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Separation of Cobalt and Nickel by Liquid Surfactant Membranes Containing a Synthesized Cationic Surfactant

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ABSTRACT

Separation of cobalt(II) and nickel(II) by using a hydroxyoxime extractant has been investigated both in liquid–liquid extraction and in a liquid surfactant membrane (LSM) system. In the liquid–liquid equilibrium extraction studies, hydroxyoximes showed significant extractability for nickel ions, although LIX 84 was found to have exceptional chelating affinity for nickel ions. In the LSM system functionalized by hydroxyoxime, the cobalt ions were efficiently separated from nickel ions as a result of slower permeation of nickel chelates across the emulsion membrane. More complete cobalt recovery was achieved in the LSMs dosed with LIX 860 than when the same carrier was applied to the liquid–liquid extraction system. Furthermore, cobalt permeation rate was enhanced threefold when a quaternary ammonium type of cationic surfactant was used as an emulsifier due to carrier interaction with surfactant at the reaction interface. The permeation mechanism of ions in LSMs was elucidated by an interfacial reaction model which took into account the adsorption of the carrier and surfactant at the reaction interface.

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INTRODUCTION

The need to develop efficient metal recovery processes for rare metals has become extremely necessary to industry owing to diminishing metal resources and environmental pollution control measures. Solvent extraction processes are among the most widely used techniques for the recovery of metal ions, and a huge collection of published research work is available. Although extensive studies on the extraction of cobalt and nickel have been conducted (1–3), in most of these studies either an organophosphorus compound such as di(2-ethylhexyl)phosphoric acid (D2EHPA) or 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC-88A) has been used as an extractant. Studies which have utilized hydroxyoxime extractants are relatively few. The extraction rate of nickel ions with a hydroxyoxime extractant is known to be very slow, therefore it is necessary to introduce an advanced extraction system to improve on the rate. A liquid surfactant membrane (LSM) process is an attractive technique because of faster extraction and stripping kinetics facilitated by a huge reaction interfacial area.

Many investigations concerning metal extraction with LSMs have been performed since the invention of LSM by Li in 1968 (4). Because an LSM has a thin membrane and a large interfacial area constituting a reaction interface between metal ions and an extractant, a rapid extraction rate of metal ions is realizable. Strzelbicki and Charewicz (5, 6) studied the separation of cobalt by LSMs using several commercial extractants and surfactant, and achieved satisfactory permeation rates of cobalt. Gu et al. (7) investigated the ligand-accelerated effect of cobalt extraction by LSMs containing D2EHPA and polyamine, and reported that rapid extraction of cobalt was achieved by adding acetate to the feed solution. However, in most research, conventional commercial surfactants have been used and little attention has been paid to the effect of surfactants on the performance of extractants.

In a previous study (8) we performed the separation of cobalt and nickel by LSMs containing phenylphosphonic acid mono-4-*tert*-octylphenyl ester as a novel carrier. The carrier is more selective for cobalt ions than commercial carriers such as D2EHPA and PC-88A. Furthermore, an acceleration effect was observed in the extraction of zinc or rare earth metals with PC-88A by LSMs (9, 10). The LSM technique may be effectively adapted to the extraction of cobalt ions by using a hydroxyoxime extractant.

In the present work, commercial hydroxyoxime extractants LIX65N, LIX84, and LIX860 were used as mobile carriers for the separation of cobalt and nickel ions in LSMs; these extractants have similar functional groups but their hydrophobic parts are a little different from each other. Further, these extractants are chelate reagents developed to extract copper ions efficiently from lower pH feed solutions, and they also have the potential to extract

various metal ions at different pH values. Our aim of this study was to establish an efficient separation system of cobalt and nickel using LSMs. First, equilibrium extraction experiments were performed by varying the pH and extractant concentration with a view to determine the reaction stoichiometry between metal ions and the extractants. Second, permeation experiments for cobalt and nickel in LSMs were carried out under various operating conditions, and the effect of the synthesized cationic surfactants on metal extraction was investigated using three different quaternary ammonium types of surfactants. Finally, the permeation mechanism of cobalt and nickel in LSMs was elucidated by an interfacial reaction model which took into account the adsorption of the carrier and surfactant.

EXPERIMENTAL

Materials

Three different commercial extractants, LIX 65N, LIX 84, and LIX 860 (Fig. 1), supplied by Henkel Hakusui Co. Ltd. (Japan), were used without further purification. The surfactants shown in Fig. 1 were synthesized as described in previous papers (8, 9, 11). L-Glutamic acid dioleyl ester quaternary ammonium phosphoric acid (abbreviated $2C_{18}\Delta^9GEC_2QAC_2PA$, commercial name My Surf 181) was supplied by Mitsui Cytec Co. Ltd. Analytical grade *n*-heptane was used as the organic diluent. All other reagents used were of guaranteed reagent grade and were used as received.

