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Synergistic Extraction of Nickel by Liquid Surfactant Membranes

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ABSTRACT

Synergistic extraction of Ni(II) by a mixture of the active component in the commercial extractant LIX63, 5,8-dimethyl-7-hydroxydodecane-6-oxime, and dioleylphosphoric acid (DOLPA) has been investigated by liquid surfactant membranes (LSMs) containing a commercial surfactant, Span 80. Solvent extraction of Ni(II) with the mixture of LIX63 and an ordinary extractant, di(2-ethylhexyl)-phosphoric acid (D2EHPA) was carried out. The results show that the LIX63–DOLPA mixture has a high synergistic effect on the extraction of Ni(II) in the LSM system compared with the LIX63–D2EHPA mixture. The synergistic effect of the LIX63–DOLPA mixture is attributed to a mixed ligand complex formation with the stoichiometry of Ni^{2+}/LIX63/DOLPA = 1/2/2. Besides extractant synergism, the effects of several operation factors in the LSMs were investigated: permeation of Ni(II), pH of external aqueous phase, and concentrations of extractant and surfactant. The permeation mechanism of Ni(II) in LSMs has been elucidated by using the interfacial reaction model which takes into account the complex formation at the interface.

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INTRODUCTION

Rare earth metals are important materials for developing novel functional devices, and their demand is expanding with the advances of new technologies. However, as the primary high-grade metal ores diminishes, the recycle processes of spent valuable materials are becoming attractive from the viewpoint of energy conservation and reducing environmental pollution. Secondary resources such as spent electric goods or scrap metals generally contain high-grade metals compared with primary resources. Japan, in particular, imports all its required metal resources from abroad, thus establishing a recycle system is strongly recommended. In this study we focused on the liquid membrane technique and performed the recovery of nickel(II) ions as a model for recovering valuable metals from dilute solutions. Nickel is one of the rare metals and is employed as a catalyst and in batteries. However, nickel ions are well know to be inactive in the ion-exchange reaction between a nickel hydrate and a chelate ligand due to the high stability of nickel hydrates in aqueous solutions. This characteristic often causes a slow metal extraction rate in a liquid–liquid extraction system.

It takes several hours to attain the equilibrium state in an ordinary extraction system for Ni(II). In the present study, in order to raduce this problem, we have introduced two techniques. One is the liquid surfactant membrane technique and the other is the synergistic effect caused by a mixture of two appropriate extractants. The use of a liquid surfactant membrane is a promising method applicable to the recovery of metal ions from a very dilute solution. This membrane has a large interfacial area formed by dispersing water-in-oil (W/O) emulsion droplets, and it is capable of performing forward and backward extraction at the same time. Furthermore, since the metal carrier contained in a liquid membrane system can be recycled, the carrier concentration may be significantly reduced relative to that in an ordinary solvent extraction system.

It is well known that the equilibrium extraction or extraction rate of metals can be strongly enhanced by employing a combination of appropriate extractants. This is called the synergistic effect in a liquid–liquid extraction system. Castresana et al. (1–3) reported that a synergistic effect is evident in the extraction of Cu and Ni by a mixture of 1-phenyl-1,3-decanedione (LIX54) and several extractants. Flett et al. reported that the combination of 5,8-diethyl-7-hydroxydodecan-6-oxime (LIX63) and a long-chain carboxylic acid shows a synergistic effect and is effective for the separation of Cu and Fe, or Ni and Co (4–6). A mixture of LIX63 and an organophosphorus extractant was recently reported to show a strong synergistic effect to the extraction of nickel ions (7). However, to date there has been no report of extractant synergism as applied to metal separation by a liquid surfactant membrane system.

A new liquid surfactant membrane technique utilizing a synergistic effect is reported in this paper for the extraction of nickel ions. The carrier mixture of LIX63 and DOLPA was employed as a mobile carrier in the liquid membrane system. Although each extractant has a low extraction ability, the mixture shows excellent extraction and permeation properties for nickel ions. Extraction behavior of nickel ions by liquid surfactant membranes was examined in detail along with extraction equilibrium using the mixture of LIX63 and DOLPA. The permeation mechanism and extraction behavior of Ni(II) was explained using an interfacial reaction model in the liquid membrane system.

EXPERIMENTAL

Reagents

The commercial extractant 5,8-diethyl-7-hydroxydodecan-6-oxime (LIX63) was supplied from Henkel Hakusui Co. Ltd. (Japan), and di(2-ethylhexyl)phosphoric acid (D2EHPA) was purchased from Tokyo Chemical Industry Co. Ltd. (Japan). The commercial surfactant Span 80 was purchased from Kishida Chemical Co. Ltd. (Japan). These extractants and surfactant were used without further purification. Dioleylphosphoric acid (DOLPA) was synthesized and purified according to our previous paper (8). Toluene and *n*-heptane were used as organic diluents. All the other reagents used were of guaranteed reagent grade and were used as received.

Extraction Equilibrium of Ni(II)

An aqueous solution was prepared by dissolving 0.2 mol/m^3 Ni$(NO_3)_2 \cdot 6H_2O$ in deionized water. Nitric acid (100 mol/m^3) and sodium acetate (100 mol/m^3) were used to adjust the pH and ionic strength. An organic solution containing a mixture of LIX63 and DOLPA or D2EHPA at different concentration levels was prepared. Toluene was used as an organic solvent.

