SEPARATIONS

Photoreductive Stripping of Cobalt Loaded on Hydroxyoxime Extractant in a Liquid−Liquid Extraction System

Syouhei Nishihama,[†] Nobuya Sakaguchi,[†] Takayuki Hirai,*[,†] and Isao Komasawa[†,‡]

Department of Chemical Science and Engineering, Graduate School of Engineering Science, and Research Center for Photoenergetics of Organic Materials, Osaka University, Machikaneyama-cho 1-3, Toyonaka, Osaka 560-8531, Japan

The photoreductive stripping of cobalt from hydroxyoxime extractants was investigated, employing 2-hydroxy-5-nonylacetophenone oxime (LIX-84I) and 2-hydroxy-5-nonylbenzophenone oxime (LIX-65N) as extractants, *n*-dodecane as the diluent, and a halogen lamp as the light source. The stripping of cobalt is barely achieved by conventional stripping, in this extraction system, because of the oxidation of the cobalt−hydroxyoxime complex by electron attraction with the O_2 molecule. The stripping of cobalt is, however, substantially improved by photoirradiation using light of visible radiation wavelength. The organic solution obtained following photoirradiation can be reused for repeated extraction and photoreductive stripping processing.

1. Introduction

Liquid−liquid extraction has been applied successfully for many industrial separation, purification, and recovery processes in the field of rare metals, and many commercial extractants have been developed. Chelating extractants, especially those having selectivity for copper, have also been developed for use in extractive separation processes[1] and have been used for the separation and recovery of copper from leach liquor containing impurities such as cobalt, iron, nickel, etc.[2] Cobalt(II), however, when extracted via commercial chelating extractants such as hydroxyoxime-type extractants, is difficult to recover by stripping, because of so-called cobalt poisoning.[2−5] This poisoning occurs because the cobalt(II)−extractant complex formed is easily oxidized to the trivalent state under atmospheric air and is then stabilized in the organic phase. Several attempts have been made to improve the stripping of cobalt from the extractant or even to prevent the cobalt from being extracted. Skarbo has reported a method for stripping cobalt from hydroxyoxime extractant.[3] In this process, however, an aqueous stripping reagent, containing 2−4 mol/L of HCl and 50−200 g/L of sodium chloride, is needed at elevated temperature conditions (40−60 °C). Rokukawa has investigated the separation of cobalt, nickel, and copper from ammoniacal alkaline leach liquor and reported that cobalt is prevented from being extracted by being oxidized to the trivalent state in the aqueous phase prior to extraction.[6]

The photochemical redox reaction, based on the principle that the distribution ratios for those metals having the smaller valences are lower than those of the metals having the larger valences, has also recently been studied for improving separation.[7−10] Selective stripping or extraction has also been achieved by photochemical reduction using liquid−liquid extraction systems with acidic organophosphorus compounds.[9,10] In such systems, the extracted species obtained in the organic phase is easier to photoreduce than the metal ion, which exists in the aqueous phase. One can therefore expect to achieve effective stripping if the oxidized cobalt(III) complex can be photoreduced within the organic phase.

In the present work, the stripping of cobalt from the more familiar hydroxyoxime-type extractants, such as 2-hydroxy-5-nonylacetophenone oxime (LIX-84I) or 2-hydroxy-5-nonylbenzophenone oxime (LIX-65N), is investigated by employing the photochemical reduction of cobalt in the organic phase. The stripping behavior of cobalt, when loaded on these extractants, was investigated first. The mechanism of oxidation of the extracted species was then explored using ESR spectrometry. Finally, the photoreductive stripping of the cobalt was investigated, including the question of the reusability of the organic phase for further extraction.

2. Experiment

2.1. Reagents. 2-Hydroxy-5-nonylacetophenone oxime (marketed as LIX-84I by Henkel Hakusui Co., Ltd.) and 2-hydroxy-5-nonylbenzophenone oxime (marketed as LIX-65N by Henkel Hakusui Co., Ltd.) were used as extractants without further purification. The inorganic chemicals and *n*-dodecane were supplied by Wako Pure Chemical Industries as analytical-grade reagents. Deionized water was purified by simple distillation prior to use. The aqueous feed solution was prepared by dissolving $CoCl_2{\cdot}6H_2O$ into dilute HCl solution, and the organic solution was prepared by diluting the extractant with *n*-dodecane as the diluent.

