are: sensitivity to temperature, pH and chemical environment (Noble, 1987), plasticizer effects (Sugiura, 1990), and loss of their mechanical stability in modular operation (Teramoto and Tanimoto, 1983). These needs suggest the use of ceramic membranes for the porous matrix, which show the potential to overcome the above difficulties. They exhibit reliability and long life, neither creep nor deformation occurs during cooling, and high permeabilities can be achieved.

Accordingly, these membranes, impregnated with suitable chelation agents, show promise for selective removal of metal ions. Examination of the potential of this concept provides the basis for this study.

No work has been found in the literature for impregnated ceramic membranes used for the above purpose. Relevant to this work, however, are the studies of copper ion transport through supported liquid membranes in polymeric supports using commercially available oxime extractants (Baker et al., 1977; Lee et al., 1978; Volkel et al., 1980; Martin and Davis, 1980; Danesi et al., 1981; Chiarizia et al., 1983). It was observed that the copper flux was sensitive to the pH gradient across the membrane and the concentration of extractants. The types and concentrations of strip solutions also affect the copper ion flux through the supported liquid membranes (Teramoto and Tanimoto, 1983). Further, it was reported that membrane performance was significantly dependent on the operation conditions (Chiarizia et al., 1983). These authors suggested that the membrane diffusion process was probably the rate-determining step in fresh membranes, but interfacial chemical reaction was proposed as the rate-determining step in aged membrane (Largman and Sifniades, 1978; Kataoka et al., 1982).

Theoretical analyses of these transport phenomena in supported liquid membranes have been reported for the limiting cases of the fast chemical reactions at the interfaces (for example, Cianetti and Danesi, 1983; Danesi et al., 1983b) or of negligible solute concentration in the strip solution (Danesi et al., 1981). Experimental results, however, show that aqueous film diffusion processes, interfacial chemical reactions, and membrane diffusion simultaneously control the flux through the membranes (Yi, 1991).

The analysis of metal ion transfer phenomena using the chemically active liquid membrane process for metal ion separation is complicated by the presence of both external mass-transfer and interfacial reaction kinetic effects. It is difficult to completely remove the effect of the external mass-transfer resistance experimentally from the kinetics at the interfaces between membrane and contacting fluids by increasing the rotational speed (for rotational diffusion cell experiments) and flow rate of liquid streams for tubular module application. Hence, the kinetic behavior of the chemically active liquid membrane process for the metal ion separation process must be studied with a model that takes into account the mass transfer in the boundary layers and reaction kinetics at the interfaces. This model equation also should allow one to estimate the parameters directly from the experiments.

In this work, a model equation is proposed to describe the effects of chemical and physical parameters on the flux in the supported liquid membrane process, and flux experiments are executed to evaluate these parameters using a rotating diffusion cell equipped with on-line UV-visible spectrophotometry. 2-hydroxy-5-nonylacetophenone oxime is used as an impregnating solution, since this oxime contains no added modifier and is available as a commercial product (LIX84, Henkel Co.). It is widely used for copper recovery from dilute sulfuric acid leach solutions and has other applications for the recovery of copper and nickel (Kordosky, 1987-1988; Pandey et al., 1989; Piotrowicz et al., 1989).

Also, an analytical solution is presented that models the metal ion separation using this impregnated ceramic membrane process for batch operation of the rotating diffusion cell, and it is compared with experimental results.

## Experiments

The rotating diffusion cell is employed to obtain overall mass-transfer rates and kinetic rate coefficients for the metal ion transport across membranes. Figure 1 shows the apparatus, in which instantaneous monitoring of the internal or external fluid is possible using an on-line UV-visible spectrophotometer (Perkin Elmer: Model 559). Also, a pH-static controller (Brinkman: Impulsomat 614, Dosimat 665, pH Meter 632) permits maintenance of constant pH during experiments. The system is isothermally controlled, a nitrogen gas purge prevents oxidation of the solutions, and a controller is used to maintain constant rotational speeds.

The organic mixture for ceramic membrane impregnation is 2-hydroxy-5-nonylacetophenone oxime (LIX84; Henkel) in kerosene (100% LIX84 and 50% LIX84 by weight were used). Copper sulfate solutions are prepared from copper sulfate powder (Fisher). The ceramic membranes have been selected from commercially available products (P-55; Coors Ceramic Co.). They are composed mostly of $\alpha$-alumina/silica with average pore size of 49-55 $\mu$m and porosity of 41.7 vol. %. The thickness and diameter of the ceramic membranes studied are 2 mm and 2.54 cm, respectively. Details of experimental procedures are shown elsewhere (Yi, 1991).

## Theoretical Background

### *Model equation for steady-state flux and parameter estimation*

A model equation for the flux through the membrane is necessary to predict the performance of the impregnated ce-