Extraction Equilibrium of Cobalt and Nickel

Aqueous solutions containing cobalt and nickel ions were prepared by dissolving their metal nitrates in deionized water. The pH and ionic strength in the aqueous solutions were adjusted using acetic acid and sodium acetate. Organic solutions were prepared by dissolving each extractant into *n*-heptane. Equal volumes of the aqueous and organic solutions were shaken in a glass vial immersed in a thermostatically controlled water bath (303 K), and allowed to reach equilibrium. After about 4 days the aqueous and organic phases were separated, and the concentrations of cobalt and nickel were determined by an atomic absorption spectrophotometer (SEIKO, SAS-760).

Extraction of Cobalt and Nickel by LSMs

The experimental apparatus used for metal extraction by LSMs was a batch-type stirred tank equipped with four 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.

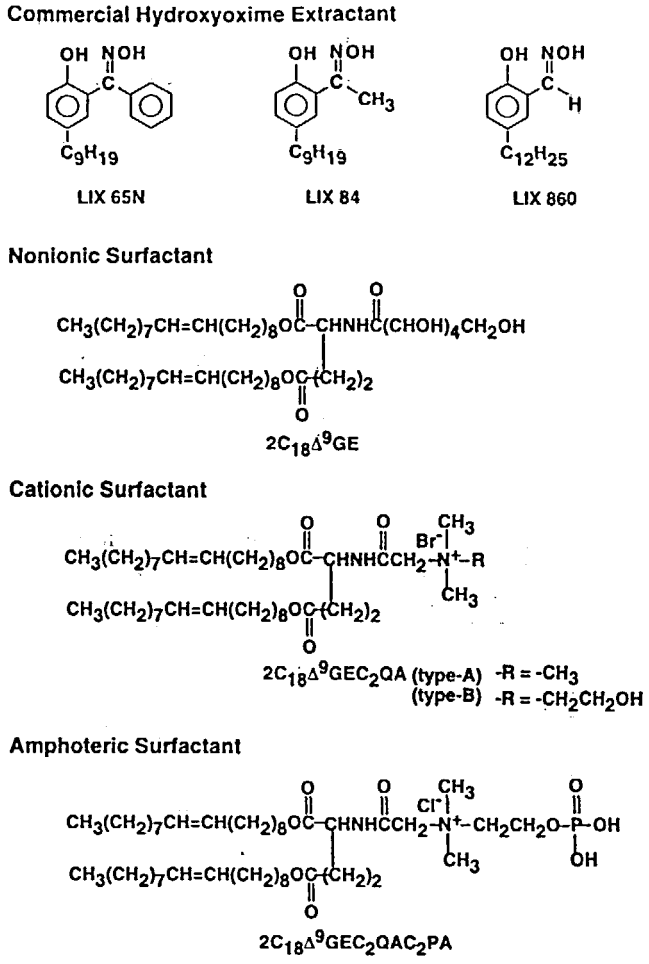


FIG. 1 Molecular structure of commercial extractants and synthesized surfactants.

A W/O emulsion was made from equal volumes of the two immiscible solutions listed in Table 1 by stirring under ultrasonic irradiation for 120 seconds in a large test tube. Fifty milliliters of this emulsion was then added to the feed aqueous solution (700 mL) containing cobalt and nickel ions in the tank and was stirred at 300 rpm. The tank was placed in a bath through which water maintained at 303 K was circulated. Zinc nitrate in the internal aqueous solution of the emulsion was employed as an indicator to measure

TABLE 1
Experimental Conditions for Metal Extraction by LSM

Internal aqueous phase	$V_{i,0}$ = 50 mL
	$C_{H_2SO_4}$ = 500 mol/m^3
Break-up tracer	$C_{Zn(NO_3)_2}$ = 10 mol/m^3
Organic phase	V_{org} = 50 mL
	Solvent: *n*-heptane
	Extractant: LIX 65N, LIX 84, LIX 860
	C_{HR} = 10–100 mol/m^3
	Surfactant: $2C_{18}\Delta^9GE$, $2C_{18}\Delta^9GEC_2QA(A)$, $2C_{18}\Delta^9GEC_2QA(B)$, $2C_{18}\Delta^9GEC_2QAC_2PA$
	C_S = 5–50 mol/m^3
External aqueous phase	$V_{e,0}$ = 700 mL
	C_{Co} = C_{Ni} = 10 mol/m^3
	pH = 5.5
	$C_{Mg(NO_3)_2}$ = 340 mol/m^3
Stirring speed	300 rpm
Temperature	303 K

the degree of breakup. Under the present experimental conditions the ionic strength in the internal solution was kept higher than that in the external material solution, therefore magnesium nitrate was added to the material solution to prevent osmotic swelling of the W/O emulsion. Samples of about 3–4 cm^3 were taken at intervals. After the emulsion and the aqueous phases in the samples were separated, the metal concentrations in the feed aqueous solution were determined with an atomic absorption spectrophotometer. The detailed experimental conditions for LSMs are summarized in Table 1.

