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Interfacial Phenomena in the Extraction Kinetics of Nickel(II) with 2′-Hydroxy-5′-nonylacetophenone Oxime

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The interfacial adsorption of (*E*)-2′-hydroxy-5′-nonylacetophenone oxime and its role in the extraction kinetics of the nickel(II) ion with the oxime were investigated in heptane/aqueous phase systems by means of a high-speed stirring apparatus. The interfacial oxime concentration was correlated to the organic phase concentration, obeying the Langmuir isotherm. The interfacial activity of the oxime was also measured by means of interfacial tension measurements. The initial extraction rate of nickel(II) ion was linearly proportional to the interfacial concentration of the oxime (rather than to the bulk-phase concentration), to the nickel-ion concentration, and inversely to the hydrogen-ion concentration. These results supported the mechanism that the rate-determining step in the extraction is the 1:1 complex formation at the interface.

Recently, one of the present authors has pointed out the importance of interfacial reaction in the extraction kinetics of zinc(II) and nickel(II) with alkyl-substituted dithizones by means of the high-speed stirring method.[1] The advantages of the new method are (a) that an extraction rate is measured with a high accuracy, even in liquid–liquid dispersions generated by vigorous stirring, and (b) that the amount of extractant adsorbed at the interface in the same dispersed system is determined.[2,3] Therefore, this method is very promising for studies of interfacial phenomena in solvent-extraction kinetics.

In the present study, the role of the interface in the extraction of nickel(II) with (*E*)-2′-hydroxy-5′-nonylacetophenone oxime (HL), the active species of the commercial extractant SME 529, was investigated by means of the high-speed stirring apparatus.

Although the mechanism of the extraction kinetics of nickel(II) with β-hydroxy oxime has recently been discussed,[4,5] the assignment of the location, whether an interface or an aqueous phase, of the rate-determining reaction in a highly agitated extraction system has been remained ambiguous.

Experimental

The oxime was isolated from SME 529 donated by the Shell Chemical Co. and purified by the copper-complex method[6] and silica-gel chromatography. The fraction of the *E*-form in the purified oxime was not less than 0.98. Heptane, Wako G.R., was purified by distillation and used as an organic-phase solvent. The ionic strengths of all the aqueous phases were adjusted to 0.1 by the use of sodium perchlorate, and the pH of the aqueous phase was controlled by employing the acetate buffer (0.002 M, 1 M=1 mol dm^{-3}) and the phosphate buffer (0.002 M).

The high-speed stirring apparatus used in the present study is shown in Fig. 1. Although the principle of this apparatus is the same as that of a previous one,[3] the reproducibility of the stirring conditions, the stability of the spectrophotometric measurement, and the accuracy of the data analysis are much improved by the use of an Ono Sokki HT-431 digital tachometer and a Jasco UVIDEC 430 double-beam spectrophotometer interfaced by means of RS-232C with a NEC PC microcomputer system.

The amount of the oxime adsorbed at the interface in the stirred liquid–liquid system was determined at 25±0.1 °C by employing an equal volume (50 ml) of an organic solution of the oxime and an aqueous solution. When stirring was begun at 4700 rpm, the absorbance of the organic phase observed with a cell with an optical length of 1 cm decreased and reached a constant value. When it was stopped, the absorbance was restored to the initial state. The change in the absorbance was continuously recorded on the chart recorder. Figure 2 shows some typical results of the reversible absorbance decrease caused by stirring. The absorbance decrement, ΔA, defined as the difference between the equilibrium absorbance under no stirring, A, and the one under stirring, A', is considered to be proportional to the interfacial amount of the oxime or to the interfacial concentration, provided that the interfacial area remains constant.[2,6–8] A strong influence of the stirring rate on the magnitude of ΔA was observed in the range of 1000—4000 rpm, suggesting a contribution from the interfacial area, but it was diminished above 4500 rpm.[6] In the present study, 4700 rpm was adopted as the stirring rate.

