EFFECTS OF THE BOUNDARY LAYER AND INTERFACIAL REACTION ON THE TIME LAG IN SUPPORTED LIQUID MEMBRANES

Jongheop Yi

Department of Chemical Engineering, Seoul National University, Seoul 151-742, Korea

Abstract—A mathematical model is proposed to describe the effects of boundary layer resistance and interfacial reaction on the time lag in supported liquid membranes for metal ion separation. The model shows that the presence of boundary layer resistance and interfacial reaction delays the time-lag, compared with the limiting case that rapid equilibrium at the interfaces and negligible boundary layer resistance are assumed. Calculated result describes the expected trend and the model equation allows one to predict the lumped parameters which represent the ratios of the diffusion time in the membrane to the characteristic time for boundary layer transfer and interfacial reactions.

Key words: Supported Liquid Membrane, Time-lag, Interfacial Reaction, Boundary Layer

INTRODUCTION

Time-lag is the time required to reach the steady state in membrane processes. The time-lag solution given by Crank [1975] has been widely used as a method to obtain the diffusivity by analyzing the transport phenomena through a membrane. It assumes negligible boundary layer resistance, constant concentrations of feed and strip solutions on both sides of membrane, and rapid equilibrium at the membrane/fluid interface during the operation. Resulting expression shows that the amount of solute transported approaches to the steady-state asymptotically after a long time and the time-lag, τ_L, is related to the diffusivity for the membrane thickness of L by the relationship:

$$\tau_L = \frac{1}{6} = \frac{\overline{D}t}{L^2} \tag{1}$$

where $\overline{D}$ is the diffusivity in the membrane and t is the time estimated from experiments. The time, t, is obtained from the intercept of the asymptote of the solute accumulation transported to the strip solution through the membrane [Crank, 1975]. However, this approach may lead to an error, since Eq. (1) neglects the effects of both boundary layer resistance and interfacial reaction between membrane and fluid phases on the mass transfer. Specifically, the performance dependence of supported liquid membranes on the operating conditions has been reported. The diffusion process through the supported liquid membranes was the rate determining step for the fresh membranes [Chiarzia et al., 1983], while the interfacial chemical reactions were the rate determining step for the aged membranes [Largman and Sifiniades, 1978; Kataoka et al., 1982]. Also, theoretical analyses of the supported liquid membranes have been reported for the limiting cases of fast chemical reactions at the interfaces [Cianetti and Danesi, 1983; Danesi et al., 1983] or of negligible solute concentration in the strip solution [Danesi et al., 1981]. However, experimental results show that aqueous film diffusion, interfacial reactions, and membrane diffusion simultaneously control the flux through the supported liquid membrane [Yi and Tavlarides,

1992; Juang, 1993].

In the supported liquid membrane process, solutions of chelating agent are impregnated into the pores of a solid matrix support. 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. It is difficult to completely remove experimentally the effect of the external mass transfer resistance from the kinetics at the interfaces between membrane and contacting fluids by increasing the flow rate of liquid streams for membrane module applications. Hence, in order to estimate the correct diffusion coefficient in the supported liquid membranes, a time-lag model should take into account mass transfer limitations in the boundary layers along with reaction kinetics at the interfaces.

In this study, a model equation is proposed to describe the effects of boundary layer resistance and interfacial reaction on the time lag in the supported liquid membrane processes. The case system considered is copper ion extraction from acidic solution employing LIX84 (Henkel Co.) as a chelating agent impregnated in ceramic membranes, since the kinetic behavior of the systems has been characterized [Yi and Tavlarides, 1992].

MODEL EQUATION FORMULATION

A schematic of the supported liquid membrane process for the separation of copper ion from the feed solution is shown in Fig. 1. Copper ion in feed solution is transported from the feed to the strip solution through the intervening membrane. The copper ion experiences a series of resistances as: transport through the boundary layer in the feed-side, reversible reaction at the membrane/feed solution at the interface, diffusion across the membrane, stripping reaction at the membrane/strip solution. The fluids in feed and strip chambers 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.