RESULTS AND DISCUSSION

Extraction Equilibrium of Cobalt and Nickel

The degree of metal extraction increased with an increase in the aqueous pH due to promotion of acid dissociation of the extractant. Using LIX 65N, LIX 84, and LIX 860 as extractants in the liquid–liquid system, nickel ions were preferentially extracted over cobalt ions although only LIX 84 showed better selectivity. All the hydroxyoxime extractants appeared to have an affinity for forming chelate complexes with nickel ions, which is directly opposite of the results reported for organophosphorus extractants (1–3, 8). Based on the relationship between the logarithm of metal distribution and pH, two protons are released from the extractant according to the valence of the reactants, cobalt(II) and nickel(II) cations. Furthermore, from a slope analysis

based on the extractant concentration, two hydroxyoxime molecules are the stoichiometric requirement needed to form the metal complex with a cobalt or a nickel ion. Cobalt and nickel are known to form a tetrahedral and an octahedral complex, respectively, with an organophosphorus extractant such as D2EHPA or PC-88A. Therefore, four organophosphorus extractant molecules are needed to extract a cobalt ion, while six molecules of a similar extractant are needed to extract a nickel ion.

Based on the results of slope analysis, it was found that the stoichiometric extraction of cobalt and nickel, using the three hydroxyoxime extractants, is similar to the mode of extraction for copper ions with LIX65N (12), as shown in the following equation:

$$M^{2+} + 2HR = MR_2 + 2H^+, \qquad K_{ex} \tag{1}$$

where HR is the extractant and K_{ex} is the extraction equilibrium constant written as follows:

$$K_{ex} = (C_{M,org}C_H^2)/(C_{M,aq}C_{HR,org}^2) \tag{2}$$

The distribution ratio of metal, D, defined by

$$D = C_{M,org}/C_{M,aq} \tag{3}$$

is rewritten from Eqs. (2) and (3) as follows:

$$\log D = 2 \log(C_{HR,org}/C_H) + \log K_{ex} \tag{4}$$

Based on Eq. (4), the relationship between log D and $\log(C_{HR,org}/C_H)$ was plotted in Figure 2. Straight lines with a slope of about 2 were obtained for

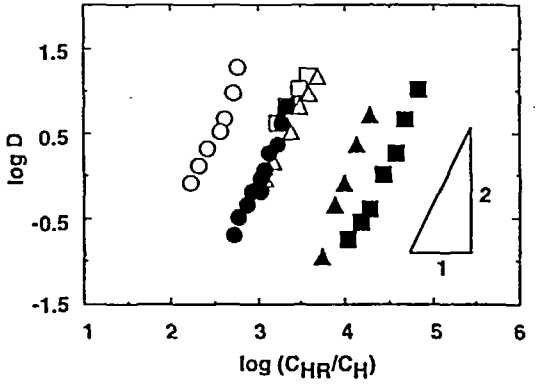


FIG. 2 Relationship between logarithmic distribution ratio of metal ions and $\log(C_{HR}/C_H)$: LIX65N (△) Ni, (▲) Co, LIX84 (□) Ni, (■) Co, LIX860 (○) Ni, (●) Co.

TABLE 2
Equilibrium Constants and Separation Coefficient in the Extraction of Cobalt and Nickel

Extractant	K_{ex} (—) Co	K_{ex} (—) Ni	β (—), Ni/Co
LIX 65N	9.7×10^{-9}	8.1×10^{-7}	84
LIX 84	1.6×10^{-9}	1.2×10^{-6}	750
LIX 860	6.2×10^{-7}	9.0×10^{-6}	15

