

# Roles of Extractant Concentration and Flow Rate of Organic Phase in Countercurrent Multistage Metal Solvent Extraction-Stripping Process for Metal Ions

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The effects of the extractant concentration,  $C_{HA}^o$ , and the flow rate of the organic phase,  $S$ , on the metal recovery in a steady-state countercurrent multi-stage metal solvent extraction-stripping process (ESP) using cation-exchange reagents have been assessed by computer simulation. The results show that, with increasing  $C_{HA}^o$  or  $S$ , (i) the recovery fraction monotonically increases when the number of stages in the extraction or stripping section ( $N$  or  $N'$ , respectively) is unity and (ii) the recovery fraction first increases, then reaches a maximum, and thereafter very slowly decreases when  $N$  and  $N'$  are larger than unity. The optimum combination of  $C_{HA}^o$  and  $S$  will be determined by using the equilibrium-recovery-fraction and equi-operating-cost curves. In order to obtain in-depth understanding of the simulation results, steady-state local linearization (SLL) analysis which theoretically considers the infinitesimal variations in the metal concentrations in each stage caused by the infinitesimal variation in the operational parameters has been done. As a result, it is proved that the balance between the quantities  $\psi(C_{HA}^o)$  of the extraction and stripping sections determines the trend of the recovery fraction with  $C_{HA}^o$ , where  $\psi(C_{HA}^o)$  is the partial derivative of the metal molarity in the organic phase at the outlet of the extraction or stripping section with respect to  $C_{HA}^o$ : At the maximum recovery fraction, these values are equal to each other. Similar results are obtained also in the effect of  $S$ . Furthermore, it is proved that, with increasing  $C_{HA}^o$  or  $S$ , (i) the maximum of the recovery fraction never appears when  $N$  or  $N'$  is unity and (ii) the decrease in the recovery fraction after reaching the maximum is much slower than the increase before reaching the maximum when  $N$  and  $N'$  are larger than unity.

## Introduction

The industrial metal solvent extraction process is usually composed of the extraction and stripping sections (ESP), which are often operated by a countercurrent multistage sequence, respectively. Some researchers studied multistage extraction-stripping processes at steady state by computer simulation. These studies paid much attention to the stage sequence in order to enhance metal recovery. The metal recoveries by the countercurrent and crossflow stage sequences were examined, where the extraction of copper(II) ion with hydroxyoximes was dealt with as the model system (Rod, 1984; Hughes and Parker, 1985, 1987; Bogacki and Szymanowski, 1990). The copper extraction-strip-

ping processes containing different hydroxyoximes in various extraction-stripping loops were also simulated (Bogacki and Szymanowski, 1992). Little attention, however, has been paid to the roles of the extractant concentration and the flow rate of the organic phase. Furthermore, no attempt has been made to clarify the symbolic relation underlying the simulation results of the ESP except our previous paper (Tanaka *et al.*, 1998).

Generally in metal solvent extraction, the analytical solutions of the multistage process cannot be obtained because the equilibrium relation is nonlinear; however, the differential metal concentration of aqueous output in the countercurrent multistage extraction process (EP) was derived theoretically by a steady-state local linearization (SLL) as a linear combination of the differential values of the operational parameters (Tanaka *et al.*, 1997).

Tanaka *et al.* (1998) carried out the computer simulation and the SLL analysis of the ESP using the cation-exchange reagent by varying the extraction equilibrium constant,  $K$ . It was shown that there is a  $K$  value

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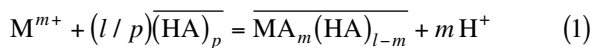
getting the maximum metal recovery fraction. The symbolic relation underlying the variation in the recovery fraction with  $K$  generated by the computer simulation was also clarified. Furthermore, the simulation result was discussed in terms of the metal loading ratio in the organic phase. Such an analysis is effective from the standpoint of in-depth understanding of process performance. The aims of the present paper are (i) to show how the metal recovery fraction in the ESP using the cation-exchange reagent varies with the number of the stages, the extractant concentration, and the flow rate of the organic phase, (ii) to discuss a guideline to determine the optimum combination of the extractant concentration and the flow rate of the organic phase, (iii) to clarify, by SLL, the symbolic relation underlying the simulation results, and (iv) to explain the dependency of the recovery fraction on the number of stages in the extraction and stripping sections in the ESP. Since the flow rates of the aqueous phases in the extraction and stripping sections in the ESP are usually determined by the close relation to the adjacent processes, the number of the stages, the extractant concentration, and the flow rate of the organic phase are chosen as adjustable parameters.

## 1. Computer Simulation

### 1.1 Assumptions

A schematic diagram of the ESP is shown in **Fig. 1**, where  $M$ ,  $N$ ,  $C$ , and  $C_{\text{HA}}^{\circ}$  denote the target metal and total number of stages in the extraction section, molarity, and total molarity of the extractant HA, respectively. The  $F$  and  $S$  are the flow rates of the aqueous and organic phases, and overbar and prime represent organic phase species and stripping section, respectively.

The cation-exchange system dealt with here has the following stoichiometric relation of extraction.

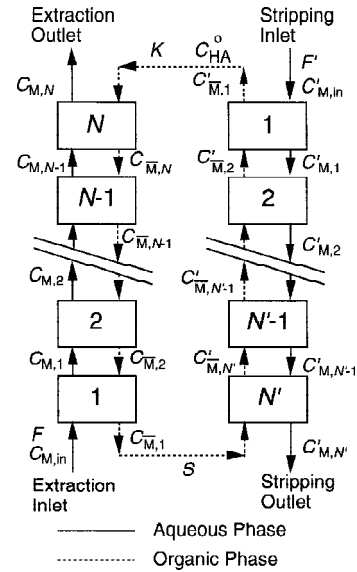


The assumptions for the computer simulation are as follows: (i) The temperature and pressure are constant. (ii) Equilibrium is immediately attained in each stage. (iii) The volume of each phase does not change during extraction. (iv) The aqueous phase consists of  $H^+$ ,  $M^{m+}$ ,  $X^{q-}$ , and water. (v) The organic phase consists of  $(HA)_p$ , the diluent, and the metal-extractant complex,  $\overline{MA}_m(HA)_{l-m}$ , where  $l$  is stoichiometry in Eq. (1). (vi) The activity coefficients of  $H^+$ ,  $M^{m+}$ ,  $(HA)_p$ , and  $\overline{MA}_m(HA)_{l-m}$  are unity.