Equal volumes (5 mL) of the aqueous and the organic solutions were mixed in glass bottles and shaken at 303 K. After about 40 hours the extraction of nickel ions was assumed to have reached the equilibrium state and each mixture was separated. The metal content in the aqueous phase was analyzed by atomic absorption spectrophotometry (Shimadzu Model AA-6700).

Extraction of Ni(II) by Liquid Surfactant Membranes

The experimental apparatus used for metal extraction with LSMs is a batch-type stirred cell equipped with four stainless baffles. The inner diameter and depth of the cell were 100 and 146 mm, 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 organic, containing a surfactant, and the internal aqueous phases listed in Table 1 under ultrasonic irradiation for 180 seconds in a large test tube. A measured volume of this emulsion was then added to the feed aqueous solution containing Ni(II) in the stirred cell, and stirred at 300 rpm. The stirred cell was placed in a water bath through which water maintained at 303 K was circulated. Magnesium nitrate in the internal aqueous solution of the emulsion was used as an indicator to measure the degree of breakup. Samples of about 4–5 mL were taken at intervals. After the emulsion and feed aqueous phases in the samples were separated, the concentrations of Ni(II) and Mg(II) in the feed solution were determined by atomic absorption spectrophotometry (Shimadzu Model AA-6700). The detailed experimental conditions for the LSM operation are listed in Table 1.

RESULTS AND DISCUSSION

Extraction Equilibrium of Ni(II)

Figure 1 shows the degree of Ni(II) extraction as a function of pH with the extractant LIX63 or DOLPA alone, or their mixtures in toluene. The

TABLE 1
Experimental Conditions for Nickel Extraction by LSMs

Internal aqueous phase	$V_{i,0} = 50$ mL
	$C_H = 1000$ mol/m^3
	$C_{Mg,0} = 20$ mol/m^3
Organic phase	$V_{org} = 50$ mL
	$C_{HR} = 0$–20 mol/m^3
	$C_{HL} = 0$–25 mol/m^3
	$C_{Sf} = 10$–75 mol/m^3
External aqueous phase	$V_{e,0} = 700$ mL
	$C_{Ni,0} = 0.2$ mol/m^3
	pH 2.5–3.5
Stirring speed	300 rpm
Temperature	303 K

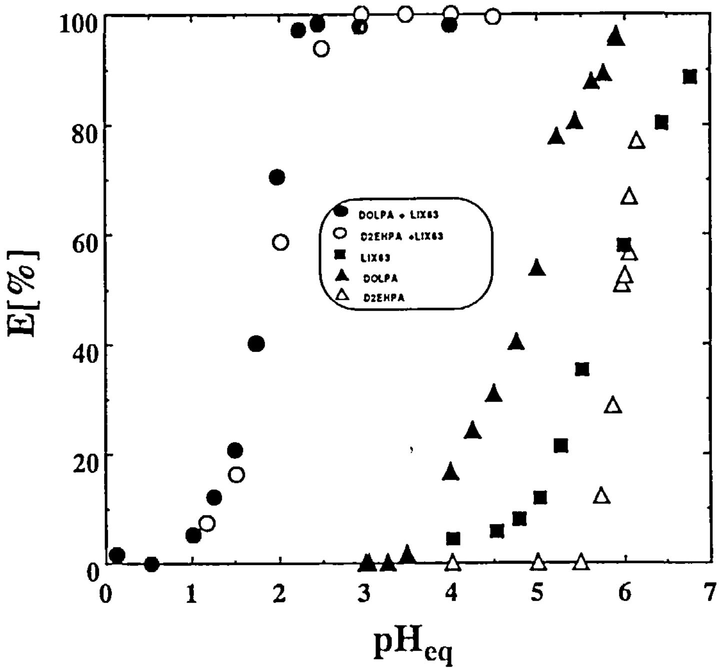

FIG. 1 Degree of Ni(II) extraction as a function of pH.

percentage of Ni(II) extraction increased with an increase in the pH value. This result suggest that complex formation proceeds by an ordinary ion-exchange mechanism. Furthermore, a large synergistic effect was observed when the two extractants were mixed. A highly extractable complex is believed to be formed by coordinating the two extractants. The degree of Ni(II) extraction versus the ratio of extractant mixtures of DOLPA or D2EHPA to LIX63 at an initial pH of 1.9 is shown in Fig. 2. The mixture of LIX63 and DOLPA shows a larger synergistic effect than that of LIX63 and D2EHPA, since the pK_a value of DOLPA (3.84) is lower than that of D2EHPA (4.21); that is, DOLPA is more acidic than D2EHPA and has a high extractability for metal ions. The pK_a values were measured by titrimetric analysis following the method of Martell and Smith (9).