---

* Author to whom correspondence should be addressed. Tel.: +81-6-6850-6272. Fax: +81-6-6850-6273. E-mail: hirai@cheng.es.osaka-u.ac.jp.

[†] Graduate School of Engineering Science.

[‡] Research Center for Photoenergetics of Organic Materials.

10.1021/ie000617p CCC: $19.00

2.2. Procedure. The extraction equilibrium data were obtained by shaking the organic and aqueous solutions, at an organic/aqueous (O/A) volume ratio of 1, at 298 K for a period of 10 h. It was found in the preliminary experiment that the equilibrium was attained for a period of less than 1 h. The concentrations of cobalt in the resulting aqueous-phase samples were analyzed using an inductively coupled argon plasma atomic emission spectrometer (ICP-AES, Nippon Jarrell-Ash ICAP-575 Mark II), and the corresponding organic phase concentrations were determined through mass balance calculations. The equilibrium pH value was measured using an Orion 920A pH meter, equipped with a glass combination electrode. The ESR spectra for the cobalt−LIX-84I complex in the organic solution were measured at liquid-nitrogen temperature using an EPR spectrometer (Bruker EMX 10/12) operating at 9.61 GHz under 4.0 mW of power. Absorption spectra for the organic solution were measured using a UV−vis spectrophotometer (Hewlett-Packard HP 8452A).

The photoreductive stripping of cobalt was carried out using a beaker-type glass bottle (32 mm in diameter). A 500-W halogen lamp (Eikohsha Co., Ltd., EHC-500) was used as the light source, which was set 7 cm apart from the reaction bottle. Only a part of the light from the lamp was used for the photoreductive stripping in the present experiments. The wavelength of irradiated light was adjusted by virtue of the Pyrex glass material of the reaction bottle (greater than 300 nm) or by using appropriate cutoff filters (greater than 450 or 550 nm). HCl aqueous solution (10 mL) and the cobalt-loaded organic solution (10 mL) were agitated together and were bubbled with Ar gas for 30 min prior to irradiation. The resulting mixture was then agitated at over 4000 rpm by a magnetic stirrer and irradiated at an irradiation intensity (under the conditions without the cutoff filter) of 7.06×10^5 W/m^2. The photointensity was measured by a thermopile (The Eppley Laboratory, Inc.). The resulting aqueous samples were analyzed for cobalt concentration using ICP-AES. The concentration of the HCl solution was determined by a potentiometric titration method using $AgNO_3$ (Hiranuma Comtite-550).

3. Results and Discussion

3.1. Extraction Equilibrium Formulations. The extraction equilibrium formulation for cobalt with LIX-84I or LIX-65N as the extractant, when diluted with *n*-heptane, has been investigated and expressed according to eq 1.[11]

$$\mathrm{Co}^{2+} + 2\overline{\mathrm{RH}} \leftrightarrow \overline{\mathrm{CoR}_2} + 2\mathrm{H}^+ \qquad (1)$$

Figure 1 shows the effect of the equilibrium pH value on the distribution ratio for the *n*-dodecane diluent system. Linear relationships with slope of about 2 were obtained in the present systems as for the reported *n*-heptane system, thus indicating that only divalent cobalt takes part in the extraction. Figure 2 shows the effect of the HCl concentration on the stripping efficiency for cobalt at an O/A volume ratio of 0.5. The extraction−stripping was carried out both with Ar or O_2 bubbling and also without bubbling. For both zero bubbling and bubbling with O_2, the stripping efficiency obtained with 6 mol/L HCl was at most about 80%, and thus quantitative stripping, by the conventional method, cannot be achieved using either extractant system. In the case of Ar bubbling and thus the absence of oxygen molecules in the system during the extraction−stripping process, the stripping is substantially improved, and quantitative stripping is achieved at 6 mol/L HCl. These results, therefore, indicate that the cobalt is stabilized in the organic phase by the presence of oxygen, which thus suppresses quantitative stripping.