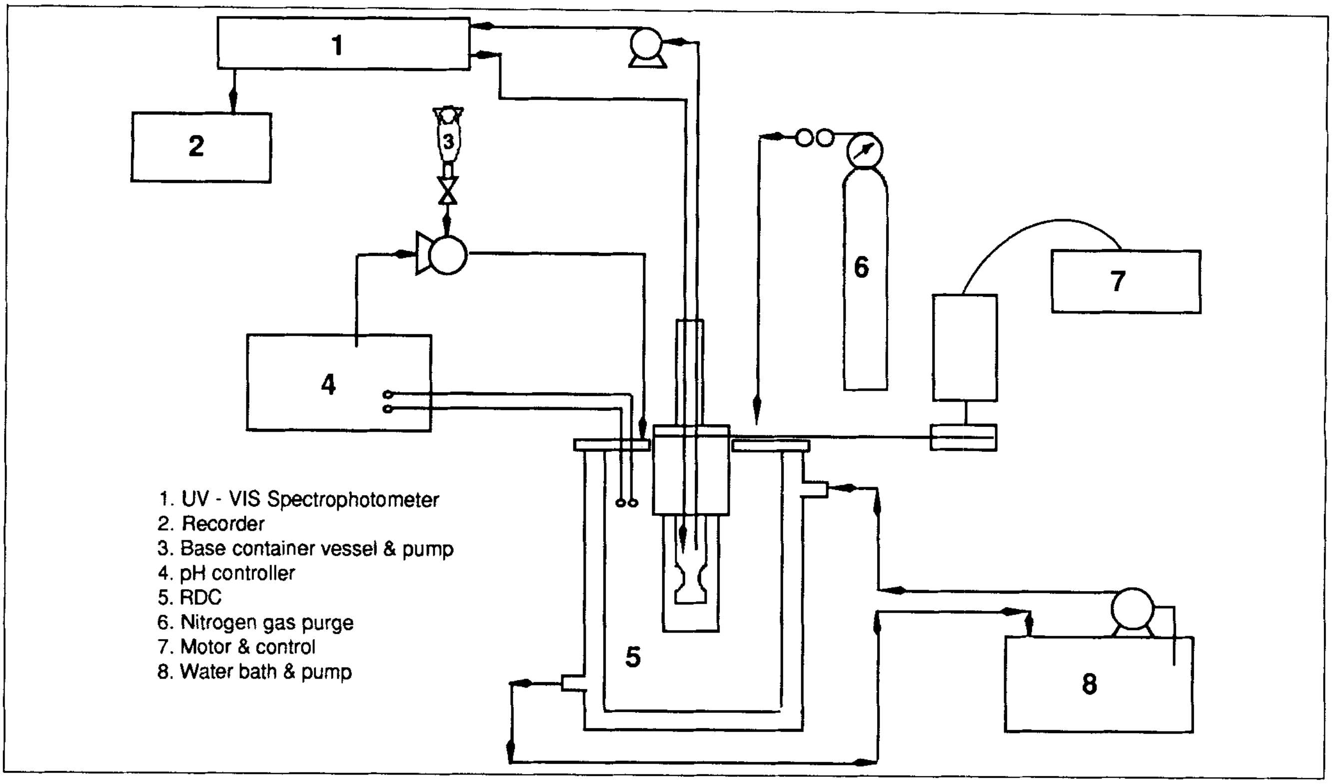

**Figure 1. Experimental apparatus.**

ramic membranes. This equation can also be employed to estimate parameters with the appropriate kinetic models and flux information. The flux model can then be used with the appropriate material balance equations to design modular extraction equipment and verify the efficiency of these ceramic membranes for metal ion removal on bench-scale equipment.

The model for the steady-state flux through the impregnated ceramic membranes assumes that the metal ions experience a series of resistances (see Figure 2): transport through the aqueous feed, complexation reversible reaction at the membrane/feed solution interface, diffusion across the membrane, stripping reaction at the membrane/strip solution interface, and transport through the aqueous strip solution.

The following stoichiometric expression is assumed to describe the overall extraction process which occurs on either side of the membrane/solution interface:

$$Cu^{2+} + 2\overline{HR} \rightleftharpoons \overline{CuR_2} + 2H^+ \tag{1}$$

A kinetic model for the interfacial reaction can be derived based on a series of five elementary reactions at the interface in a similar fashion as suggested earlier (Danesi et al., 1980; Teramato and Tanimoto, 1983; Komasawa et al., 1983; and Lee and Tavlarides, 1986).

a. $\overline{HR} \rightleftharpoons HR$

b. $HR \rightleftharpoons H^+ + R^-$

c. $M^{2+} + R^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} MR^+$ (RDS)

d. $MR^+ + R^- \rightleftharpoons MR_2$

e. $MR_2 \rightleftharpoons \overline{MR_2}$

where $M$ and $\overline{HR}$ represent the copper metal ion species and the chelation acid, respectively. The overbar indicates concentrations in the organic phase. In step a, the chelation acid partitions into the aqueous side of the interface; in step b, dissociation occurs; in steps c and d, sequential addition of the chelated acid anion occurs with the metal cation; and in step e, the metal complex partitions into the organic phase at

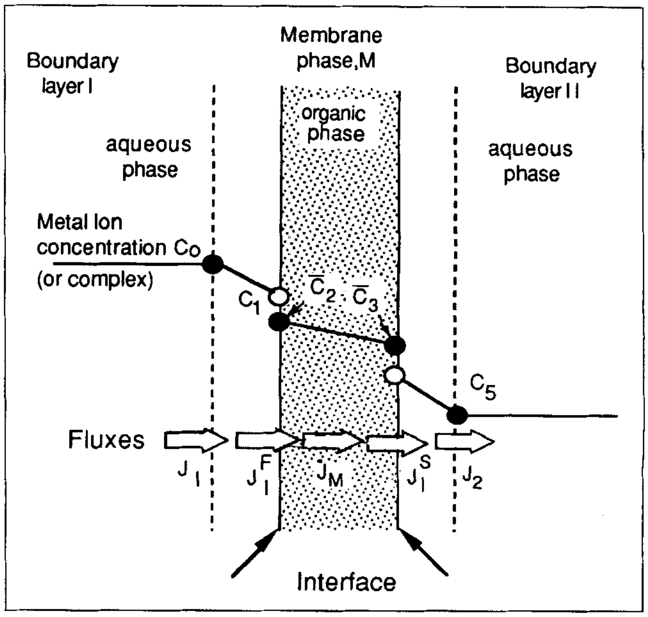

**Figure 2. Metal ion extraction flux using through a supported liquid membrane.**

the membrane interface. The rate-determining step (RDS) is assumed to be step c, the dehydration of the free metal ion. Since other kinetic models derived based on different (RDS) assumptions did not provide for acceptable data analysis, this model was accepted *a posteriori*. Accordingly, the lumped expression for the interfacial reaction, $R^i$, can be written as:

$$R^i = k'_{+i} C_M^{i*} \frac{C_{\overline{HR}}^{i*}}{C_H^{i*}} - k'_{-i} C_{\overline{MR}_2}^{i*} \frac{C_H^{i*}}{C_{\overline{HR}}^{i*}} \tag{2}$$

where superscript $i^*$ denotes the interfacial concentration at the $i$-side, $i$ = feed or strip solution. Kinetic expressions of this form have been reported for the copper ion extraction rates in similar systems (Danesi et al., 1980; Kojima and Miyauchi, 1981; Teramoto and Tanimoto, 1983; Komasawa et al., 1983; Komasawa and Otake, 1983; Tallarico et al., 1989).

For the conditions of these experiments, the reaction takes place at high concentrations of chelation acid as compared to the metal ion concentration, and the pH is maintained constant and/or the hydrogen ions concentrations are larger than the metal ion or metal complex concentrations. Accordingly, the interfacial reaction expressions at both interfaces, $R^F$ and $R^S$, can be written as:

$$R^F = k_{+F} C_M^{F*} - k_{-F} C_{\overline{MR}_2}^{F*} \tag{3a}$$

$$R^S = k_{-S} C_{\overline{MR}_2}^{S*} - k_{+S} C_M^{S*} \tag{3b}$$

where

$$k_{+i} = k'_{+i} \frac{C_{\overline{HR}}^{i*}}{C_H^{i*}} \tag{4a}$$

$$k_{-i} = k'_{-i} \frac{C_H^{i*}}{C_{\overline{HR}}^{i*}} \tag{4b}$$

Here $C_M^{F*}$ and $C_M^{S*}$ are the interfacial metal ion concentrations at the feed and strip solution side, respectively, $k_{+i}$ and $k_{-i}$ are the lumped rate coefficients at the $i$-side, and

$$C_{\overline{MR}_2}^{F*} \text{ and } C_{\overline{MR}_2}^{S*}$$

are the metal complex concentrations in organic phase at the interface at the feed or strip solution side, respectively. These approximations admit a linear kinetic form which facilitates the analyses and is adequate to represent the data.

