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HIGH FUNCTIONAL LIQUID-LIQUID EXTRACTION SYSTEM USING PHOTOCHEMICAL REDUCTION FOR METAL IONS

Syouhei NISHIHAMA, 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 560-8531, Japan

A high functional liquid-liquid extraction system using photochemical reduction for metal ions has been investigated. The distribution of the target metals between the aqueous and organic phases in the extraction system can be controlled by the reduction of the metals, and selective extraction or stripping progresses. Kinetic studies for such extraction systems revealed that the photochemical reduction of the metals is the rate-determining step. The photochemical reduction of the metals mainly progressed at the interface and in the organic phase, following photoabsorption at the absorption band for the metal extracted. The technique can be applied to the cobalt-poisoning problem in the hydroxyoxime type extractant systems.

1. Introduction

Liquid-liquid extraction is a major method employed for separation of rare metals on an industrial scale. Such extractive separation processes are generally based on differences in the complex formation abilities between metals and their extractants. Separation of some metals is, therefore, difficult when using a conventional extraction system. For the development of more effective separation processes, introduction of functional chemical reactions to the system, such as complexing reactions [1-3], synergistic reactions [4,5], and redox reactions [6-13], into the extraction system has been investigated. In the case of an extraction system combined with a redox reaction, photochemical reaction has recently been investigated as the reaction source, since there is very little discharge of waste. Several investigations of extraction systems combined with photochemical redox reactions have been reported [8,10-15]. There are, however, relatively few reports concerning the mechanism for such extraction systems.

In the present work, high functional liquid-liquid extraction systems combined with the photochemical reduction of target metals have been investigated. The photochemical reduction of Fe(III) and V(V) in separate aqueous or organic phases was first investigated. The photochemical reduction was then applied to the extraction (stripping) system, and the mechanism of extraction was investigated based on kinetic studies in Fe(III) [14] and V(V) [15] systems. The effect of the wavelength of the irradiated light on the reaction and the possibility for the reuse of the organic phase were also investigated. The extraction system was then applied to the cobalt-poisoning problem in hydroxyoxime extractant systems [16]. The problem is caused by the oxidation of the cobalt species in the organic phase, and the resultant complex cannot be stripped by conventional means.

2. Experimental

The commercial extractants, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHPNA, marketed as PC-88A by Daihachi Chemical Industry Co., Ltd.), bis(2-ethylhexyl)phosphoric acid (D2EHPA, marketed as DP-8R by Daihachi Chemical Industry Co., Ltd.), 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. It has been shown by a vapor phase osmometric study that the majority of organophosphorus acids are dimerized in nonpolar diluents [17]. The inorganic chemicals, *n*-dodecane, and formic acid (90 %) were supplied by Wako Pure Chemical Industries as analytical-grade reagents. In the cases of the Fe and Co systems, aqueous feed solutions were prepared by dissolving each metal chloride in diluted HCl solutions. In the case of the V system, the aqueous feed solution was prepared by dissolving either $NaVO_3$ or $VOSO{\cdot}nH_2O$ into dilute H_2SO_4. The organic solutions were prepared by diluting each extractant with *n*-dodecane.

The extraction equilibrium data were obtained by conventional procedures, at an organic/aqueous (O/A) volume ratio of 1, at 298 K. The photochemical reaction of metals in both single aqueous and organic solutions and photoreductive stripping or extraction were carried out using a beaker-type glass bottle (32 mm in diameter). A 500 W xenon lamp (Ushio, UXL-500D-0) with an irradiation intensity of 580 kW/m^2 was used as the light source for the Fe and V systems, and a 500 W halogen lamp (Eikohsha Co., Ltd., EHC-500) with an irradiation intensity of 706 kW/m^2 was used for the Co system.

The wavelength of irradiated light was adjusted by the Pyrex glass material of the reaction bottle (greater than 300 nm) or by using appropriate cutoff filters. The concentration of metals in the aqueous solutions were analyzed using an inductively coupled argon plasma atomic emission spectrophotometer (Nippon Jarrell-Ash ICAP-575 Mark II). The absorption spectra were measured using an UV-vis spectrophotometer (Hewlett-Packard HP 8452A). The water concentration in the organic phase was determined by Karl Fischer titration using a Kyoto Electronics MKS-1. The photointensity was measured by a thermopile (The Eppley Laboratory, Inc.).

3. Results and Discussion

3.1 Extraction Equilibrium Formulations.

Figure 1 shows the effect of the equilibrium pH value on the distribution ratios in Fe/EHPNA and V/D2EHPA systems. Generally, the distribution ratios for the metals having the larger valences are larger than those of the metals having the smaller valences [18]. For the Fe system, the distribution ratio for Fe(II) is much lower than that for Fe(III) over the pH range investigated, thus indicating that selective stripping of Fe may be expected to progress by reduction during the stripping process. The slope analysis method revealed that the extraction equilibria for these metals could be expressed as in Eqs. (1) and (2).