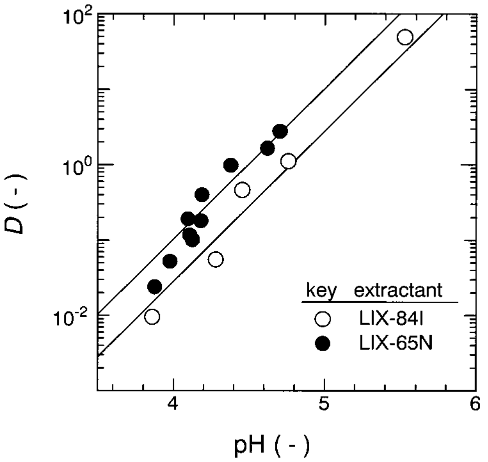

Figure 1. Effect of the aqueous-phase pH on the distribution ratio for the *n*-dodecane diluent. $[\overline{\mathrm{RH}}]_{\mathrm{feed}}$ = 10 vol % and $[\mathrm{Co}^{2+}]_{\mathrm{feed}}$ = 0.01 mol/L. LIX-84I system: slope = 2.24, $|r|$ = 0.99. LIX-65N system: slope = 2.35, $|r|$ = 0.97.

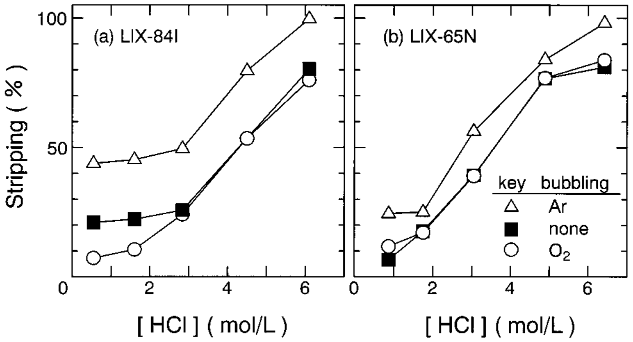

Figure 2. Effect of HCl concentration on the stripping efficiency in the (a) LIX-84I and (b) LIX-65N systems, at an O/A ratio of 0.5. $[\overline{\mathrm{RH}}]_{\mathrm{feed}}$ = 10 vol %, and $[\overline{\mathrm{Co}}]_{\mathrm{feed}}$ = (a) 6.76 mmol/L and (b) 7.13 mmol/L.

3.2. Mechanism for the Oxidation of Extracted Species. The species of cobalt extracted using LIX-84I was analyzed by ESR spectroscopy. Cobalt(III) is known to be ESR silent, because it is not paramagnetic. Figure 3 shows the ESR spectra for cobalt−LIX-84I complexes, prepared by extraction under sets of differing conditions. In the case of Ar bubbling, a broad signal caused by a cobalt(II)−LIX-84I complex, shown by spectrum a, is observed. However, when the sample is in contacting with air, new split sharp signals, as shown by spectrum b, appear. For both zero bubbling and O_2 bubbling, only the sharp signals are observed, spectra c and d, and the broad signal corresponding to the resulting cobalt(II)−LIX-84I complex is no longer observed. Cobalt(II) complexes are well-known to add easily to an O_2 molecule and to be oxidized to cobalt(III) to form a superoxo complex, as expressed by eq 2.[12−14]

$$\overline{\mathrm{Co(II)}} + \mathrm{O}_2 \rightarrow \overline{\mathrm{Co(III)}\text{−}\mathrm{O}\text{−}\mathrm{O}\cdot} \qquad (2)$$

The split sharp signals are thus caused by the superoxide anion added to cobalt, thus indicating that the cobalt(II) molecule is oxidized to the trivalent state by