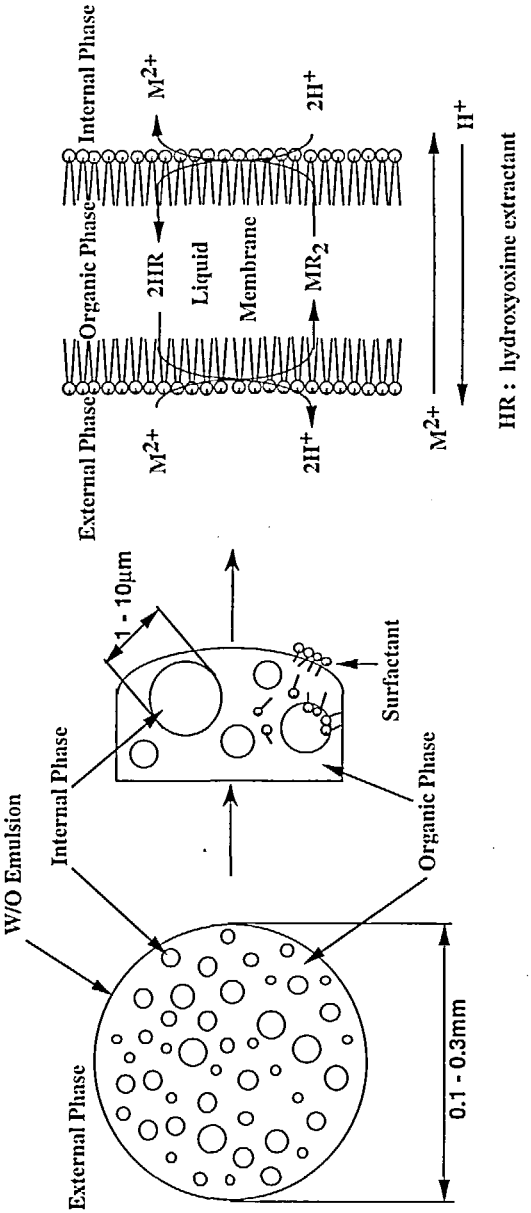
all extractants as shown in the figure, and the validity of Eq. (1) was confirmed. The K_{ex} values for each metal and extractant were determined from the intercept of the straight lines by a linear regression method and are summarized in Table 2. β is the separation coefficient evaluated as the ratio of K_{ex} values for the respective metals. The separation coefficient associated with cobalt and nickel in the liquid–liquid system increased in the order LIX860 < LIX65N < LIX84, although the extractability was largest with LIX860 among the three extractants. The effective pH region for cobalt and nickel extraction was higher compared with that for copper.

Permeation Mechanism of Cobalt and Nickel through LSM

Figure 3 illustrates the permeation mechanism of cobalt and nickel in an LSM process utilizing a hydroxyoxime extractant as a mobile carrier. A metal ion forms an oil-soluble complex with the hydroxyoxime extractant on the surfaces of W/O emulsions and is extracted into the liquid membrane phase. As shown in the figure, because surfactant molecules preferentially adsorb on the surface, the extractive reaction between the metal ion and the carrier at the interface is inhibited by the surfactant molecules. However, in the case of favorable interaction between the surfactants and the carrier or metal ions, the permeation rate of metal ions is enhanced significantly. Subsequently, the metal complexes extracted at the external interface diffuse to the other side of a thin liquid membrane and are rapidly recovered in the acidic internal aqueous phases by an ion-exchange reaction. The separation of cobalt and nickel is achieved in the extraction step at the external interface. Under the present experimental conditions, cobalt, which is extracted faster than nickel, was preferentially concentrated in the internal recovery phase of emulsions.

Stability of Emulsion

In an LSM process a surfactant plays an important role of forming and maintaining an emulsion, and thus the efficiency of metal recovery is strongly



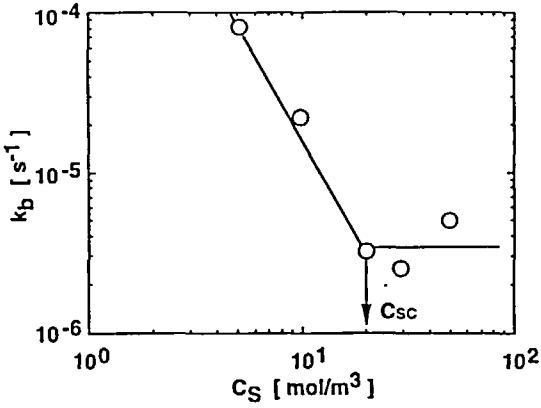


FIG. 4 Relationship between k_b and surfactant concentration (surfactant $2C_{18}\Delta^9GEC_2QA(B)$, LIX860 concentration 50 mol/m^3).

influenced by the emulsion conditions. In particular, the surfactant concentration affects the rate of metal permeation as well as the stability of emulsions. Therefore, surfactant concentration must be kept at optimized levels in order to maintain stable emulsions in the LSM system.

