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Separation of Cobalt and Nickel with Phenylphosphonic Acid Mono-4-*tert*-octylphenyl Ester by Liquid Surfactant Membranes

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ABSTRACT

The separation of cobalt and nickel with liquid surfactant membranes (LSMs) was carried out in a stirred cell using a newly synthesized extractant. The effect of a surfactant on the kinetics of cobalt and nickel extraction was investigated to elucidate the role of a surfactant used in LSMs. The extraction equilibrium of these metals was also examined. Further, the interfacial tension between the organic and aqueous phases was measured to elucidate the adsorption equilibrium of a surfactant. It was found that the interfacial activity of the extractant is as high as that of a surfactant. In the extraction equilibrium study of these metals, extraction equilibrium constants were obtained for cobalt and nickel for the following equations:

$$Co^{2+} + 2(HR)_2 = CoR_2(HR)_2 + 2H^+$$

$$Ni^{2+} + 3(HR)_2 = NiR_22(HR)_2 + 2H^+$$

The effects of the extractant and surfactant on the extraction rate of cobalt and nickel in LSMs were studied. The results were analyzed by a proposed model with an interfacial reaction, and rate constants were obtained for each metal. It was found that the new extractant has a very strong extractability for each metal compared with a conventional commercial extractant such as 2-ethylhexylphos-

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phonic acid mono-2-ethylhexyl ester (commercial name, PC-88A) or di(2-ethylhexyl)phosphoric acid (D2EHPA). Further, a surfactant strongly affected the extraction rate and the separation of these metals, and a cationic surfactant was selected.

INTRODUCTION

As new scientific technology is developed, the demand for advanced materials has increased. In particular, the need for metallic materials has extended from the conventional structural side to the functional side such as for superconductivity and semiconductivity. Therefore, rare metals which possess physically and chemically specific properties will occupy important position in many industries. However, rare metals are very rare, as indicated in the name, and difficult to separate from each other, and therefore it is very important to develop effective recovery processes for them.

Separation and concentration processes of rare metals by liquid membranes have many advantages such as possibilities of selective separation, large-scale treatment, and continuous operation, and have been anticipated for the recycling of industrial resources or energy conservation in the fields of hydrometallurgical and wastewater treatment as an effective and selective separation method. The liquid surfactant membrane (LSM) process was invented by Li in 1968 (1). It has been studied by many investigators because of the advantages of rapid separation and concentration of metal ions through its very thin liquid membrane and large interfacial area, and it has been used in an industrial process to remove zinc from the wastewater at a textile plant in Austria (2).

In the present work, separation of cobalt and nickel ions with LSMs was carried out using acidic organophosphorus extractants. Di(2-ethylhexyl)phosphoric acid (abbreviated D2EHPA), 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (commercial name, PC-88A), and di(2,4,4-trimethylpentyl)phosphinic acid (commercial name, CYANEX272) are typical commercial extractants, and many investigators have studied the extraction behavior of cobalt and nickel by solvent extraction or liquid membranes using these extractants. Komasawa et al. (3–5) investigated solvent extraction of many metals using D2EHPA or PC-88A in several experimental systems and obtained extraction equilibrium constants. Teramoto et al. (6, 7) and Danesi et al. (8, 9) reported the separation of cobalt and nickel by supported liquid membranes using PC-88A or CYANEX272, respectively. In LSMs, Strzelbicki et al. (10, 11) and Gu et al. (12) studied the separation of cobalt and nickel using a commercial carrier such as D2EHPA and a commercial surfactant such as Span 80 or Polyamine.

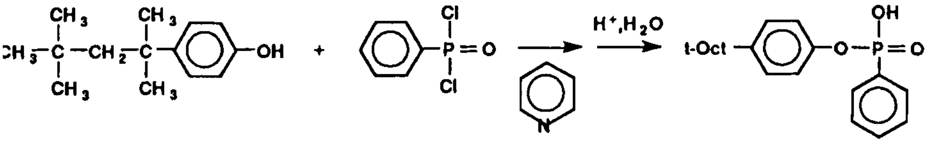
In the LSM system based on solvent extraction, the selection of a carrier (extractant) and surfactant is important because the carrier mainly determines the selectivity of metals and the surfactant affects the extraction rate and the stability of the liquid membrane in the system. We synthesized a new organophosphorus compound, phenylphosphonic acid mono-4-*tert*-octylphenyl ester (4TOPPPA), for the extraction and separation of rare metals. This compound contains two phenyl groups and is expected to have a high potential for the extraction of metals. In previous papers (13–15) we developed new surfactants, and it was confirmed that a derivative of glutamic acid dioleyl ester formed a stable emulsion compared with commercial surfactants. In this work, new cationic surfactants were synthesized for the purpose of effectively separating cobalt and nickel by utilizing the difference in permeation rates of the two ions.

In the present study the extraction equilibrium of cobalt and nickel with the new organophosphorus extractant and the separation of these metals by LSMs were carried out. In addition, measurement of the interfacial tension of the carrier and surfactants was conducted to elucidate their adsorption equilibrium at the interface. In a LSM system the effects of the extractant and surfactant on the extraction rates of cobalt and nickel were investigated. The results obtained were analyzed by the proposed model with an interfacial reaction, and rate constants in LMSs were obtained for each metal.

EXPERIMENTAL

Materials

Figure 1 shows the structure of the carrier and surfactants used. The commercial extractant PC-88A was supplied by Daihachi Chemical Industry Co. Ltd., and D2EHPA was purchased from Tokyo Chemical Industry Co. Ltd. These extractants were used without further purification. 4TOPPPA was synthesized according to the following reaction scheme:



Phenyldichlorophosphine was dissolved in pyridine in an ice bath. *p-tert*-Octylphenol dissolved in pyridine was added dropwise to the solution in a stream of nitrogen. After the reaction, ice and concentrated hydrochloric acid were added to the solution until the pH was about 1, and then the solution was stirred for about a day. After the stirring, benzene was added to the solution and the product was extracted in the benzene phase. The