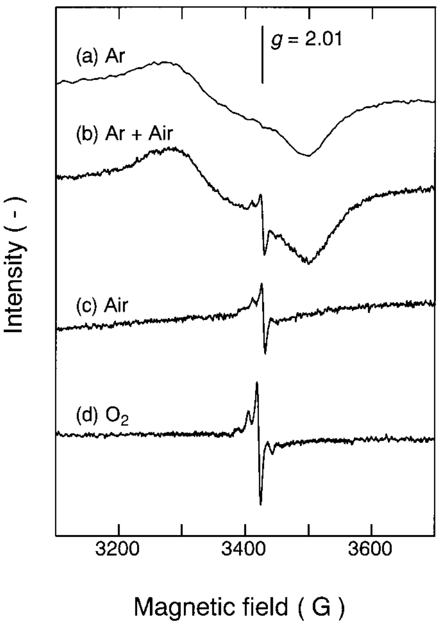

Figure 3. ESR spectra for cobalt loaded on LIX-84I in *n*-dodecane. The cobalt–LIX-84I complexes were prepared by extraction under the differing conditions of (a) Ar atmosphere, (b) Ar atmosphere but measured following exposure to air, (c) air atmosphere, and (d) O_2 atmosphere $[\overline{RH}]_{feed}$ = 30 vol %, and $[\overline{Co}]_{feed}$ = (a) 0.0734 mol/L, (b) 0.0732 mol/L, (c) 0.0738 mol/L, and (d) 0.0735 mol/L.

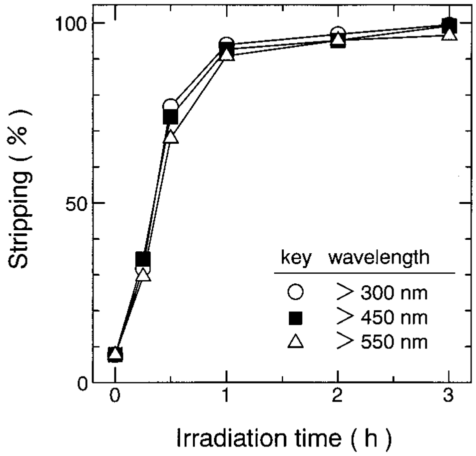

Figure 4. Effect of the wavelength of the light source on the time-course variation in the stripping efficiency for the LIX-84I system. $[\overline{RH}]_{feed}$ = 10 vol %, $[\overline{Co}]_{feed}$ = 7.64 mmol/L, and [HCl] = 3 mol/L.

electron attraction with O_2 in the extraction system. This superoxo complex is reported to react further with a second cobalt(II) to form a μ-peroxo complex (eq 3).[15]

$$\overline{\text{Co(III)}-\text{O}-\text{O}\cdot} + \overline{\text{Co(II)}} \rightarrow \overline{\text{Co(III)}-\text{O}-\text{O}-\text{Co(III)}} \quad (3)$$

3.3. Photoreductive Stripping of Cobalt. The photoreductive stripping of cobalt was then carried out using both extractant systems. In these experiments, the extractant *n*-dodecane solution, containing cobalt, was first put into contact with the HCl solution at an O/A volume ratio of 1. The mixture was then photoirradiated following Ar bubbling with agitation by magnetic stirrer. Figure 4 shows the time-course variation in the stripping efficiency for cobalt, in the LIX-84I system with 3 mol/L of HCl, under the conditions of vigorous stirring with photoirradiation at three different wavelengths. The photoreductive stripping of cobalt into the HCl solution progresses successively, with the concentration of cobalt in the aqueous phase increasing with irradiation time. In addition, the rate of the photoreductive stripping of cobalt appears to be insensitive to the wavelength of the irradiated light. Figure 5 shows the absorption spectra for the organic solutions containing the cobalt–LIX-84I complex. A large absorption band, caused by the cobalt–LIX-84I complex is seen at 400–800 nm. These results indicate that the photochemical reduction of cobalt occurs following photoabsorption at wavelengths of 400–800 nm, and thus, the photoreductive stripping progresses with photoirradiation by visible as well as UV light.