### 1.2 Method

The relaxation method (Rod, 1984) was applied to simulation of the ESP by using the following equations.

(1) The nonsteady-state material balance equation for the metal in each stage:



**Fig. 1** Schematic diagram of ESP

$$\frac{dC_{M,n}}{dT} = C_{M, \text{inlet to the } n\text{th stage}} - C_{M,n} + \frac{S}{F} \left[ \overline{C}_{M, \text{inlet to the } n\text{th stage}} - \overline{C}_{M,n} \right] \quad (2)$$

Here  $n$  and  $T$  denote the stage number and dimensionless time equal to  $tF/V_{\text{aq}}$ , respectively, where  $t$  and  $V_{\text{aq}}$  are time and the volume of the aqueous phase in each stage, respectively.

(2) The equation for the extraction equilibrium constant,  $K$ :

$$K = \overline{C}_{M,n} C_{H,n}^m / \left( C_{M,n} C_{(HA)_p,n}^{l/p} \right) \quad (3)$$

(3) The material balance equation for the extractant:

$$C_{\text{HA}}^{\circ} = pC_{(HA)_p,n} + lC_{M,n} \quad (4)$$

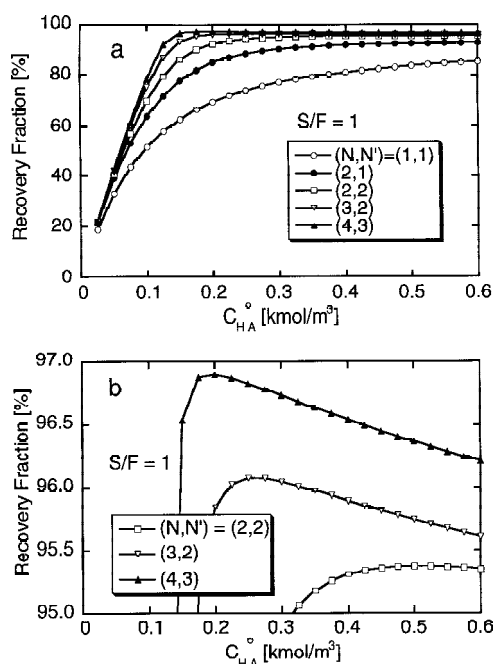
(4) The charge balance equation:

$$m \left( C_{M, \text{inlet to the } n\text{th stage}} - C_{M,n} \right) + C_{H, \text{inlet to the } n\text{th stage}} - C_{H,n} = 0 \quad (5)$$

The conditions for the computer simulation are listed in **Table 1**. These conditions are set up in reference to the leaching-solvent extraction-electrowinning process for copper oxide ores (Szymanowski, 1993); the target metal ion is copper(II) ion and the extractant is  $\beta$ -hydroxyoxime. The  $K$  value is fixed at 10, because this value gives a high metal recovery fraction in the

**Table 1** Conditions for computer simulation

$l$ [—]	2
$m$ [—]	2
$p$ [—]	1
$K$ [—]	10
$C_{M,in}$ [kmol/m <sup>3</sup> ]	0.05
$C'_{M,in}$ [kmol/m <sup>3</sup> ]	0.5
$C_{H,in}$ [kmol/m <sup>3</sup> ]	0.01
$C'_{H,in}$ [kmol/m <sup>3</sup> ]	2
$C_{HA}^o$ [kmol/m <sup>3</sup> ]	0.2
$F/F'$ [—]	5

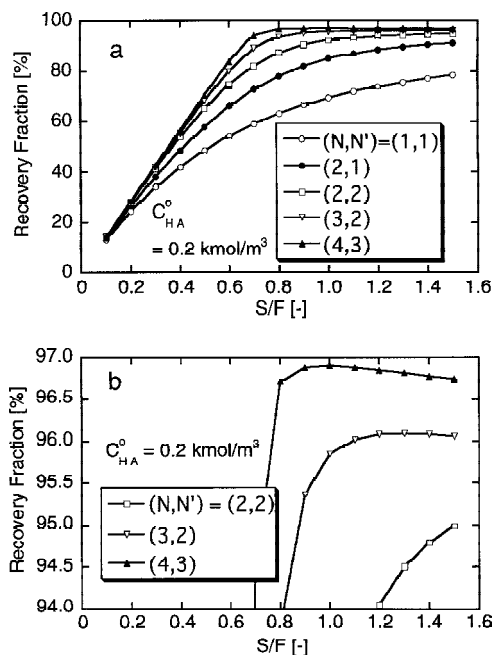


**Fig. 2** Variation in recovery fraction with  $C_{HA}^o$  when  $S/F$  is unity. Recovery fraction: (a) 0–100%; (b) 95–97%

ESP under the same compositions of the aqueous phases at the extraction and stripping inlets as those in Table 1 (Tanaka *et al.*, 1998). The  $N$ ,  $N'$ ,  $C_{HA}^o$ , and  $S$  values are varied. The recovery fraction (%) was defined as  $100(1 - C_{M,N}/C_{M,in})$ .

### 1.3 Effect of extractant concentration

Figures 2(a) and (b) show the variation in the recovery fraction with  $C_{HA}^o$  under various combinations of  $N$  and  $N'$  when  $S/F$  is unity. When  $(N, N')$  is (1, 1) and (2, 1), the recovery fraction regularly increases with  $C_{HA}^o$ , although the rates of the increase become small. It was also found that the recovery fraction regularly increases with  $C_{HA}^o$  for  $N > 1$  and  $N' = 1$ . On the other hand, when  $(N, N')$  is (2, 2), (3, 2), and (4, 3), the recovery fraction first increases with  $C_{HA}^o$ , then reaches



**Fig. 3** Variation in recovery fraction with  $S$  when  $C_{HA}^o$  is 0.2 kmol/m<sup>3</sup>. Recovery fraction: (a) 0–100%; (b) 94–97%

maximum at a  $C_{HA}^o$  of 0.51, 0.26, and 0.19 kmol/m<sup>3</sup>, respectively, and decreases very slowly thereafter (Fig. 2(b)). From Eq. (3), the increase in  $C_{HA}^o$  enhances the metal transfer fraction from the aqueous to organic phases in the extraction section, but reduces the metal transfer fraction from the organic to aqueous phases in the stripping section. This fact results in a reduction in the increasing rate of the recovery fraction when  $(N, N')$  is (1, 1) and (2, 1) and the very slow decrease in the recovery fraction when  $(N, N')$  is (2, 2), (3, 2), and (4, 3) in the high  $C_{HA}^o$  region. This trend is compared with the effect of  $K$  on the recovery fraction in the ESP (Tanaka *et al.*, 1998). With increasing  $K$ , the recovery fraction first increases, reaches a maximum, and decreases much faster than the cases shown in Fig. 2.