As depicted in Figure 2, assuming the forms of the reaction rate expressions in Eq. 3, and quasi-steady state, the overall flux equation can be written as:

$$J = K_W \Delta C \tag{5}$$

where

$$\Delta C = \frac{C_M^F}{K^F} - \frac{C_M^S}{K^S} \tag{6}$$

$$\frac{1}{K_W} = \frac{\delta^F}{D_M^F K^F} + \frac{1}{\epsilon k_{-F}} + \frac{L}{D_{\overline{MR}} \epsilon} + \frac{1}{\epsilon k_{-S}} + \frac{\delta^S}{D_M^S K^S} \tag{7}$$

and

$$K^i = k_{-i}/k_{+i} \quad i = F, S \tag{8}$$

Here $K_W$ is an overall mass-transfer coefficient and $\Delta C$ is the normalized concentration difference between the bulk concentrations of the feed and the strip solution. A value of 1 is assumed for the tortuosity of the porous membrane. It is seen in Eqs. 5-8 that a number of parameters are related to the individual transport and kinetic expressions. Here, $D_M^i$ *and* $D_{\overline{MR}}$ are the diffusivities of the copper ion in the $i$-side, and the copper complex in the membrane pores, respectively, $\delta^i$ is the mass-transfer boundary layer thickness on either side of the membrane, $L$ is the membrane thickness, $\epsilon$ is the porosity of the membrane, and $K^F$ and $K^S$ are lumped coefficients on the feed and strip side of the membrane. Equation 7 implies that the inverse of the overall mass-transfer coefficient is the summation of the inverse of five resistances. The first and fifth terms represent the effect of the boundary layer resistances on the metal flux, the second and fourth terms indicate the extraction and strip kinetics rates as the resistance on the metal ion extraction flux, and the third term represents the diffusional resistance of the metal complex through the membrane.

We have shown for the RDC case (Yi, 1991) that an expression for the thickness of diffusion boundary layer, given in Eq. 7, is analogous to the well known form of the Levich solution (Levich, 1962):

$$\delta^i \propto (D_M^i)^{1/3} \omega^{-1/2} (\nu^i)^{1/6} \quad i = F, S \tag{9}$$

where $\omega$ is the rotating speed of disk and $\nu^i$ is the kinematic viscosity.

Experiments were executed on the RDC to evaluate chemical and physical parameters which affect the inorganic ceramic membrane capability. Table 1 shows the fluid-contacting mode in the three phases of the RDC which permit independent determination of the above parameters. For example, experiments in row 3 in Table 1 were executed with aqueous-phase compositions to describe either the feed or strip solution and the organic phase at corresponding conditions. Thus, data to determine the rate constants for both cases were generated. Experimental conditions for parameter estimations are given in the Results section with calculated parameter values.

### Aqueous-phase equilibria

The above kinetic models assume the reactive species in the aqueous phase are the dissociated copper ion and the hydrogen ion. Thus it becomes necessary to determine these concentrations to calculate kinetic rates and fluxes. It is well known that copper sulfate solutions exist as a mixture of free copper, $Cu^{++}$, free sulfate, $SO_4^=$, and hydrate copper sulfate, $CuSO_4$ (Freeman and Tavlarides, 1981; Whewell et al., 1975). Copper hydroxide ions also are formed at certain conditions, as listed in Table 2. When the expressions for the equilibrium reactions and mass balance equations for the copper, hydrogen, and sulfate are solved using the equilibrium constants of Table 2, equilibrium concentrations of the various species present in the aqueous phase can be calculated (Freeman and Tavlarides, 1981; Schecher and Westall, 1990). These results are used to calculate the fractions of free ion to the total ions present in the aqueous phase for the different pH and copper concentration solutions. Results are discussed later.

### Analysis of the chemically active liquid membrane reactor

A schematic for the chemically active liquid membrane reactor for continuous flow or batch operation is shown in Figure

**Table 1. Experiments for Parameter Estimation**

| Exp. | Feed Phase | Impregnated Phase | Strip Phase | Parameters Observed |
|---|---|---|---|---|
| 1 | Aqueous | Aqueous | Aqueous | Diffusivity of metal ion in the aqueous phase ($D_M^F$,$D_M^S$) |
| 2 | Organic | Organic | Organic | Diffusivity of metal-chelating agent complex |
| 3 | Aqueous | Organic | Organic | Reaction kinetic constants |
| 4 | Aqueous | Organic | Aqueous | Flux |

3. Metal and hydrogen ions are transported between the two chambers through the intervening inorganic membrane as described above. The fluids in each chamber could be processed either in the batch or continuous flow mode, and are assumed well mixed, isothermal and with constant densities. One-dimensional transport is assumed to occur across the membrane.

Under these conditions, the material balances for the transporting metal ion in the feed-side and the strip-side bulk solutions may be given as:

$$V^F \frac{dC_M^F}{dt} = q^F(C_{MO}^F - C_M^F) - A^F J^F \tag{10}$$

$$V^S \frac{dC_M^S}{dt} = q^S(C_{MO}^S - C_M^S) + A^S J^S \tag{11}$$

where $V^i$ $(i=F, S)$ is the volume of $i$-side solutions, $q^i$ $(i=F, S)$ is the volumetric flow rate, $A^i$ is the membrane area, and $J^i$ $(i=F, S)$ is the flux through the boundary layer of $i$-side solution. $C_M^F$ *and* $C_M^S$ are metal ion concentrations in exiting streams of feed and strip chambers, respectively, and $C_{MO}^F$ and $C_{MO}^S$ are the metal ion concentrations for the inlet streams.

For a more general development, it is assumed that first-order irreversible reaction takes place in the membrane phase, in the form of $k_R\ C_{\overline{MR}_2}$, simultaneously with the diffusion process (in this study, $k_R = O$). For this case, the material balance equation for the metal ion in the membrane can be written as:

$$\frac{\partial C_{\overline{MR}_2}}{\partial t} = D_{\overline{MR}} \nabla^2 C_{\overline{MR}_2} + k_R C_{\overline{MR}_2} \tag{12}$$

where $D_{\overline{MR}}$ is the diffusion coefficient of the metal complex, and $C_{\overline{MR}_2}$ is the metal complex concentration.

**Table 2. Relevant Aqueous-Phase Reactions with Equilibrium Constants for Copper Sulfate Ion Equilibrium**

| Aqueous-Phase Reaction | Equilibrium Constant* |
|---|---|
| $H_2O \rightleftharpoons H^+ + OH^-$ | $10^{-14}$ |
| $CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-}$ | 204.2 |
| $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$ | 97.7 |
| $Cu^{2+} + 2OH^- \rightleftharpoons Cu(OH)_2\downarrow$ | $2.3 \times 10^{-9}$ |
| $Cu^{2+} + OH^- \rightleftharpoons Cu(OH)^+$ | $10^{-8}$ |
| $Cu^{2+} + SO_4^{2-} \rightleftharpoons CuSO_4\downarrow$ | $9.8 \times 10^{-4}$ |

*Schecher and Westall (1990).