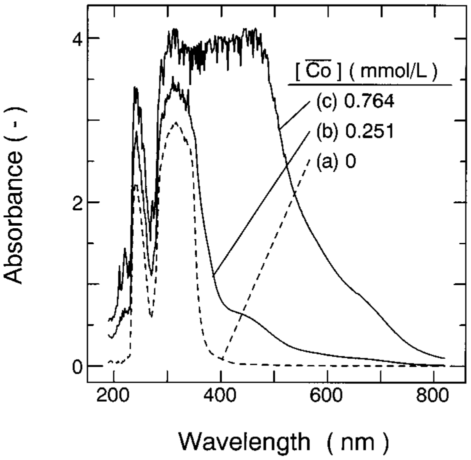

Figure 5. Absorption spectra for the organic solution containing LIX-84I and cobalt. $[\overline{RH}]_{feed}$ = 2.5 vol %, and $[\overline{Co}]_{feed}$ = (a) 0 mol/L, (b) 0.251 mmol/L, and (c) 0.764 mmol/L. Reference: air.

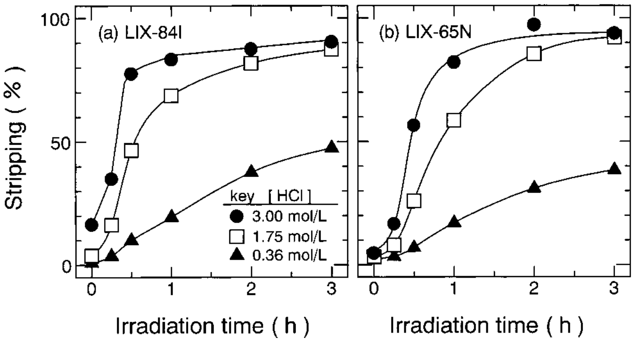

Figure 6. Effect of the HCl concentration on the time-course variation of photoreductive stripping in the (a) LIX-84I and (b) LIX-65N systems. $[\overline{RH}]_{feed}$ = 10 vol %, and $[\overline{Co}]_{feed}$ = (a) 6.53 mmol/L and (b) 9.37 mmol/L.

The effect of HCl concentration on the photoreductive stripping of cobalt with photoirradiation at wavelengths greater than 550 nm in the LIX-84I and LIX-65N systems is shown in Figure 6a and b, respectively. Successive stripping also progresses in the LIX-65N system as well as in the LIX-84I system. The photoreductive stripping of cobalt is improved by increasing the concentration of HCl in both systems, and a stripping efficiency of about 90% can be achieved with 3 mol/L of HCl following photoirradiation for 3 h. More successful stripping may progress when the extraction is carried out under the conditions of Ar bubbling (in the absence of oxygen molecule), as the oxidation of the cobalt(II) complex during extraction may have been much suppressed. In the present work, a long irradia-

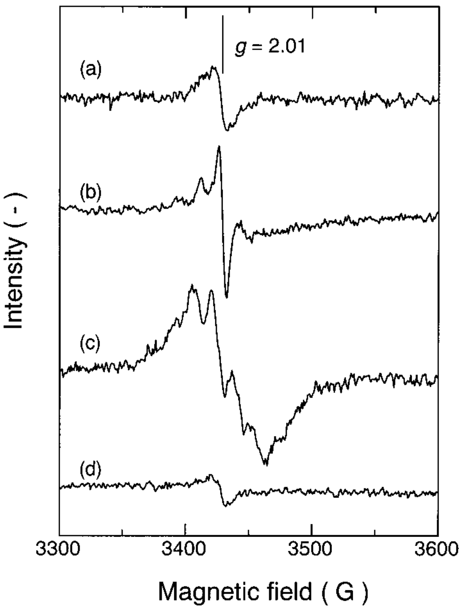

Figure 7. Effect of photoirradiation on the ESR spectra for cobalt loaded on LIX-84I in *n*-dodecane. $[\overline{\mathrm{RH}}]_{\mathrm{feed}}$ = 30 vol %; $[\overline{\mathrm{Co}}]$ = (a) 0 mol/L, (b) 0.082 mol/L, (c) 0.030 mol/L, and (d) 1.1 mmol/L; and [HCl] = (c) 0.6 mol/L and (d) 3 mol/L.

tion time was needed for the photoreductive stripping of cobalt. Because the experimental setup was made as simple as possible, the development of an appropriate reaction apparatus will allow the irradiation time be shortened and the irradiation intensity to be decreased.