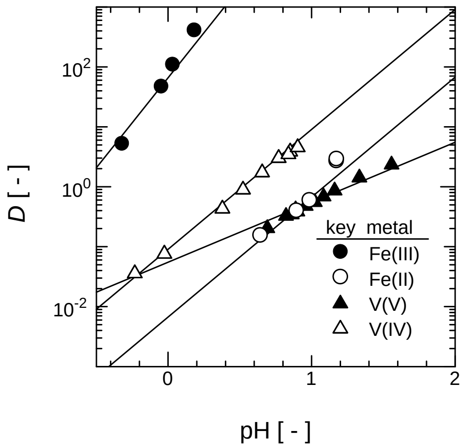

Figure 1. Effect of the aqueous pH on the distribution ratio for Fe with EHPNA and V with D2EHPA. $[\overline{(RH)_2}]_{feed}$ = 0.5 mol/*l* and $[M]_{feed}$ = 0.01 mol/*l*.

$$Fe^{3+} + 3\overline{(RH)_2} \leftrightarrow \overline{FeR_3(RH)_3} + 3H^+ \quad (1)$$

$$Fe^{2+} + 2\overline{(RH)_2} \leftrightarrow \overline{FeR_2(RH)_2} + 2H^+ \quad (2)$$

For the V system, however, the distribution ratio for V(V) is smaller than that for V(IV), which is contrary to the valences, since, in an acidic solution with a pH value of 0-2, V(V) and V(IV) exist as VO_2^+ and VO^{2+} , respectively [19]. Selective extraction of V is thus expected by reduction, especially at high pH. The slope analysis method revealed that the extraction equilibria for these metals could be expressed as in Eqs. (3) and (4).

$$VO_2^+ + \overline{(RH)_2} \leftrightarrow \overline{VO_2R(RH)} + H^+ ; K_{ex,V(V)} = 1.12 \times 10^{-1} \quad (3)$$

$$VO^{2+} + 2\overline{(RH)_2} \leftrightarrow \overline{VOR_2(RH)_2} + 2H^+ ; K_{ex,V(IV)} = 3.79 \times 10^{-1} \quad (4)$$

3.2 Photochemistry of the Metals in the Aqueous and Organic Solutions.

In the case of Fe(III), no photochemical reduction occurs without a radical scavenger in both aqueous and organic solutions. In aqueous solution, however, the reaction progresses in the presence of a radical scavenger, such as formic acid. This is because the photochemical reduction of Fe(III) in aqueous solution occurs by electron donation from water, and the OH radical produced, which promotes the reverse reaction, is scavenged by formic acid. The photochemical reduction of Fe(III) is expressed by Eqs. (5) and (6).

$$\mathrm{Fe^{3+} + H_2O \rightarrow Fe^{2+} + H^+ + {\bullet}OH} \qquad (5)$$

$$\mathrm{{\bullet}OH + HCOOH \rightarrow H_2O + {\bullet}COOH} \qquad (6)$$

In the case of V(V), photochemical reduction occurs in both aqueous and organic solutions without a radical scavenger. The rate of photochemical reduction was investigated following Ar bubbling in order to purge dissolved oxygen. A pseudo-first order kinetic plot for the variation in the concentration of V(V) revealed that the rate of photochemical reduction of V(V), in both aqueous and organic solutions, is first order with respect to V(V) concentration and is independent of pH, sulfuric ion concentration, and extractant concentration, as shown by Eqs. (7) and (8).

$$r_{\mathrm{V,a}} = -\frac{\mathrm{d[V(V)]}}{\mathrm{d}t} = k_{\mathrm{V,a}}[\mathrm{V(V)}]\,;\ k_{\mathrm{V,a}} = 3.58 \text{ x } 10^{-4} \text{ min}^{-1} \qquad (7)$$

$$r_{\mathrm{V,o}} = -\frac{\mathrm{d}[\overline{\mathrm{V(V)}}]}{\mathrm{d}t} = k_{\mathrm{V,o}}[\overline{\mathrm{V(V)}}]\,;\ k_{\mathrm{V,o}} = 9.84 \text{ x } 10^{-2} \text{ min}^{-1} \qquad (8)$$

In aqueous solution, the photochemical reduction of V(V) is likely to occur by electron donation from water, as indicated in Eqs. (9)-(11).

$$\mathrm{VO_2(H_2O)_4{}^+ + H_2O \rightarrow VO_2(H_2O)_4 + H^+ + \cdot OH} \qquad (9)$$

$$\mathrm{VO_2(H_2O)_4 + 2H^+ \rightarrow VO(H_2O)_5{}^{2+}} \qquad (10)$$

$$\mathrm{\cdot OH \rightarrow \frac{1}{2}H_2O + \frac{1}{4}O_2} \qquad (11)$$

The overall reaction is thus shown by Eq. (12), which is identical with that found by Jeliazkowa *et al* [20].

$$\mathrm{VO_2(H_2O)_4{}^+ + \frac{1}{2}H_2O + H^+ \rightarrow VO(H_2O)_5{}^{2+} + \frac{1}{4}O_2} \qquad (12)$$

If the reduction of V(V) is the rate-determining step as shown by Eq. (9), then the overall reaction rate may also be expressed by means of Eq. (7). For the organic solution, the photochemical reduction of V(V) also seems to occur via electron donation from water dissolved in the organic phase. **Figure 2** shows the water concentration in the organic solution versus the concentration of extracted V(V) or Fe(III). In the V(V)/D2EHPA system, the quantity of water in the organic phase is much larger than that of V(V), and thus the photochemical reduction progresses in the separate organic solution. In the Fe(III)/EHPNA system, however, the quantity of water is smaller than that in the V system. This difference in the quantity of the water is likely to affect the ability of photochemical reduction in the organic solution between the two metals.