Ni(II) is well known to be extracted by forming an octahedral complex with an organophosphorus extractant. Komasawa et al. (10–12) reported that the extracted species of nickel with PC-88A or D2EHPA [abbreviated

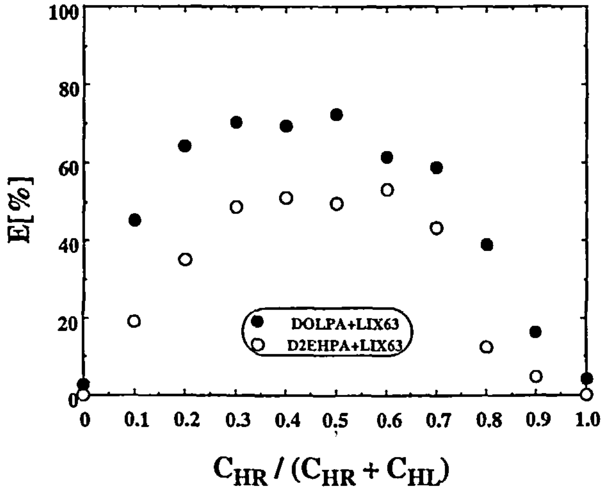

FIG. 2 Percentage of Ni(II) extraction versus ratio of extractant mixture of DOLPA (HR) or D2EHPA (HR) to LIX63 (HL) at the initial pH 1.9.

HR, where $(HR)_2$ is a dimer of the extractant] is $NiR_22(HR)_2$. Preston (13) reported that the extracted complex of Ni(II) with a mixture of carboxylic acids (H_2A_2) and nonchelating oximes is $NiA_2(oxime)_2$. Osseo-Asare et al. (14) performed the synergistic extraction of Ni(II) with a mixture of LIX63 (H_2Ox) and dinonylnaphtalene sulfonic acid (HDNNS), and reported that synergistic extraction was attributed to the formation of a mixed ligand complex with the stoichiometry of Ni(II)/H_2Ox/HDNNS = 1/3/2.

As shown in Fig. 2, when the mixed concentration ratio of the two extractants approaches are close to 1, a maximum extraction percentage was obtained. This result suggests that the large synergistic effect of Ni(II) extraction mainly depends on the formation of an extracted complex with the stoichiometry Ni(II)/LIX63/DOLPA, D2EHPA = 1/2/2.

Permeation Mechanism of Ni(II) through an LSM

An LSM process is an efficient extraction technique for metal ions, particularly in the case in which the rate of metal extraction is very slow, such as for nickel ion, because the LSM is capable of rapidly performing the extraction and transport of metal ions through a large interfacial area and a thin liquid membrane. In previous studies (15, 16) we investigated the extraction of copper ions by LSMs containing LIX65N as a mobile carrier. We found that copper ions are rapidly extracted by LSMs and, furthermore, that the extraction rate was accelerated by adding DOLPA.

The permeation mechanism of nickel ions with an LSM containing a mixed extractant of LIX63 and DOLPA is illustrated in Fig. 3. A nickel ion first forms an adsorbed intermediate complex with an adsorbed DOLPA which is more interfacially active than LIX63. The adsorbed complex reacts with LIX63, which is in an organic solution part of the liquid membrane. It is assumed that LIX63 forms a stable chelate complex with the nickel ion and that DOLPA acts as a ligand, similarly to cases using other acid extractants (7, 17). The oil-soluble complex is released from the interface and is extracted into the liquid membrane phase. The extraction of nickel ions can be synergistically accelerated by mixing the two extractants. The two extractants are considered to have a different role in the permeation of nickel ions in the LSM system. First, the surface-active DOLPA concentrates nickel ions at the interface to form an intermediate complex. Then two LIX63 molecules bonds with the adsorbed intermediates to form more stable complexes. Subsequently, the extracted metal complexes diffuse to the other side of the interface through the liquid

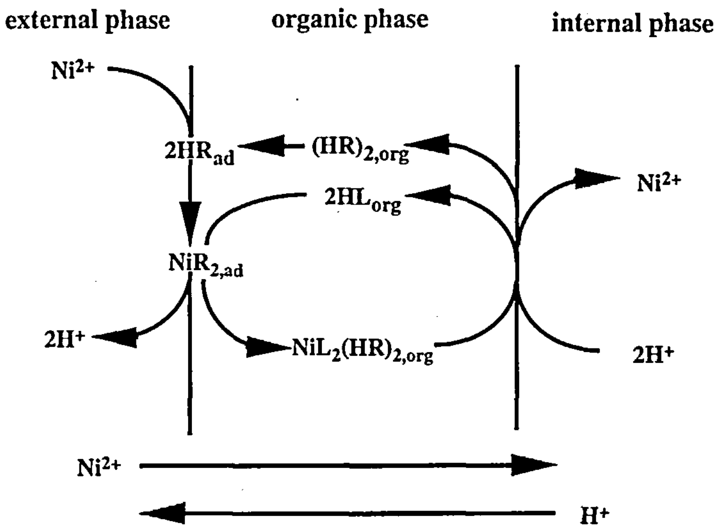

FIG. 3 Schematic permeation mechanism of nickel by LSM (HR: DOLPA, HL: LIX63).

membrane and are recovered in the inner droplets of the W/O emulsions by stripping reaction with an acid.