The extraction rate of nickel(II) was measured at

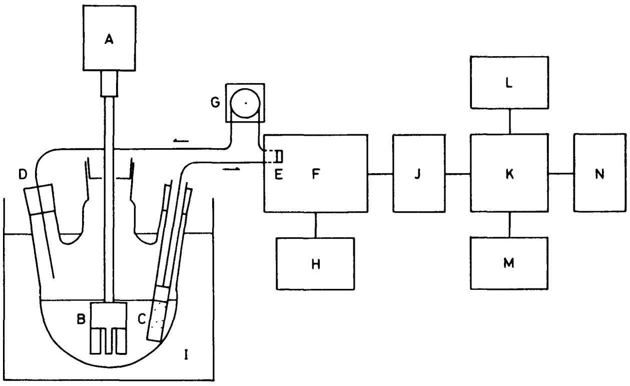

Fig. 1. Schematic diagram of the computer-assisted extraction kinetics measurement system. (A): Electric motor, (B): Teflon stirring bar, (C): Teflon phase separater, (D): sample inlet, (E): flow cell, (F): spectrophotometer, (G): peristaltic pump, (H): chart recorder, (I): thermostated water bath, (J): controlled device with RS-232C interface, (K): microcomputer, (L): printer, (M): dual-floppy disk drive, (N): CRT.

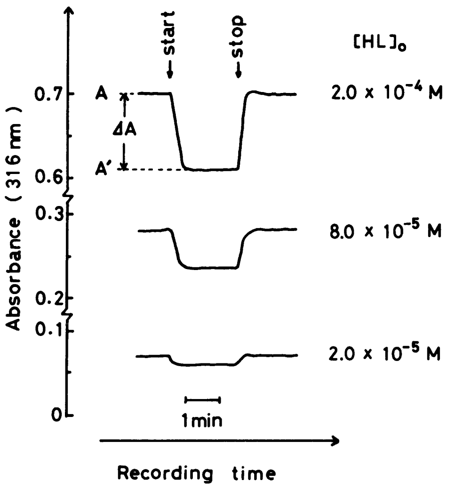

Fig. 2. Reversible change in the organic phase absorbance resulting from stirring at 4700 rpm, pH=3.01.

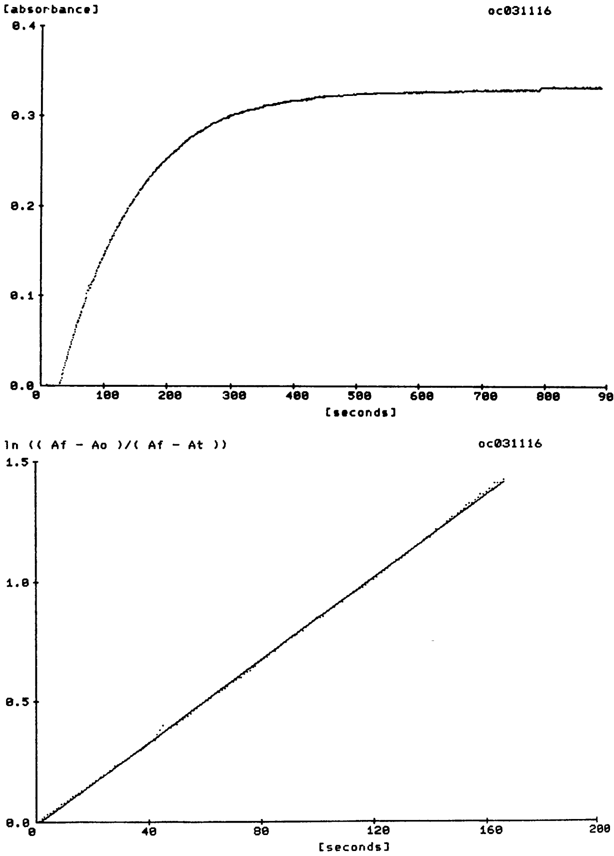

Fig. 3. Typical results of a recorded extraction kinetic run (upper) and a first-order kinetic analysis (lower). $[\mathrm{Ni}^{2+}]_{\mathrm{init}}=1.0\times10^{-2}$ M, $[\mathrm{HL}]_{\mathrm{o,init}}=1.0\times10^{-3}$ M, pH=4.52. $k_{\mathrm{obsd}}=(8.57\pm0.01)\times10^{-3}\ \mathrm{s}^{-1}$.