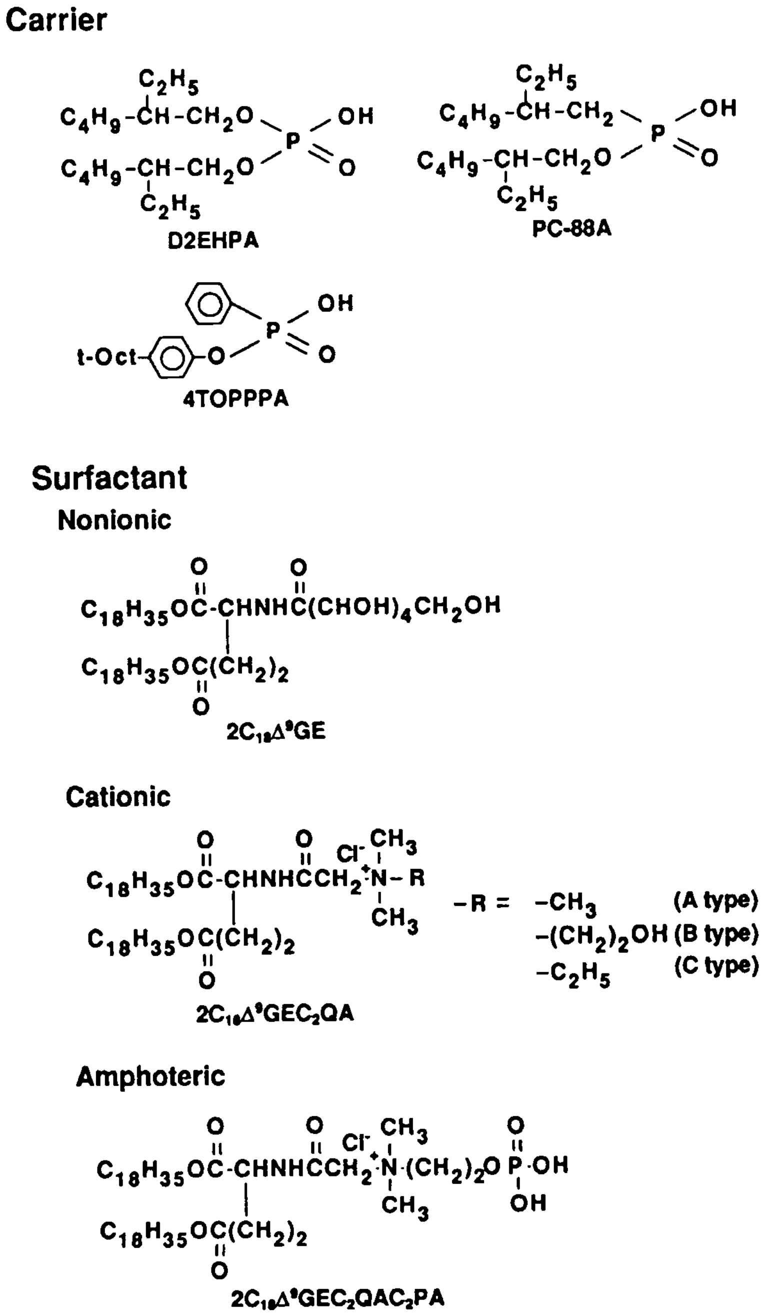


FIG. 1 Molecular structure of carrier and surfactants used.

benzene solution was separated from the aqueous solution and washed with 1000 mol/m^3 hydrochloric acid, and then dried over anhydrous magnesium sulfate after separation from the aqueous solution. The benzene was removed under reduced pressure, and the residue was recrystallized from ethyl acetate. The final product was identified by IR, NMR, and elemental analysis.

L-Glutamic acid dioleyl ester ribitol (abbreviated $2C_{18}\Delta^9GE$) and L-glutamic acid dioleyl ester quaternary ammonium chloride (B) [abbreviated $2C_{18}\Delta^9GEC_2QA(B)$] were synthesized as described in previous papers (13, 15). The preparation method of L-glutamic acid dioleyl ester quaternary ammonium chloride (A) and (C) [abbreviated $2C_{18}\Delta^9GEC_2$-QA(A) and $2C_{18}\Delta^9GEC_2QA(C)$] is approximately as same as that of $2C_{18}\Delta^9GEC_2QA(B)$, and $2C_{18}\Delta^9GEC_2QA(A)$ and $2C_{18}\Delta^9GEC_2QA(C)$ were prepared by adding trimethylamine and dimethylethylamine, respectively, instead of dimethylethanolamine. L-Glutamic acid dioleyl ester quaternary ammonium phosphoric acid (abbreviated $2C_{18}\Delta^9GEC_2$-QAC_2PA, commercial name My Surf 181) delivered by Mitsui Cyanamid Co. Ltd. was used as recieved. Span 80 purchased from Kishida Chemical Co. Ltd. was used without further purification.

Toluene and *n*-heptane were used as the organic diluents for extractants and surfactants. All the other reagents used were of guaranteed reagent grade and were used as received.

Interfacial Tension of Extractant and Surfactants

The aqueous solution was prepared by dissolving hydrochloric acid in deionized water, whereas the organic solution was prepared by weighting the extractant and surfactants in an organic solvent of mixed toluene and *n*-heptane.

Equal volumes of the aqueous and organic solutions of known concentrations were shaken in a flask and allowed to attain equilibrium in a thermostated bath maintained at 303 K, then the solutions were separated. The interfacial tension of the extractant and surfactants with different concentrations of an organic solution and 1000 mol/m^3 hydrochloric acid solution was measured by the drop volume method at 303 K. The specific gravity of both solutions was also measured by a digital densimeter (Paar DMA35).

Extraction Equilibrium of Cobalt and Nickel

An aqueous solution was prepared by dissolving cobalt and nickel nitrate into deionized water. Hydrochloric acid (100 mol/m^3) and glycine (100 mol/m^3) were used to maintain the pH and the ionic strength. An organic solution was prepared as mentioned above. Toluene was used as an organic solvent.

After both the aqueous and organic solutions attained an equilibrium state, the solutions were separated and each was analyzed for its metal content. The concentration of cobalt and nickel in the aqueous solution was determined directly by atomic absorption spectrophotometry (SEIKO Model SAS-760).

Extraction of Cobalt and Nickel by LSM

The experimental apparatus used for metal extraction with a LSM is a batch-type stirred cell equipped with four glass baffles. The inner diameter and the depth of the tank were 10 and 15 cm, respectively. Stirring was carried out using a turbine impeller having six flat blades and a speed controller. A W/O emulsion was made from equal volumes of the two immiscible solutions listed in Table 1 by stirring at 13,500 rpm for 120 seconds in a large test tube. A measured volume of this emulsion was then added to the third phase in the vessel (the feed aqueous solution containing cobalt and nickel), and was stirred at 300 rpm. The vessel was placed in a bath through which water maintained at 303 K was circulated. Samples of about 3–4 cm^3 were taken at intervals. After several phases in the samples were separated, the concentrations of cobalt and nickel in the feed solution were determined by atomic absorption spectrochemical analysis. Dioxane was added to the emulsion phase separated from the feed solution until the emulsion phase became homogeneous, and the volume of an internal aqueous solution in the emulsion phase was determined by the Karl-Fisher method (MCI Model CA-05). The detailed conditions of the experiment by LSMs are listed in Table 1.