Stability of Emulsion

An LSM is stabilized by surfactant molecules as emulsifiers at the oil–water interface. The stability of emulsions is very important for the success of metal recovery by LSMs because the leakage of concentrated metal and hydrogen from the internal aqueous phase into the external aqueous phase is caused by the breakup of emulsion globules. In order to discuss the emulsion stability, the degree of breakup, ϵ, was defined by

$$\epsilon = \frac{V_e C_{Mg,e}}{V_i C_{Mg,i,0}} \tag{1}$$

where the subscripts, e, i, and 0 denote the external and internal phases and the initial value, respectively. The value of ϵ is obtained by the amount of brakeup tracer released from the internal aqueous phase to the external aqueous phase (15). In an LSM an organic solvent in the liquid membrane phase is well-known to affect the permeation rate of metals. In previous papers we found that *n*-heptane of aliphatic solvents is better than toluene with regard to the breakup, the swelling, and the demulsification rate of a W/O emulsion and the enrichment of metal ions (18–20). Kinugasa et al. (21) reported that an organic solvent having a long aliphatic hydrocarbon stabilizes a W/O emulsion relative to an aromatic solvent. Therefore, *n*-heptane was selected as the membrane phase in the present LSM operation.

Figure 4 exhibits the time course of emulsion stability for the different concentrations of surfactant Span 80. In a surfactant concentration of 10 mol/m^3, the emulsion was significantly broken at the initial state and the ϵ value showed approximately 60% at 1800 seconds. Under a low surfactant concentration of less than 10 mol/m^3, good recovery of nickel ions by LSMs did not occur due to the low stability of the emulsions. On the other hand, the emulsion stability increased with an increase in the concentration of surfactant, and a stable emulsion was formed with a surfactant concentration of more than 30 mol/m^3.

Extraction Behavior of Ni(II) by LSMs

The extraction of Ni(II) by LSMs has been performed by changing operational conditions. The effect of various mixed ratios of DOLPA and LIX63 on nickel extraction by LSMs is shown in Fig. 5. Nickel ions were not extracted at all under the present experimental conditions when LIX63

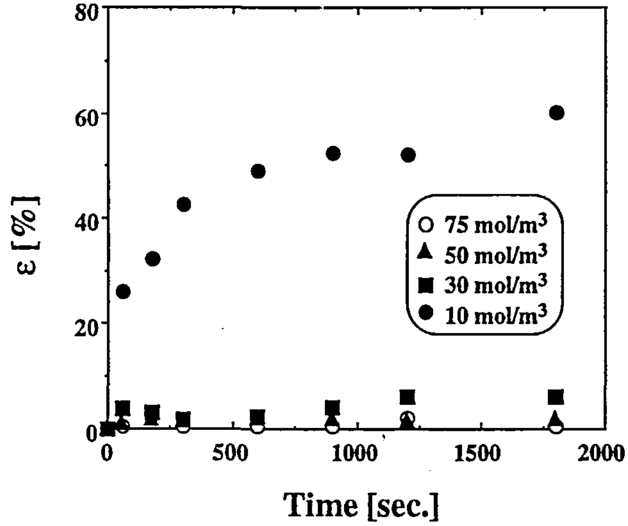

FIG. 4 Time course of emulsion stability at different concentrations of surfactant.

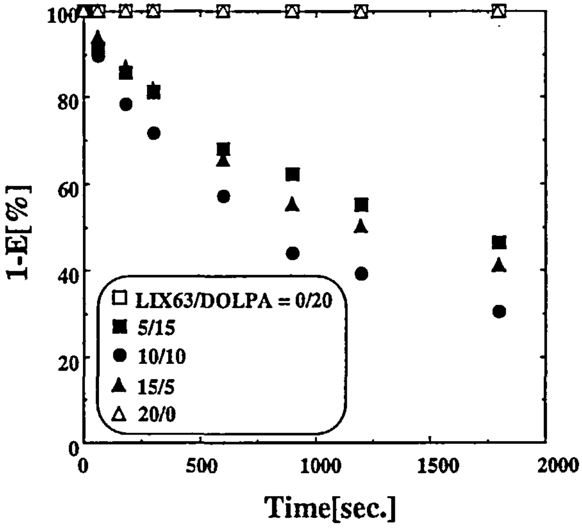

FIG. 5 Effect of the mixed ratio of DOLPA and LIX63 on Ni(II) extraction.

or DOLPA alone was used as a mobile carrier in LSMs. On the other hand, by mixing the two extractants, nickel ions were extracted and the rate of nickel extraction showed the maximum value at the equivalent ratio similar to the extraction equilibrium.