25±0.1 °C by means of a microcomputer-assisted system (Fig. 1). Fifty ml of a heptane solution of oxime and 45 ml of an aqueous buffer solution were poured into the three-necked flask, and stirring was begun at 4700 rpm. The organic phase was pumped out through a Teflon phase-separator (Kokuboseiki Co.) and circulated through the flow cell (8 µl; 0.25 cm in optical length) at the flow rate of 16 ml min^{-1}. Extraction was started by injecting 5 ml of a nickel(II) stock solution through a glass syringe into the dispersed mixture. The absorbance of the organic phase was read by the computer at the acquisition rate of 1 data/sec, and it was displayed graphically on CRT as a function of the time. Soon after the termination of the data acquisition, the absorbance data, stored on a floppy disk, were analyzed according to the first-order rate law. The extraction rate constant, k_{obsd}, was calculated by the use of the following equation;

$$\ln\frac{A_{\mathrm{f}}-A_{\mathrm{o}}}{A_{\mathrm{f}}-A_{\mathrm{t}}}=k_{\mathrm{obsd}}\cdot t \tag{1}$$

where A_{o}, A_{t}, and A_{f} correspond to the absorbances of the nickel(II) complex in the organic phase at the start of extraction, at a certain time t, and at the extraction equillibrium. Some typical results of kinetic measurement are shown in Fig. 3. From the observed extraction rate constant, the observed initial extraction rate (in absorbance units), $r^{\circ}_{\mathrm{obsd}}$, was calculated by the use of this relation;

$$r^{\circ}_{\mathrm{obsd}}=(A_{\mathrm{f}}-A_{\mathrm{o}})k_{\mathrm{obsd}}. \tag{2}$$

In several experiments, the agreement of $r^{\circ}_{\mathrm{obsd}}$ calculated by Eq. 2 and of $r^{\circ}_{\mathrm{obsd}}$ directly obtained from $r^{\circ}_{\mathrm{obsd}}=(\mathrm{d}A_{\mathrm{t}}/\mathrm{d}t)_{t=0}$, which is the definition of $r^{\circ}_{\mathrm{obsd}}$, was confirmed.

The acid dissociation constant (K_{a}) of the oxime was estimated as $10^{-9.79\pm0.09}$ from the apparent dissociation constants, $10^{-10.28}$, $10^{-10.45}$, and $10^{-10.76}$, which were obtained in 30, 40, and 50% ethanolic aqueous solution by means of spectrophotometry.

The experiments on the distribution equilibrium of the oxime and the extraction equilibrium of nickel(II) with the oxime were done by means of the conventional batch method and by means of spectrophotometry at 25±1 °C. The distribution constant (K_{D}) was calculated as $10^{3.99\pm0.21}$ from the distribution ratio determined in the alkaline region and the acid dissociation constant. The extraction equilibrium of;

$$\mathrm{Ni}^{2+}+2\mathrm{HL}_{\mathrm{o}} \rightleftharpoons \mathrm{NiL}_{2,\mathrm{o}}+2\mathrm{H}^{+} \tag{3}$$

was confirmed and the extraction constant of $10^{-3.99\pm0.41}$ was determined from a slope analysis of the distribution ratio plotted against the pH.

The interfacial tension in heptane/water systems containing the oxime was measured by means of the drop-volume method at 25±0.1 °C, applying the Harkins-Brown correction.[9,10]

Results and Discussion

Interfacial Adsorption of the Oxime. The reversible absorbance decrease caused by stirring was measured while varying the concentration of the oxime. Figure 4 shows the concentration effect as a plot of ΔA against A'. As may be noted in this figure, ΔA approaches a saturated value with the increase in A', which means that the saturation in the interfacial amount of the oxime occurs at a higher-organic-phase concentration than 10^{-3}M. The effect of the pH on ΔA was not observed under the acidic and neutral conditions (pH=3—6) where the kinetic experiments were conducted.

The interfacial tension in the heptane/water system decreased with an increase in the oxime concentration, as is shown in Fig. 5, demonstrating an interfacial activity of the neutral form of the oxime. Also, Fig. 5 indicates that the heptane/water interface is saturated by oxime when the oxime concentration becomes as concentrated as 10^{-3} M, corresponding to the result observed in the stirring experiment (Fig. 4).