Figure 7 shows the effect of photoirradiation on the ESR spectra of the cobalt−LIX-84I complex. Spectrum a applies to the case without cobalt being present, with the appearance of the signal seeming to indicate addition of oxygen to the extractant. Spectrum b applies to the case of organic solution containing 0.082 mol/L cobalt. Here, the spectrum differs from spectrum a in that it is split, indicating that the electronic state of the oxygen is different for the case of superoxide anion added to cobalt−LIX-84I complex for spectrum b as compared to that for oxygen added to LIX-84I in spectrum a. Spectrum c applies to the case of the solution containing cobalt−LIX-84I, stripped with 0.6 mol/L HCl with photoirradiation for 12 h, and containing a residual 0.030 mol/L cobalt. In this case, the broad signal caused by cobalt(II), as shown by spectrum a in Figure 3, is absent, although the conditions provide sufficient time for the cobalt in the organic phase to be reduced to the divalent state. Spectrum d applies to the case in which 3 mol/L HCl was used for the stripping and most of the cobalt was stripped into the aqueous phase. Here, the spectrum shows both the absence of cobalt(II) and the absence of superoxide anion added to the cobalt(III)−LIX-84I complex, leaving only a sharp signal, the shape of which is identical to that observed for oxygen added to extractant, as in spectrum a. The reduced cobalt is, therefore, immediately reoxidized by the oxygen in the organic phase, unless stripped into the aqueous phase.

3.4. Reusability of the Organic Phase. The possible reuse of the organic solution following photoirradiation was also investigated for the case of the LIX-84I system. A 3 mol/L HCl solution and the cobalt-containing organic solution were put into contact at an O/A volume ratio of 1 and were photoirradiated for 5 h. The resulting organic solution, after being washed with water, was then used for extraction, and the extracted organic solution was then used again for repeated processing. Figure 8 shows the concentration of cobalt in the organic phase for the repeated extraction−photoreductive stripping processing. The results thus show that the organic phase retains sufficient loading and stripping capacity for use in repeated processing and confirm the possible reuse of the organic phase.

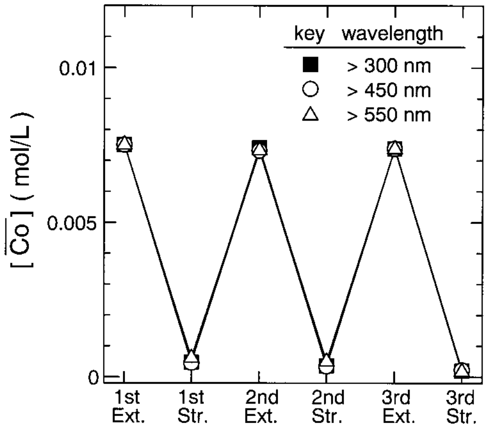

Figure 8. The concentration of cobalt, obtained in the organic phase, following the repeated extraction−photoirradiation processing. $[\overline{\mathrm{RH}}]_{\mathrm{feed}}$ = 10 vol% and $[\mathrm{Co}^{2+}]_{\mathrm{feed}}$ = 0.01 mol/L.

4. Conclusion

The photoreductive stripping of cobalt loaded on hydroxyoxime extractant has been investigated, with the following results: (1) The quantitative stripping of cobalt loaded on LIX-84I or LIX-65N is not achieved by the conventional extraction procedure because of the inevitable oxidation of the cobalt−hydroxyoxime complex in the organic phase. The oxidation of cobalt progresses by electron attraction with the O_2 molecule in the extraction system. (2) The photoreductive stripping of cobalt progresses by photoirradiation, using the wavelengths of visible light. The photoreductive stripping is improved by increasing the concentration of HCl, and a stripping efficiency of about 90% can be achieved following photoirradiation for 3 h. (3) The organic solution following photoirradiation can be reused for repeated extraction−photoreductive stripping processing.

Acknowledgment

The authors are grateful to the Division of Chemical Engineering for the Lend Lease Laboratory System. S.N. is grateful to the Research Fellowships of the Japan Society for Promotion of Science for Young Scientists and to the Morishita Zintan Scholarship Foundation.