The concentration change of nickel ion in the stirred cell with time is shown by the following equation:

$$-\frac{dC_{\mathrm{Ni}}}{dt} = ak_f' \cdot \frac{C_{\mathrm{Ni}}}{\alpha_{\mathrm{H}}^2} \tag{2}$$

where a [$= (V_E/V_e)(6/d_E)$] is the specific interfacial area; k_f' is the observed rate constant of metal at the external interface of emulsion globules; V_E and V_e are the volumes of emulsion and external aqueous solution, respectively; d_E is the diameter of the emulsion globule; and α_H is the activity of hydrogen ion in the feed aqueous solution. 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:

$$\frac{d\alpha_{\mathrm{H}}}{dt} = -2\gamma_{\mathrm{H}} \cdot \frac{dC_{\mathrm{Ni}}}{dt} \tag{3}$$

Assuming that the activity coefficient of the hydrogen ion is 1, Eq. (4) can be derived by combining Eqs. (2) and (3):

$$(\alpha_{\mathrm{H},0} + 2\gamma_{\mathrm{H}} C_{\mathrm{Ni},0})^2 \cdot \ln \frac{C_{\mathrm{Ni},0}}{C_{\mathrm{Ni},t}} - (4\alpha_{\mathrm{H},0}\gamma_{\mathrm{H}} + 8\gamma_{\mathrm{H}}^2 C_{\mathrm{Ni},0})(C_{\mathrm{Ni},0} - C_{\mathrm{Ni},t}) + 2\gamma_{\mathrm{H}}^2(C_{\mathrm{Ni},0}^2 - C_{\mathrm{Ni},t}^2) = ak_f' \cdot t \tag{4}$$

where subscript t is the operation time (seconds) Figure 6 shows the relationship between the left-hand side of Eq. (4) and t at various surfactant concentrations. Based on the results in the figure, the values of ak_f' are obtained by using the linear regression method.

Figure 7 shows the relationship between log ak_f' and the logarithm of the initial hydrogen ion concentration in the external aqueous phase. The value of log ak_f' did not depend on the initial hydrogen ion concentration. It was confirmed that the order of hydrogen ion activity in Eq. (2) is appropriate.

Figure 8 shows the relation between log ak_f' and the logarithm of the surfactant concentration. The values of log ak_f' decreased gradually with an increase in the surfactant concentration, and they showed a negative second-order dependence on the surfactant concentration. The decrease in the extraction rate is due to the coating effect of the reaction interface by the surfactant molecules. The role of surfactant in an LSM process is

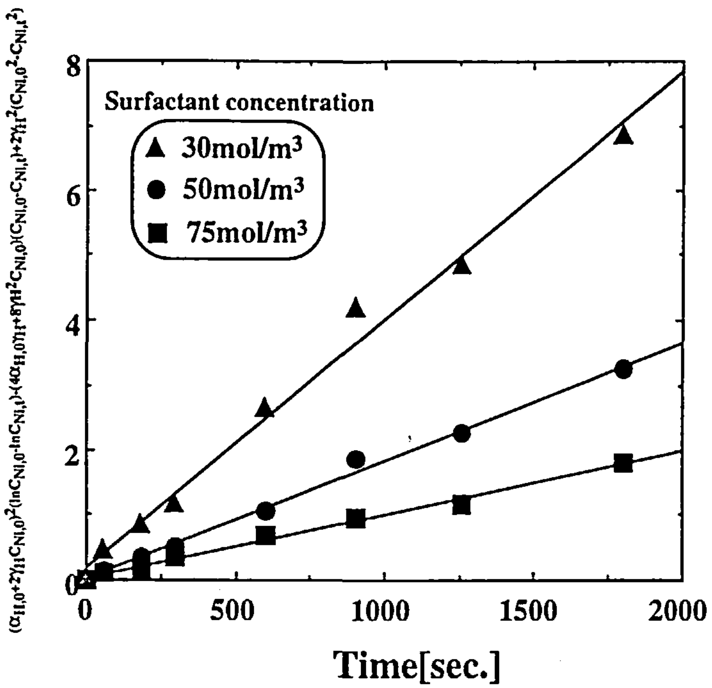

FIG. 6 Relationship between the left-hand side of Eq. (4) and *t*.

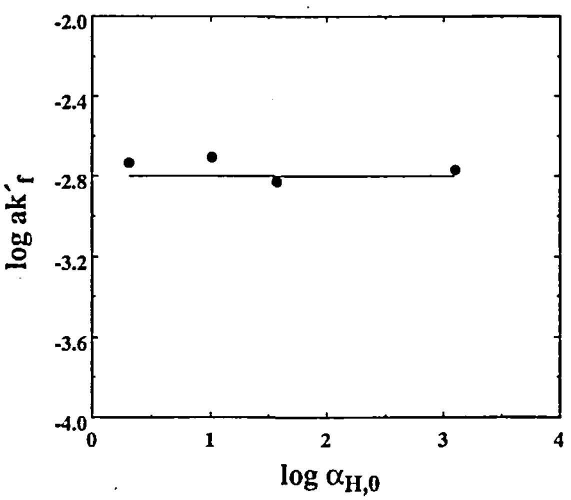

FIG. 7 Relationship between log ak'_f and the logarithm of initial concentration of hydrogen ion.