TABLE 1
Experimental Conditions for Metal Extraction by LSM

Internal aqueous phase	$V_{i,0}$ = 50 mL
	C_H = 1000 mol/m^3
Organic phase	V_{org} = 50 ml
	C_{HR} = 10–30 mol/m^3
	C_{sf} = 10–30 mol/m^3
External aqueous phase	$V_{e,0}$ = 700 ml
	C_{Co} = 2 mol/m^3
	C_{Ni} = 2 mol/m^3
	pH = 3.0
Stirring speed	300 rpm
Temperature	303 K

RESULTS AND DISCUSSION

Interfacial Tension of Extractant and Surfactants

The relation between an interfacial tension and concentration of extractant or surfactants is shown in Figs. 2a and 2b. It was found that all surfactants used in this study have interfacial activity, and that the extractant of 4TOPPPA also has interfacial activity, although the interfacial tension of the extractant is small compared with that of the surfactants. These results suggest that the permeation model in LSM must take into account the interfacial activity of the surfactant and extractant at the surface of an emulsion.

The adsorption equilibrium of the surfactant is expressed as

$$Sf_{\text{org}} = Sf_{\text{ad}}, \qquad K_{\text{Sf}} \tag{1}$$

where K_{Sf} is the adsorption equilibrium constant of a surfactant, and Sf and the subscript ad denote the surfactant and the adsorption state at the interface, respectively. The relation between interfacial tension and the amount of surfactant adsorbed at the interface is expressed by Gibbs' adsorption equation. Assuming a Langmuir adsorption isotherm between the amount of surfactant adsorbed and the bulk concentration of surfactant, C_{Sf}, the relation between interfacial tension, γ, and C_{Sf} at temperature T is expressed as

$$\gamma = \gamma_0 - (RT/S_{\text{Sf}}) \ln(1 + K_{\text{Sf}}C_{\text{Sf}}) \tag{2}$$

where γ_0 is the interfacial tension between an organic solvent and an aqueous solution, R is the gas constant, and S_{Sf} is the interfacial area occupied by a unit mole of the surfactant. The values of K_{Sf} and S_{Sf} can be obtained from the experimental results for the interfacial tension and Eq. (2) by the nonlinear regression method. The results are shown in Table 2. The solid curves in Fig. 2 are calculated by Eq. (2) by using the constants obtained above.

Extraction Equilibrium of Cobalt and Nickel

Many investigations of the extraction of cobalt and nickel with an acidic organophosphorus extractant have been carried out for several systems (3–7). It is well known that cobalt is extracted by forming a regular tetrahedral complex with an extractant, while nickel is extracted by forming an octahedral complex with an extractant. Komasawa et al. (3–5) reported that the extraction species of cobalt and nickel by PC-88A or D2EHPA [abbreviated HR, where $(HR)_2$ is a dimer of extractant] are $CoR_2(HR)_2$ and $NiR_22(HR)_2$ respectively.

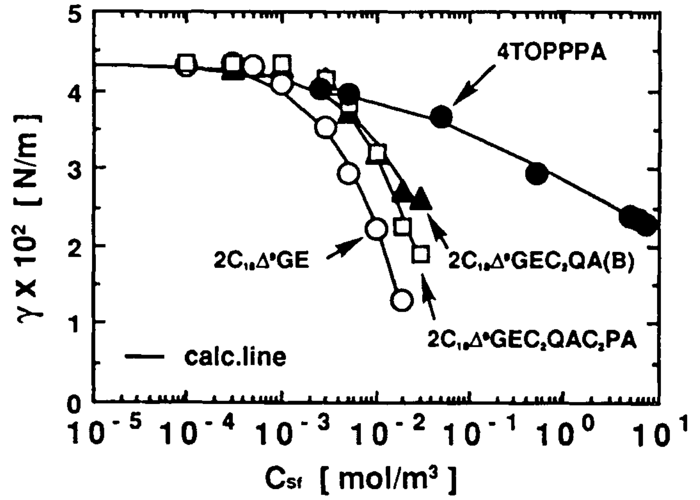


FIG. 2a Relation between interfacial tension and concentration of surfactants (aqueous phase: HCl 1000 mol/m^3; organic phase: solvent toluene:n-heptane = 1:4).

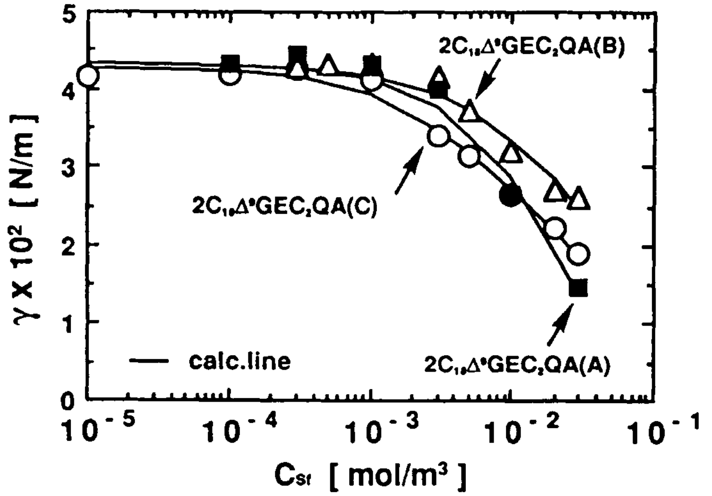


FIG. 2b Relation between interfacial tension and concentration of cationic surfactants (aqueous phase: HCl 1000 mol/m^3; organic phase: solvent toluene:n-heptane = 1:4).

