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Analysis of Transport Rate of Zinc Extraction through Liquid Surfactant Membrane

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Abstract

Analysis of the transport rate of a metal ion through a liquid surfactant membrane is important for understanding an extraction system. A facilitated transport model for zinc extraction through a liquid surfactant membrane is proposed for the analysis of the transport rate. Based on the model, the transport rates, including the interfacial reaction rates and the diffusion rate of the zinc ion, are analyzed. From an analysis of the model, it is shown that the reactions at both interfaces are not in equilibrium before extraction is complete. It is also shown that the transport rates are not equal value in the early stage of a run. Parametric effects on the transport rates are also illustrated.

INTRODUCTION

Liquid surfactant membrane technology has attracted increasing attention for its potential capability in the field of separation, and it has been demonstrated to be an effective tool in many applications such as resource recovery, pollutant removal, and bioseparation. The technology is particularly attractive when very dilute solutions are involved since the treating ratio between the receiving phase and the source phase can be drastically reduced. Liquid surfactant membrane extraction is a three-phase process. Two miscible phases are separated by a membrane phase which is immiscible with the other two phases. Extraction of solute is achieved by mass transfer between the two miscible phases through the membrane phase. Theoretical analysis of this system is important for an understanding of separation behavior and in the design and scale-up of such a process. Most models developed for theoretical analysis are based on the "emulsion globule model." Chan and Lee (*1*) presented a review of the various models usually used to describe this type of extraction process.

Some past theoretical treatments of extraction behavior have been restricted to extreme conditions where the chemical reactions occurring at both interfaces are so fast that chemical equilibrium is assumed (*2–5*). In this way, the whole extraction is treated as solely a diffusion process in the membrane phase. As pointed out by Komasawa et al. (*6*) and Oritz Uribe et al. (*7*), the reason for such treatment is most likely due to the lack of available information on the kinetic behavior of the chemical reactions occurring at the interfaces.

On the other hand, some facilitated models (*2–4*, *8–10*), although they take the chemical reactions into consideration, assume all the transport rates, including the external interfacial reaction rate, the permeation rate of the metal complex in the membrane, as well as the stripping rate at the internal interface, are of equal value, i.e., the system is at steady state.

In this paper a mathematical model based on the mobilized globule flat plate configuration is proposed. The main purposes are to analyze the transport rate of the metal ion through the membrane and to verify if chemical equilibrium and/or the steady-state situation do exist in the system.

THEORY

The theory is built on the mobilized emulsion globule model with a flat plate configuration, as shown in Fig. 1. Both the external film resistance and the membrane diffusional resistance are taken into consideration, while the internal mass transfer resistance is neglected.

1. Zinc Extraction System

The extraction of zinc through a liquid surfactant membrane is schematically shown in Fig. 1. Due to the driving force of the concentration gradient, zinc ions in the external phase transport through the aqueous film surrounding the emulsion globule and move toward the membrane. On reaching the external interface of the membrane, zinc ions react with chelating agent, D2EHPA, to form zinc complexes. The complex formation is according to the following stoichiometric reaction:

$$\mathrm{Zn}^{2+} + \tfrac{2}{3}(\mathrm{RH})_2 \rightleftharpoons \overline{\mathrm{ZnR_2 \cdot RH}} + 2\mathrm{H}^+ \qquad (1)$$