In order to evaluate the surfactant effect on emulsion stability, the break-up rate of emulsions, k_b, was defined by the following equation (11):

$$\ln(1 - \epsilon) = -k_b \cdot t \tag{5}$$

where ϵ is the degree of break-up defined by $(V_e C_{Zn,e})/(V_i C_{Zn,i,0})$, and the subscripts, e, i and 0, denote the external and internal phases, and the initial value, respectively. ϵ is determined from the amount of break-up tracer released from the internal to the external aqueous phase.

Figure 4 shows the relationship between k_b and the surfactant concentration. The k_b value decreases with an increase in the surfactant concentration up to 20 mol/m^3, above which it approaches a constant value signifying formation of a stable emulsion. The k_b value remain constant mainly due to saturation of the interface between the aqueous and the organic phases by surfactant molecules (11). Under the present conditions, the critical surfactant concentration was found to be approximately 20 mol/m^3, therefore a surfactant concentration of 20 mol/m^3 was added to the membrane phase in all subsequent experiments.

Extraction of Cobalt and Nickel by LSMs

Figure 5 shows the effect of carriers on the extraction of cobalt and nickel ions by LSMs. It is clear that there is preferential extraction of cobalt ions

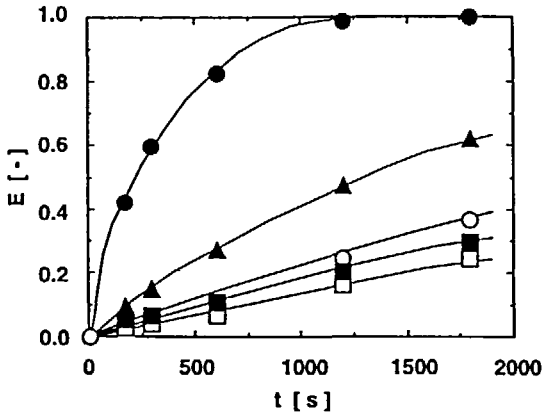


FIG. 5 Effect of carriers on the permeation of cobalt and nickel by LSMs; LIX65N (△) Ni, (▲) Co, LIX84 (□) Ni, (■) Co, LIX860 (○) Ni, (●) Co (pH 5.5, extractant concentration 50 mol/m^3, $2C_{18}\Delta^9GEC_2QA(B)$ concentration 20 mol/m^3).

in LSMs over that of nickel ions under the present conditions. However, in the liquid–liquid equilibrium extraction trials all the hydroxyoxime extractants employed showed a higher extractability for nickel ions than cobalt ions. The metal permeation in the LSM system is governed by the kinetic state at the reaction interface. The formation of oil-soluble a cobaltous–organometallic complex appears to be faster than that of nickel, and as a result cobalt is preferentially recovered over nickel. Therefore, separation behavior was quite different between the liquid–liquid extraction and LSM extraction systems. Furthermore, because the metal complexes permeate rapidly through the thin liquid membrane and are simultaneously stripped into the interior phase, the contribution of the reverse reaction as a rate-determining step can be neglected.

It was found that slight structural differences in the carriers affect the permeation behavior of the metal ions. With respect to the extractability of the metal ions in the LSM system, LIX 860 showed the highest extraction affinity for cobalt, and subsequently yielded the best separation results between cobalt and nickel. The order of extraction potential of the three extractants for cobalt and nickel was similar to the results obtained in the equilibrium extraction experiments, although the selectivity is completely opposite.

The initial reaction rate of metals with LSMs is expressed as follows (12):

$$r = k'_{f,M} C_M \tag{6}$$

where $k'_{f,M}$ is the apparent interfacial reaction rate constant for each metal M

(= Co, Ni). The concentration change of metal ions in an external aqueous solution in the stirred tank with time can be shown by the following equation:

$$-dC_M/dt = a \cdot r \tag{7}$$

where a is the specific interfacial area defined by $(V_E/V_e)(6/d_E)$. From Eqs. (6) and (7), the following equation is obtained:

$$\ln(C_{M,e}/C_{M,e,0}) = -ak'_{f,M} \cdot t \tag{8}$$

Under the present experimental conditions, the change of hydrogen ion activity in the external aqueous solution was negligible due to the buffer condition effect. Based on the relationship between $\ln(C_{M,e}/C_{M,e,0})$ and the reaction time, the $ak'_{f,M}$ value is obtained from the slope of the straight line. The values obtained from the results in Fig. 5 are summarized in Table 3. Using LIX 860 as the carrier, both the rate of metal extraction and the separation coefficient between cobalt and nickel were found to be satisfactory. Using LIX 65N or LIX 84, the separation coefficient was very small compared to those obtainable in liquid–liquid equilibrium extraction. Based on these results, LIX 860 was selected as the mobile carrier for the recovery of cobalt from an impure nickel solution.