TABLE 2
Adsorption Equilibrium Constant and Interfacial Area Occupied by Unit Mole of Each Surfactant in Organic Solvent of Mixed Toluene and *n*-Heptane

Surfactant	K_j (m^3/mol)	S_j (m^2/mol)
4TOPPPA (dimer)	5.0×10^1	8.8×10^5
$2C_{18}\Delta^9$GE	1.5×10^2	1.2×10^5
$2C_{18}\Delta^9GEC_2QA$ (A)	9.3×10^1	1.2×10^5
$2C_{18}\Delta^9GEC_2QA$ (B)	1.3×10^2	2.3×10^5
$2C_{18}\Delta^9GEC_2QA$ (C)	5.0×10^2	3.0×10^5
$2C_{18}\Delta^9GEC_2QAC_2PA$	5.6×10^1	1.0×10^5

We confirmed that the extractant of 4TOPPPA exists as a dimer in such a nonpolar solvent by vapor-phase osmometry (Corona 117 type). Therefore, it was anticipated that the extraction equilibrium of cobalt and nickel with 4TOPPPA is as same as that with PC-88A or D2EHPA, as shown in the following equations:

$$Co^{2+} + 2(HR)_2 = CoR_2(HR)_2 + 2H^+, \quad K_{ex,Co} \tag{3}$$

$$Ni^{2+} + 3(HR)_2 = NiR_22(HR)_2 + 2H^+, \quad K_{ex,Ni} \tag{4}$$

$K_{ex,M}$ is the extraction equilibrium constant and is written as

$$K_{ex,M} = C_{MR2(m-1)(HR)2} \cdot C_H^n / (C_M \cdot C_{(HR)2}^m) \tag{5}$$

where C_j is the concentration of species j, $n = 2$, and $m = 2$ for cobalt and $m = 3$ for nickel. The distribution ratio of metal, D_M, is defined by Eq. (6), and Eq. (7) is obtained from Eqs. (5) and (6):

$$D_M = C_{MR2(m-1)(HR)2} / C_M \tag{6}$$

$$\log D_M = \log C_{(HR)2}^m / C_H^n + \log K_{ex,M} \tag{7}$$

According to Eq. (7), when the relation between log D_M and log $C_{(HR)2}$ is plotted, straight lines with a slope of 2 for cobalt and 3 for nickel will be obtained. The slope of the straight lines was -2 for both metals with respect to the relation between log D_M and log C_H. From these results it was confirmed that Eqs. (3) and (4) are correct. The experimental results according to Eq. (7) are shown in Fig. 3. Straight lines with a slope of 1 were obtained for each metal, from which the $K_{ex,M}$ values were obtained for each. The results are listed in Table 3, and the solid curves shown in Fig. 3 were calculated by Eq. (7) using the above constants. The values of K_{ex} using PC-88A or D2EHPA are also listed in the same table.

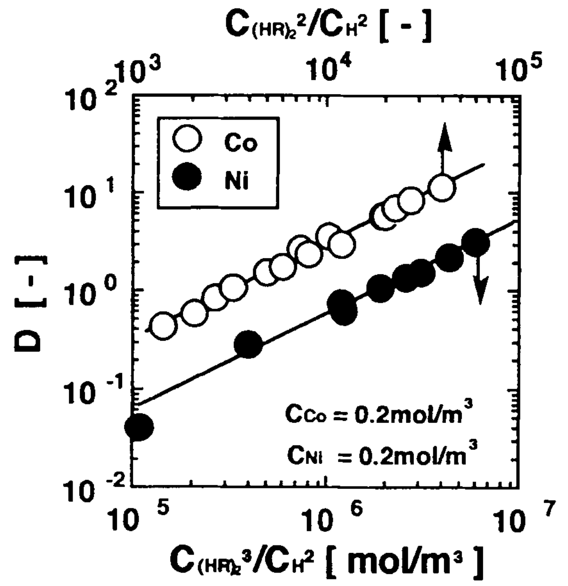


FIG. 3 Relation between distribution ratio of metal and $C_{(HR)_2}^{3}/C_{H}^{2}$ (aqueous phase: Co 0.2 mol/m³, Ni 0.2 mol/m³, HCl + glycine 100 mol/m³; organic phase: solvent toluene, extractant 4TOPPPA).

4TOPPA has a higher potential for the extraction of cobalt and nickel than do PC-88A or D2EHPA.

Permeation Mechanism of Metal Ion through LSM

Figure 4 shows the permeation mechanism of cobalt and nickel with LSM containing an acidic organophosphorus extractant as a carrier. Cobalt and nickel ions form an oil-soluble complex with the extractant at Interface 1. The complexes diffuse to Interface 2 through the liquid membrane, and are stripped at Interface 2 by hydrogen ions whose concentra-

TABLE 3
Equilibrium Constants of Metal Extraction in Toluene

Extractant	$K_{ex,Co}$ (—)	$K_{ex,Ni}$ (m³/mol)
4TOPPPA	3.2×10^{-4}	3.1×10^{-7}
D2EHPA	1.2×10^{-5}	2.5×10^{-9}
PC-88A	5.4×10^{-7}	

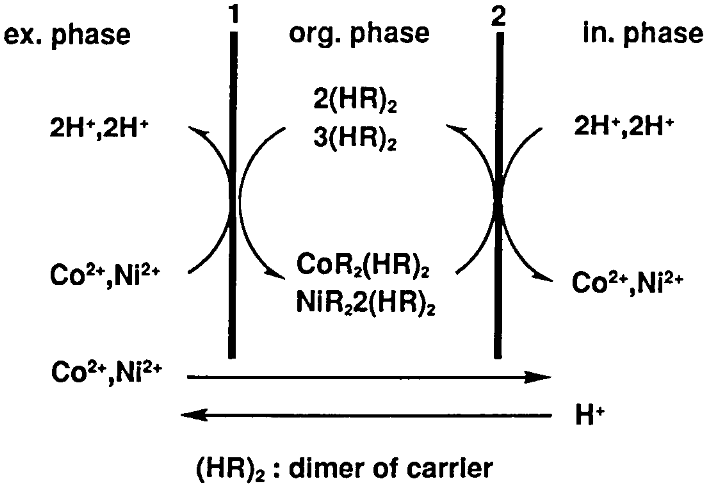


FIG. 4 Schematic permeation mechanism of metal with LSM.

tion is very high. In conclusion, cobalt and nickel are separated at Interface 1 and are concentrated in the internal aqueous phase.