As depicted in Fig. 1, the mass conservation equation for che-

---

†To whom any correspondences should be addressed.
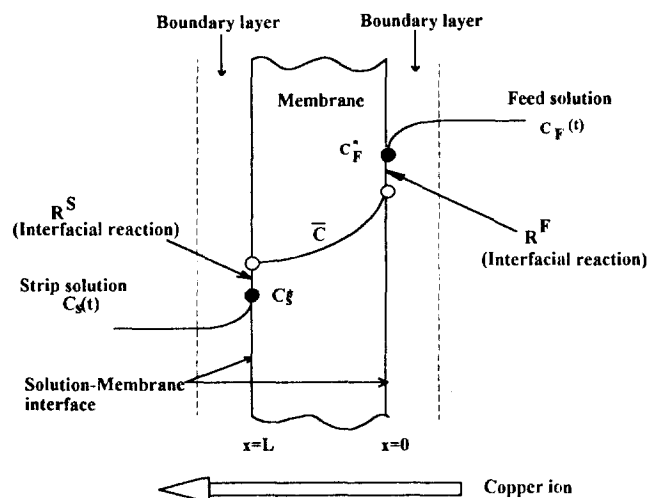
J. Yi

Fig. 1. Schematic of membrane process with boundary layers and interfacial reactions.

lated molecules with copper ion in the supported liquid membrane can be given as:

$$\frac{\partial \overline{C}(x,t)}{\partial t} = \overline{D}\frac{\partial^2 \overline{C}(x,t)}{\partial x^2} \qquad (2)$$

where $\overline{C}$ and $\overline{D}$ are the concentration and diffusivity of chelated molecules in the membrane, respectively.

At the interface as in Fig. 1, it is assumed that interfacial reactions between the feed solution and membrane take place and are represented by R^F and R^S. Accordingly, the boundary conditions at the interfaces applicable for Eq. (2) can be given as:

$$-\overline{D}\frac{\partial \overline{C}}{\partial x} = R^F \qquad \text{at } x=0 \qquad (3a)$$

$$-\overline{D}\frac{\partial \overline{C}}{\partial x} = R^S \qquad \text{at } x=L \qquad (3b)$$

A kinetic model for the interfacial reaction expressions, R^F and R^S, can be derived, based on a series of elementary reactions as described elsewhere [Yi and Tavlarides, 1992] as:

$$R^F = k_+^F C_F^* 0(t) - k_-^F \overline{C}(0, t) \qquad (4a)$$

$$R^S = k_-^S \overline{C}(L, t) - k_+^S C_S^*(t) \qquad (4b)$$

where k_+^i are k_-^i the forward and backward reaction rate coefficients at the i-side, i=Feed or Strip, respectively. C_F^* and C_S^* are the interfacial concentrations of the copper ion at the feed and strip solution side, and $\overline{C}(0, t)$ and $\overline{C}(L, t)$ are the concentrations of chelated agent with copper ion in the membrane at the feed-side and strip-side, respectively.

For the mass-transfer flux through boundary, the film model assumes the transfer occurs through the fluid film formed at the boundary layers between the fluid and membrane. The flux through the boundary layer can be given by:

$$J^F = k_M^F(C_F - C_F^*) \qquad (5a)$$

$$J^S = k_M^S(C_S^* - C_S) \qquad (5b)$$

where k_M^i is the mass-transfer coefficient at boundary layer, C_i is the bulk concentration and $C_i^*(i=F$ and $S)$ is the concentration at the interface between the fluid and membrane. Using Eq. (4)

Table 1. Dimensionless terms

$$g=\overline{C}/C_T^0 \quad f=C_F(t)/K^F C_T^0 \quad u=C_S(t)/K^S C_T^0$$

$$\eta = x/L \quad \tau = \overline{D}t/L^2 \quad \Delta^i = \left(\frac{1}{k_M^i} + \frac{1}{k_+^i}\right)^{-1}$$

$$K^i = k_-^i/k_+^i$$

$$B^i = \frac{K^i L}{\overline{D}} \quad \Delta^i = K^i \frac{L^2/\overline{D}}{L/\Delta^i}$$