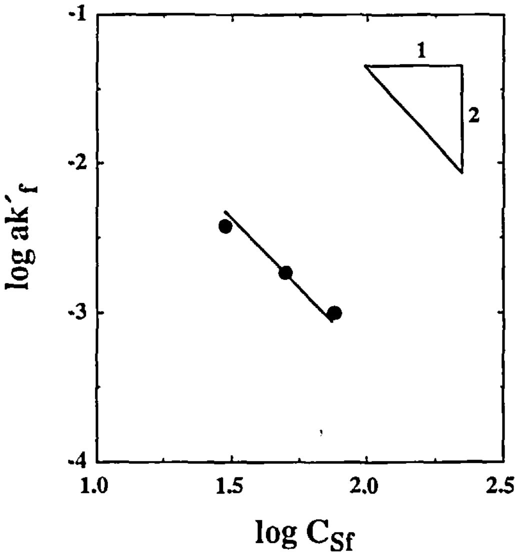

FIG. 8 Relationship between log ak_f' and the logarithm of surfactant concentration.

mainly to stabilize the emulsions; however, an excess addition of surfactant into the liquid membrane phase causes the extraction rate of metals to be lowered. Therefore, there is an optimum condition for the surfactant concentration in LSM extraction.

The relationship between log ak_f' and the logarithm of the DOLPA concentrations at a constant concentration of LIX63 at 10 mol/m^3 and the logarithm of the LIX63 concentrations at a constant concentration of DOLPA at 10 mol/m^3 are shown in Fig. 9 and Fig. 10 respectively. The rate of nickel extraction increased with the increase in the concentration each carrier. In Fig. 9 the dependence of ak_f' on DOLPA concentration is less than first order, while in Fig. 10 the value of ak_f' shows a first-order dependence on the concentration of LIX63.

Extraction Mechanism of Ni(II)

The rate of Ni(II) permeation in LSMs has been found to depend on 1) the hydrogen activity in the external aqueous phase, 2) the first-order of either LIX63 or DOLPA concentration in the extractant mixture when the concentration of the other extractant was kept constant, 3) and the second-order of surfactant concentration. The extraction mechanism

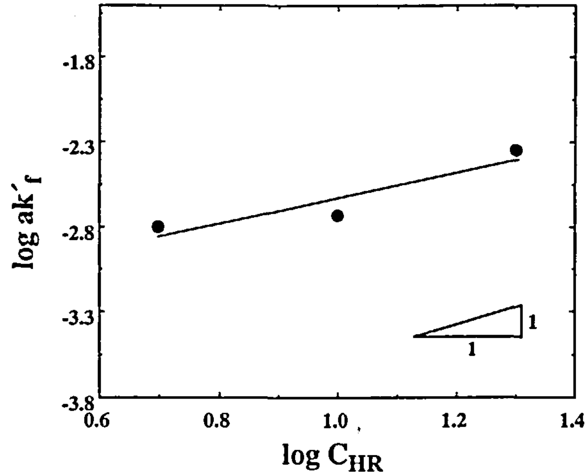

FIG. 9 Relationship between log ak'_f and the logarithm of DOLPA concentration at a constant concentration of LIX63.

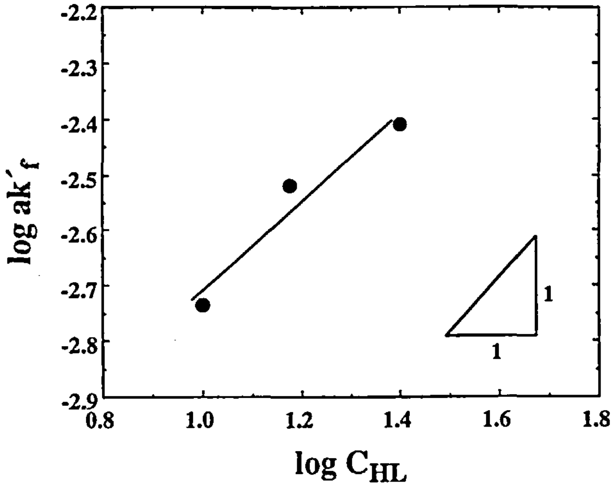

FIG. 10 Relationship between log ak'_f and the logarithm of LIX63 concentration at a constant concentration of DOLPA.

which explains this extraction behavior at the external surface of the emulsion globules is elucidated as follows:

$$2\mathrm{HR}_{\mathrm{org}} = (\mathrm{HR})_{2,\mathrm{org}} \qquad :K_{\mathrm{d}} \tag{5}$$

$$\mathrm{Sf}_{\mathrm{org}} = \mathrm{Sf}_{\mathrm{ad}} \qquad :K_{\mathrm{Sf}} \tag{6}$$

$$\mathrm{HR}_{\mathrm{org}} = \mathrm{HR}_{\mathrm{ad}} \qquad :K_{\mathrm{HR}} \tag{7}$$

$$\mathrm{Ni}^{2+}_{\mathrm{aq}} + \mathrm{HR}_{\mathrm{ad}} = \mathrm{NiR}^{+}_{\mathrm{ad}} + \mathrm{H}^{+}_{\mathrm{aq}} \qquad :K_{1} \tag{8}$$

$$\mathrm{NiR}^{+}_{\mathrm{ad}} + \mathrm{HR}_{\mathrm{ad}} = \mathrm{NiR}_{2,\mathrm{ad}} + \mathrm{H}^{+}_{\mathrm{aq}} \qquad :K_{2} \tag{9}$$