or

$$Z + \tfrac{2}{3}R \rightleftharpoons M + 2H \qquad (2)$$

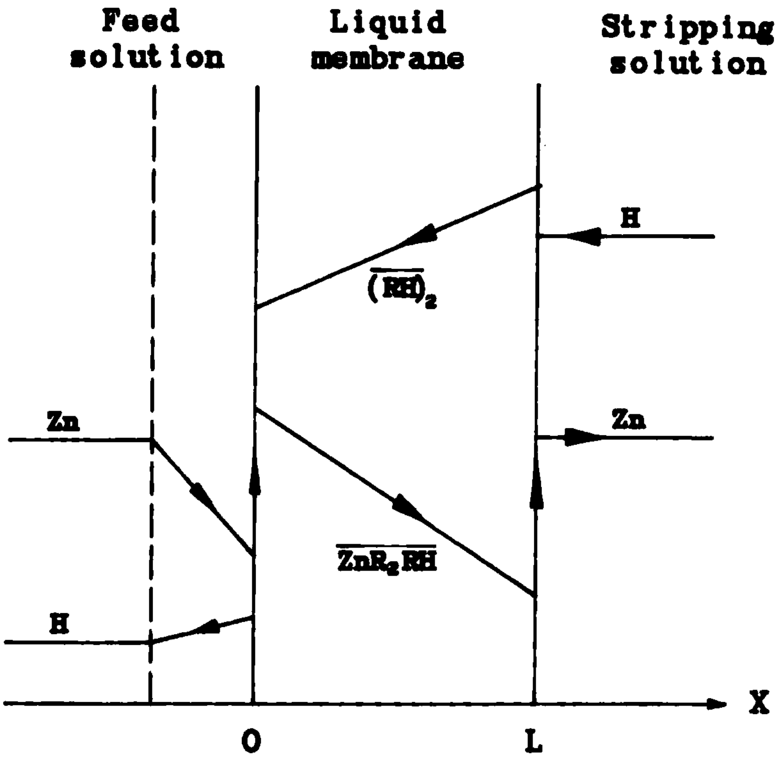

FIG. 1. Schematic diagram of carrier-mediated zinc ion transport across a liquid membrane.

The formation rate of zinc complex at the external interface will be

$$J_1 = k_f[Z_1\overline{R}^{1.5}/H_1^2 - \overline{M}/K_{ex}] \tag{3}$$

where k_f and K_{ex} are the forward interfacial reaction rate constant and the equilibrium constant, respectively. The superscript bar denotes that the species are in the membrane phase.

The complexes formed at the external interface then diffuse across the membrane toward the other side. The diffusion rate of metal complex in the membrane is

$$J_x = D\frac{\partial\overline{M}}{\partial x} \tag{4}$$

where D is the diffusivity of zinc complex in the organic membrane phase and can be calculated based on the Wilke–Chang equation (*11*).

On reaching the internal interface, metal ions are then stripped from metal complexes by the assistance of strong acid present in the internal phase. The stripping rate is

$$J_2 = k_f[\overline{M}/K_{ex} - Z_2\overline{R}^{1.5}/H_2^2] \tag{5}$$

2. Transport Model

The flat plate configuration was selected for model development. In order to simplify the mathematics and model development, the following assumptions were made:

1. The system is under ideal batch operation.
2. All physical and transport properties are constant during the process operation.
3. No breakage of the emulsion globules occurs.
4. The droplets dispersed in the emulsion globules are completely mobile and well mixed.
5. The concentrations in each droplet are uniform.
6. The globule size and droplet size are uniform.
7. No interfacial mass-transfer resistance exists between the oil membrane and the internal aqueous phase.

By knowing the extraction steps of the zinc ions from the external aqueous solution toward the internal solution and by using the above-mentioned assumptions, the following mass balance equations may be formulated.

For the external bulk solution,

$$-V_1\frac{dZ_1}{dt} = kA(Z_1 - Z_1^*) \tag{6}$$

where k is the mass transfer coefficient of zinc in the aqueous solution, Z_1 is the zinc concentration in the feed solution, and Z_1^* is the zinc concentration outside the external interface of the membrane.

In the membrane phase,

$$\frac{\partial\overline{M}}{\partial t} = D\frac{\partial^2\overline{M}}{\partial x^2} \tag{7}$$

For the internal aqueous phase,

$$V_2\frac{dZ_2}{dt} = AJ_2 \tag{8}$$

where A is the interfacial area of the emulsion globules.

The initial and boundary conditions at the membrane interfaces are as follows:

Initial conditions:

$$t = 0, \qquad Z_1 = Z_{10}, \qquad Z_2 = 0, \qquad \overline{M} = 0 \tag{9}$$

Boundary conditions:

$$x = 0, \qquad k(Z_1 - Z_1^*) = J_1 = J_x \tag{10}$$

$$x = l, \qquad J_x = J_2 \tag{11}$$

Additional contrains for the system are

$$2Z_{10} + H_{10} = 2Z_1 + H_1 \tag{12}$$

$$2Z_2 + H_2 = H_{20} \tag{13}$$

$$1.5\overline{M} + \overline{R} = \overline{R}_0 \tag{14}$$

Equations (6)–(14) can be solved numerically by the PDEONE and Runge–Kutta numerical method.