Extraction of Cobalt and Nickel by LSM

The extraction of cobalt and nickel by LSM using several carriers was conducted in toluene as a diluent. The results are shown in Fig. 5. These metals are not extracted by PC-88A or D2EHPA under the following conditions: the carrier concentration is 20 mol/m^3, the concentration of $2C_{18}\Delta^9$GE is 20 mol/m^3, and the operation time is 900 seconds. Only cobalt is extracted to about 40% by 4TOPPPA. 4TOPPPA is excellent for cobalt extraction in the LSM because the extraction equilibrium constant of 4TOPPPA to cobalt is very large compared to that of commercial extractants.

It is well known that in LSM an organic solvent as a liquid membrane affects the permeation rate of metals. In previous papers we found that *n*-heptane as an aliphatic solvent is better than toluene as an aromatic one with regard to the breakup and swelling of a W/O emulsion, the enrichment of copper, and the demulsification rate (16, 17). Kinugasa et al. (18) reported that a longer aliphatic hydrocarbon stabilizes the W/O emulsion and an aromatic one is unstable in comparison to it because of a difference in such properties of the membrane solvent as viscosity. However, 4TOPPPA as a carrier is only slightly dissolved in *n*-heptane. Therefore, a mix-

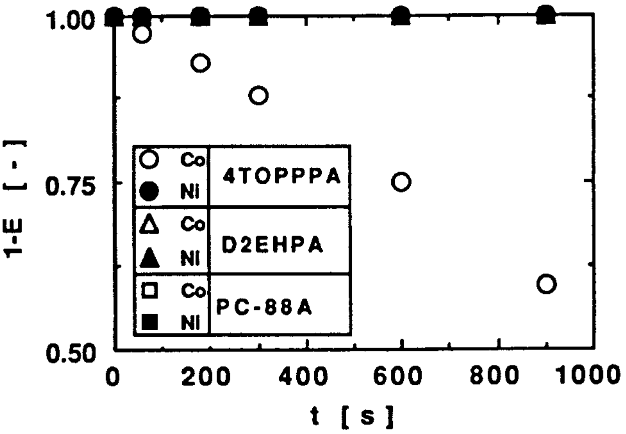


FIG. 5 Effect of carrier on metal extraction by LSM (aqueous phase: Co 2 mol/m^3, Ni 2 mol/m^3, pH 3.0; organic phase: solvent toluene, carrier 20 mol/m^3, 2C$_{18}\Delta^9$GE 20 mol/m^3).

ture of *n*-heptane and toluene was used as the membrane solvent. Figure 6 shows the effect of an organic solvent on the extraction of metals. The extraction rate of each metal is accelerated by adding *n*-heptane to toluene.

It is well known that the surfactant plays an important role in the LSM process. Many investigations using a commercial surfactant have been

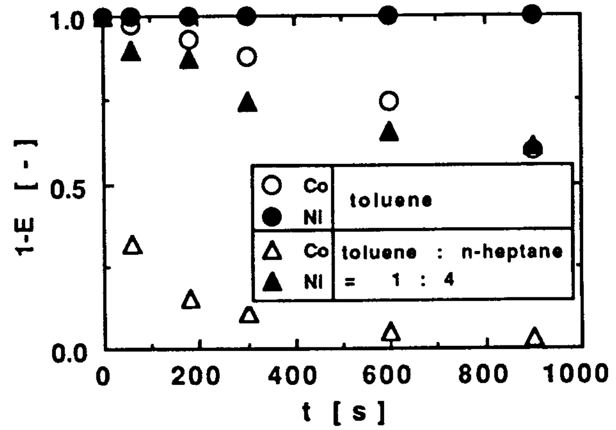


FIG. 6 Effect of organic solvent on metal extraction by LSM (aqueous phase: Co 2 mol/m^3, Ni 2 mol/m^3, pH 3.0; organic phase: 4TOPPPA 20 mol/m^3, 2C$_{18}\Delta^9$GE 20 mol/m^3).

carried out with respect to the breakup, the swelling, and the permeation rate of metals (19–22). Mikucki et al. (20, 21) reported that there was an optimum value in the surfactant concentration with respect to the stability of the emulsion and the kinetics of metal extraction, and that the value changed widely with the type of surfactant used. In previous papers (15, 23, 24) we synthesized several new surfactants and studied their role in LSMs. From those investigations it was found that an anionic or amphoteric surfactant accelerates the extraction of copper and a cationic one accelerates the extraction of zinc or rare earth metals. Figure 7a shows the effect of the kinds of surfactants on the extraction rate of cobalt and nickel. When a cationic or amphoteric surfactant is used as an emulsifier, the extraction rates of both cobalt and nickel are accelerated compared with a nonionic surfactant. In particular, the extraction rate of nickel increases considerably by using an amphoteric surfactant. It is believed that the acceleration of the metal extraction is caused by an enrichment effect of the carrier and the promotion of acid dissociation of the carrier because of an electrostatic interaction between the cationic surfactant and the anionic carrier at the interface. The extraction rate of nickel, which is extracted slowly, is significantly accelerated by using an amphoteric surfactant because of electrostatic interaction between a metal ion and a hydrophilic phosphoric group of the surfactant. Figure 7b shows the effect of the hydrophilic structure in a cationic surfactant on the extraction rate of cobalt and nickel. It was found that the extraction rate of metals when using an A-type cationic surfactant is lower than that when using a B- or C-type cationic surfactant. The adsorption equilibrium constant of an A-type cationic surfactant was found to be smaller than that of a B- or C-type cationic surfactant. Therefore, it is assumed that the difference in the extraction rate is caused by the difference of the concentration effect of the carrier at the interface. A more detailed study is now under way.

Figure 8 shows the effect of the carrier concentration on the extraction of metals. As the carrier concentration increases, the extraction rate of metals increases.