$$\mathrm{NiR}_{2,\mathrm{ad}} + \mathrm{HL}_{\mathrm{org}} = \mathrm{NiLR(HR)}_{\mathrm{org}} \qquad :k''_{\mathrm{f}}/k''_{r} \tag{10}$$

$$\mathrm{NiLR(HR)}_{\mathrm{org}} + \mathrm{HL}_{\mathrm{org}} = \mathrm{NiL}_{2}(2\mathrm{HR})_{\mathrm{org}} \qquad :K_{3} \tag{11}$$

where HR and HL are the carriers DOLPA and LIX63, respectively, and Sf is the surfactant Span 80. K_{d} is the dimerization constant of DOLPA, K_{Sf} and K_{HR} are the adsorption equilibrium constants of Span 80 and DOLPA, respectively. K_1 is the formation constant expressed by Eq. (8), and K_2 and K_3 are similar constants expressed by Eqs. (9) and (11), respectively. Assuming that Eq. (10) is the rate-determining step, the interfacial reaction rate, r, is written as follows:

$$r = k''_{\mathrm{f}}\cdot\left(\frac{K_{\mathrm{HR}}}{S_{\mathrm{HR}}}\right)^{2}\cdot\frac{C^{2}_{\mathrm{HR,org}}\cdot C_{\mathrm{HL,org}}\cdot C_{\mathrm{Ni,aq}}}{C^{2}_{\mathrm{H}}\cdot\sigma^{2}_{\mathrm{ad}}} - k''_{r}\cdot C_{\mathrm{NiLR(HR),org}} \tag{12}$$

$$\sigma_{\mathrm{ad}} = 1 + K_{\mathrm{HR}}C_{\mathrm{HR,org}} + K_{\mathrm{NiR}}C_{\mathrm{NiR,org}} + K_{\mathrm{NiR2}}C_{\mathrm{NiR2,org}} + K_{\mathrm{Sf}}C_{\mathrm{Sf,org}} \tag{13}$$

where σ_{ad} is the sum of terms representing the adsorption characteristics of extractant, the metal complex, and the surfactant, and S_{HR} is the interfacial area occupied by the unit mole of the extractant, DOLPA. The third and fourth terms are considerably smaller than the first, second, and fifth terms on the right-hand side of Eq. (13) (20). Assuming that the stripping rate is extremely fast compared with the extraction rate at the external interface of the emulsion globules, and the amount of carrier in the liquid membrane can be considered to be almost constant at the initial concentration (16), Eq. (12) can be rewritten as follows:

$$r = k_{\mathrm{f}}\cdot\left(\frac{K_{\mathrm{HR}}}{S_{\mathrm{HR}}}\right)^{2}\cdot C_{\mathrm{Ni,aq}}\cdot\left(\frac{C_{\mathrm{HR,org}}}{1 + K_{\mathrm{Sf}}C_{\mathrm{Sf,org}} + K_{\mathrm{HR}}C_{\mathrm{HR,org}}}\right)^{2}\cdot\frac{C_{\mathrm{HL,org}}}{C^{2}_{\mathrm{H}}} \tag{14}$$

An apparent interfacial reaction rate constant, k'_{f}, previously defined, can

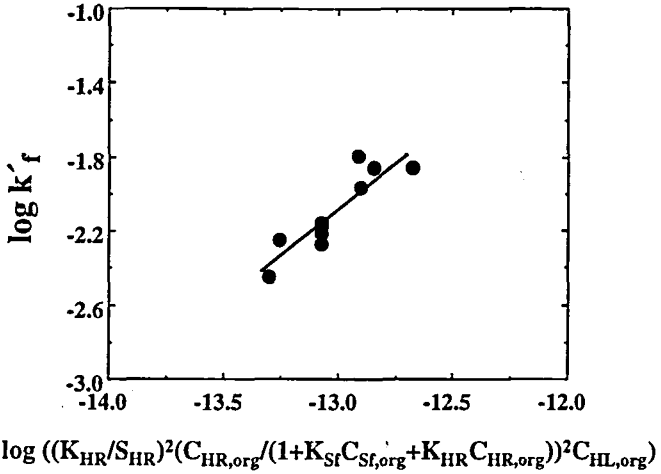

FIG. 11 Relationship between k_f' and the right-hand side of Eq. (15).

be expressed as a function of the concentrations of DOLPA, LIX63, and Span 80 as follows:

$$k_f' = k_f \cdot \left(\frac{K_{HR}}{S_{HR}}\right)^2 \cdot \left(\frac{C_{HR,org}}{1 + K_{Sf}C_{Sf,org} + K_{HR}C_{HR,org}}\right)^2 \cdot C_{HL,org} \qquad (15)$$

The relationship between k_f' and the right-hand side of Eq. (15) is shown in Fig. 11. Under the present experimental conditions, the average diameter of emulsion globules was 0.3 mm. Based on these experimental results and the interfacial tension measurement determined by the drop volume method (16), the overall rate constant, k_f, can be evaluated. The values of k_f, K_{HR}, K_{Sf}, and S_{HR} obtained are listed in Table 2. Experimental

TABLE 2
The Values of k_f, K_{HR}, K_{Sf}, and S_{HR} Determined by Interfacial Reaction Model

k_f	8.3×10^{10} (m^3/mol·s)
K_{HR}	3.1×10^3 (m^3/mol)
K_{Sf}	52 (m^3/mol) (16)
S_{HR}	4.5×10^5 (m^2/mol)

results were well simulated by using the above interfacial reaction parameters over a wide range of extractions.