RESULTS AND DISCUSSION

The main purpose of this study was to analyze the transport rates of zinc ions during the course of extraction, including the external interfacial reaction rate (J_1), the membrane diffusion rate (J_x), and the internal interfacial reaction rate (J_2). Before analysis, the validity of the model was verified by experimental runs. The rate constants and diffusion coefficients used for the model calculation were as follows: the forward reaction rate constant was adopted from Ref. *12* as 0.00015 cm·(mol/L)$^{1/2}$/min, the equilibrium constant was determined by experiment to be 0.065 (mol/L)$^{1/2}$, and the diffusivity was estimated by using the Wilke–Chang equation to be 0.00016 cm/min. The experimental procedure is similar to Ref. *13*. The

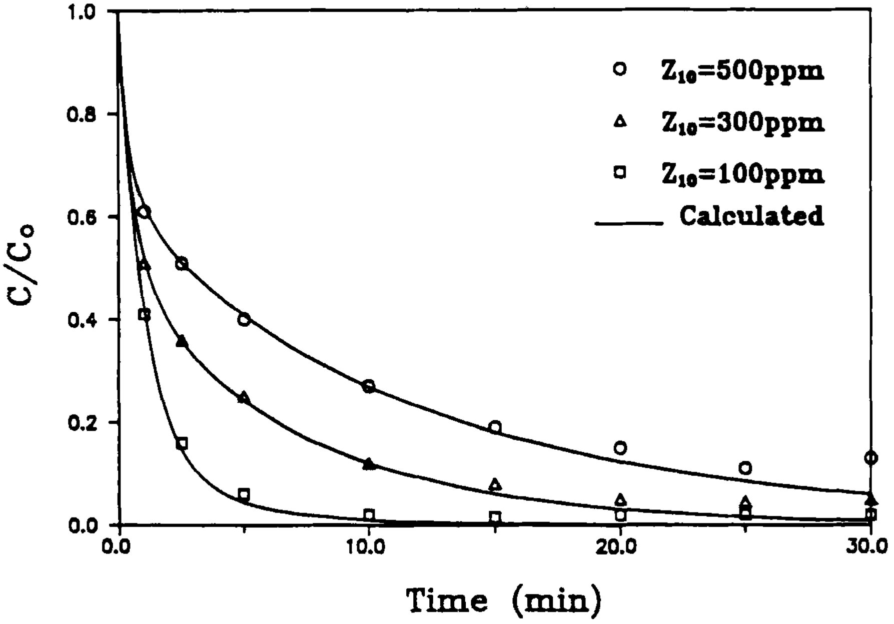

FIG. 2. Comparison of experimental and calculated data. Experimental conditions: feed, 200 mL; membrane, 10 mL; internal, 10 mL; D2EHPA, 10%; $H_{10} = 10^{-5}\ M$; $H_{20} = 1\ M$.

calculated results are compared with the respective experimental data in Fig. 2. The model meets the experimental results satisfactorily. The deviations at higher extraction times are due to emulsion globule break-up, which was not taken into account in the theoretical model.

1. Analysis of Permeation Rate

The variation of zinc transport rate with extraction time at various position along the x-direction is shown in Table 1. Table 1 clearly indicates that the net extraction rate at the external interface (J_1), the diffusion rates in the membrane (J_x's), and the net stripping rate of zinc at the internal interface (J_2) are not of equal value during extraction, especially in the early stage of the run. Table 1 shows that at the beginning of the run, the transport rates near the external interface are much greater than those near the internal interface; for instance, J_1 is about 100 times greater than J_2. However, this large difference among the transport rates quickly decreases with extraction time. When the extraction time reaches about 1.5 min, the difference becomes quite small, and the transport rates are almost

TABLE 1
Transport Rate Variation with Time at Various Positions along the x-Direction

	Transport rate × 10^5 (mol/min/cm^2)					
Extraction time (min)	J_1	J_x				J_2
	$x = 0$	$x = 0.2l$	$x = 0.4l$	$x = 0.6l$	$x = 0.8l$	$x = l$
0.0	115	0.0	0.0	0.0	0.0	0.0
0.1	99.3	77.6	55.3	34.9	17.0	0.93
0.3	59.9	52.6	42.8	31.2	18.4	5.17
0.5	37.0	33.1	27.9	21.7	14.9	7.76
1.0	16.1	15.4	14.3	13.1	11.6	10.1
2.0	7.67	8.30	8.87	9.40	9.90	10.4
3.0	5.87	6.64	7.40	8.13	8.85	9.55
5.0	4.53	5.20	5.87	6.52	7.15	7.77
10.0	2.80	3.17	3.55	3.92	4.28	4.63
15.0	1.79	2.00	2.22	2.43	2.63	2.83
20.0	1.17	1.29	1.42	1.54	1.67	1.78
30.0	0.51	0.56	0.61	0.66	0.71	0.75

equal. As the extraction proceeds further, the transport rates near the internal interface become even larger, although only about 50% greater.