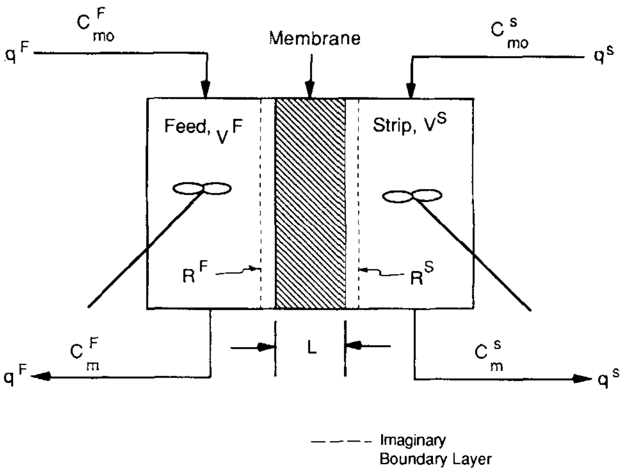

**Figure 3. Batch ($q^F = q^S = 0$) and continuous flow with well-mixed chamber membrane module.**

At the interfaces depicted in Figure 3, it is assumed that interfacial reactions between the metal ion in the aqueous phase and the chelation acid in the membrane take place and are represented by $R^F$ and $R^S$. Accordingly, the boundary conditions at the membrane interfaces applicable for Eq. 12 can be given as:

$$-D_{\overline{MR}} \frac{\partial C_{\overline{MR}_2}}{\partial X} = R^F \quad \text{at } X = O \tag{13}$$

$$-D_{\overline{MR}} \frac{\partial C_{\overline{MR}_2}}{\partial X} = R^S \quad \text{at } X = L \tag{14}$$

The interfacial reaction expressions, $R^F$ and $R^S$, can be derived theoretically based on the appropriate chemistry. For this study, the approximations in forms of first-order reversible reactions as given in Eqs. 3 and 4 can be rewritten as:

$$R^F = k_{+F} C_M^{F*}(t) - k_{-F} C_{\overline{MR}_2}(0,t) \tag{15}$$

$$R^S = k_{-S} C_{\overline{MR}_2}(L,t) - k_{+S} C_M^{S*}(t) \tag{16}$$

For the mass-transfer flux through boundary, the film model assumes that the transfer occurs through the fluid film formed at the boundary in the aqueous side. The flux through the aqueous boundary layer can be given by:

$$J^i = k_M^i (C_M^i - C_M^{i*}) \quad i = F,S$$

where $k_M^i$ is the mass-transfer coefficient at boundary layer, $C_M^i$ is the bulk concentration, and $C_M^{i*}$ is the metal ion concentration at the interface between the aqueous and organic phase.

Using Eqs. 15 and 16, and the expression for the fluxes from the bulk solution to membrane, $J^F$ and $J^S$ can be written as:

$$J^F = \Delta^F \{ C_M^F - K^F C_{\overline{MR}_2}(0,t) \} \tag{17}$$

$$J^S = \Delta^S \{ K^S C_{\overline{MR}_2}(L,t) - C_M^S \} \tag{18}$$

where

$$\Delta^i=\left(\frac{1}{k^i_M}+\frac{1}{k_{+i}}\right)^{-1} \tag{19}$$

$$K^i=\frac{k_{-i}}{k_{+i}} \quad i=F,S \tag{20}$$

It is noted that the concentrations at the interface are related to both the flux through the boundary layer, $J^i$, and the flux due to the reaction at the interface, $R^i$, $(i=F, S)$. For example, the interfacial concentration at the feed-side, $C^{F*}_M$, can be written as:

$$C^{F*}_M(t)=\frac{k^F_M C^F_M+k_{-F}C_{\overline{MR}_2}(0,t)}{k^F_M+k_{+F}} \tag{21}$$

A similar equation can be written for the strip-side.

The interfacial metal ion concentration can be calculated directly with Eq. 21 for any given metal complex concentration at the membrane side as all coefficients and the bulk concentration can be measured or determined experimentally.

For ease of solution and analysis, it is convenient to use dimensionless forms of Eqs. 10–12. Using Eqs. 15–18, these are written as follows:

$$\frac{\partial f}{\partial \tau}=\theta^F F-\beta^F f+E^F g(\tau,\eta=0) \tag{22}$$

$$\frac{\partial u}{\partial \tau}=\theta^S U-\beta^S u+E^S g(\tau,\eta=1) \tag{23}$$

$$\frac{\partial g}{\partial \tau}=\nabla^2 g+\phi g \tag{24}$$

$$\frac{\partial g}{\partial \eta}=B^F(g-f) \quad \text{at } \eta=0 \tag{25}$$

$$\frac{\partial g}{\partial \eta}=B^S(u-g) \quad \text{at } \eta=1 \tag{26}$$

$$f=f_o, \quad u=u_o, \quad g=g_o \quad \text{at } \tau=0 \tag{27}$$

The dimensionless terms which arise above can be grouped as in Table 3.

### Analytical solution

Analytical solution can be obtained through the separation of variables. This analytical solution allows one not only to verify the numerical solutions, but also to evaluate the sensitivity of the chemically active liquid membrane reactor performance to kinetic and physical parameters more efficiently.

The approach for an analytical solution for Eqs. 22–24 assumes a series expansion form for the dependent variables exist such that

$$g(\eta,\tau)=\sum_{n=0}^{\infty} G_n(\eta)T_n(\tau) \tag{28a}$$

$$f(\tau)=\sum_{n=0}^{\infty} F_n T_n(\tau) \tag{28b}$$

$$u(\tau)=\sum_{n=0}^{\infty} U_n T_n(\tau) \tag{28c}$$

The $G_n(n)$ terms are the eigenfunctions given by the solution to the eigenvalue problem:

$$\frac{1}{G_n}\frac{d^2G_n}{d\eta^2}+\beta_n^2 G_n=0 \tag{29a}$$

$$E^F\{G_n|_{\eta=0}-F_n\}=F_n(\phi-\beta_n^2) \tag{29b}$$

**Table 3. Dimensionless Terms**

| | |
|---|---|
| *Dependent and independent variables* | |
| $f=C^F_M/K^FC^o_T$ | $F=C^F_{Mo}/K^FC^o_T$ |
| $u=C^S_M/K^SC^o_T$ | $U=C^S_{Mo}/K^SC^o_T$ |
| $g=C_{\overline{MR}_2}/C^o_T$ | |
| $\eta=X/L$ | $\tau=D_{\overline{MR}}t/L^2$ |
| *Dimensionless parameter groups* | |
| $\phi=\frac{K_RL^2}{D_{\overline{MR}}}=\frac{L^2/D_{\overline{MR}}}{1/k_R}$ | $=\frac{\text{diffusion time of metal complex in membrane}}{\text{reaction time in membrane}}$ |
| $\theta^j=\frac{L^2/D_{\overline{MR}}}{V^j/q^j}$ | $=\frac{\text{diffusion time of metal complex in membrane}}{\text{residence time in chamber } j}$ |
| $\alpha^j=\frac{A^jL\epsilon}{K^jV^j}$ | $=\frac{\text{membrane phase capacity}}{\text{solution phase capacity}}$ |
| $B^j=\frac{K^jL}{D_{\overline{MR}}}\ \Delta^j=K^j\frac{L^2/D_{\overline{MR}}}{L/\Delta^j}$ | $=\frac{\text{diffusion time of metal complex in membrane}}{\text{characteristic time of diffusion and reaction}}$ |
| $E^j=\alpha^jB^j$ | $j$ = feed or strip |
| *Dimensionless performance parameters* | |
| $X(\tau)=\frac{\text{feed concentration at } \tau}{\text{initial feed concentration}}$ | |
| $Y(\tau)=\frac{\text{strip concentration at } \tau}{\text{initial feed concentration}}$ | |