The results of metal extraction by LSMs using several different synthesized surfactants are listed in Table 4. When using a cationic surfactant, there was significant increase in the rate of cobalt extraction compared with a nonionic surfactant; however, the change in the rate of nickel extraction was negligible for both surfactants. The hydrophilic parts of the quaternary ammonium surfactant were found to enhance the extraction of cobalt with LIX 860. In a previous paper (8) we reported that the rate of cobalt extraction by LSMs containing an organophosphorus extractant increased remarkably when similar cationic surfactants were used. The increase in extraction rate is considered to be due to both the enrichment effect of the carrier and the promotion of

TABLE 3
Effect of Extractants on the Extraction of Cobalt and Nickel by LSM [HR: 50 mol/m^3; $2C_{18}\Delta^9GEC_2QA(B)$: 20 mol/m^3]

Extractant	ak'_f (s^{-1})		β_{LSM} (—),[a] Co/Ni
	Co	Ni	
LIX 65N	5.3×10^{-4}	1.5×10^{-4}	3.5
LIX 84	1.9×10^{-4}	1.5×10^{-4}	1.3
LIX 860	2.8×10^{-3}	1.7×10^{-4}	16

[a] β_{LSM} is defined by the ratio of ak'_f between Co and Ni.

TABLE 4
Effect of Surfactants on the Extraction of Cobalt and Nickel by LSM
(LIX 860: 50 mol/m^3; surfactant: 50 mol/m^3)

Surfactant	ak_f' (s^{-1}) Co	ak_f' (s^{-1}) Ni	β_{LSM} (—), Co/Ni
$2C_{18}\Delta^9GE$	3.5×10^{-4}	6.3×10^{-5}	5.6
$2C_{18}\Delta^9GEC_2QA(A)$	9.9×10^{-4}	5.7×10^{-5}	17
$2C_{18}\Delta^9GEC_2QAC_2PA$	1.9×10^{-4}	1.5×10^{-4}	1.3

acid dissociation of the carrier which we consider to arise from electrostatic interaction between the head group of the cationic surfactant and the hydroxyoxime carrier at the reaction interface. In the case of using an amphoteric surfactant, it was found that the extraction rate of nickel improved significantly as compared with a nonionic surfactant, though the permeation rate of cobalt decreased. In a previous paper (8) we observed that when an organophosphorus extractant was used as a mobile carrier in LSMs, the extraction rate of both cobalt and nickel increased significantly in the presence of an amphoteric surfactant owing to the favorable interaction of hydrophilic phosphorus groups to both metal ions. However, when a hydroxyoxime carrier replaced the organophosphorus type in the same LSM system, nickel extraction was preferentially accelerated due to the high affinity of the hydroxyoxime group to nickel ions. As the result, the separation factor between cobalt and nickel ions was reduced. By contrast, a cationic surfactant of type B showed the best results with respect to both the rate of cobalt extraction and the separation of cobalt and nickel. Hence, in subsequent experiments a more detailed study using cationic surfactants was performed to elucidate the permeation mechanism by LSMs.

The results of metal extraction by LSMs using two different cationic surfactants are summarized in Table 5. The surfactants differ in their respective

TABLE 5
Effect of Cationic Surfactants on the Extraction of Cobalt and Nickel by LSM
(LIX 860: 50 mol/m^3; surfactant: 20 mol/m^3)

Surfactant	ak_f' (s^{-1}) Co	ak_f' (s^{-1}) Ni	β_{LSM} (—), Co/Ni
$2C_{18}\Delta^9GEC_2QA(A)$	2.2×10^{-3}	1.5×10^{-4}	15
$2C_{18}\Delta^9GEC_2QA(B)$	2.8×10^{-3}	1.7×10^{-4}	16

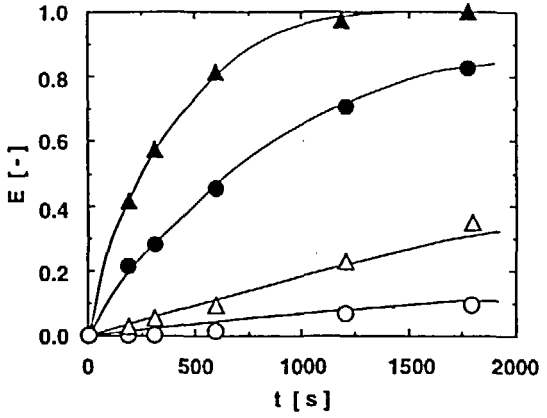


FIG. 6 Effect of cationic surfactants on the permeation of cobalt and nickel by LSMs; $2C_{18}\Delta^9GEC_2QA(A)$ (○) Ni, (●) Co, $2C_{18}\Delta^9GEC_2QA(B)$ (△) Ni, (▲) Co (pH 5.5, LIX860 concentration 50 mol/m^3, surfactant concentration 20 mol/m^3).