Regarding the dynamic change of the individual transport rate, Table 1 shows that J_1, although starting at a quite high value, drops quickly within the first few minutes. This quick drop is mainly attributed to the fast increase in hydrogen ion concentration in the feed solution. On the other hand, all J_x's, the zinc complex transport rate in the membrane, increase drastically within the first few seconds. This is mainly due to a quick build-up of metal complex concentration within the membrane phase. After passing a maximum, all J_x's then gradually decrease with extraction time. J_2 shows a trend similar to J_x's but with slower steps and a smaller maximum. Table 1 also reveals that no equilibrium exists at either interface before extraction is complete. The simulation shows that the forward reaction is dominant at the external interface while the stripping reaction is dominant at the internal interface.

2. Parametric Effect on the Permeation Rate

The parameters affecting the transport rate are the initial zinc concentration in the feed solution (Z_{10}), the carrier concentration in the membrane phase (R_0), the initial hydrogen ion concentration of the feed solution (H_{10}), and the initial hydrogen ion concentration present in the internal solution (H_{20}). The results presented below are based on the experimental conditons Z_{10} = 500 ppm, R_0 = 10%, $H_{10} = 10^{-5}\ M$, $H_{20} = 1\ M$.

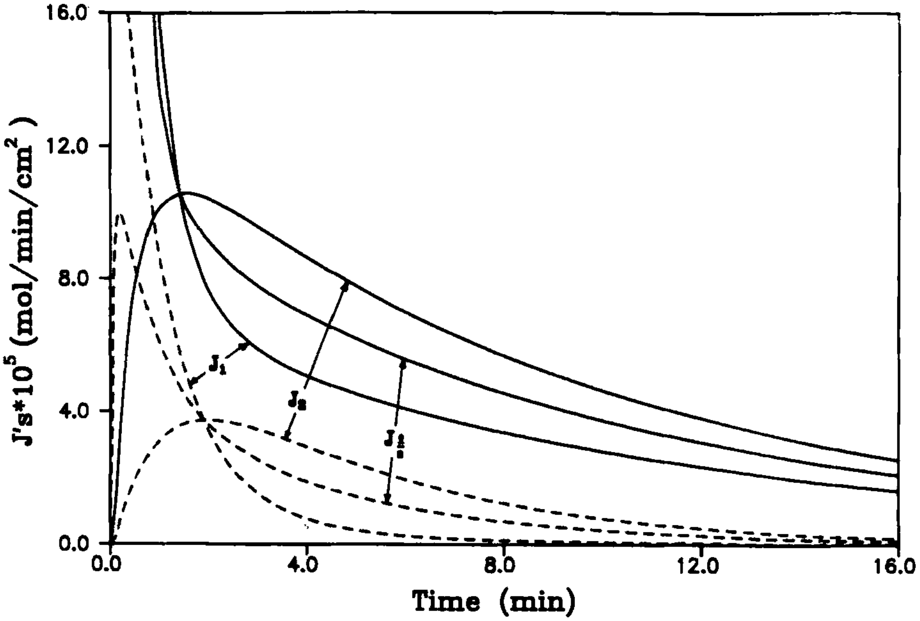

FIG. 3. Effect of initial zinc concentration on the transport rates. Solid line: Z_{10} = 500 ppm. Broken line: Z_{10} = 100 ppm.

Figure 3 shows how the transport rates are affected by the initial zinc concentration. Obviously, increasing the initial zinc concentration increases all the transport rates. However, this increase was not linearly proportional. For a 5-fold increase in the initial zinc concentration, the transport rates increased only by a factor of approximately 2.5 to 4 (in the first 3 min). In other words, if the permeation coefficient is defined as the transport rate divided by the initial zinc concentration, the permeation coefficient decreases with increasing initial zinc concentration.