$$E^S\{G_n|_{\eta=1} - U_n\} = U_n(\phi - \beta_n^2) \qquad (29c)$$

The boundary conditions from Eqs. 25-26 take the form:

$$F_n = G_n(0) - \frac{1}{B^F}\left.\frac{dG_n}{d\eta}\right|_{\eta=0} \qquad (30a)$$

$$U_n = G_n(1) + \frac{1}{B^S}\left.\frac{dG_n}{d\eta}\right|_{\eta=1} \qquad (30b)$$

The formal solution of Eq. 29 is given by:

$$G_n(\eta) = \cos(\beta_n\eta) + \frac{B_i^F}{\beta_n^2 - E^F}\beta_n\sin(\beta_n\eta) \qquad (31)$$

where the eigenvalues, $\beta_n$, are the ordered roots of the characteristic Eq. 32:

$$\frac{\tan\beta_n}{\beta_n} = \frac{\beta_n^2(B^F + B^S) - (B^FE^S + B^SE^F)}{(\beta_n^2 - E^S)(\beta_n^2 - E^F) - B^FB^S\beta_n^2} \qquad (32)$$

The eigenfunctions of Eq. 29 obey the orthogonality relation:

$$\int_o^1 G_nG_m d\eta + \Delta_{nm} = \delta_{nm}R_n \qquad (33)$$

where

$$\Delta_{mn} = \frac{B^S}{E^S}U_mU_n + \frac{B^F}{E^F}F_nF_m$$

and $\delta_{mn}$ is the Kronecker delta. This leads to:

$$R_n = \int_o^1 G_n^2 d\eta + \Delta_{nn} \qquad (34)$$

The time-dependent solutions of $T_n(\tau)$ can be given as the solutions of:

$$\frac{dT_n}{d\tau} - (\phi - \beta_n^2)T_n = 0 \qquad (35)$$

The solution can be written as:

$$T_n(\tau) = C_n\exp\{(\phi - \beta_n^2)\tau\} \qquad (36)$$

The coefficients, $C_n$, can be obtained from the initial conditions, which are:

$$g(\tau = o, \eta) = g_o = \sum_{n=0}^{\infty} C_nG_n(\eta) \qquad (37a)$$

$$f(\tau = o) = f_o = \sum_{n=0}^{\infty} C_nF_n \qquad (37b)$$

$$u(\tau = o) = u_o = \sum_{n=0}^{\infty} C_nU_n \qquad (37c)$$

Using these conditions and applying the orthogonality relation to the result yields:

$$C_n = \frac{1}{R_n}\left[g_o\int_o^1 G_n^2 d\eta + \frac{B^F}{E^F}f_oF_n + \frac{B^S}{E^S}u_oU_n\right] \qquad (38)$$

where $R_n$ is given by Eq. 34, and the integral on the right hand side of Eq. 38 is

$$\int_o^1 G_n^2 d\eta = \frac{1}{2} + \frac{\sin(2\beta_n)}{4\beta_n} - \frac{B^F}{2(\beta_n^2 - E^F)}\cos(2\beta_n) + \frac{B^F}{2(\beta_n^2 - E^F)} + \frac{(\beta_nB^F)^2}{2(\beta_n^2 - E^F)^2} - \frac{(B^F)^2\beta_n}{4(\beta_n^2 - E^F)^2}\sin(2\beta_n) \qquad (39)$$

$F_n$ and $U_n$ can be obtained from Eqs. 29. They are given by:

$$F_n = \frac{E^F}{E^F - \beta_n^2} \qquad (40a)$$

$$U_n = \left(1 + \frac{B^F\beta_n^2}{\beta_n^2 - E^F}\right)\beta_n\cos(\beta_n) + \frac{B^FB^S + E^F - \beta_n^2}{B^S(\beta_n^2 - E^F)}\beta_n\sin(\beta_n) \qquad (40b)$$

Substitution of the above into Eq. 28 provides the required solutions whose analysis is discussed later.

## Results

### *Aqueous-phase equilibria*

Calculations were conducted to obtain the concentrations of free copper and hydrogen ions in the aqueous solution by solving the associated algebraic equations for the aqueous-phase reaction given in Table 2. Figure 4 displays the change in the fractions of free ions to the total ions present in the aqueous phase with the solution acidity (pH) at two different total copper concentrations. The copper, hydrogen, and sulfate ion fractions are displayed. In Figures 4 and 5, the free copper ion fraction is defined as the ratio of dissociated copper ion concentration ($C_{Cu^{+2}}$) to the total concentration of copper-containing species ($C_{Cu^{+2}} + C_{CuSO_4} + C_{Cu(OH)_2} + C_{Cu(OH)^+}$), and the free hydrogen ion fraction is the ratio of free hydrogen ion concentration ($C_{H^+}$) to the summation of hydrogen ion and hydroxy sulfate ion concentrations ($C_{H^+} + C_{HSO_4^-}$). The free sulfate ion fraction also is defined in a similar way. The results demonstrate that the actual free ions calculated are lower than the total copper concentration. For example, at the total copper concentration of $3.02 \times 10^{-2}$ mol/L and pH = 4, 33.0% of total copper ions are present as free ions, whereas at the total copper concentration of $3.02 \times 10^{-3}$ mol/L and pH = 4, 69.5% of total copper ions are free ions. Figure 4 also shows that the free ion fraction changes rapidly with the solution pH below 3. When the solution pH is larger than 3, these values are nearly constant.