The concentration change of each metal ion in the stirred tank with time is shown by the following equation:

$$-dC_{\mathrm{Co}}/dt = a(1/k_{\mathrm{Co}} + \alpha_{\mathrm{H}}^{2}/k'_{\mathrm{f,Co}})^{-1}C_{\mathrm{Co}} \tag{8}$$

$$-dC_{\mathrm{Ni}}/dt = a(1/k_{\mathrm{Ni}} + \alpha_{\mathrm{H}}^{2}/k'_{\mathrm{f,Ni}})^{-1}C_{\mathrm{Ni}} \tag{9}$$

where $a\ [= (V_{\mathrm{E}}/V_{\mathrm{e}})(6/d_{\mathrm{E}})]$ is the specific interfacial area, k_{M} is the mass transfer coefficient of a metal in the external aqueous phase side, $k'_{\mathrm{f,M}}$ is the observed rate constant of a metal at the external interface of the emulsion globule, V_{E} and V_{e} are the volumes of emulsion and external aqueous

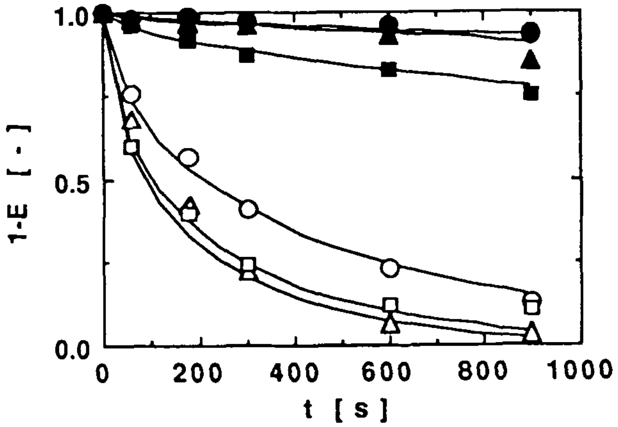


FIG. 7a Effect of surfactant on metal extraction by LSM [aqueous phase: Co 2 mol/m^3, Ni 2 mol/m^3, pH 3.0; organic phase: 4TOPPPA 10 mol/m^3, surfactant 10 mol/m^3; (○) Co (●) Ni $2C_{18}\Delta^9GE$, (△) Co (▲) Ni $2C_{18}\Delta^9GEC_2QA$ (B), (□) Co (■) Ni $2C_{18}\Delta^9GEC_2QAC_2PA$].

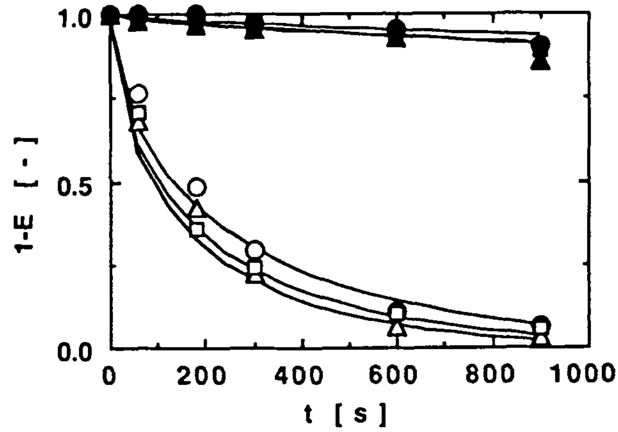


FIG. 7b Effect of cationic surfactant on metal extraction by LSM [aqueous phase: Co 2 mol/m^3, Ni 2 mol/m^3, pH 3.0; organic phase: 4TOPPPA 10 mol/m^3, surfactant 10 mol/m^3; (○) Co (●) Ni $2C_{18}\Delta^9GEC_2QA$ (A), (△) Co (▲) Ni $2C_{18}\Delta^9GEC_2QA$ (B), (□) Co (■) Ni $2C_{18}\Delta^9GEC_2QA$ (C)].

solutions, respectively, d_E is the diameter of the emulsion globule, and α_H is the activity of the hydrogen ion. If the change of the activity coefficient of the hydrogen ion, γ_H, is small, the following equation is obtained from the mass balance of hydrogen ion activity in the external solution:

$$-d\alpha_H/dt = -2\gamma_H(dC_{Co}/dt + dC_{Ni}/dt) \qquad (10)$$

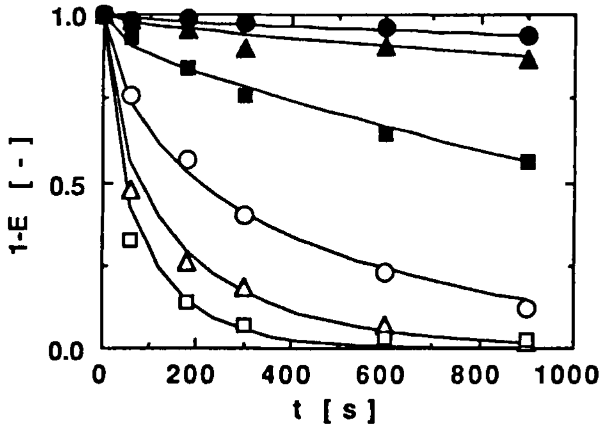


FIG. 8 Effect of carrier concentration on metal extraction by LSM [aqueous phase: Co 2 mol/m^3, Ni 2 mol/m^3, pH 3.0; organic phase: carrier 4TOPPPA, 2C$_{18}\Delta^9$GE 10 mol/m^3; (○) Co (●) Ni 10 mol/m^3, (△) Co (▲) Ni 14 mol/m^3, (□) Co (■) Ni 20 mol/m^3].

In this experimental condition, emulsion swelling takes place because the concentration of electrolytes in the internal aqueous solution is higher than that in the external aqueous solution. Actually, the swelling rate of an emulsion increases as the concentration of the carrier or surfactant is increased. Therefore, the time dependence of each phase volume has to be considered. Assuming that the permeation rate of water through the liquid membrane is proportional to the difference of electrolyte concentration between the internal and external solutions, the swelling rate of the emulsion globules is expressed as

$$dY/dt = (1/V_{i,0})(dV_i/dt) = k_w\ (C_{el,i} - C_{el,e}) \tag{11}$$

where Y is the swelling ratio expressed by the normalized volume of the internal aqueous solution, k_w is the swelling factor defined by Eq. (11), and the subscript el denotes electrolytes. The values of k_w were determined for each condition by using Eq. (11).

Assuming that the activity coefficient of the hydrogen ion is 1, the value of d_E is constant and the value of k_M is 1.1×10^{-5} m/s (7). From the experimental results, $k'_{f,M}$ can be evaluated by analyzing Eqs. (8)–(11) using the Runge–Kutta–Gill method. Figure 9 shows the relation between $k'_{f,M}$ and the dimer concentration of the carrier. $k'_{f,Co}$ and $k'_{f,Ni}$ show a second-order and a third-order dependence on the dimer concentration of the carrier, respectively.