Figure 4 shows the effect of carrier concentration on the transport rates. When the carrier concentration in the membrane phase is increased from 5 to 10%, all the transport rates are increased. Raising the carrier concentration will apparently speed up the extraction of zinc ion through the membrane. However, doubling the carrier concentration results in only a 60–80% increase in J_1 and J_x, and a 30–60% increase in J_2.

Figure 5 shows the effect of hydrogen ion concentration in the feed solution on the transport rates. This figure shows that almost no effect was imposed on the transport rates when the pH value of the feed solution was varied from 5 to 3. This result is attributed to the fact that whenever the initial pH value is greater than 3, the pH value in the feed solution will

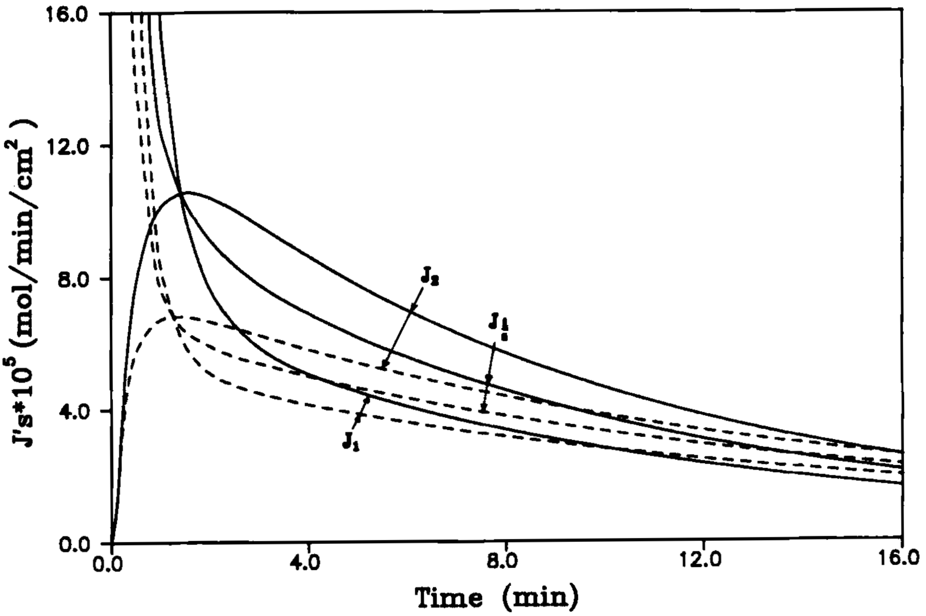

FIG. 4. Effect of initial carrier concentration on the transport rates. Solid line: R_0 = 10%. Broken line: R_0 = 5%.

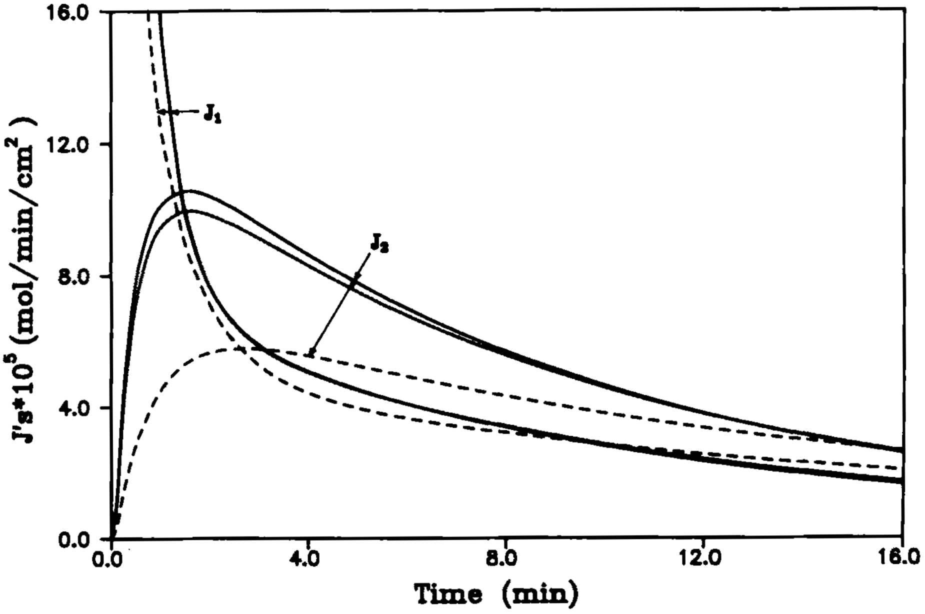

FIG. 5. Effect of initial pH value of feed solution on the transport rates. (——) $H_{10} = 10^{-5}$ M, (- - -) $H_{10} = 10^{-3}$ M, (– – –) $H_{10} \geq 10^{-2}$ M.