hydrophilic terminal groups. The difference in structure probably affects the adsorption ability at the oil–water interface. Based on the results in the table, the extraction rate of metals using the A-type cationic surfactant was lower than that for the B-type cationic surfactant as shown in Fig. 6 (8). This is mainly due to strong interaction between the B-type surfactant and the mobile carrier at the reaction interface. However, similar separation profiles of cobalt and nickel were obtained in both surfactants.

Figure 7 shows the relationship between ak_f' and the extractant concentration. The rate of metal extraction increased with an increase in the carrier concentration and showed a second-order dependence upon carrier concentration. The dependence agreed well with the stoichiometric number of extracted complexes, and therefore the rate-determining step in metal permeation by the LSM-containing hydroxyoxime carrier was considered to be the first step associated with complex formation of extracted species at the exterior interface.

Figure 8 shows the relationship between ak_f' and the surfactant concentration. The rate of metal permeation decreased with an increase in the surfactant concentration, and a slope of approximately -1 was obtained. This behavior is explained on the basis of an interfacial reaction model in which the decrease in the extraction rate is deduced to be due to the blocking effect of adsorbed surfactant molecules at the reaction interface. Further, the extraction rate also decreased in the surfactant concentration range of less than 20 mol/m^3 due to emulsion instability. Results are not shown in the figure.

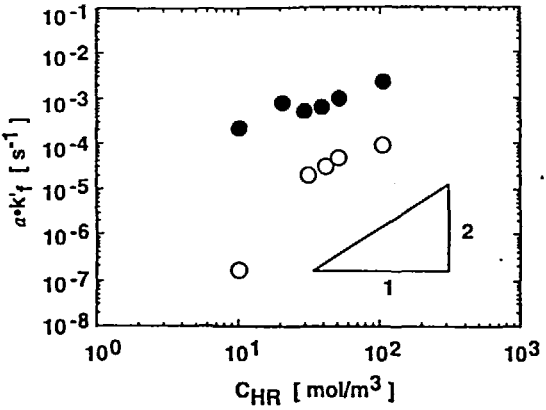


FIG. 7 Relationship between ak'_f and extractant concentration; (○) Ni, (●) Co [pH 5.5, $2C_{18}\Delta^9GEC_2QA(B)$ concentration 20 mol/m^3, extractant LIX860].

Extraction Mechanism of Cobalt and Nickel by LSMs

As described above, the extraction rate of both cobalt and nickel depends upon the second order of carrier concentration and the inverse first order of surfactant concentration. Therefore, the extraction mechanism on the surface of emulsions is expressed as follows:

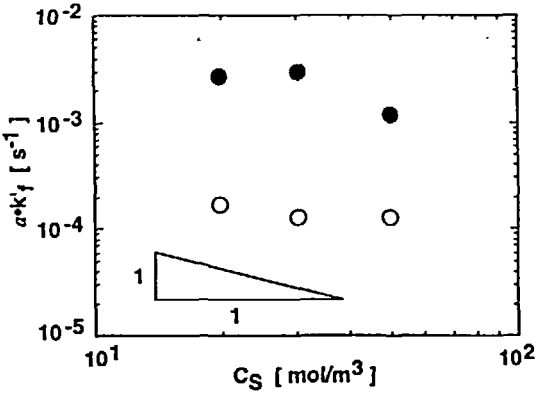


FIG. 8 Relationship between ak'_f and surfactant concentration; (○) Ni, (●) Co [pH 5.5, surfactant $2C_{18}\Delta^9GEC_2QA(B)$, LIX860 concentration 50 mol/m^3].

$$Sf_{org} = Sf_{ad}, \qquad K_S \qquad (9)$$

$$HR_{org} = HR_{ad} \qquad K_{HR} \qquad (10)$$

$$M^{2+} + HR_{ad} = MR_{ad}^{+} + H^{+}, \qquad K_1 \qquad (11)$$

$$MR_{ad}^{+} + HR_{org} = MR_{2,org} + H^{+}, \qquad k_2/k_{-2} \qquad (12)$$

where K_S and K_{HR} are the adsorption equilibrium constants at the oil–water interface with surfactant and extractant, respectively, K_1 is the formation constant expressed by Eq. (11), and k_2 and k_{-2} are the forward and the reverse reaction rate constant expressed by Eq. (12). Assuming that Eq. (12) is the rate-determining step to satisfy the dependence, the interfacial reaction rate is expressed by the following equation on the basis of the Langmuir adsorption isotherm for the adsorbed carrier and surfactant:

$$r = k_2 K_1 \left(\frac{K_{HR}}{S_{HR}}\right) \frac{C_{HR,org}^2}{1 + K_{HR}C_{HR,org} + K_{MR}C_{MR,org} + K_S C_{S,org}} \frac{C_M}{C_H} - k_{-2} C_{MR2,org} C_H \qquad (13)$$

where S_{HR} is the interfacial area occupied by a unit mole of the carrier, and K_{MR} is the adsorption equilibrium constant of the interfacial metal complex MR^+. The term $K_{MR}C_{MR}$ may be neglected because the concentration of MR^+ is considerably smaller than those of HR and Sf. Furthermore, the stripping rate of the metal complexes extracted in the membrane phase is extremely fast compared with the extraction rate because the acid concentration is high enough for it to be a stripping reagent and the reaction interfacial area is very large (12). Therefore, the second term of Eq. (13) can be neglected and Eq. (13) is rewritten as follows:

$$r = k_f \left(\frac{K_{HR}}{S_{HR}}\right) \frac{C_{HR,org}^2}{1 + K_{HR}C_{HR,org} + K_S C_{S,org}} \frac{C_M}{C_H} \qquad (14)$$

where k_f ($= k_2 K_1$) is the overall interfacial reaction rate constant. The degree of separation between cobalt(II) and nickel(II) in the LSM system depends on the k_2 value in the rate-determining step (12). The rate of complex formation is considered to be influenced by the adsorption of surfactants at the reaction interfaces. Based on Eqs. (6) and (14), the apparent interfacial reaction rate constant, k_f', was found to increase with increasing carrier concentration and to decrease with increasing surfactant concentration. Furthermore, the experimental results in Figs. (6) and (7) can be explained by the proposed interfacial reaction model.

CONCLUSION

The conclusion to this study is twofold.

1. LSMs functionalized by hydroxyoxime have been successfully employed to separate cobalt and nickel in acetate media, and the effect of the nature of a surfactant on the metal extraction rate has been established. As a mobile carrier, LIX 860 promotes rapid permeation of cobalt ions across a W/O interface and yields satisfactory cobalt and nickel separation factors up to 17. Cationic surfactants enhance the cobalt permeation rate 3-fold compared with nonionic surfactants mainly due to favorable carrier–surfactant interaction at the interface. The extraction mechanism fits well into the interfacial reaction model.
2. The liquid–liquid extraction of cobalt and nickel with LIX 65N, LIX 84, and LIX 860 was examined, and the equilibrium extraction constants were determined for each extractant. All extractants showed an affinity to form chelates with nickel ions, although the same extractants show an affinity for cobalt ions in a LSM system. LIX 84 yielded the largest separation coefficient, averaging 750 between cobalt and nickel under equilibrium conditions. The extractability was ranked in the order LIX 860 > LIX 65N, LIX 84.

NOMENCLATURE

a	interfacial area defined by $(V_E/V_e)(6/d_E)$ (1/m)
C_j	concentration of species j (mol/m^3)
D	distribution coefficient of metal (—)
d_E	diameter of emulsion globule (m)
E	degree of metal extraction (—)
K_1	equilibrium constant of reaction expressed by Eq. (11) (—)
K_{ex}	extraction equilibrium constant (—)
K_j	adsorption equilibrium constant of species j (m^3/mol)
k_2	rate constant of forward reaction expressed by Eq. (12) (m^3/mol·s)
k_{-2}	rate constant of reverse reaction expressed by Eq. (12) (m^4/mol·s)
k_b	break-up rate constant of emulsion defined by Eq. (5) (1/s)
k_f	overall interfacial reaction rate constant defined by K_1k_2 (m^3/mol·s)
k_f'	apparent interfacial reaction rate constant defined by Eq. (6) (m/s)
r	extraction rate (mol/m^2·s)
S_j	interfacial area occupied by unit mole of species j (m^2/mol)
t	time (s)
V	volume of solution (m^3)

Greek Letters

β separation factor between cobalt and nickel (—)
ϵ degree of break-up of emulsion (—)

Subscripts

ad adsorption state
aq aqueous phase
Co cobalt ion
E emulsion phase
e external aqueous solution
H hydrogen ion
i internal aqueous solution
HR extractant
M metal ion
MR primary metal–extractant complex
MR_2 extractable species of metal
Ni nickel ion
0 initial value
org organic phase
S surfactant

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