$$= \frac{\text{diffusion time of chelated molecules in the membrane}}{\text{characteristic time of boundary layer transport and interfacial reaction}}$$

i=F or S

and (5), the interfacial concentrations of c_i^* can be calculated and are related both the flux through the boundary layer and the flux due to the reaction at the interface [Yi and Tavlarides, 1992]. After substituting c_i^* into Eq. (4), Eq. (2) and (3) can be written in dimensionless forms as:

$$\frac{\partial g}{\partial \tau} = \frac{\partial^2 g}{\partial \eta^2} \qquad (6)$$

$$\frac{\partial g}{\partial \eta} = B^F(g-f) \qquad \text{at } \eta=0 \qquad (7a)$$

$$\frac{\partial g}{\partial \eta} = B^S(u-g) \qquad \text{at } \eta=1 \qquad (7b)$$

$$g=g_0 \text{ at } \tau=0$$

Here, f and u are the dimensionless concentrations in the feed and strip solutions, respectively. The dimensionless terms which arise above can be given in Table 1. Note that B^i, i=F or S, is the ratio of diffusion time in the membrane to the characteristic time of boundary layer transport and interfacial reaction.

Equations of the lag time for solute transport can be derived through the amount of solute transported from the feed to the membrane, M_τ^f (at $\eta=0$), or from the membrane to the strip solution, M_τ^u (at $\eta=1$), during the operation time of τ as:

$$\frac{M_\tau^f}{M_\infty} = -\int_0^\tau \left(\frac{\partial g}{\partial \eta}\right)_{\eta=0} d\tau' \qquad (8a)$$

$$\frac{M_\tau^u}{M_\infty} = -\int_0^\tau \left(\frac{\partial g}{\partial \eta}\right)_{\eta=1} d\tau' \qquad (8b)$$

where M_∞ represents the maximum amount of solute that would be retained in the membrane after an infinite period of time, as defined by $A_m L C_T^0$. After Laplace transform of Eq. (6) with the boundary conditions of Eq. (7), Eq. (8) can be given as:

$$L\left\{\frac{M_\tau^f}{M_\infty}\right\} = \frac{B^F B^S \overline{u} \cosech\sqrt{s} - B^F \overline{f}(\sqrt{s}+B^S\coth\sqrt{s})}{\sqrt{s}\{(B^F+B^S)\sqrt{s} \coth\sqrt{s}+(s+B^F B^S)\}} \qquad (9a)$$

$$L\left\{\frac{M_\tau^u}{M_\infty}\right\} = \frac{B^S\overline{u}(\sqrt{s}+B^F \coth\sqrt{s}) - B^F B^S\overline{f} \cosech\sqrt{s}}{\sqrt{s}\{(B^F+B^S)\sqrt{s} \coth\sqrt{s}+(s+B^F B^S)\}} \qquad (9b)$$

where s is the Laplace time variable. $\overline{f}$ and $\overline{u}$ are the Laplace transform of f and u, respectively. For the long time operation of τ, s is very small compared to one, and the hyperbolic functions in Eq. (9) may be approximated by the power series [Spiegel, 1968]

$$\coth\sqrt{s} \cong \frac{1}{\sqrt{s}} - \frac{\sqrt{s}}{6} \qquad (10a)$$

$$\operatorname{cosech}\sqrt{s} \cong \frac{1}{\sqrt{s}} + \frac{\sqrt{s}}{3} \tag{10a}$$

Thus, Eq. (9) can be written as

$$L\left\{\frac{M_\tau^f}{M_\infty}\right\} = \frac{v - ws}{s(ps + q)} \tag{11a}$$

$$L\left\{\frac{M_\tau^u}{M_\infty}\right\} = \frac{v + w's}{s(ps + q)} \tag{11b}$$

where $v = B^F B^S(\bar{u} - \bar{f})$, $w = B^F\left\{\frac{B^S}{6}\bar{u} + \left(1 + \frac{B^S}{3}\right)\bar{f}\right\}$, $p = \frac{B^F + B^S}{3} + 1$,

$$q = B^F B^S + B^F + B^S, \quad w' = B^S\left\{\frac{B^F}{6}\bar{f} + \left(1 + \frac{B^F}{3}\right)\bar{u}\right\} \tag{11c}$$

The time-lag for the membrane process can be derived from M_τ^i/M_∞ expression after extrapolation back to M_τ^i/M_∞ of zero, $i = f$ or u. Inversion of Eq. (11) gives the M_τ^f/M_∞ and M_τ^u/M_∞ expressions as a function of time, τ, and allows one to estimate the time lag in the presence of the resistances by the boundary layer and interfacial reactions.