As the extraction reaction proceeds, the total copper con-

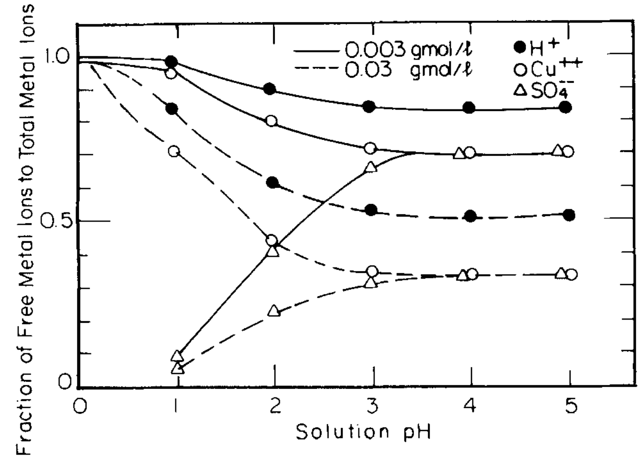

**Figure 4. Calculated values of free ion fractions in the aqueous phase at various conditions.**

centration in the aqueous solution will decrease and the fraction of free ions will change. Figure 5 shows the fraction of free ions to the total number of ions calculated for different copper concentrations at the constant solution acidity of pH = 3. The free copper ion fraction is 33.0% at the initial condition of the total copper concentration of 0.03 mol/L and pH of 3, while the free copper ion fraction value changes to 36.1% after extraction of one-third of total amount of copper ion present in the aqueous phase at the total copper ion concentration of 0.02 mol/L and pH of 3, as shown in Figure 5. These results show that the free ion fractions change smoothly with the change of total copper concentration in the aqueous phase over the range of interest in this investigation. Also, the free ion fraction can be considered as a constant for a small change of total copper concentration in the aqueous phase. This constancy of the fraction is useful in parameter lumping in the kinetic model development, since experiments for parameter estimations were executed over the range of small changes of conditions.

These calculation results are applied to the kinetic model to obtain the true response of extraction and stripping reaction rates.

### *Determination of parameters*

Since only free forms of copper and hydrogen ions are reacted with the chelation acid, these concentrations in Eq. 2 should be calculated from the total concentrations of copper and hydrogen ions presented in the aqueous phase, as described in the previous section. We proposed a lumped parameter method that permits the use of the linear model.

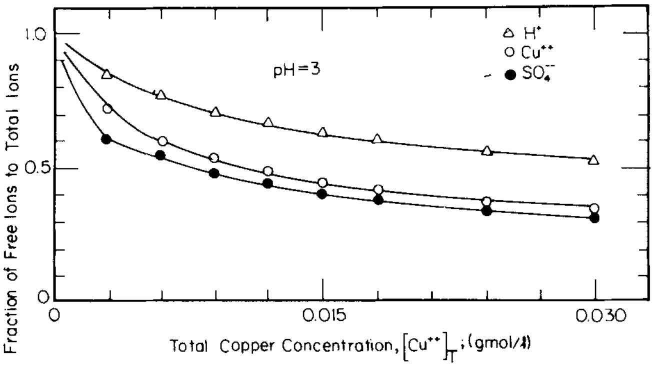

**Figure 5. Calculated fractional changes of free ions in the aqueous phase.**

Free ion concentrations can be expressed as:

$$C_i^j = f_i^j C_{i,\text{tot}}^j \quad i = \text{Cu or H, and } j = F \text{ or } S$$

where $C_i^j$ represents the free ion concentration as an active form, and $C_{i,\text{tot}}^j$ is the total concentration of compound which contain species $i$. $f_i^j$ is the fraction of free ion to the total ion concentration. $f_i^j$ can be determined from the aqueous-phase equilibrium as described above.

Using this relation for the free copper ion concentration, the kinetic coefficients shown in Eqs. 3a and 3b can be rewritten with the experimentally measured concentrations as:

$$R^F = k_{+F} f_{\text{Cu}}^F C_{\text{Cu,tot}}^{F*} - k_{-F} C_{\overline{\text{Cu}R_2}}^{F*} \tag{41a}$$

$$R^S = k_{-S} C_{\overline{\text{Cu}R_2}}^{S*} - k_{+S} f_{\text{Cu}}^S C_{\text{Cu,tot}}^{S*} \tag{41b}$$

where $C_{\text{Cu,tot}}^j$ are measured experimentally using atomic absorption spectrophotometry, $k_{+i}$ and $k_{-i}$ are given as shown in Eq. 4. $f_{\text{Cu}}^j$ are the calculated results as shown in Figure 4. Note that the pH-static technique was employed in this study, which allows one to maintain constant hydrogen concentration during experiments. Thus, hydrogen concentration terms can be lumped with the kinetic coefficients, as shown in Eqs. 4 and 41.

Analysis of calculated flux values from a set of experiments as specified in Table 1 yields the values of chemical and physical parameters in Table 4. Details of the experiments are provided elsewhere (Yi, 1991). These parameters were used to calculate the performance of the rotating diffusion cell for the copper ion extraction process. This high concentration of 2-hydroxy-5-nonylacetophenone oxime was achieved using near 100% reagent material as obtained from the supplier and calculated using a molecular weight of 277 kg/kg·mol and density of 0.9 kg/m³.

It is of interest to compare the numerical values obtained for the kinetic coefficients in this work with those given by

**Table 4. Parameter Values by Steady-State Flux Model**

| Parameters in Eq. 7 | Values | Membrane and Exp. Conditions |
|---|---|---|
| $D_{\text{Cu}++}$ | $4.69 - 5.33 \times 10^{-6}$ cm²/s | P55B<br>$C_{\text{Cu}}^F = 0.03$ mol/L,<br>$\text{pH}_f = 3.0$ |
| $D_{\overline{\text{Cu}R_2}}$ | $2.26 \times 10^{-7}$ cm²/s | P55D<br>$C_{\overline{\text{Cu}R_2}} = 0.0023$ mol/L |
| $k_{+F}$ | $7.3 \times 10^{-4}$ cm/s | P55B, P55D,<br>$C_{\text{Cu}}^F = 0.02$ mol/L,<br>$C_{\overline{HR}} = 3.2$ mol/L<br>$\text{pH}_f = 2.98 - 3.4$ |
| $k_{-F}$ | $7.1 \times 10^{-6}$ cm/s | |
| $K^F$ | $9.7 \times 10^{-3}$ | |
| $k_{+S}$ | $6.9 \times 10^{-8}$ cm/s | |
| $k_{-S}$ | $3.6 \times 10^{-6}$ cm/s | P55C<br>$C_{\overline{\text{Cu}R_2}} = 0.03$ mol/L<br>$\text{pH}_s = 0.3$ |
| $K^S$ | 52.17 | |

deHaan et al. (1989). These investigators studied the same chemical systems and supported 20 wt. % LIX 84 solution in decane (as opposed to our 100% wt. % and 50 wt. % solutions) in polymeric membranes constructed into tubular capillary modules. One module was operated in the extraction mode and the other module in the stripping mode. Thus, their reactions were separated, while these reactions occur simultaneously on either side of the membrane in this work. They used literature values for the diffusivity of copper ion, the diffusivity of copper complex, and the extraction equilibrium constant, $K_{ex}$. The parameters of interest to compare, therefore, is the forward kinetic rate coefficients under extraction and stripping conditions. The kinetic expressions used by these authors can be written in the following form using their notation:

*extraction*

$$\frac{1}{2\pi R_i}\Phi^e_{Cu}=\left[k_e\frac{C_{Cu}C_{\overline{HR}}}{C_H}-\frac{k_e}{K_{ex}}\frac{C_{\overline{CuR_2}}C_H}{C_{\overline{HR}}}\right]$$

*regeneration* (*or stripping*)

$$\frac{1}{2\pi R_i}\Phi^r_{Cu}=\left[(k_rC_{\overline{HR}})\left(\frac{C_{\overline{CuR_2}}C_H}{C_{\overline{HR}}}\right)-(k_rK_{ex}C_{\overline{HR}})\left(\frac{C_{Cu}C_{\overline{HR}}}{C_H}\right)\right]$$

where $\Phi^e_{Cu}$ and $\Phi^r_{Cu}$ are the flux per unit capillary length and $R_i$ is the capillary radius. The above two equations are comparable to Eq. 2 used in this work, and the relationship between the forward rate coefficients can be written using Eq. 4a as:

$$k_e=k'_{+F}=k_{+F}\frac{C^i_H}{C^i_{\overline{HR}}}$$

and

$$k_rC_{\overline{HR}}=k'_{-S}=k_{-S}\frac{C^i_{\overline{HR}}}{C^i_H}.$$

For pH of 3.0 and $\overline{HR}$ concentration of 0.18 mol/L, our calculated values of $k_e$ and $k_r$ are $2.0\times10^{-8}$ m/s and $7.6\times10^{-11}$ $m^4/s\cdot mol$. These values compare favorably to their values of $3.0\times10^{-8}$ m/s and $1.5\times10^{-10}$ $m^{-4}/s\cdot mol$. It should be noted that deHaan and coworkers determined these parameters under experimental conditions which are diffusion-limited and reaction-rate-limited. In this work, these parameters are obtained over the range of conditions which include these regimes as well as the cases when both mass transfer and reaction rates are of the same order. Further, all our parameters were determined by independent experiments as outlined above.

Table 5. Comparison of Analytical Results with Numerical Calculations

| $\tau$ | $x(\tau)=C^F_M/C^F_{MO}$ for $\alpha=0.1$ | |
|---|---|---|
| | Analytical Solution* | Numerical Solution** |
| 0.01 | 0.876415 | 0.876162 |
| 0.1 | 0.493551 | 0.494038 |
| 1.0 | 0.137038 | 0.137549 |
| 10.0 | $0.510767\times10^{-3}$ | $0.509676\times10^{-3}$ |

*Analytical solutions are described in the text.
**EPISODE package used for the numerical solution.

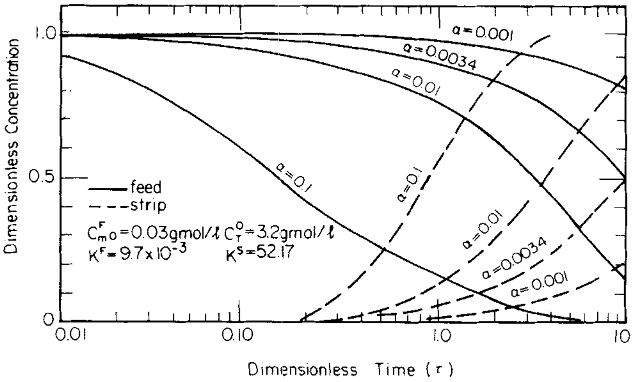

Figure 6. Dimensionless concentrations in the feed and strip solution vs. dimensionless operation time.

The dimensionless equations (Eqs. 22-27), for $k_R=0$, were solved numerically and analytically as described in the previous section to evaluate the performance of the rotating diffusion cell. The numerical calculations provide a comparison test of the analytical solution to verify the validity of the analytical solutions. In the numerical solution procedure, a material balance was performed on the copper metal at each time interval to insure the consistency of the numerical solution. In the EPISODE routine, the step size in the $\eta$ direction is set automatically to meet the specific tolerance. The tolerance was set to $10^{-7}$. Errors less than 2% also indicated the results were satisfactory. Table 5 shows the comparison of the analytical solutions obtained with the numerical calculation. The results are in good agreement.

Figures 6 and 7 are results of calculations for batch operation for the parameters given in Table 4. Figure 6 plots the dimensionless concentration in the feed $X(\tau)$ and strip $Y(\tau)$ solutions as a function of dimensionless separation time $\tau$. The capacity parameter $\alpha$ varies from 0.1 to 0.001 and is defined as the ratio of the volume of chelation acid in the membrane to the volume of aqueous solution being contacted. As expected, for a given $\alpha$, as dimensionless time increases, the metal concentration decreases in the feed and increases in the strip solution. Thus, for $\alpha=0.01$ and $\tau=1$, the metal ion concen-

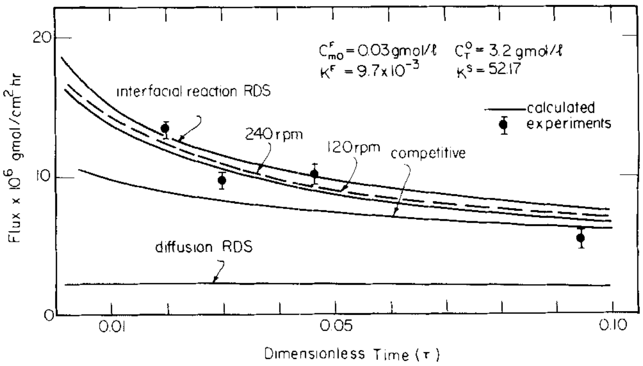

Figure 7. Calculated fluxes vs. experimental results.

tration in the feed is decreased to 75% of the initial concentration, and the strip solution extracts 17% of initial feed metal ions. $\tau = 1$ represents approximately 50 hours of contact time for 2-mm-thick membrane.

Figure 7 shows the comparison of the calculated fluxes with the experimental results as a function of operation time. The calculations indicate how flux depends on the operating parameters at a given feed metal ion concentration, the chemical system parameters, and operating time. The upper curve is for the maximum flux possible when interfacial reaction controls whereas the bottom line represents the minimum flux when diffusion controls. Curves for intermediate situations are also presented and are indicated with the disk rotational speed. Calculated fluxes from the model equations are in good agreement with experimental results as shown in Figure 7. These results suggest that the model contains the basic features of the processes which affects transport across these supported membranes and that the model has the capability to predict the performance of the rotating diffusion cell as a reactor.

## Discussion and Conclusions

This study reports an analysis of a chemically active liquid membrane process using inorganic membranes for the separation of copper ions from aqueous solutions. A steady-state model is proposed to describe the metal ion flux through impregnated ceramic membranes. This flux model considers the effects of both the boundary layer mass-transfer resistances and the kinetic rates resistances at the interfaces. Separately designed experiments were executed using a precise pH-static technique to obtain these parameters which are used to calculate fluxes for comparison with experimentally determined values from batch experiments.