Nomenclature

D = distribution ratio
g = g value for ESR measurement
$|r|$ = correlation coefficient
RH = LIX-84I or LIX-65N

Subscripts

feed = aqueous or organic feed solution

Superscripts

$\overline{}$ = organic-phase species

Literature Cited

(1) Ritcey, G. M.; Ashbrook, A. W. *Solvent Extraction*; Elsevier: Amsterdam, 1984; Part I, Chapter 3.II.

(2) Ritcey, G. M.; Ashbrook, A. W. *Solvent Extraction*; Elsevier: Amsterdam, 1979; Part II, Chapter 4.5.

(3) Skarbo, R. R. Cobalt Stripping. U.S. Patent 3,849,534, 1974.

(4) Ritcey, G. M. Commercial Processes for Nickel and Cobalt. In *Handbook of Solvent Extraction*; Lo, T. C., Baird, M. H. I., Hanson, C., Eds.; John Wiley & Sons: New York, 1983.

(5) Takahashi, M.; Ogata, T.; Okino, H.; Abe, Y. The Deterioration of Nickel Extractant LIX 64N and Its Regeneration. *Proc. Int. Solvent Extr. Conf.* **1983**, 359.

(6) Rokukawa, N. Separation of Cobalt, Nickel and Copper from Ammoniacal Alkaline Leach Liquor of Cobalt Crusts by Solvent Extraction. *Shigen-to-Sozai* **1993**, *109*, 373 (in Japanese).

(7) Hirai, T.; Komasawa, I. Separation of Eu from Sm/Eu/Gd Mixture by Photoreductive Stripping in Solvent Extraction Process. *Ind. Eng. Chem. Res.* **1995**, *34*, 237.

(8) Hirai, T.; Manabe, T.; Komasawa, I. Photoreductive Stripping of Vanadium Using 2-Propanol as Radical Scavenger in Liquid−Liquid Extraction Process of Vanadium and Molybdenum. *J. Chem. Eng. Jpn.* **1997**, *30*, 268.

(9) Nishihama, S.; Hirai, T.; Komasawa, I. Mechanism of Photoreductive Stripping of Iron(III) in a Liquid−Liquid Extraction System and Its Application for a Hydrometallurgical Process. *Ind. Eng. Chem. Res.* **1999**, *38*, 4850.

(10) Nishihama, S.; Hirai, T.; Komasawa, I. Mechanism of Photoreductive Extraction of Vanadium in a Liquid−Liquid Extraction System Using Bis(2-ethylhexyl)phosphoric Acid. *Ind. Eng. Chem. Res.* **2000**, *39*, 3018.

(11) Kakoi, T.; Ura, T.; Kasaini, H.; Goto, M.; Nakashio, F. Separation of Cobalt and Nickel by Surfactant Membranes Containing a Synthesized Cationic Surfactant. *Sep. Sci. Technol.* **1998**, *33*, 1163.

(12) Hoffman, B. M.; Diemente, D. L.; Basolo, F. Electron Paramagnetic Resonance Studies of Some Cobalt(II) Schiff Base Compounds and Their Monomeric Oxygen Adducts. *J. Am. Chem. Soc.* **1970**, *92*, 61.

(13) Wong, C. L.; Switzer, J. A.; Balakrishnan, K. P.; Endicott, J. F. Oxidation Reduction Reactions of Complexes with Macrocyclic Ligands. Oxygen Uptake Kinetics, Equilibria, and Intermediates in Aqueous $Co^{II}(N_4)$ Systems. *J. Am. Chem. Soc.* **1980**, *102*, 5511.

(14) Drago, R. S.; Cannady, J. P.; Leslie, K. A. Hydrogen Bonding Interactions Involving Metal-Bound Dioxygen. *J. Am. Chem. Soc.* **1980**, *102*, 6014.

(15) Vaska, L. Dioxygen Metal Complexes: Toward a Unified View. *Acc. Chem. Res.* **1976**, *9*, 175.

Received for review June 27, 2000
Revised manuscript received September 6, 2000
Accepted September 9, 2000

IE000617P