### 1.4 Effect of organic phase flow rate

Figures 3(a) and (b) show the variation in the recovery fraction with  $S/F$  ( $F$  is kept constant) under various combinations of  $N$  and  $N'$  when  $C_{HA}^o$  is 0.2 kmol/m<sup>3</sup>. The general trend is the same as that in Fig. 2. When  $(N, N')$  is (2, 2), (3, 2), and (4, 3), the recovery fraction first increases with  $S$ , reaches a maximum, at an  $S/F$  of 2.3 (outside of Fig. 3), 1.3, and 1.0, respectively, and decreases very slowly thereafter (Fig. 3(b)). The increase in  $S$  enhances the metal transfer fraction from the aqueous to organic phases in the extraction section, but reduces the metal transfer fraction from the organic to aqueous phases in the stripping section. This fact results in a reduction in the increasing rate of the recovery fraction for  $(N, N')$  of

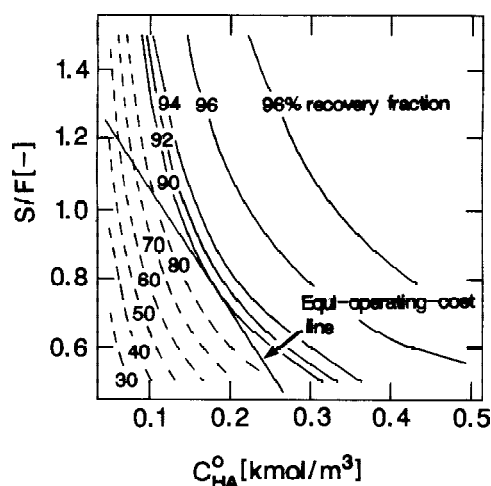


Fig. 4 Equi-recovery-fraction curves and an equi-operating-cost line when  $(N, N') = (3, 2)$ ,  $\log K = 1$

(1, 1) and (2, 1) and a decrease in the recovery fraction for  $(N, N')$  of (2, 2), (3, 2), and (4, 3) in the high  $S$  region.

### 1.5 Optimum combination of $C_{HA}^0$ and $S$

The  $C_{HA}^0$  or  $S$  value getting a maximum recovery fraction is not necessarily the optimum value, because, generally, the larger  $C_{HA}^0$  and  $S$  result in a greater loss of the extractant to the aqueous phase and the greater power consumption for pumping the organic phase, respectively. In this section, a guideline to determine the optimum values of  $C_{HA}^0$  and  $S$  is discussed.

By fixing  $(N, N')$  at (3, 2), the recovery fractions were calculated at various combinations of  $C_{HA}^0$  (every 0.025 kmol/m<sup>3</sup> from 0.05 to 0.5 kmol/m<sup>3</sup>) and  $S$  (every 0.1 from 0.5 to 1.5 as  $S/F$ ) (200 points in total). The result is interpolated and presented as equi-recovery-fraction curves in Fig. 4. A ridge lying between two 96%-recovery-fraction curves corresponds to the recovery fraction between 96.04 and 96.09% and divides the figure into two parts. The increases in  $C_{HA}^0$  and  $S$  enhance the recovery fraction at the left side of the ridge but slightly reduce the recovery fraction at the right side of the ridge.

The operating cost would be a very complicated function of the various operational parameters. As a first approximation, however, the operating cost per unit time,  $f$ , could be expressed by a linear combination of  $C_{HA}^0$  and  $S$  as

$$f = aC_{HA}^0 + bS + c \quad (6)$$

where  $a$ ,  $b$ , and  $c$  are constant, respectively. From Eq. (6), the following equation is obtained.

$$\frac{S}{F} = -\frac{a}{Fb}C_{HA}^0 + \frac{f-c}{Fb} \quad (7)$$

In Fig. 4, straight lines with a slope of  $-a/Fb$  called equi-operating-cost lines can be drawn. In order to achieve, for example, a 90% recovery fraction at minimum  $f$ , a point of contact between the 90%-recovery-fraction curve and one of the equi-operating-cost lines gives the optimum combination of  $C_{HA}^0$  and  $S$ . In Fig. 4, the equi-operating-line with a slope of  $-3.5$  (arbitrarily set at this value as an example) is drawn. Even when  $f$  is a more complicated function of  $C_{HA}^0$  and  $S$ , superimposing the equi-operating-cost curve on the equi-recovery-fraction curve would be useful to determine the optimum combination of  $C_{HA}^0$  and  $S$  at the given conditions.

## 2. Analysis of the Computer Simulation Results by SLL

In this section, by SLL, we derive symbolic relationships underlying the simulation results and show why these trends are observed.

### 2.1 Extension of differential equilibrium relation to EP

Tanaka *et al.* (1997) derived the equation expressing the relationship among the differential of  $C_{M,N}$ ,  $dC_{M,N}$ , and the differentials of the operational parameters for the EP. The procedure is as follows. (i) The equation for the  $n$ th stage in the EP is derived based on the differential forms of Eqs. (3), (4), and (5). This equation expresses the relationship among the differentials of the outlet metal molarities and the operational parameters and can be called differential equilibrium relation. When the operational parameters other than  $C_{M,in}$ ,  $C_{HA}^0$ , and  $S$  are constant, the differential equilibrium relation for the  $n$ th stage in the EP is written as

$$dC_{M,n} = \alpha_n dC_{M,n} + \beta(C_{HA}^0)_n dC_{HA}^0 \quad (8)$$

where the coefficients  $\alpha_n$  and  $\beta(C_{HA}^0)_n$  are expressed as follows, respectively.