Further, the steady-state model, as shown in Eqs. 5-8, implies that uphill transport of metal ions can be achieved with the application of chemically active liquid membranes for the concentration and separation processes. The driving force for the metal ion separation using these membranes is shown in Eq. 6. When the chemical system and the operating conditions are such that $K^F$ is smaller than one and $K^S$ is greater than one, the metal ion concentration of strip solution ($C_M^S$) can be larger than that of feed solution ($C_M^F$), as shown in Eq. 6, and flux still occurs against the concentration gradients.

Calculation results of uphill transport are shown in Figure 6 for the batch operation case: at $\tau = 0.51$ for $\alpha = 0.1$, the strip solution concentration ($C_M^S$) is higher than the feed concentration ($C_M^F$) and metal ions extraction from the feed to the strip solution still occurs until the driving force of $\Delta C$ in Eq. 6 goes to zero.

The model equations to estimate the performance of the chemically active liquid membrane reactor predict expected trends, and calculated results are in good agreement with the experimental results for the batch operation of the rotating diffusion cell.

The model equation proposed in this study can be applied to more general cases, when the hydrogen mass-balance equation is added. For the general case, the interfacial reaction expressions can be rewritten as:

$$R^F = k''_{+F} \frac{C_M^{F*}}{C_H^{F*}} - k''_{-F} C_{\overline{MR}_2}^{F*} C_H^{F*}$$

$$R^S = k''_{-S} C_{\overline{MR}_2}^{S*} C_H^{S*} - k''_{+S} \frac{C_M^{S*}}{C_H^{S*}}$$

where

$$k''_{+j} = k'_{+j} C_{\overline{HR}}^{j*}$$
$$k''_{-j} = k'_{-j} / C_{\overline{HR}}^{j*}$$

It should be noted that in these expressions reaction rates can be given as functions of aqueous-phase concentrations, which are relatively easy to determine experimentally. Based on the obtained results under the experimental conditions, kinetic expressions can be calculated as:

$$R^F = (3.87 \times 10^{-7}) \frac{C_{\mathrm{Cu}}^{F*}}{C_H^{F*}} - (0.013) C_{\overline{\mathrm{Cu}R}_2}^{F*} C_H^{F*}$$

$$R^S = (1.22 \times 10^{-5}) C_{\overline{\mathrm{Cu}R}_2}^{S*} C_H^{S*} - (2.03 \times 10^{-7}) \frac{C_{\mathrm{Cu}}^{S*}}{C_H^{S*}}$$

In these calculations it was assumed that the mass-transfer resistances of hydrogen ion through the boundary layers are negligibly small compared to those of copper ion.

These expressions can be applied to model the chemically active liquid membrane process when hydrogen ions concentrations also vary, although in this study the pH-static technique is employed to maintain constant hydrogen ion concentration during experiments.

A major operational problem is the lifetime of such supported liquid membranes. The problem is compounded when the support is hydrophilic and the liquid is hydrophobic as is the case here. Danesi et al. (1987) provide a thorough discussion of the problem. The problem of expression of the liquid from the pores was minimized here by essentially eliminating the hydraulic pressure drop across the membrane. Operational methods to control this problem for tubular cocurrent flow membranes have also been studied and reported elsewhere (Yi, 1991). Long-term experiments were executed to determine deactivation during use (Yi et al., 1992; Yi, 1991). Operation times of up to nine days were achieved. Runs of greater length are possible in large-scale units which can avoid mechanical problems peculiar to our small-scale apparatus. Permanent deactivation of the membranes was observed due to repeated use. This deactivation is apparently caused by destruction of membrane pores leading to decrease in membrane porosity. Regeneration techniques have been tested and explored for flux recovery. These results are described elsewhere (Yi, 1991).

The approach employed here can be extended to the analysis of multiple metal systems if kinetic data and diffusivities are obtained, and to the extent that they exist, coupling effects between the metal species are properly incorporated into the model.

The model equations reported here could provide a basis for the design and scale-up of these units. Also, these models can serve as the basis of selecting more promising chelation agent systems and desirable operating conditions for high separation efficiencies.

## Acknowledgment

The financial support of the State University of New York, Center for Hazardous Waste Management, Buffalo, NY, through Grant No. 150-W009A is gratefully acknowledged.

## Notation

$A^i$ = contacting membrane area of *i*-side
$\Delta C$ = normalized concentration difference
$\mathrm{Cu}^{++}$ = copper ion
$C_{\overline{HR}}$ = Chelation acid concentration
$C_M^i$ = metal ion concentration at *i* phase
$C_{MO}^i$ = metal ion concentration of inlet solution
$C_M^{i*}$ = metal ion concentration at the interface
$C_{\overline{MR_2}}$ = metal complex concentration in the membrane
$\overline{CuR_2}$ = copper-chelating complex species
$C_T^o$ = initial metal chelating agent concentration
$D_M^i$ = diffusivity of metal ion in the aqueous phase
$D_{\overline{MR}}$ = diffusivity of metal complex component
$f$ = dimensionless metal ion concentration in feed
$f_i^j$ = fraction of free ion of species *i* at *j*-side solution
$F$ = dimensionless concentration of inlet solution of feed
$g$ = dimensionless metal complex concentration in membrane
$H^+$ = hydrogen ion
$\overline{HR}$ = chelating agent
$J^i$ = flux
$k_e$ = forward reaction rate coefficient for the extraction reaction
$k_r$ = forward reaction rate coefficient for the regeneration (stripping) reaction
$k_R$ = homogeneous reaction rate coefficient
$k_M^i$ = boundary layer mass transfer coefficient
$k_{+i}$ = forward reaction rate coefficient
$k_{-i}$ = reverse reaction rate coefficient
$K^i$ = ratio of reverse of forward reaction rate coefficients
$K_W$ = overall mass transfer coefficient
$L$ = membrane thickness
$q^i$ = flow rate
$R^i$ = interfacial reaction rate expression
$R_i$ = capillary radius
$u$ = dimensionless metal ion concentration in strip solution
$U$ = dimensionless concentration of inlet strip solution
$V^i$ = solution volume of feed or strip
$X$ = dimensionless feed concentration
$Y$ = dimensionless strip concentration

### *Greek letters*

$\delta^i$ = boundary layer thickness
$\epsilon$ = membrane porosity
$\Phi_{\mathrm{Cu}}$ = flux per unit capillary length
$\nu^i$ = kinematic viscosity
$\tau$ = dimensionless time
$\omega$ = rotational speed

### *Superscripts*

$\overline{\phantom{x}}$ = organic phase
$e$ = extraction
$r$ = regeneration
$j$ = *j* phase, $j$ = feed or strip phase

### *Subscripts*

$+j$ = forward reaction at *j*-phase
$-j$ = reverse reaction at *j*-phase

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*Manuscript received Sept. 3, 1991, and revision received June 22, 1992.*