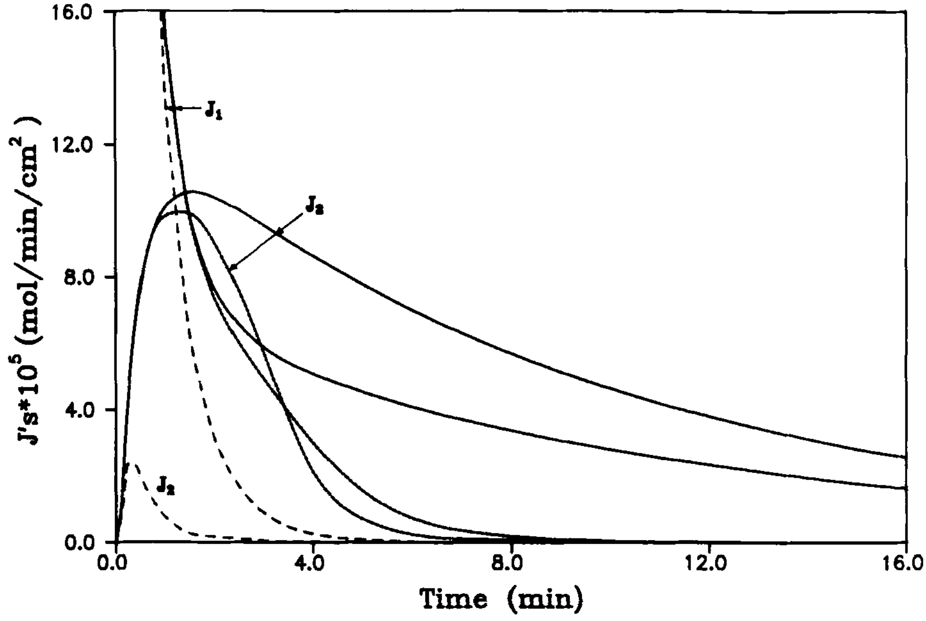

Fig. 6. Effect of initial pH value of internal solution on the transport rates. (——) $H_{20} \geq 1$ *M*, (- - -) $H_{20} = 0.1$ *M*, (– – –) $H_{20} = 0.01$ *M*.

quickly drop to the pH 3 level within the first few seconds due to the fast increase in hydrogen ion concentration. This leads to experimental conditions almost identical for the case where the external pH value is greater than 3. However, when the initial pH value of the feed solution is smaller than 3, the permeation rate will drop quickly with pH, especially J_2, as indicated in Fig. 5.

The effect of internal solution acidity on the permeation rates is shown in Fig. 6. When the acidity in the internal phase was greater than 1.0 *M*, the degree of zinc extraction as well as the transport rates were not affected by the change of acidity. However, when the acidity in the internal phase was less than 1.0 *M*, the influence of the acidity on the transport rate became significant. As soon as the acidity was less than 0.01 *M*, J_2 became quite small and extraction became difficult, as illustrated in Fig. 6.

CONCLUSION

The transport rate of zinc extraction through a liquid membrane containing D2EHPA as the carrier agent was analyzed, and the following information was obtained.

1. The transport rates, including the extraction rate occurring at the external interface of the membrane, the transport rate in the membrane, and the stripping rate taking place at the internal interface, are not of equal value, i.e, the system is not in the steady state.
2. Equilibrium is not attained at either interfaces. The forward reaction is dominant at the external interface and the stripping reaction is dominant at the internal interface.
3. All the transport rates are affected to some extent by the initial zinc concentration, the carrier concentration, and the pH values in the feed solution and the internal solution.

NOTATION

A	total mass transfer area of emulsion globules
D	diffusivity of zinc complex in the membrane phase
J	zinc transport rate
k	zinc ion mass transfer coefficient in aqueous solution
k_f	forward reaction rate constant
K_{cx}	equilibrium constant
M	concentration of zinc complex
R	carrier concentration
t	time
V	liquid volume

Superscript

*	concentration outside external interface of the membrane

Subscripts

$_1$	external phase
$_2$	internal phase
$_0$	initial concentration

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