$$\alpha_n = \frac{1/C_{M,n} + m^2/C_{H,n}}{1/C_{M,n} + l^2/\left(p^2 C_{(HA)_p,n}\right)} \quad (9)$$

$$\beta(C_{HA}^0)_n = \frac{l/\left(p^2 C_{(HA)_p,n}\right)}{1/C_{M,n} + l^2/\left(p^2 C_{(HA)_p,n}\right)} \quad (10)$$

(ii) The differential equilibrium relation for each stage is combined with the steady-state material balance equation for the metal around each stage. As a result, the nonhomogeneous second-order difference equation

with variable coefficients expressing the relationship between the  $dC_{M,n}$  values in the EP and the differentials of the operational parameters is obtained. (iii) This difference equation is solved with respect to  $dC_{M,N}$  by using Cramer's rule. When the operational parameters, other than  $C_{M,in}$ ,  $C_{HA}^o$ , and  $S$  are constant, the final equation obtained is written as

$$dC_{M,N} = B(C_{M,in})dC_{M,in} + B(C_{HA}^o)dC_{HA}^o + B(S)dS \quad (11)$$

where the coefficients,  $B(C_{M,in})$ ,  $B(C_{HA}^o)$ , and  $B(S)$  are expressed as follows, respectively.

$$B(C_{M,in}) = \frac{\sum_{i=1}^N \left( \prod_{j=1}^{i-1} \alpha_j \right) r^{-i}}{1 + \sum_{i=1}^N \left( \prod_{j=1}^i \alpha_j \right) r^{-i}} \quad (12)$$

$$B(C_{HA}^o) = - \frac{\sum_{i=1}^N \left( \prod_{j=1}^{i-1} \alpha_j \right) \beta(C_{HA}^o)_i r^{-i}}{1 + \sum_{i=1}^N \left( \prod_{j=1}^i \alpha_j \right) r^{-i}} \quad (13)$$

$$B(S) = \frac{S^{-1} \sum_{i=1}^N \left( \prod_{j=1}^{i-1} \alpha_j \right) (C_{M,in} - C_{M,i}) r^{-i}}{1 + \sum_{i=1}^N \left( \prod_{j=1}^i \alpha_j \right) r^{-i}} \quad (14)$$

Here,  $\prod_{j=1}^{i-1} \alpha_j = 1$  when  $i = 1$ , and  $r = F/S$ . The suffixes  $i$  and  $j$  denote the stage number.

Equation (8) can be modified in order to express the differential mole flow rate of the metal at the organic outlet of the  $n$ th stage in the EP,  $d(SC_{M,n})$ , as

$$d(SC_{M,n}) = S\alpha_n dC_{M,n} + S\beta(C_{HA}^o)_n dC_{HA}^o + C_{M,n} dS \quad (15)$$

From Eq. (11) and the differential material balance of the metal around the EP with  $N$  stages, one can express the differential mole flow rate of the metal at the organic outlet of the EP as

$$d(SC_{M,1}) = S\theta dC_{M,N} + S\psi(C_{HA}^o) dC_{HA}^o + \psi(S) dS \quad (16)$$

where

$$\theta = \frac{1 - rB(C_{M,in})}{B(C_{M,in})} = \frac{\left( \prod_{i=1}^N \alpha_i \right) r^{-N}}{\sum_{i=1}^N \left( \prod_{j=1}^{i-1} \alpha_j \right) r^{-i}} \quad (17)$$

$$\psi(C_{HA}^o) = - \frac{B(C_{HA}^o)}{B(C_{M,in})} = \frac{\sum_{i=1}^N \left( \prod_{j=1}^{i-1} \alpha_j \right) \beta(C_{HA}^o)_i r^{-(i-1)}}{\sum_{i=1}^N \left( \prod_{j=1}^i \alpha_j \right) r^{-(i-1)}} \quad (18)$$

$$\psi(S) = - \frac{SB(S)}{B(C_{M,in})} + C_{M,in} = \frac{\sum_{i=1}^N \left( \prod_{j=1}^{i-1} \alpha_j \right) C_{M,i} r^{-(i-1)}}{\sum_{i=1}^N \left( \prod_{j=1}^i \alpha_j \right) r^{-(i-1)}} \quad (19)$$

Equation (15) indicates that  $\alpha_n$ ,  $\beta(C_{HA}^o)_n$ , and  $C_{M,n}$  are the partial derivatives,  $(\partial C_{M,n} / \partial C_{M,n})_{C_{HA}^o}$ ,  $(\partial C_{M,n} / \partial C_{HA}^o)_{C_{M,n}}$ , and  $[\partial(SC_{M,n}) / \partial S]_{C_{M,n}, C_{HA}^o}$ , respectively. On the extraction isotherm ( $C_{M}^o$  vs.  $C_M$  diagram) drawn under the constant anion molarity,  $\alpha_n$  expresses the slope of the tangent to the equilibrium curve at the  $n$ th stage in the EP, and  $\beta(C_{HA}^o)_n dC_{HA}^o$  is equal to the infinitesimal variation in  $C_{M,n}$  caused by the infinitesimal variation in  $C_{HA}^o$  (Tanaka *et al.*, 1997). The equilibrium relation is not affected by the variation in  $S$  under constant  $C_{M,n}$  and  $C_{HA}^o$ ; thus, the partial derivative,  $(\partial C_{M,n} / \partial S)_{C_{M,n}, C_{HA}^o}$ , is zero. Equation (16) indicates that  $\theta$ ,  $\psi(C_{HA}^o)$ , and  $\psi(S)$  are the partial derivatives,  $(\partial C_{M,1} / \partial C_{M,N})_{C_{HA}^o, S}$ ,  $(\partial C_{M,1} / \partial C_{HA}^o)_{C_{M,N}, S}$ , and  $[\partial(SC_{M,1}) / \partial S]_{C_{M,N}, C_{HA}^o}$ , respectively.