Figure 10 shows the relation between $k'_{f,M}$ and the surfactant concentration. It was found that both $k'_{f,Co}$ and $k'_{f,Ni}$ decrease gradually as the surfac-

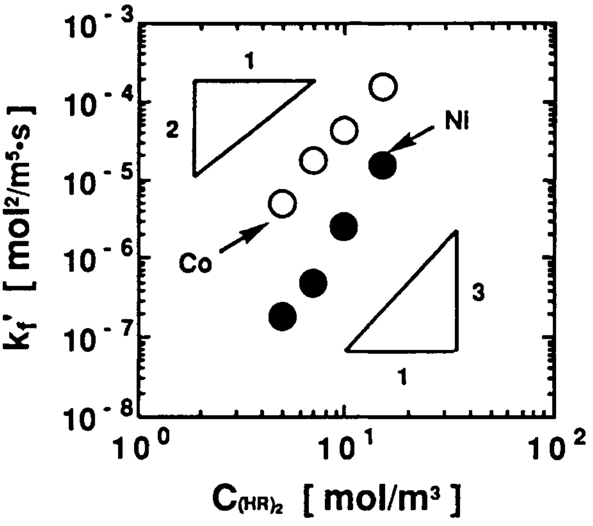


FIG. 9 Relation between $k'_{f,M}$ and $C_{(HR)_2}$ (aqueous phase: Co 2 mol/m^3, Ni 2 mol/m^3, pH 3.0; organic phase: carrier 4TOPPPA, 2C$_{18}\Delta^9$GE 10 mol/m^3).

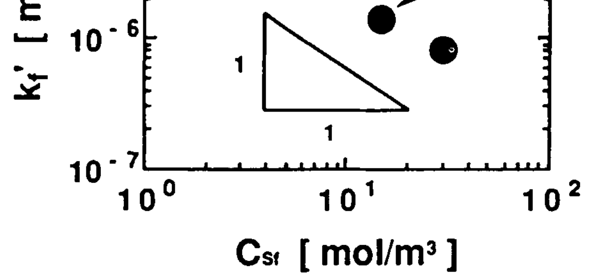


FIG. 10 Relation between $k'_{f,M}$ and C_{sf} (aqueous phase: Co 2 mol/m^3, Ni 2 mol/m^3, pH 3.0; organic phase: 4TOPPPA 20 mol/m^3, surfactant 2C$_{18}\Delta^9$GE).

tant concentration increases, and they show a negative first-order dependence on the surfactant concentration. The decrease of the extraction rate is due to the coating effect of the reaction interface by the surfactant.

The values of $k'_{f,M}$ evaluated from the results in Figs. 7a and 7b are listed in Table 4. Among the three kinds of cationic surfactants, the value of $k'_{f,M}$ using an A-type cationic surfactant is the lowest. This result is interesting, for the value of K_{Sf} using an A-type cationic surfactant is lower than that using a B- or C-type cationic surfactant. It is assumed that the concentration of the extractant at the interface increases because of the interaction between the extractant and the cationic surfactant, and that it depends on the concentration of the cationic surfactant at the interface. Therefore, the extraction mechanism for a cationic surfactant will be very complex. By using an amphoteric or a cationic surfactant, the value of $k'_{f,Co}$ increases. However, the separation factor of cobalt and nickel decreases because of the considerable increment of $k'_{f,Ni}$.

Extraction Mechanism of Cobalt And Nickel

The observed rate constants of cobalt and nickel show a second-order and third-order dependence on the dimer concentration of 4TOPPPA, respectively, while they showed a negative first-order dependence on the concentration of the surfactant, $2C_{18}\Delta^9GE$. Therefore, the extraction mechanism at the surface of the emulsion globules (Interface 1) is

$$(HR)_{2org} = (HR)_{2ad}, \qquad K_{(HR)2} \tag{12}$$

$$Sf_{org} = Sf_{ad}, \qquad K_{Sf} \tag{13}$$

$$Co^{2+} + (HR)_{2ad} = CoR_{2ad} + 2H^+, \qquad K_{1,Co} \tag{14}$$

$$CoR_{2ad} + (HR)_{2org} = CoR_2(HR)_{2org}, \qquad k''_{f,Co}/k_{r,Co} \tag{15}$$

$$Ni^{2+} + (HR)_{2ad} = NiR_{2ad} + 2H^+, \qquad K_{1,Ni} \tag{16}$$

$$NiR_{2ad} + (HR)_{2org} = NiR_2(HR)_{2ad}, \qquad K_{2,Ni} \tag{17}$$

$$NiR_2(HR)_{2ad} + (HR)_{2org} = NiR_22(HR)_{2org}, \qquad k''_{f,Ni}/k_{r,Ni} \tag{18}$$

TABLE 4
Apparent Interfacial Reaction Rate Constants for Metal Extraction by LSM

Surfactant	$k'_{f,Co}$ (mol^2/m^5·s)	$k'_{f,Ni}$ [mol^2/m^5·s]	$\beta_{Co/Ni}$ (—)
$2C_{18}\Delta^9GEC_2QA$ (A)	8.4×10^{-6}	1.9×10^{-7}	44
$2C_{18}\Delta^9GEC_2QA$ (B)	1.4×10^{-5}	3.0×10^{-7}	47
$2C_{18}\Delta^9GEC_2QA$ (C)	1.2×10^{-5}	3.0×10^{-7}	40
$2C_{18}\Delta^9GEC_2QAC_2PA$	1.3×10^{-5}	9.1×10^{-7}	14

where $K_{1,\mathrm{M}}$ is the formation constant expressed by Eq. (14) for cobalt and Eq. (16) for nickel, $K_{2,\mathrm{M}}$ is the same one expressed by Eq. (17), and $k''_{\mathrm{f,M}}$ or $k_{\mathrm{r,M}}$ is the forward or the reverse reaction rate constant, respectively. Assuming that Eq. (15) for cobalt and Eq. (18) for nickel are the rate-determining steps, the interfacial reaction rate, r, is written as follows:

$$r = \sigma_{\mathrm{ad}}^{-1}(k_{\mathrm{f,M}}(K_{\mathrm{(HR)2}}/S_{\mathrm{(HR)2}})C^{m}_{\mathrm{(HR)2org}}C_{\mathrm{M}}/C^{2}_{\mathrm{H}} - k_{\mathrm{r,M}}C_{\mathrm{MR2(m-1)(HR)2org}}) \tag{19}$$

$$\sigma_{\mathrm{ad}} = 1 + K_{\mathrm{(HR)2}}C_{\mathrm{(HR)2org}} + K_{\mathrm{MR2}}C_{\mathrm{MR2org}} + (m-2)\,K_{\mathrm{MR2(HR)2}}C_{\mathrm{MR2(HR)2org}} + K_{\mathrm{s}}C_{\mathrm{Sorg}} \tag{20}$$

where σ_{ad} is the lumped term representing the adsorption characteristics of the extractant, the metal complex, and the surfactant, and m is 2 and 3 for cobalt and nickel, respectively. The third and fourth terms are considerably smaller than the first, second, and fifth terms on the right-hand side of Eq. (20). Assuming that the stripping rate is extremely fast compared with the extraction rate at the external interface of emulsion globules (14), and that the amount of carrier in the liquid membrane can be considered to be almost constant at the initial concentration, Eq. (19) is rewritten