RESULTS AND DISCUSSION

As a model case, consider a continuous flow system that the feed concentration is constant during the operation and the strip concentration is negligible, because of large flow rate. $\bar{f}$ and $\bar{u}$ can be given as: $f(\tau) \cong f_0 = $ constant and $u(\tau) \cong 0$.

Under the conditions, inversion of Eq. (11) gives

$$\frac{M_\tau^f}{M_\infty} = \frac{-f_0}{\frac{1}{B^F} + \frac{1}{B^S} + 1}\left\{\left(\frac{p}{q} - \beta\right)(1 - e^{-(q/p)\tau}) - \tau\right\} \tag{12a}$$

$$\frac{M_\tau^u}{M_\infty} = \frac{-f_0}{\frac{1}{B^F} + \frac{1}{B^S} + 1}\left\{\left(\frac{p}{q} + \frac{1}{6}\right)(1 - e^{-(q/p)\tau}) - \tau\right\} \tag{12b}$$

where $\beta = \frac{1}{3} + \frac{1}{B^S}$

At the long times of τ for much greater than one, the exponential term will be very small and thus the lag-time is given by setting $M_\tau^i = 0$ ($i = f$ or u) as:

$$\tau_L^f = \frac{p}{q} - \beta \tag{13a}$$

$$\tau_L^u = \frac{1}{6} + \frac{p}{q} \tag{13b}$$

where τ_L^i ($i = f$ or u) is the time-lag solution estimated based on the amount of solute transported from the feed to the membrane [Eq. (13a)] and from the membrane to the strip solution [Eq. (13b)]. Also, Eq. (13) implies that the time lag of the membrane process depends on the ratio of diffusion time in the membrane to the characteristic time of boundary layer transport and interfacial reaction.

The slope of Eq. (12), S, after long time τ, is given by

$$S = \frac{f_0}{\frac{1}{B^F} + \frac{1}{B^S} + 1} \tag{14}$$

The lumped parameters of B^F and B^S can be obtained from the time lag of Eq. (13) and the slope S of Eq. (14).
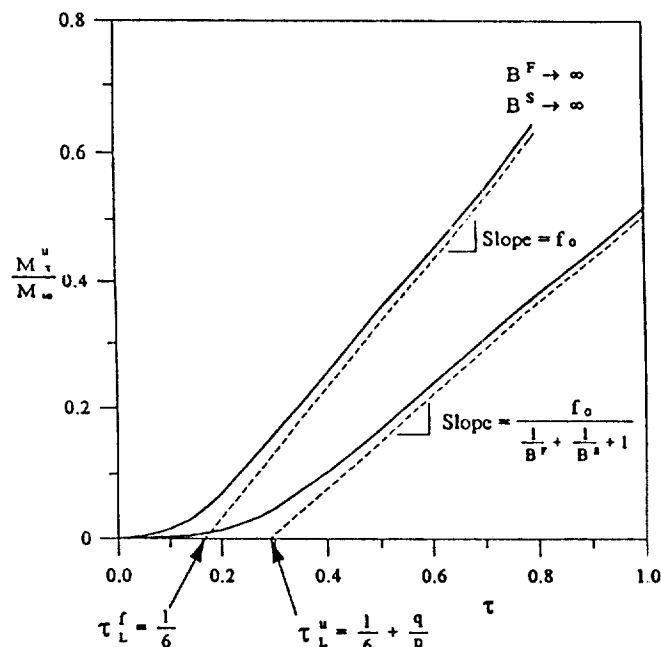