A comparison between Eqs. (15) and (16) allows one to realize that Eq. (16) is an extension of Eq. (15) to the EP. Also, Eq. (18) states that  $\psi(C_{HA}^o)$  is the

weighted average  $\beta(C_{HA}^{\circ})$  of each stage in the EP, where the relative weight of the  $n$ th stage,  $\rho_n$ , is expressed as

$$\rho_n = \frac{\left(\prod_{i=1}^{n-1} \alpha_i\right) r^{-(n-1)}}{\sum_{i=1}^N \left(\prod_{j=1}^{i-1} \alpha_j\right) r^{-(i-1)}} \quad (20)$$

Similarly, Eq. (19) states that  $\psi(S)$  is the weighted average of  $C_{M,n}^{\circ}$  of each stage in the EP, where the relative weight of the  $n$ th stage is  $\rho_n$ . Equations (16), (18)–(20) mean that the contributions of the infinitesimal variations in  $C_{HA}^{\circ}$  and  $S$  of the  $n$ th stage in the EP to  $d(SC_{M,1}^{\circ})$  are rewritten by  $S\rho_n\beta(C_{HA}^{\circ})_n dC_{HA}^{\circ}$  and  $\rho_n C_{M,n}^{\circ} dS$ , respectively. This fact is analogous to our previous result with respect to the contribution of the variation in  $K$  to the output of the EP (Tanaka *et al.*, 1998). The results obtained here indicate that by the infinitesimal variation in  $C_{HA}^{\circ}$ , (i) the  $\beta(C_{HA}^{\circ})_1$  value mainly affects the variation in  $C_{M,1}^{\circ}$  when  $\alpha_1$  is very low, because  $\rho_1 \gg \rho_n$  ( $n \geq 2$ ) and (ii) the  $\beta(C_{HA}^{\circ})$  values in the second or higher stages substantially contribute to the variation in  $C_{M,1}^{\circ}$  when  $\alpha_1$  is large.

## 2.2 SLL of ESP

In the ESP, Eq. (16) and the following equation hold true for the extraction and stripping sections, respectively.

$$d(SC'_{M,1}) = S\theta' dC'_{M,N'} + S\psi'(C_{HA}^{\circ}) dC_{HA}^{\circ} + \psi'(S) dS \quad (21)$$

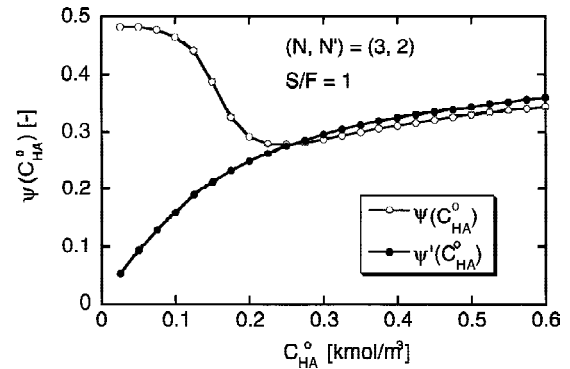
A combination of Eqs. (16) and (21) with the differential material balance equations for the metal around the ESP and around the extraction section of the ESP yields the following equation.

$$\begin{aligned} & \left(r + \theta + \frac{F}{F'}\theta'\right) dC_{M,N} \\ & = \left[\psi'(C_{HA}^{\circ}) - \psi(C_{HA}^{\circ})\right] dC_{HA}^{\circ} + \left[\psi'(S) - \psi(S)\right] dS / S \end{aligned} \quad (22)$$

This equation relates the infinitesimal variation in  $C_{M,N}$  to the infinitesimal variations in  $C_{HA}^{\circ}$  and  $S$  in the ESP.

## 2.3 Interpretation of the results of computer simulation for ESP

**2.3.1 Effect of extractant concentration** The coefficient of  $dC_{M,N}$  of Eq. (22) is always positive; thus, the variation in the recovery fraction shown in Fig. 2 is connected to the relative balance between the values of  $\psi(C_{HA}^{\circ})$  and  $\psi'(C_{HA}^{\circ})$ , when  $S$  is constant. When



**Fig. 5** Variations in  $\psi(C_{HA}^{\circ})$  and  $\psi'(C_{HA}^{\circ})$  with  $C_{HA}^{\circ}$  when  $(N, N')$  and  $S/F$  are  $(3, 2)$  and unity, respectively

$C_{HA}^{\circ}$  is increasing, the following classification holds true: (i) When the recovery fraction is increasing,  $\psi'(C_{HA}^{\circ}) < \psi(C_{HA}^{\circ})$ , (ii) at the maximum recovery fraction,  $\psi'(C_{HA}^{\circ}) = \psi(C_{HA}^{\circ})$ , and (iii) when the recovery fraction is decreasing,  $\psi'(C_{HA}^{\circ}) > \psi(C_{HA}^{\circ})$ . As far as the metal ion is transferred from the extraction to stripping sections, the inverses of these relationships also hold true. One can confirm that these relationships really hold by calculating the  $\psi(C_{HA}^{\circ})$  values from the results of the computer simulation. **Figure 5** shows the variations in the  $\psi(C_{HA}^{\circ})$  and  $\psi'(C_{HA}^{\circ})$  values with  $C_{HA}^{\circ}$  when  $(N, N')$  and  $S/F$  are  $(3, 2)$  and unity, respectively. The  $\psi(C_{HA}^{\circ})$  and  $\psi'(C_{HA}^{\circ})$  values intersect when the recovery fraction is at its maximum, and the signs of  $\psi'(C_{HA}^{\circ}) - \psi(C_{HA}^{\circ})$  are in agreement with the variation in the recovery fraction shown in Fig. 2.

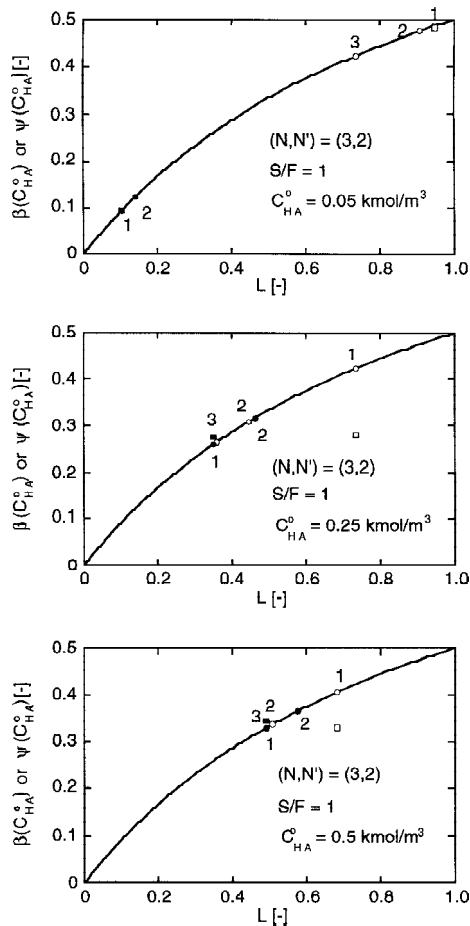
The metal loading ratio of the  $n$ th stage,  $L_n$ , is defined as