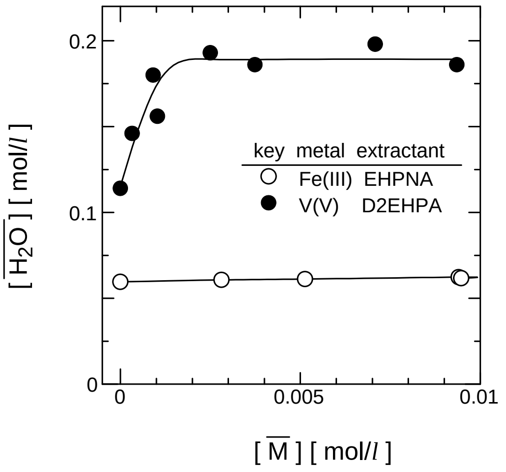

Figure 2. Effect of the concentration of Fe(III) and V(V) extracted on the concentration of water in the organic phase. $[\overline{(RH)_2}]_{feed}$ = 0.5 mol/*l*.

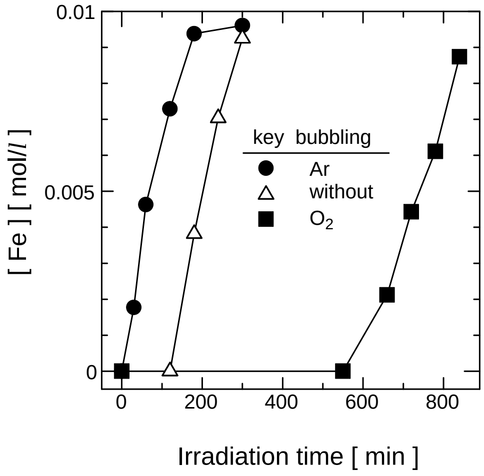

Figure 3. Effect of Ar or O_2 bubbling on the photoreductive stripping of Fe(III). $[\overline{(RH)_2}]_{feed}$ = 0.24 mol/*l*, $[\overline{Fe(III)}]_{feed}$ = 0.01 mol/*l*, and $[HCl]_{feed}$ = 0.24 mol/*l*.

3.3 Mechanism of the Extraction Systems Combined with Photochemical Reduction.

3.3.1 Photoreductive Stripping of Fe(III).

The organic solution following extraction of Fe(III) was contacted with a dilute HCl solution at O/A = 1, which was not expected to strip Fe(III), and then photoirradiated with the Xe lamp with vigorous agitation by a magnetic stirrer at over 4000 rpm. **Figure 3** shows the variation of the aqueous phase Fe concentration with time. Photoreductive stripping of Fe(III) is seen to progress without a radical scavenger. For the case of zero bubbling treatment, the reaction only started after an induction period. In the case of bubbling with O_2, this induction period was prolonged, whereas in the case of Ar bubbling, the reaction was seen to start immediately. Donohue has reported that, for the photochemical reduction of Yb or Sm in a methanol solution, no reaction was found to occur until most or all of O_2 was excluded [21]. In addition, following the induction period, no difference was seen in the rate of stripping for all three cases studied here. Therefore, during the induction period, the dissolved oxygen suppresses the reduction of Fe(III) to Fe(II), and stripping only starts to progress when all of the oxygen in the extraction system has been consumed.

The investigation, at which phase the photochemical reduction of Fe(III) occurs, was carried out with the rate of agitation being kept at 500 rpm to maintain a flat interface and each phase being shielded from photoirradiation. Photoreductive stripping hardly occurred in the case of irradiation of the aqueous phase alone. In the case of irradiation of the organic phase alone, however, photoreductive stripping was seen to occur, and the reaction progressed at a rate that was almost identical with that in the case of irradiation of both phases. Because photochemical reduction is found not to occur in the organic solution, Fe(III) is likely to be photoexcited in the organic phase and to be reduced at the interface by electron donation from water.

A kinetic study of the photoreductive stripping of Fe(III) was carried out. The pseudo-first-order plot, for the variation in the concentration of Fe(III) in the organic phase with respect to irradiation time, shows the rate of photoreductive stripping is of first order with respect to the Fe(III) concentration in the organic phase. The rate of photoreductive stripping can, therefore, be expressed as shown in Eq. (13).

$$r_{\mathrm{Fe}} = -\frac{d[\overline{\mathrm{Fe}}]}{dt} = k_{\mathrm{Fe}}'[\overline{\mathrm{Fe}}] \qquad (13)$$