The mechanism of interfacial adsorption in the vigorously stirred systems can be understood in terms of the following discussion. The total amount of oxime in the dispersed system is represented by;

$$[\mathrm{HL}]_{\mathrm{init}}V_o \simeq [\mathrm{HL}]_oV_o + [\mathrm{HL}]_iS10^3, \tag{4}$$

where $[\mathrm{HL}]_{\mathrm{init}}$, $[\mathrm{HL}]_o$, and $[\mathrm{HL}]_i$ refer to an initial organic-phase concentration before contact with the aqueous phase, an organic-phase concentration under stirring, and an interfacial concentration (mol cm^{-2}) in the dispersed liquid-liquid system, V_o, to the volume (ml) of the organic phase, and S, to the total interfacial area (cm^2) of the dispersed system. If the Langmuir isotherm is assumed to be the adsorption equilibrium of the oxime, $[\mathrm{HL}]_i$ is represented by;

$$[\mathrm{HL}]_i = \frac{ab[\mathrm{HL}]_o}{1+b[\mathrm{HL}]_o}, \tag{5}$$

where a corresponds to a saturated interfacial concentration, and ab, to an adsorption equilibrium constant at an infinite dilution, K', itself defined by;

$$ab = K' = \lim_{[\mathrm{HL}]_o \to 0} \frac{[\mathrm{HL}]_i}{[\mathrm{HL}]_o}. \tag{6}$$

From Eqs. 4—6 and the Lambert-Beer equations of;

$$\begin{aligned}\Delta A &= \varepsilon([\mathrm{HL}]_{\mathrm{init}}-[\mathrm{HL}]_o)\\ A' &= \varepsilon[\mathrm{HL}]_o,\end{aligned} \tag{7}$$

the following equation can be derived upon the relationship between $1/\Delta A$ and $1/A'$:

$$\frac{1}{\Delta A} = \left(\frac{1}{a}+\frac{\varepsilon}{K'}\frac{1}{A'}\right)\frac{V_o}{\varepsilon S10^3} \tag{8}$$

where ε refers to the molar absorptivity of the oxime in heptane, ε (316 nm)=3.49×10^3 M^{-1} cm^{-1}.

The straight line shown in Fig. 6 confirmed the proposed relationship of Eq. 8, and its slope and intercept gave these two parameters: $K'S=1.0\times10^{-2}$ l and a $S=3.9\times10^{-6}$ mol. Employing $a=2.0\times10^{-10}$ mol cm^{-2}, which was determined from Fig. 5 by applying the Gibbs equation,[6] $S=2.0\times10^4$ cm^2 was estimated; by its use, $K'=5.1\times10^{-7}$ l cm^{-2} was then calculated. The value of S is consistent with that obtained previously.[8]

Extraction Mechanism of Nickel(II). The dependence of $r^{\circ}_{\mathrm{obsd}}$ on the oxime concentration was examined at a constant pH; the results are shown in Fig. 7. The plot of $r^{\circ}_{\mathrm{obsd}}$ against $[\mathrm{HL}]_o$ was curved, and

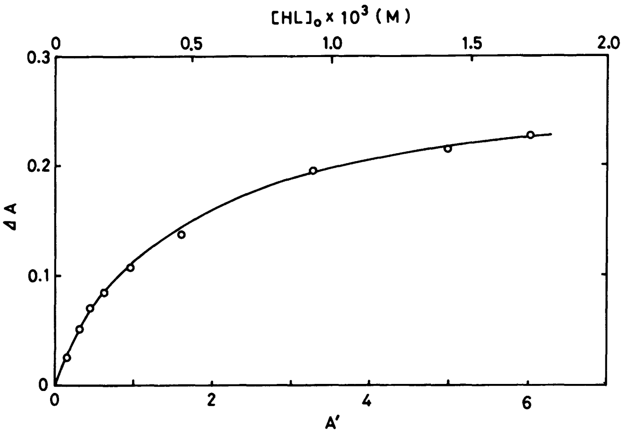

Fig. 4. Dependence of the absorbance decrement, ΔA, on the organic phase absorbance, A,' under stirring. $[\mathrm{HL}]_{o,\mathrm{init}}=2.0\times10^{-5}$ M—2.0×10^{-3} M, pH=3.0—6.2, λ=316 nm, 4700 rpm.