$$L_n = \frac{C_{M,n}^{\circ}}{C_{HA}^{\circ} / l} \quad (23)$$

Equation (11) is rewritten by using Eqs. (4) and (23) as

$$\beta(C_{HA}^{\circ})_n = \frac{L_n}{(l-p)L_n + p} \quad (24)$$

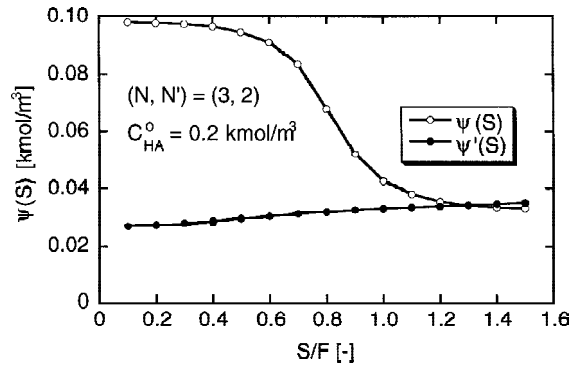
The derivative of  $\beta(C_{HA}^{\circ})_n$  with respect to  $L_n$  is always positive; thus,  $\beta(C_{HA}^{\circ})_n$  monotonically increases with  $L_n$ . The solid curve in **Fig. 6** represents  $\beta(C_{HA}^{\circ})_n$  as a function of  $L_n$ . Here, the variation in the recovery fraction with  $C_{HA}^{\circ}$  observed in the computer simulation can be discussed in connection with the variation in  $L_n$  in each stage. On the premise that the metal ion transfers from the extraction to stripping sections, the relative balance between  $\psi(C_{HA}^{\circ})$  and  $\psi'(C_{HA}^{\circ})$  can be discussed depending on the situations classified into the following two cases.



**Fig. 6**  $\beta(C_{HA}^o)_n$  vs.  $L_n$  and  $\psi(C_{HA}^o)_n$  vs.  $L_n$  plots at extraction and stripping sections of ESP when  $(N, N')$  and  $S/F$  are (3, 2) and unity, respectively. Numerals on the curve denote  $n$  or  $n'$ :  $\circ$ ,  $\beta(C_{HA}^o)$ ;  $\bullet$ ,  $\beta'(C_{HA}^o)$ ;  $\square$ ,  $\psi(C_{HA}^o)$ ;  $\blacksquare$ ,  $\psi'(C_{HA}^o)$

(a) Case where  $N$  or  $N'$  is unity. When  $N'$  is unity, the relationship  $L_1 > \dots > L_n > \dots > L_N > L'_1$  holds true; thus,  $\beta(C_{HA}^o)_1 > \dots > \beta(C_{HA}^o)_n > \dots > \beta(C_{HA}^o)_N > \beta'(C_{HA}^o)_1$ . This inequality and Eq. (18) lead to  $\beta(C_{HA}^o)_1 > \psi(C_{HA}^o) > \beta(C_{HA}^o)_N > \psi'(C_{HA}^o)$ . Thus, from the relationship (i) previously mentioned in this section, the recovery fraction monotonically increases with  $C_{HA}^o$ . When  $N$  is unity, similar inequalities can be derived; thus, the recovery fraction also increases monotonically with  $C_{HA}^o$ .

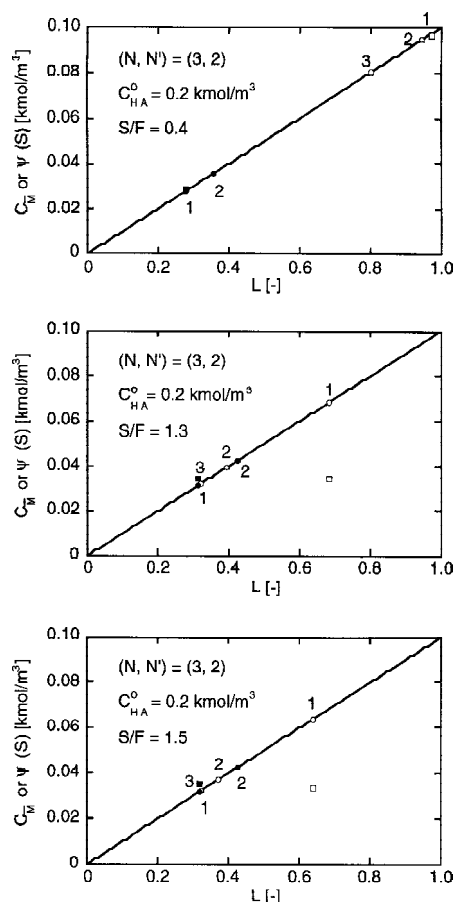
(b) Case where  $N$  and  $N'$  are larger than unity. In this case, the relative balance between  $L_N$  and  $L'_{N'}$  is unclear, although the inequalities of  $L_1 > \dots > L_n > \dots > L_N > L'_1$  and  $L_1 > L'_{N'} > \dots > L'_{n'} > \dots > L'_1$  hold true. Therefore, the relative balance between  $\beta(C_{HA}^o)_N$  and  $\beta'(C_{HA}^o)_{N'}$  is unclear, although the inequalities of  $\beta(C_{HA}^o)_1 > \dots > \beta(C_{HA}^o)_n > \dots > \beta(C_{HA}^o)_N > \beta'(C_{HA}^o)_1$  and  $\beta(C_{HA}^o)_1 > \beta'(C_{HA}^o)_{N'} > \dots > \beta'(C_{HA}^o)_{n'} > \dots > \beta'(C_{HA}^o)_1$  hold true. As a result, the relative balance between  $\psi(C_{HA}^o)$  and  $\psi'(C_{HA}^o)$  depends on the conditions. Figure 6 shows the points of  $(L_n, \beta(C_{HA}^o)_n)$  and  $(L_1,$



**Fig. 7** Variations in  $\psi(S)$  and  $\psi'(S)$  with  $S$  when  $(N, N')$  and  $C_{HA}^o$  are (3, 2) and  $0.2 \text{ kmol/m}^3$ , respectively