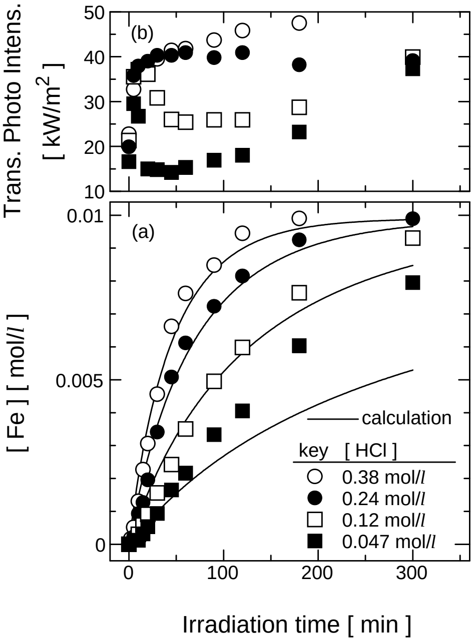

Figure 4. Effect of photoirradiation time on (a) the concentration of Fe(III) in the aqueous phase and (b) the transmitted photointensity. Comparison of observed data with prediction shown by solid lines. $[\overline{(\mathrm{RH})_2}]_{\mathrm{feed}}$ = 0.1 mol/*l* and $[\overline{\mathrm{Fe(III)}}]_{\mathrm{feed}}$ = 0.01 mol/*l*.

The effects of the initial hydrogen ion concentration and the free dimeric EHPNA concentration, $[\overline{(\mathrm{RH})_2}]_{\mathrm{feed}} - 3[\overline{\mathrm{Fe}}]_{\mathrm{feed}}$, on the apparent rate constant k' were then investigated and it was shown that the rate of photoreductive stripping of Fe(III) can be expressed as Eq. (14).

$$r_{\mathrm{Fe}} = -\frac{d[\overline{\mathrm{Fe}}]}{dt} = k_{\mathrm{Fe}}\frac{[\overline{\mathrm{Fe}}][\mathrm{H}^+]}{[\overline{(\mathrm{RH})_2}]^{0.5}} \qquad (14)$$

where $k_{\mathrm{Fe}} = 0.0275\ l^{0.5}\mathrm{mol}^{-0.5}\mathrm{min}^{-1}$.

Figure 4(a) shows the effect of photoirradiation time on the concentration of Fe in the aqueous phase as compared with the calculated value based on Eq. (14). The magnitude of the experimental values agrees well with the calculated values during the initial part of the run but with increasing irradiation time these become greater than the calculated value. This deviation becomes notable in the run with the solution of lower HCl concentration. Figure 4(b) shows the variation with time on the photointensity of transmitted light. In the case of low HCl concentration at 0.047 mol/*l*, the transmitted light intensity increased as the photoreductive stripping of Fe(III) progressed, and the photoreaction progressed more effectively than that predicted based on the initial photoreductive stripping rate.

The overall reaction mechanism for the photoreductive stripping of Fe(III) can be divided into two reaction stages, the photochemical reduction of extracted species of

Fe(III) to Fe(II) at the interface, followed by the stripping of Fe(II) into the aqueous phase, as follows.

$$\overline{\mathrm{FeR_3(RH)_3}} + \mathrm{H_2O} \leftrightarrow \overline{\mathrm{FeR_2(RH)_2}} + \overline{\mathrm{(RH)_2}} + {}^{\bullet}\mathrm{OH} \qquad (15)$$

$$\overline{\mathrm{FeR_2(RH)_2}} + 2\mathrm{H^+} \leftrightarrow \mathrm{Fe^{2+}} + 2\overline{\mathrm{(RH)_2}} \qquad (16)$$

This reaction scheme is deduced on the assumptions that the rate-determining step is the photochemical reduction of Fe(III), as shown by Eq. (15), and that the rate of distribution of the reduced Fe(II) is fast. The Fe(III)-extractant complex is found to be excited in the organic phase and to be donated an electron from the water at the aqueous/organic interface. Assuming the extractant to exist as a monomeric species at the interface, as was found in the case of D2EHPA [22], the elementary reaction of Eq. (15) can be expressed in more detail as in Eqs. (17)-(22).

$$\overline{\mathrm{(RH)_2}} \leftrightarrow 2\overline{\overline{\mathrm{RH}}} \qquad ;K_1 \qquad (17)$$

$$\overline{\mathrm{FeR_3(RH)_3}} \leftrightarrow \overline{\mathrm{FeR_3(RH)_3}}^{*} \qquad ;K_2 \qquad (18)$$

$$\overline{\mathrm{FeR_3(RH)_3}}^{*} \leftrightarrow \overline{\overline{\mathrm{FeR_3(RH)_3}}}^{*} \qquad ;K_3 \qquad (19)$$

$$\overline{\overline{\mathrm{FeR_3(RH)_3}}}^{*} + \mathrm{H^+} \leftrightarrow \overline{\overline{\mathrm{FeR_2(RH)_3}}}^{+} + \overline{\overline{\mathrm{RH}}} \qquad ;K_4 \qquad (20)$$

$$\overline{\overline{\mathrm{FeR_2(RH)_3}}}^{+} + \mathrm{H_2O} \rightarrow \overline{\overline{\mathrm{FeR_2(RH)_3}}} + \mathrm{H^+} + {}^{\bullet}\mathrm{OH} \qquad ;k_1 \qquad (21)$$

$$\overline{\overline{\mathrm{FeR_2(RH)_3}}} \rightarrow \overline{\overline{\mathrm{FeR_2(RH)_2}}} + \overline{\overline{\mathrm{RH}}} \qquad (22)$$

If the rate-determining step is the photochemical reduction of Fe(III) as shown by Eq. (21), the overall reaction rate equation can be expressed by Eq. (23).

$$r = -\frac{d[\overline{\mathrm{Fe}}]}{dt} = k_1[\overline{\overline{\mathrm{FeR_2(RH)_3}}}^{+}] = \frac{k_1K_2K_3K_4}{K_1^{0.5}}\frac{[\overline{\mathrm{FeR_3(RH)_3}}][\mathrm{H^+}]}{[\overline{\mathrm{(RH)_2}}]^{0.5}} \qquad (23)$$

This agrees with the result from the experimental kinetic study, as shown by Eq. (14), indicating that the mechanism of photoreductive stripping of Fe(III) is expressed by the proposed scheme.