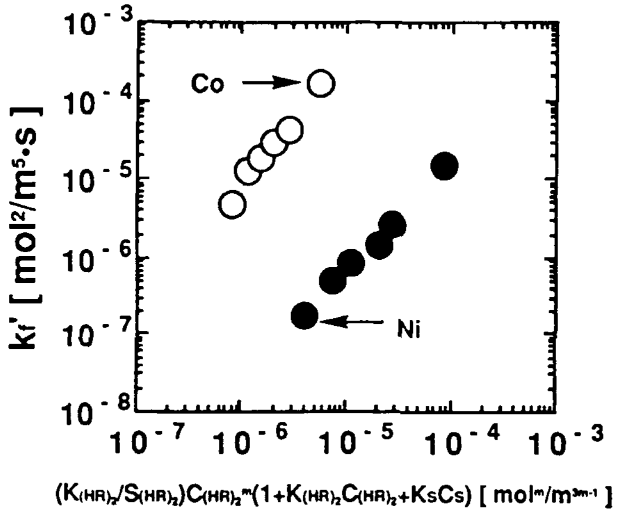


FIG. 11 Determination of $k_{\mathrm{f,M}}$ in Eq. (22) (aqueous phase: Co 2 mol/m^3, Ni 2 mol/m^3, pH 3.0; organic phase: carrier 4TOPPPA, surfactant $2\mathrm{C}_{18}\Delta^{9}\mathrm{GE}$).

as

$$r = k_{f,M}(K_{(HR)2}/S_{(HR)2})\, C^{m}_{(HR)2org} C_M / C^2_H / (1 + K_{(HR)2}C_{(HR)2org} + K_s C_{sorg}) \quad (21)$$

An apparent interfacial reaction rate constant, $k'_{f,M}$, previously defined by Eqs. (8) and (9), can be expressed as a function of the concentration of 4TOPPPA dimer and surfactant as follows:

$$k'_{f,M} = k_{f,M}(K_{(HR)2}/S_{(HR)2})\, C^{m}_{(HR)2org}/(1 + K_{(HR)2}C_{(HR)2org} + K_s C_{sorg}) \quad (22)$$

The relation between $k'_{f,M}$ and the right hand side of Eq. (22) is shown in Fig. 11. From these experimental results, the overall rate constant, $k_{f,M}$, for $2C_{18}\Delta^9GE$ can be evaluated as follows: $k_{f,Co} = 1.5 \times 10^1$ s^{-1}, $k_{f,Ni} = 7.9 \times 10^{-2}$ m^3/mol·s. However, when an ionic surfactant was used, the interfacial reaction mechanism was more complex. A detailed study is under way.

CONCLUSION

Using 4TOPPPA as a carrier and several synthesized surfactants, the separation of cobalt and nickel ions with LSMs was carried out and the following information was obtained.

Measurements of the interfacial tensions of 4TOPPPA and surfactants were carried out, and their adsorption equilibrium constants were obtained. The new carrier, 4TOPPPA, was surface active.

The extraction equilibria of cobalt and nickel with 4TOPPPA, D2EHPA, and PC-88A were examined, and the extraction equilibrium constants for each extractant were obtained. 4TOPPPA has a larger potential for metal extraction than does D2EHPA or PC-88A.

The extraction rate of cobalt and nickel with LSMs was explained by an interfacial reaction model taking into account the adsorption of a surfactant and 4TOPPPA at the interface. A cationic or amphoteric surfactant accelerated the extraction rate of metals compared with a nonionic surfactant.

NOMENCLATURE

a	interfacial area defined by $(V_E/V_e)(6/d_E)$ (m^{-1})
C_j	concentration of species j (mol/m^3)
D_M	distribution ratio of metal (—)
d_E	diameter of emulsion globule (m)

$K_{1,\mathrm{M}}$	equilibrium constant of reaction expressed by Eq. (14) or (16) (mol/m^3)
$K_{2,\mathrm{M}}$	equilibrium constant of reaction expressed by Eq. (17) (m^3/mol)
$K_{\mathrm{ex,M}}$	equilibrium constant of metal extraction (for cobalt) (—) (for nickel) (m^3/mol)
K_j	adsorption equilibrium constant of species j (m^3/mol)
$k_{\mathrm{f,M}}$	interfacial reaction rate constant (for cobalt) (s^{-1}) (for nickel) (m^3/mol·s)
$k'_{\mathrm{f,M}}$	apparent interfacial reaction rate constant defined by Eq. (8) or (9) (mol^3/m^5·s)
$k''_{\mathrm{f,M}}$	rate constant of forward reaction expressed by Eq. (15) or (18) (m^3/mol·s)
k_{M}	mass transfer coefficient of metal (m/s)
$k_{\mathrm{r,M}}$	rate constant of reverse reaction expressed by Eq. (15) or (18) (m/s)
k_{W}	swelling factor defined by Eq. (11) (m^3/mol·s)
R	gas constant (N·m/mol·K)
r	extraction rate (mol/m^2·s)
S_j	interfacial area occupied by unit mole of species j (m^2/mol)
T	temperature (K)
t	time (s)
V	volume of solution (m^3)
Y	normalized volume of internal aqueous solution (—)
α_{H}	activity of hydrogen ion (mol/m^3)
β	separation factor defined by $k'_{\mathrm{f,Co}}/k'_{\mathrm{f,Ni}}$ (—)
γ	interfacial tension (—)
γ_{H}	activity coefficient of hydrogen ion (N/m)

Subscripts

ad	adsorption state
aq	aqueous phase
Co	cobalt ion
E	emulsion phase
e	external aqueous solution
el	electrolyte
H	hydrogen ion
HR	monomer of extractant
$(\mathrm{HR})_2$	dimer of extractant
i	internal aqueous solution
j	species

M	metal
$MR_2(m-1)(HR_2)$	metal–extractant complex
Ni	nickel ion
0	initial value
org	organic phase
Sf	surfactant

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