CONCLUSION

The synergistic extraction of Ni(II) with LSMs has been carried out successfully using 5,8-dimethyl-7-hydroxydodecane-6-oxime (an active component of LIX63), DOLPA as a mobile carrier, and the surfactant Span 80. The associated extraction mechanism is elucidated using an interfacial reaction model.

Owing to its higher acidity and larger interfacial activity, the synthesized extractant DOLPA was superior to the commercial extractant D2EHPA with respect to the synergistic extraction of Ni(II) with LIX63.

The synergistic effect was observed not only in the extraction equilibrium of Ni(II) but also in the extraction rate of Ni(II) by LSMs. A huge synergistic effect occurred with an equivalent mixture of DOLPA and LIX63. The efficient recovery of Ni(II) was achieved under this condition.

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_E	diameter of emulsion globule (m)
K_1	equilibrium constant of reaction expressed by Eq. (8) (—)
K_2	equilibrium constant of reaction expressed by Eq. (9) (m^{-1})
K_3	equilibrium constant of reaction expressed by Eq. (11) (m^3/mol)
K_d	dimerization constant (m^3/mol)
K_j	adsorption equilibrium constant of species j (m^3/mol)
k_f	interfacial reaction rate constant ($m^3/mol \cdot s$)
k_f'	apparent interfacial reaction rate constant defined by Eq. (2) ($mol^2/m^5 \cdot s$)
k_f''	rate constant of forward reaction expressed by Eq. (10) ($m^3/mol \cdot s$)
k_r''	rate constant of reverse reaction expressed by Eq. (10) (m/s)
r	extraction rate ($mol/m^2 \cdot s$)
t	time (s)
V	volume of solution (m^3)
α_H	activity of hydrogen ion (mol/m^3)
γ_H	activity coefficient of hydrogen ion (—)
ϵ	degree of break-up (%)

Subscript

ad	adsorption state
aq	aqueous phase

E	emulsion phase
e	external aqueous phase
HL	LIX63
HR	DOLPA
i	internal aqueous phase
Mg	magnesium ion
Ni	nickel ion
0	initial value
org	organic phase
Sf	surfactant

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REFERENCES

1. J. M. Castresana, N. Etxebarria, and M. J. Zapatero, *Solv. Extr. Ion Exch.*, *10*(5), 861 (1992).
2. M. A. Olazabal, M. J. Zapatero, M. P. Elizalde, and J. M. Castresana, *Ibid.*, *10*(1), 19 (1992).
3. M. J. Zapatero, M. P. Elizalde, and J. M. Castresana, *Ibid.*, *10*(2), 281 (1992).
4. D. S. Flett and D. W. West, *ISEC '71*, *1*, 214 (1971).
5. M. Cox and D. S. Flett, *Ibid.*, *1*, 204 (1971).
6. D. S. Flett, M. Cox, and J. D. Heels, *ISEC '74*, *3*, 2560 (1974).
7. M. P. Elizalde, M. Cox, and M. Aguilar, *Solv. Extr. Ion Exch.*, *14*(5), 833 (1996).
8. T. Ono, M. Goto, F. Nakashio, and T. A. Hatton, *Biotechnol. Prog.*, *12*, 793 (1996).
9. A. E. Martell and R. J. Motekaitis, *Determination and Use of Stability Constant*, VCH Publishers, New York, NY, 1988.
10. I. Komasawa, T. Otake, and Y. Higaki, *Inorg. Nucl. Chem.*, *43*, 3351 (1981).
11. I. Komasawa, T. Otake, and I. Hattori, *J. Chem. Eng. Jpn.*, *16*, 210, 384 (1983).
12. I. Komasawa and T. Otake, *Ind. Eng. Chem.*, *Fundam.*, *22*, 367 (1983).
13. J. S. Preston, *Hydrometallurgy*, *11*, 105 (1983).
14. K. Osseo-Asare and D. R. Renninger, *Ibid.*, *13*, 45 (1984).
15. M. Goto, K. Kondo, and F. Nakashio, *J. Chem. Eng. Jpn.*, *22*, 79 (1989).
16. *Idem.*, *Ibid.*, *22*, 71 (1989).
17. J. M. Castresana and M. P. Elizalde, *Solv. Extr. Ion Exch.*, *6*,(2), 265 (1988).
18. F. Nakashio, M. Goto, M. Matsumoto, J. Irie, and K. Kondo, *J. Chem. Eng. Jpn.*, *38*, 249 (1988).
19. M. Goto, J. Irie, K. Kondo, and F. Nakashio, *Ibid.*, *22*, 401 (1989).
20. T. Kakoi, M. Goto, K. Sugimoto, K. Ohto, and F. Nakashio, *Sep. Sci. Technol.*, *30*(4), 637 (1995)
21. T. Kinugasa, K. Watanabe, and H. Takeuchi, *J. Chem. Eng. Jpn.*, *22*, 593 (1989)

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