3.3.2 Photoreductive Extraction of V(V).

The extractant D2EHPA in *n*-dodecane was contacted with the aqueous solution, containing $\mathrm{NaVO_3}$, at O/A = 1. The mixture was then photoirradiated following Ar bubbling with agitation by a magnetic stirrer. **Figure 5** shows the effect of photoirradiation time on the distribution ratio for V under conditions of vigorous stirring at over 4000 rpm. In the extraction system, the variation with time of the distribution ratio can be predicted by assuming that the rate of the reaction is dominated by the photochemical reduction of V in the aqueous and organic phases, and the distribution of both V(V) and V(IV) between the two phases is attained immediately. Such predictions, which are shown by dotted lines in Figure 5, however, lead to much lower values for the distribution ratio than given by the experimental results. This difference may be caused by photochemical reduction of V at the interface between the aqueous and organic phases, as was also found in the case for the photoreductive stripping of Fe(III). The photochemical reduction of V(V) at the interface may be thought to be expressed by the mechanisms indicated in Eqs. (24)-(27).

$$\overline{\mathrm{VO_2R(RH)}} \leftrightarrow \overline{\overline{\mathrm{VO_2R(RH)}}} \qquad ; K_\mathrm{i} \qquad (24)$$

$$\overline{\overline{\mathrm{VO_2R(RH)}}} + \mathrm{H_2O} \rightarrow \overline{\overline{\mathrm{VO_2R(RH)^-}}} + \mathrm{H^+} + \cdot\mathrm{OH} \qquad ; k'_\mathrm{i} \qquad (25)$$

$$\overline{\overline{\mathrm{VO_2R(RH)^-}}} + \overline{\mathrm{(RH)_2}} + \mathrm{H^+} \rightarrow \overline{\overline{\mathrm{VOR_2(RH)_2}}} + \mathrm{H_2O} \qquad (26)$$

$$\overline{\overline{\mathrm{VOR_2(RH)_2}}} \rightarrow \overline{\mathrm{VOR_2(RH)_2}} \qquad (27)$$

If the rate of photochemical reduction at the interface is first order with respect to the concentration of V(V) at the interface, as in the case of reduction in aqueous and organic solutions, then the interfacial surface rate equation can be expressed by Eq. (28),

$$r_{\mathrm{V,i}}' = -\frac{Q}{A}\frac{\mathrm{d}[\overline{\overline{\mathrm{V(V)}}}]}{\mathrm{d}t} = k_{\mathrm{V,i}}'[\overline{\overline{\mathrm{V(V)}}}] = K_{\mathrm{V,i}}k_{\mathrm{V,i}}'[\overline{\mathrm{V(V)}}] \qquad (28)$$

where Q and A are the volume of the organic phase and the area of the interface, respectively. Assuming the interface area to be constant, the overall rate equation at the interface can be expressed as Eq. (29).

$$r_{\mathrm{V,i}} = \frac{A}{Q}r_{\mathrm{V,i}}' = k_{\mathrm{V,i}}[\overline{\mathrm{V(V)}}] \qquad (29)$$

The overall rate constant for photochemical reduction of V at the interface was determined as $k_\mathrm{i} = 1.75 \times 10^{-1}\ \mathrm{min}^{-1}$, by a nonlinear least-squares fit to the experimental results. The

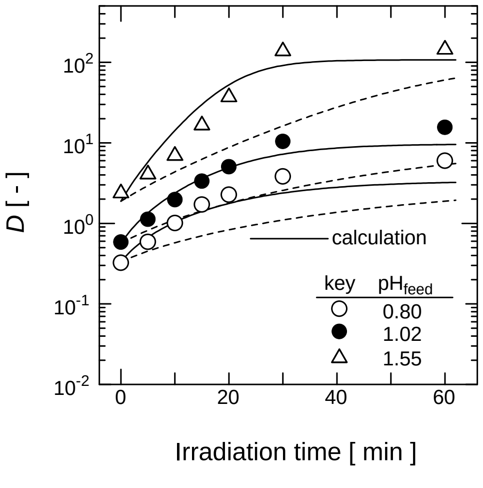

Figure 5. Effect of the photoirradiation time on the distribution ratio for V. Solid lines: photochemical reduction at the interface only, dotted lines: photochemical reduction only in the aqueous and organic phases . $[\overline{\mathrm{(RH)_2}}]_{\mathrm{feed}} = 0.5$ mol/*l* and $[\mathrm{NaVO_3}]_{\mathrm{feed}} = 0.01$ mol/*l*.