Fig. 2. Graphical representation of the total amount of solute transported from the membrane to strip solution (M_τ^u/M_∞) for the limiting case and the general case.
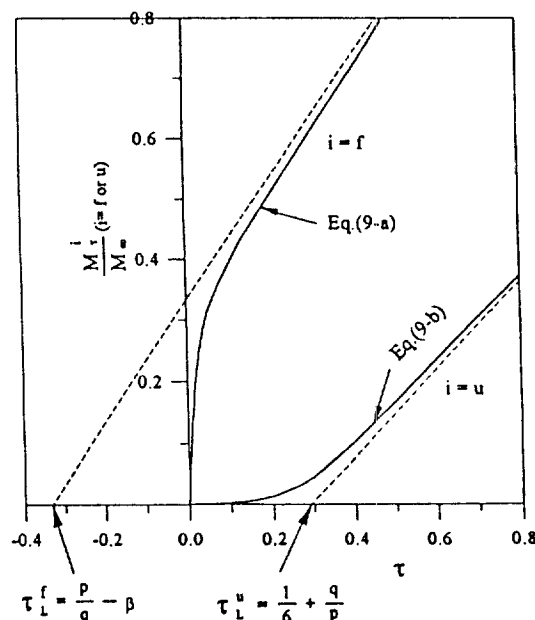

Fig. 3. Graphical representation of the total amount of solute transported from the feed to membrane (M_τ^f/M_∞) and from the membrane to strip solution (M_τ^u/M_∞) as a function of the dimensionless operating time.

For the limiting case calculation, Eq. (13b) may be compared with the time-lag expression shown by Crank [1975] for the membrane process that rapid equilibrium occurs at the interfaces and negligible boundary layer resistances are assumed. In this case, B^F and B^S approach to infinite, since the diffusion time through the membrane is very large compared with the characteristic time for boundary layer mass transfer and interfacial reaction. Conse-

quently, the time lag ($\tau_L{}^u$) of 1/6 agrees with the result by Crank [1975] as seen in Eq. (1).

Fig. 2 shows the comparison of $M_\tau{}^u/M_\infty$ for the limiting case (B^S and $B^F \to \infty$) with the general case (B^S and $B^F =$ finite values). The slope and intercept ($\tau_L{}^u$) are shifted to the large values, when the effects of boundary layer resistance and interfacial kinetics on mass transport are not negligible. As expected, the presence of boundary layer resistance and interfacial reaction delays the time lag. Also, the lumped parameters of B^F and B^S can be estimated from the intercept [Eq. (13b)] and slope [Eq. (14)] of $M_\tau{}^u/M_\infty$ plot against the operating time, as seen in Fig. 2.

Fig. 3 represents how the time-lag of $\tau_L{}^i$ (i = f or u) is determined from $M_\tau{}^i/M_\infty$ (i = f or u) plot. Note that $\tau_L{}^f$ is negative and the slope of tangential line of $M_\tau{}^f/M_\infty$ plot is parallel to that of $M_\tau{}^u/M_\infty$ plot for $\tau \to \infty$, as expected from Eq. (12).

CONCLUSIONS

One of the commonest ways to estimate the diffusivity of solute in the membrane was the use of time-lag solution as of $\tau_L = 1/6$. This approach assumes negligible boundary layer resistance and rapid equilibrium at the membrane/fluid interface. However, the complete removal of those resistances may not be easy in the supported liquid membrane process operation.

In this work, a time-lag solution is derived with the consideration of the effects of boundary layer resistance and interfacial reaction on the mass transport across the supported liquid membrane. The resulting equation shows that both of the boundary layer transport and interfacial reaction shift the time lag to the large value. The model equation also allows one to estimate the lumped parameters of B^i (i = F or S) from the intercept and slope of tangential line of $M_\tau{}^u/M_\infty$ plot against the operating time for $\tau \to \infty$. It should be noted that B^i is the ratio of diffusion time in the membrane to the characteristic time of boundary layer transport and interfacial reaction.

Model equation for the time lag estimation reported herein could provide the basis for a method to select more promising chelating agent and a desirable operating condition for high separation flux.