$\psi(C_{HA}^o)$  in the extraction and stripping sections of the ESP when  $(N, N')$  and  $S/F$  are (3, 2) and unity, respectively. In the ESP, the metal loading ratios as the extraction and stripping sections are  $L_1$  and  $L'_1$ , respectively; thus,  $\psi(C_{HA}^o)$  and  $\psi'(C_{HA}^o)$  are plotted versus  $L_1$  and  $L'_1$ , respectively. The three selected  $C_{HA}^o$  values of 0.05, 0.25, and  $0.5 \text{ kmol/m}^3$  correspond to the situations where the recovery fraction is increasing, near the maximum, and decreasing with  $C_{HA}^o$ , respectively. When  $C_{HA}^o$  is  $0.05 \text{ kmol/m}^3$ , the groups of the  $(L_n, \beta(C_{HA}^o)_n)$  plots in the extraction and stripping sections, lying on the solid curve expressed by Eq. (24), are far from each other ( $L_3 > L'_2$ ). Clearly, in this case, the  $\psi(C_{HA}^o)$  value is larger than the  $\psi'(C_{HA}^o)$  value. When  $C_{HA}^o$  is  $0.25 \text{ kmol/m}^3$ , however, the two groups overlap each other ( $L_3 < L'_2$ ). The  $\psi(C_{HA}^o)$  value is approximately equal to the  $\psi'(C_{HA}^o)$  value. When  $C_{HA}^o$  is  $0.5 \text{ kmol/m}^3$ , the  $\psi'(C_{HA}^o)$  value is larger than the  $\psi(C_{HA}^o)$  value; however, the difference between  $\psi'(C_{HA}^o)$  and  $\psi(C_{HA}^o)$  is very small. This is because  $L'_{N'}$  ( $L'_2$  in this case) never exceeds  $L_1$  and the two groups of the  $(L_n, \beta(C_{HA}^o)_n)$  plots remain overlapped. This fact results in a very slow decrease in the recovery fraction with  $C_{HA}^o$  in the higher  $C_{HA}^o$  region, which is shown in Fig. 2. In contrast with the variation in  $\beta(C_{HA}^o)$  with  $L$ , the variation in  $\beta(\ln K)$  (coefficient of  $d \ln K$  in the differential equilibrium relation) with  $L$  exhibits a concave curve in the range  $0 \leq L \leq 1$  (Tanaka *et al.*, 1998). Thus, the difference between  $\psi(\ln K)$  (coefficient of  $d \ln K$  in the equation analogous to Eq. (16) (Tanaka *et al.*, 1998)) and  $\psi'(\ln K)$  can be positively and negatively large. As a result, the increase and decrease in the recovery fraction with  $\log K$ , determined by this difference, can be rapid (Tanaka *et al.*, 1998).

**2.3.2 Effect of organic phase flow rate** The same logic as that in the former section is applied. When  $S$  is increasing at a constant  $C_{HA}^o$ , the following classification holds true from Eq. (22): (i) When the recovery fraction is increasing,  $\psi'(S) < \psi(S)$ , (ii) at the maximum recovery fraction,  $\psi'(S) = \psi(S)$ , and (iii) when the recovery fraction is decreasing,  $\psi'(S) > \psi(S)$ . **Fig-**



**Fig. 8**  $C_{M,n}$  vs.  $L_n$  and  $\psi(S)$  vs.  $L_n$  plots at extraction and stripping sections of ESP when  $(N, N')$  and  $C_{HA}^0$  are (3, 2) and 0.2 kmol/m<sup>3</sup>, respectively. Numerals on line denote  $n$  or  $n'$ :  $\circ$ ,  $C_M$ ;  $\bullet$ ,  $C'_M$ ;  $\square$ ,  $\psi(S)$ ;  $\blacksquare$ ,  $\psi'(S)$

Figure 7 shows the variations in the  $\psi(S)$  and  $\psi'(S)$  values with  $S$  when  $(N, N')$  and  $C_{HA}^0$  are (3, 2) and 0.2 kmol/m<sup>3</sup>, respectively. The  $\psi(S)$  and  $\psi'(S)$  values intersect when the recovery fraction is at its maximum, and the signs of  $\psi'(S) - \psi(S)$  are in agreement with the variation in the recovery fraction shown in Fig. 3. According to Eq. (23), the  $C_{M,n}$  vs.  $L_n$  plot lies on a straight line with a slope of  $C_{HA}^0/l$ ; namely,  $C_{M,n}$  regularly increases with  $L_n$ . Therefore, with  $S$ , the recovery fraction regularly increases when  $N$  or  $N'$  is unity, whereas the recovery fraction first increases, reaches a maximum, and decreases very slowly thereafter when  $N$  and  $N'$  are larger than unity. Figure 8 shows the points of  $(L_n, C_{M,n})$  and  $(L_1, \psi(S))$  in the extraction and stripping sections of the ESP when  $(N, N')$  and  $C_{HA}^0$  are (3, 2) and 0.2 kmol/m<sup>3</sup>, respectively. The three selected  $S/F$  values of 0.4, 1.3, and 1.5 correspond to the situations where the recovery fraction is, respectively, increasing, near the maximum, and decreasing. The situation is analogous to that in Fig. 6. When  $S/F$  is 0.4, the groups of the  $(L_n, C_{M,n})$  plots in the extraction

and the stripping sections are far from each other ( $L_3 > L'_2$ ). Obviously, in this case, the  $\psi(S)$  value is larger than the  $\psi'(S)$  value. When  $S/F$  is 1.3, however, the two groups overlap each other ( $L_3 < L'_2$ ). The  $\psi(S)$  value is approximately equal to the  $\psi'(S)$  value. When  $S/F$  is 1.5, the  $\psi'(S)$  value is larger than the  $\psi(S)$  value. The difference between  $\psi'(S)$  and  $\psi(S)$  is, however, very small, because  $L'_{N'}$  ( $L'_2$  in this case) never exceeds  $L_1$  and the two groups of the  $(L_n, C_{M,n})$  plots remain overlapped. This results in the very slow decrease in the recovery fraction with  $S$  at the higher  $S$  region when  $N$  and  $N'$  are larger than unity, which is shown in Fig. 3.