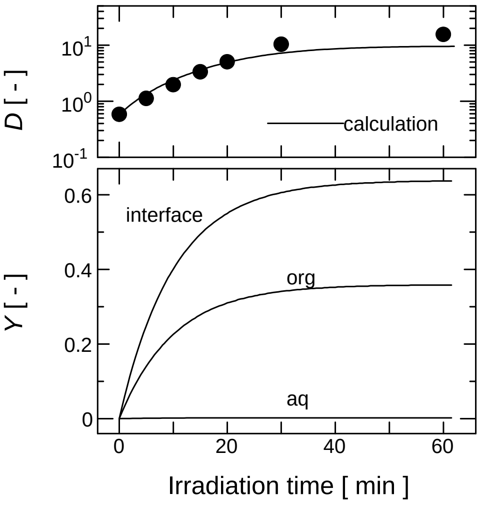

Figure 6. Effect of the photoirradiation time on the distribution ratio and reduction yield in each phase. $[\overline{\mathrm{(RH)_2}}]_{\mathrm{feed}} = 0.5$ mol/*l*, $[\mathrm{NaVO_3}]_{\mathrm{feed}} = 0.01$ mol/*l*, and $\mathrm{pH_{feed}} = 1.02$.

change in the concentrations of V(V) and V(IV) in the aqueous and organic phases for a time interval Δ*t* lying between time *t* and *t* + Δ*t* can be calculated from a knowledge of the values of the rate constants, k_a, k_o, and k_i, as indicated in Eqs. (30)-(33).

$$[\mathrm{V(V)}]_{t+\Delta t} = \frac{[\mathrm{V(V)}]_t}{\mathrm{e}^{k_\mathrm{a}\Delta t}} \tag{30}$$

$$[\mathrm{V(IV)}]_{t+\Delta t} = [\mathrm{V(IV)}]_t + \{[\mathrm{V(V)}]_t - [\mathrm{V(V)}]_{t+\Delta t}\} \tag{31}$$

$$[\overline{\mathrm{V(V)}}]_{t+\Delta t} = \left(\frac{1}{\mathrm{e}^{k_\mathrm{o}\Delta t}} + \frac{1}{\mathrm{e}^{k_\mathrm{i}\Delta t}} - 1\right)[\overline{\mathrm{V(V)}}]_t \tag{32}$$

$$[\overline{\mathrm{V(IV)}}]_{t+\Delta t} = [\overline{\mathrm{V(IV)}}]_t + \{[\overline{\mathrm{V(V)}}]_t - [\overline{\mathrm{V(V)}}]_{t+\Delta t}\} \tag{33}$$

Assuming that an equilibrium distribution of both V(V) and V(IV) between the phases is attained immediately, the distribution ratio at the new time (*t* + Δ*t*) can be calculated using the extraction equilibrium formulations previously determined. Repeated calculation, until the values of the distribution ratios and the proton concentration converge, enables the apparent distribution ratio, $D = ([\overline{\mathrm{V(V)}}] + [\overline{\mathrm{V(IV)}}])/([\mathrm{V(V)}] + [\mathrm{V(IV)}])$, to be determined. These predicted values according to the above method are shown in Figure 5 by the solid lines. The experimental data are seen to fall well on the prediction lines, thus indicating that the photochemical reduction of V progresses in the aqueous phase, in the organic phase, and at the interface. **Figure 6** shows the variation with time in the reduction yield for each phase, *Y*, defined as the ratio of the concentration of V(IV) reduced in the appropriate phase to that of the feed V(V) concentration. The photoreductive extraction progresses mainly via photochemical reduction at the interface and in the organic phase, with the reduction in the aqueous phase hardly contributing to the overall photoreductive extraction.

3.4 Effect of the Wavelength of the Irradiated Light.

Figure 7 shows the effect of the wavelength of the irradiated light, when varied by the use of appropriate cutoff filters, on the variation with time in the photoreductive stripping of Fe(III) and photoreductive extraction of V(V). In the case of Fe, the reaction hardly occurs when irradiated light of less than 400 nm is cut off. This may be caused by the ability for photoabsorption of the extracted species. **Figure 8(a)** shows the absorption spectrum for the organic solution with and without Fe(III) and indicates that the absorption band, caused by Fe(III), appears at 200-350 nm. In the case of V, the absorption band, caused by V(V), appears at 300-500 nm (Figure 8(b)), and the reaction hardly occurs when irradiated light of less than 500 nm is cut off. These results thus indicate the photochemical reduction of the metals in the organic phase and at the interface progresses following photoabsorption at the absorption band for the metal extracted.