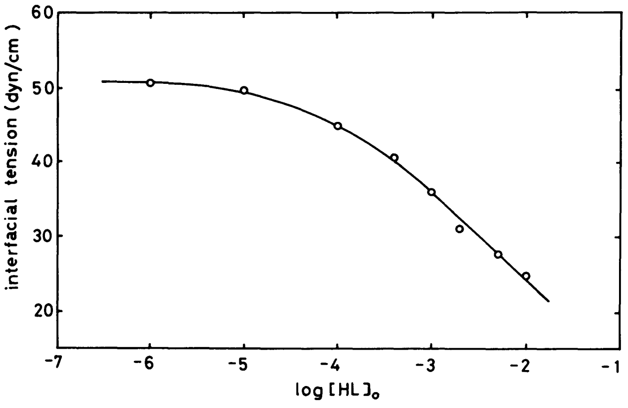

Fig. 5. Lowering of the interfacial tension with increase of the oxime concentration in the heptane/water system.

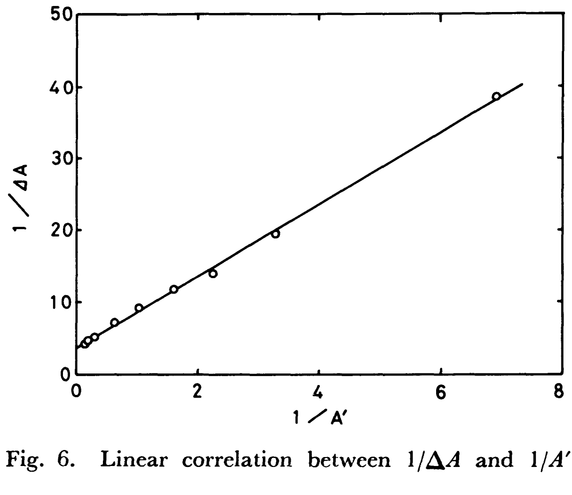

Fig. 6. Linear correlation between $1/\Delta A$ and $1/A'$.

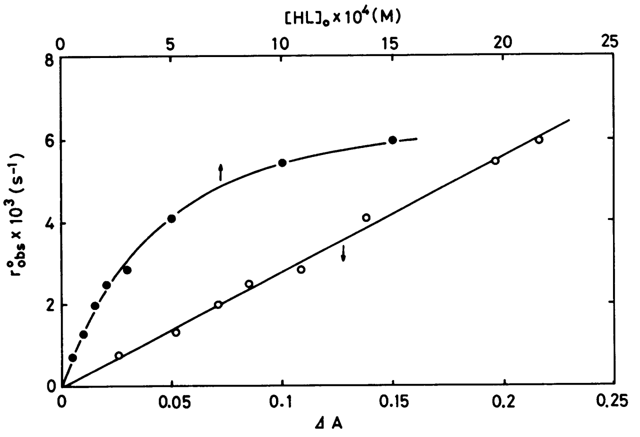

Fig. 7. Linear dependence of the initial extraction rate on ΔA, and nonlinear one on the bulk phase concentration of the oxime. $[\text{HL}]_{\text{o,init}}=1.0\times10^{-4}$ M—1.5×10^{-3}M, $[\text{Ni}^{2+}]_{\text{init}}=9.85\times10^{-3}$ M, pH=5.61.

no linear relationship was obtained between them. On the other hand, the plot of r°_{obsd} against ΔA gave a good linearity indicating that r°_{obsd} is proportional to $[\text{HL}]_i$, and not to $[\text{HL}]_o$. The effects of the nickel-ion concentration and the hydrogen-ion concentration on r°_{obsd} are shown in Figs. 8(a) and 8(b) respectively. In either figure, a linear plot was obtained, and the relation of $r^\circ_{\text{obsd}} \propto [\text{Ni}^{2+}]/[\text{H}^+]$ was experimentally concluded.

If the rate-determining step is 1 : 1 chelate formation in the aqueous phase, as has been reported for other nickel(II)-extraction systems,[11] r°_{obsd} will be represented by;

$$r^\circ_{\text{obsd}} = k_1\frac{K_a}{K_D}\frac{[\text{Ni}^{2+}][\text{HL}]_o}{[\text{H}^+]}\varepsilon_c l, \tag{9}$$

where k_1 refers to the formation-rate constant of NiL^+; ε_c, to the molar absorptivity of NiL_2 in heptane, ε_c (387 nm)=4.53×10^4 M^{-1} cm^{-1}, and l, to the optical length of the flow cell. Although Eq. 9 proposes the relation of $r^\circ_{\text{obsd}} \propto [\text{HL}]_o$, this is inconsistent with the experimental results (Fig. 7). Furthermore, the magnitude of r°_{obsd} calculated from Eq. 9 under the probable conditions of $k_1=10^5$ M^{-1} s^{-1}, pH=5, $[\text{HL}]_o=10^{-3}$ M, and $[\text{Ni}^{2+}]=10^{-2}$ M was of an order of 10^{-6} s^{-1} and 10^3 times less than the observed value of r°_{obsd} under the corresponding conditions.