## 2.4 Generality of Eqs. (16) and (22)

As discussed in our previous paper (Tanaka *et al.*, 1997), in the EP, Eqs. (8) and (9) hold true even when the activity coefficients of the species relevant to the extraction are not constant (assumption vi), although the expressions of  $\alpha_n$  and  $\beta(C_{HA}^0)_n$  need some corrections. This is understood by considering that Eq. (8) expresses the infinitesimal movement of the equilibrium point on the  $C_M$  vs.  $C_M$  diagram caused by the infinitesimal variation in  $C_{HA}^0$  (Tanaka *et al.*, 1997). Equations (16) and (22) are derived from Eq. (9) only by using the material balance and, thus, hold true even when assumption vi does not hold true, although Eqs. (10) and (11) need some corrections.

## 2.5 Significance of SLL

As shown in this paper, the SLL analysis answers questions such as (i) why the trend of the recovery fraction depends on the total number of stages in the extraction and stripping sections, (ii) what the relationship between the concentration of each species in each stage at the maximum recovery fraction is, and (iii) why the decreasing rate of the recovery fraction is very slow. These questions cannot be answered only by computer simulation. In addition, the SLL can be used as a new computer simulation method (Tanaka *et al.*, 1997, 2000) by deriving the differential equations of metal concentrations in all the stages with respect to the operational parameters. Also, the SLL would enable a theoretical approach to the process control, because the SLL deals with a small variation in the concentrations of each species in the solutions caused by a small variation in the operational parameters. From these standpoints, the SLL brings about significant results on the multistage solvent extraction processes.

## Conclusion

The effects of  $C_{HA}^0$  and  $S$  on metal recovery in the ESP using cation exchange reagents have been assessed by computer simulation. The variation in the metal recovery fraction with the increase in  $C_{HA}^0$  or  $S$  is shown to be as follows.

- (i) When  $N$  or  $N'$  is unity, the recovery fraction regularly increases, although the rate of increase becomes reduced.



(ii) When  $N$  and  $N'$  are larger than unity, the recovery fraction first increases, then reaches a maximum, and decreases very slowly thereafter.

The optimum combination of  $C_{HA}^\circ$  and  $S$  would be determined by using the equi-recovery-fraction and equi-operating-cost curves.

The quantities  $\psi(C_{HA}^\circ)$  and  $\psi(S)$ , derived by the SLL, are the partial derivatives,  $\left(\partial C_{\bar{M},1} / \partial C_{HA}^\circ\right)_{C_{M,N},S}$ , and  $\left[\partial (SC_{\bar{M},1}) / \partial S\right]_{C_{M,N},C_{HA}^\circ}$  and are expressed by the weighted averages of  $\left(\partial C_{\bar{M},n} / \partial C_{HA}^\circ\right)_{C_{M,n}}$  and  $\left[\partial (SC_{\bar{M},n}) / \partial S\right]_{C_{M,n},C_{HA}^\circ}$  values in the EP (Eqs. (18) and (19)), respectively. Here the weight is related to the slope of the  $C_{\bar{M}}$  vs.  $C_M$  diagram. The balance of the  $\psi(C_{HA}^\circ)$  or  $\psi(S)$  values for the extraction and stripping sections of the ESP determines the trend of the recovery fraction with varying  $C_{HA}^\circ$  or  $S$ , respectively: At the maximum recovery fraction, these values are equal to each other.

On the basis of the monotonically increasing nature of  $\left(\partial C_{\bar{M},n} / \partial C_{HA}^\circ\right)_{C_{M,n}}$  and  $\left[\partial (SC_{\bar{M},n}) / \partial S\right]_{C_{M,n},C_{HA}^\circ}$  with the metal loading ratio in the organic phase, it has been proved, with increasing  $C_{HA}^\circ$  or  $S$ , that (i) the maximum of the recovery fraction never appears when  $N$  or  $N'$  is unity and (ii) the decrease in the recovery fraction after reaching the maximum is much slower than the increase before reaching the maximum when  $N$  and  $N'$  are larger than unity.

#### Nomenclature

$a$	= coefficient in Eq. (6)	[m <sup>3</sup> /(kmol·s)]
$B(C_{M,in})$	= coefficient in Eq. (11) and is defined by Eq. (12)	[—]
$B(S)$	= coefficient in Eq. (11) and is defined by Eq. (14)	[kmol·s/m <sup>6</sup> ]
$b$	= coefficient in Eq. (6)	[m <sup>-3</sup> ]
$C$	= molarity	[kmol/m <sup>3</sup> ]
$C_{HA}^\circ$	= total molarity of HA	[kmol/m <sup>3</sup> ]
$c$	= constant in Eq. (6)	[s <sup>-1</sup> ]
$F$	= flow rate of aqueous phase	[m <sup>3</sup> /s]
$f$	= operating cost per unit time	[s <sup>-1</sup> ]
HA	= monomeric species of extractant	
$K$	= extraction equilibrium constant	[(kmol/m <sup>3</sup> ) <sup>m-lp</sup> ]
$L_n$	= metal loading ratio in organic phase at $n$ th stage defined by Eq. (23)	[—]
$l$	= number of extractant anions in the metal-extractant complex	[—]
M	= metal to be extracted	
$m$	= valency of metal cation	[—]
$N$	= total number of stages	[—]
$n$	= stage number	[—]

$p$	= aggregation order of extractant	[—]
$r$	= ratio of the flow rates defined by $F/S$	[—]
$S$	= flow rate of the organic phase	[m <sup>3</sup> /s]
$T$	= dimensionless time equal to $tF/V_{aq}$	[—]
$t$	= time	[s]
$V_{aq}$	= volume of the aqueous phase in each stage	[m <sup>3</sup> ]
$\alpha_n$	= coefficient in Eq. (8) and is expressed by Eq. (9)	[—]
$\beta(C_{HA}^\circ)_n$	= coefficient in Eq. (8) and is expressed by Eq. (10)	[—]
$\theta$	= coefficient in Eq. (16) and is expressed by Eq. (17)	[—]
$\rho_n$	= relative weight of the $n$ th stage defined by Eq. (20)	[—]
$\psi(C_{HA}^\circ)$	= coefficient in Eq. (16) and is expressed by Eq. (18)	[—]
$\psi(S)$	= coefficient in Eq. (16) and is expressed by Eq. (19)	[kmol/m <sup>3</sup> ]
<Subscript>		
in	= inlet	
'	= stripping section	
<Superscript>		
—	= organic phase species	

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