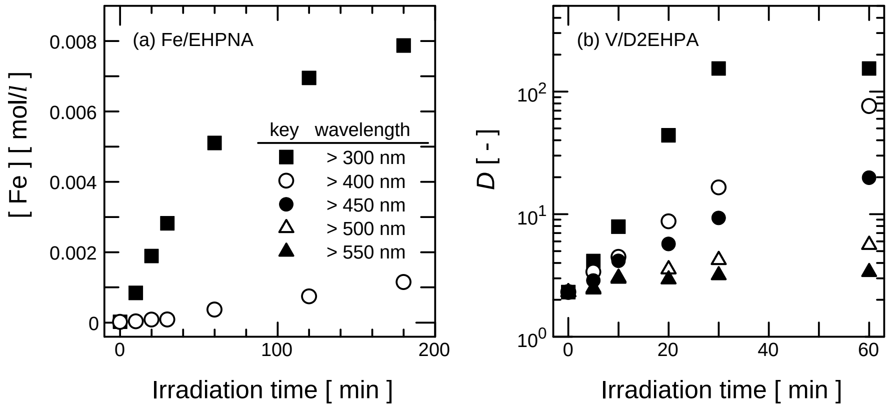

Figure 7. Effect of the wavelength of the light source on the rate of (a) photoreductive stripping of Fe(III) and (b) photoreductive extraction of V(V). (a) Fe/EHPNA system, $[\overline{(RH)_2}]_{feed}$ = 0.1 mol/*l*, $[\overline{Fe}]_{feed}$ = 0.0088 mol/*l*, and $[HCl]_{feed}$ = 0.24 mol/*l*, and (b) V/D2EHPA system, $[\overline{(RH)_2}]_{feed}$ = 0.5 mol/*l*, $[NaVO_3]_{feed}$ = 0.01 mol/*l*, and pH_{feed} = 1.52.

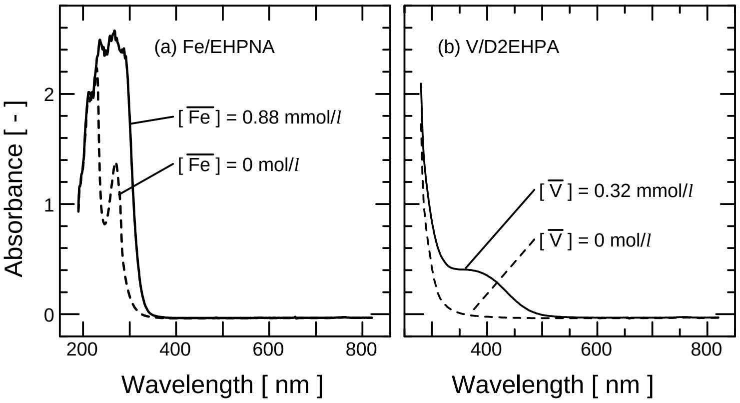

Figure 8. Absorption spectrum for organic solutions containing (a) Fe(III) and (b) V(V). $[\overline{(RH)_2}]_{feed}$ = 0.1 mol/l. Reference: air

3.5 Reusability of the Organic Phase.

The reuse of an organic solution following photoirradiation was also investigated. In the case of Fe, the aqueous feed solution and organic solution were contacted at O/A = 1. The Fe loaded organic solution was then contacted with 0.36 mol/*l* of HCl solution at O/A = 1 and the phases photoirradiated for 300 min. In the case of V, the aqueous and organic solutions were contacted at O/A = 1 and were photoirradiated for 60 min. The resultant organic solution was then stripped using 6 mol/*l* of HCl at O/A = 0.5. These resultant organic solutions were then used for repeated processing after washing with 3 mol/*l* of HCl and then water. **Figure 9** shows the concentration of Fe or V in the organic phase during the repeated extraction-stripping processing. The results thus show that the organic phase

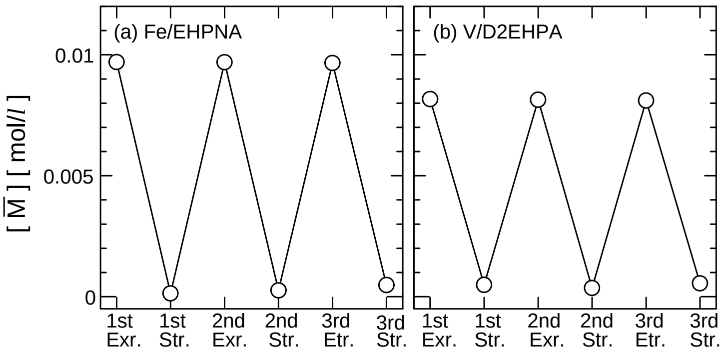

Figure 9. The concentration of (a) Fe and (b) V in the organic phase following the repeated extraction-stripping processing. $[\overline{(RH)_2}]_{feed}$ = (a) 0.1 mol/*l* and (b) 0.5 mol/*l*, $[M]_{feed}$ = 0.01 mol/*l*, and pH_{feed} = (a) 1.47 and (b) 0.86.

possesses a sufficient loading and stripping capacity for use in repeated processing and confirm the possible reuse of the organic phase following photoirradiation.