All of the experimental results and the above discussions seems to be favorable for the interfacial reaction mechanism rather than the aqueous-phase reaction mechanism. If the rate-determining step is the formation of a 1 : 1 complex at the interface, the following scheme can be assumed;

$$\text{HL}_o \rightleftharpoons \text{HL}_i \qquad ; \ \text{Langmuir isotherm} \tag{10}$$

$$\text{HL}_i \rightleftharpoons \text{L}_i^- + \text{H}^+ \qquad ; \ K_a' \tag{11}$$

$$\text{Ni}^{2+} + \text{L}_i^- \longrightarrow \text{NiL}_i^+ \qquad ; \ k_i \tag{12}$$

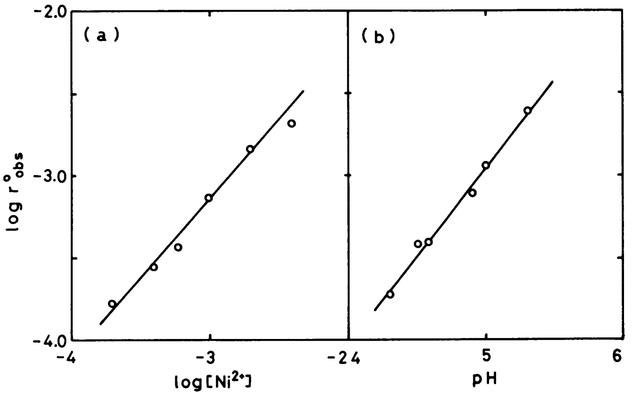

Fig. 8. First-order dependences of the initial extraction rate on nickel concentration (a), and on $[\text{H}^+]^{-1}$ (b).

where K_a' is the acid dissociation constant at the interface defined by $K_a'=[\text{L}^-]_i[\text{H}^+]/[\text{HL}]_i$ and where k_i is the formation-rate constant of NiL^+ at the interface. The final complex of NiL_2 did not show any significant interfacial adsorption in the stirring experiment. From the scheme, the following equation can be derived for the observed initial extraction rate;

$$\begin{aligned} r^\circ_{\text{obsd}} &= k_i[\text{Ni}^{2+}][\text{L}^-]_i\frac{10^3S}{V_o}\cdot\varepsilon_c l \\ &= k_iK_a'\frac{[\text{Ni}^{2+}]}{[\text{H}^+]}\cdot\frac{\varepsilon_c l}{\varepsilon}\cdot\Delta A. \end{aligned} \tag{13}$$

Equation 13 is consistent with the observed relationships between r°_{obsd} and $[\text{Ni}^{2+}]$, $[\text{H}^+]$ and ΔA, shown in Figs. 7 and 8. Consequently, the proposed mechanism of Eqs. 10—12 is considered to be reasonable. The slope of the line in Fig. 7 and the intercepts of Figs. 8(a) and 8(b) gave the combined parameter of $k_iK_a'=(2.18\pm0.09)\times10^{-5}$ s^{-1} as an averaged value. Although the value of K_a' in the present system has not been determined, if $K_a'\simeq K_a$ is assumed, as has been observed in LIX65N,[8] k_i can be estimated as 1.3×10^5 M^{-1} s^{-1}. The value of k_i is apparently close to the formation-rate constant of the mono(8-quinolinethiol)nickel(II) complex in the aqueous phase.[11]

As has been concluded in the present study, the primary step of an extraction reaction is the adsorption of an extractant at the interface when the extractant has a large distribution constant and, more or less, an interfacial activity. Therefore, the experimental determination of the interfacial concentration of an extractant is very important in evaluating the contribution of an interfacial reaction to the mechanism of extraction kinetics. Also, the utility of the high-speed stirring apparatus for the study of interfacial phenomena was demonstrated. Further studies of the interfacial phenomena in other chelate-extraction systems and ion-association extraction systems are in progress.

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