ACKNOWLEDGEMENT

NOMENCLATURE

A_m : membrane area
B : the ratio of diffusion time of solute containing species in the membrane to the characteristic time of boundary layer transport and interfacial reaction
C : bulk concentration
C^* : interfacial concentration
$\bar{C}$: concentration of the chelated agent in the membrane
$C_T{}^0$: maximum concentration in the membrane
$\bar{D}$: diffusivity in the membrane
f : dimensionless feed concentration
$\bar{f}$: Laplace transform of f
fo : initial dimensionless feed concentration
g : dimensionless concentration in the membrane
J : flux
k_M : mass transfer coefficient at the boundary layer

k_+ : forward reaction rate coefficient
k_- : backward reaction rate coefficient
K : equilibrium constant
L : membrane thickness
M_τ : the amount of metal ion transported to/from the membrane
M_∞ : the maximum amount of solute that would remain in the membrane after an infinite period of time
p : expression in Eq. (11c)
q : expression in Eq. (11c)
R : interfacial reaction rate expression
s : Laplace time variable
S : slope in Eq. (14)
t : time
u : dimensionless strip concentration
$\bar{u}$: Laplace transform of u
v : expression in Eq. (11c)
w : expression in Eq. (11c)
w' : expression in Eq. (11c)
x : axial distance

Greek Letters

β : expression in Eq. (12)
Δ : mass transfer resistance by boundary layer and interfacial reaction in Table 1
η : dimensionless axial distance
τ : dimensionless time
τ_L : time lag derived by Crank [1975]
$\tau_L{}^i$: time lag based on the amount of solute transported to the membrane from the feed solution (i = f) and to the strip solution from the membrane (i = u)

Superscripts

i : feed or strip phase
f : dimensionless feed concentration
F : feed phase
S : strip phase
* : interface

Subscripts

F : feed phase
S : strip phase

REFERENCES

Chiarzia, R., Castgnola, A., Danesi, P. R. and Horwitz, E. P., "Mass Transfer Rate through Solid Supported Liquid Membranes: Influence of Carrier Dimeriation and Feed Metal Concentration on Membrane Permeability", *J. Memb. Sci.*, **14**, 1 (1983).

Cianetti, C. and Danesi, P. R., "Facilitated Transport of HNO₃ through a Supported Liquid Membrane Containing a Tertiary Amine as Carrier", *Solv. Extrac. & Ion Exchange*, **1**, 565 (1983).

Crank, J., "The Mathematics of Diffusion", 2nd ed., Clarendon Press, Oxford, UK (1975).

Danesi, P. R., Horwitz, E. P. and Rickert, P. G., "Rate and Mechanism of Facilitated Americium Transport through a Supported Liquid Membrane Containing a Bifunctional Organophosphorus Mobile Carrier", *J. Phys. Chem.*, **87**, 4708 (1983).

Danesi, P. R., Horwitz, E. P., Vandergrift, G. F. and Chiarzia, R., "Mass Transfer Rate through Solid Supported Liquid Membranes: Interfacial Chemical Reactions and Diffusion as Simul-

taneous Permeability Controlling Factors", *Sep. Sci. & Tech.*, **16**, 201 (1981).

Juang, R., "Permeation and Separation of Zinc and Copper by Supported Liquid Membranes Using Bis(2-ethylhexyl) Phosphoric Acid as a Mobile Carrier", *Ind. Eng. & Chem. Research*, **32**, 911 (1993).

Kataoka, T., Nischiki, T. and Ueyama, K., "Mechanism of Copper Transport through a Diaphragm-type Liquid Membrane", *Bull. Chem. Soc. Japan*, **55**, 1306 (1982).

Largman, T. and Sifiniades, S., "Recovery of Copper (III) from Aqueous Solutions by Means of Supported Liquid Membranes", *Hydrometallurgy*, **3**, 153 (1978).

Spiegel, M. R., "Mathematical Handbook of Formula and Tables", McGraw Hill, New York, NY (1968).

Yi, J. and Tavlarides, L. L., "Chemically Active Liquid Membranes in Organic Supports for Metal Ion Separations", *AIChE J.*, **38**, 1957 (1992).