3.6 Application for the Cobalt-Poisoning Problem.

It is well known that Co(II) when extracted via commercial chelating extractants, such as hydroxyoxime type extractants, is difficult to recover by conventional stripping procedures, owing to cobalt poisoning [23,24]. **Figure 10** shows the effect of HCl concentration on the stripping efficiency at O/A = 0.5, without photoirradiation. The extraction-stripping was carried out using both 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

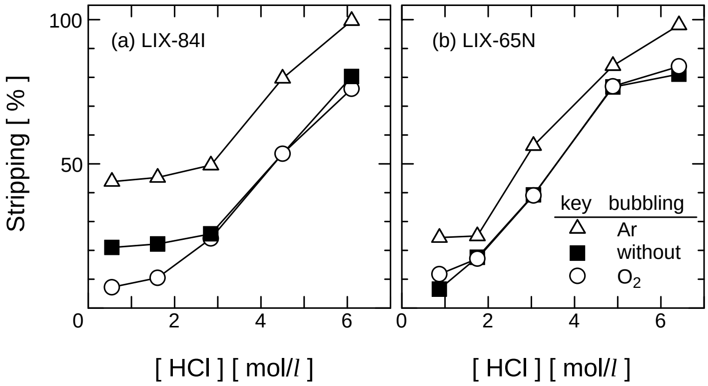

Figure 10. Effect of HCl concentration on the stripping efficiency without photoirradiation in (a) LIX-84I and (b) LIX-65N systems, at O/A ratio of 0.5. $[\overline{RH}]_{feed}$ = 10 vol%, and $[\overline{Co}]_{feed}$ = (a) 6.76 mmol/*l* and (b) 7.13 mmol/*l*.

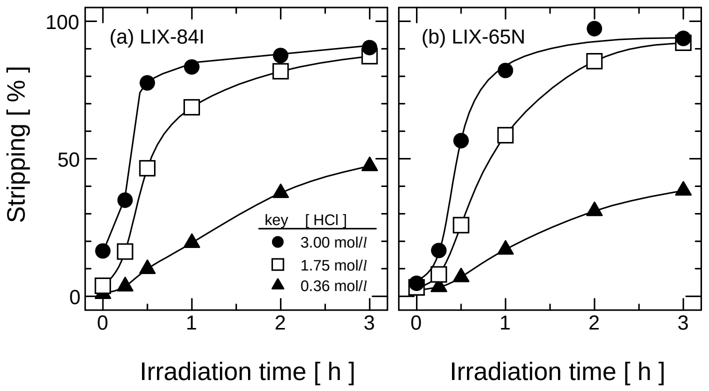

Figure 11. Effect of the HCl concentration on rate of photoreductive stripping in (a) LIX-84I and (b) LIX-65N systems. $[\overline{\mathrm{RH}}]_{\mathrm{feed}}$ = 10 vol%, and $[\overline{\mathrm{Co}}]_{\mathrm{feed}}$ = (a) 6.53 mmol/*l* and (b) 9.37 mmol/*l*.

stripping is achieved at 6 mol/*l* HCl. These results, thus, indicate that Co is oxidized to the trivalent state by oxygen in the extraction system, and is then stabilized in the organic phase, which suppresses quantitative stripping. Effective stripping is therefore expected to be carried out, if the oxidized Co(III) complex can be photoreduced within the organic phase.

The photoreductive stripping of Co was then carried out, by a similar procedure to the photoreductive stripping of Fe, using a halogen lamp. Only visible light with a wavelength greater than 550 nm was irradiated, since Co-LIX 84I has a large absorption band at 400-800 nm. **Figure 11** shows the effect of HCl concentration on the photoreductive stripping of Co in LIX-84I and LIX-65N systems. Successive stripping can be carried out in both systems using the photoreductive stripping technique. 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. The organic phase in this process also possesses sufficient loading and stripping capacity for use in repeated processing, as for the Fe and V systems.

4. Conclusion

The high functional liquid-liquid extraction systems using photochemical reduction for metal ions have been investigated, with the following results: (1) The distribution ratio of metals can be controlled by photochemical reduction of the metals. The mechanisms of the extraction system combined with photochemical reduction were elucidated based on kinetic studies, in which the photochemical reduction of the metals is the rate-determining step. (2) The photochemical reduction of the metals in the organic phase and at the interface takes place following photoabsorption at the absorption band for the extracted metal. The organic solution following photoirradiation is reusable for repeated extraction-stripping processing. (3) The photoreductive stripping technique can solve the cobalt-poisoning problem in hydroxyoxime extractant systems.

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Nomenclature

A = interface area [dm^2]
D = distribution ratio [-]
k_{Fe} = rate constant for photoreductive stripping of Fe [$l^{0.5}$/mol$^{0.5}$min]
k_{V} = rate constant for photochemical reduction of V [min^{-1}]
k_{Fe}' = apparent rate constant [min^{-1}]
$k_{\mathrm{V,i}}'$ = rate constant for photochemical reduction of V at the interface [dm/min]
K_{ex} = extraction equilibrium constant
M = Fe or V
Q = volume of the organic phase [l]
r_{Fe} = rate of photoreductive stripping of Fe [mol/l・min]
r_{V} = rate of photochemical reduction of V [mol/l・min]
r_{V}' = rate of photochemical reduction of V at the interface [mol/dm^{2}min]
RH = LIX-84I or LIX-65N
$(\mathrm{RH})_2$ = dimeric species of EHPNA or D2EHPA
Y = reduction yield [-]
[ ] = concentration of the species in the bracket [mol/l]

Subscript

a = aqueous phase
feed = aqueous or organic feed solution
i = interface
o = organic phase

Superscripts

$\overline{\quad}$ = organic phase species
$\overline{\overline{\quad}}$ = interface species

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