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# Extraction of Uranium(VI) by Emulsion Liquid Membrane Containing 5,8-Diethyl-7-hydroxy-6-dodecanone Oxime

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Extraction of uranium(VI) by a liquid surfactant membrane has been studied. The stability of water-in-oil (w/o) emulsion dispersed in the continuous aqueous phase increased with an increase in surfactant concentrations and in the fraction of the organic phase in emulsion globules. Uranium(VI) in dilute acid solutions was extracted into (w/o) emulsions containing 5,8-diethyl-7-hydroxy-6-dodecanone oxime (LIX 63) as a mobile carrier and its concentration decreased according to $[U]_t=[U]_0 \exp(-k_{obsd}t)$. The apparent rate constants ($k_{obsd}$) increased with an increase in carrier concentrations and in external pH values, while they were slightly dependent on the stripping acid concentrations. Uranium was transported and concentrated into the internal aqueous droplets. The final concentration of uranium in the external aqueous phase dropped to about $10^{-3}$ of its initial value.

Separation of metal ions by liquid-liquid extraction can be achieved through the processes of extraction into the organic phase and stripping into the aqueous phase. Liquid membranes combining simultaneously both the extraction and the stripping processes have become of interest as a new technique of selective separation and concentration of metals from dilute aqueous solutions.1,2) The extracting reagent plays a role as a mobile carrier in the membrane, and the metal ion can be concentrated by active transport against its concentration gradient across the liquid membrane.

Two types of liquid membranes, supported liquid membranes and emulsion liquid membranes, have been well known for separation of metal ions.3,4) The effectiveness of liquid membrane method for the recovery of uranium from dilute solutions has been shown by means of supported liquid membranes containing various carriers,5—7) and emulsion type liquid membranes of mixed carriers, bis(2-ethylhexyl) hydrogenphosphate and trioctylphosphine oxide, were also employed for uranium extraction from wet process phosphoric acid.8) Emulsion liquid membranes consist of small droplets of the stripping aqueous phase stabilized by a surfactant and the extracting organic phase. They could give fast extraction owing to the large surface area of emulsion globules.

Previously, we revealed that a α-hydroxy ketone oxime, 5,8-diethyl-7-hydroxy-6-dodecanone oxime (LIX 63), is an excellent reagent for uranium extraction from weak acidic media9) and also for a suitable ion carrier in the supported liquid membrane.10) The present study deals with some of important factors affecting the stabilities of emulsions and the extraction of uranium(VI) by emulsion liquid membranes containing LIX 63 as a mobile carrier.

## Experimental

*Emulsion Liquid Membranes.* The liquid membranes were composed of a nonionic surfactant, sorbitan monooleate (Span 80; Kao-Atlas) and 5,8-diethyl-7-hydroxy-6-dodecanone oxime (LIX 63; Henkel). The kerosene solutions of them were vigorously emulsified (20000 $\text{min}^{-1}$ for 2 min) with stripping solutions of sulfuric acid (most commonly pH 1.5) by a high-speed homoginizer (Ultra-Disperser; Yamato Kagaku). No membrane strengthening agent such as liquid paraffin was added in the membrane solution, because there was little change in the stability of emulsion containing liquid paraffin up to 20 (w/v)%.

*Emulsion Stability.* The water-in-oil emulsion free from carriers was dispersed in ten times as much as the volume of water by stirring at 300 $\text{min}^{-1}$. To monitor the breaking of emulsions, stirring was stopped at time intervals so that the emulsion phase rose to the top of the beaker. After phase separation, samples of the aqueous phase were withdrawn and their pH values were measured with a pH meter (F-7ss; Horiba). When emulsions break down in the course of stirring, the internal stripping acid leaks out in the external aqueous phase. The emulsion breakdown was evaluated as percentage from the hydrogen ion concentrations as follows:

$$\varepsilon(\%) = \frac{([\text{H}^+]_{\text{ext}} - [\text{H}^+]_{\text{ext,init.}})V_{\text{ext}}}{[\text{H}^+]_{\text{int}} \times V_{\text{int}}} \times 100$$

where $V$ refers to the volume and the subscripts ext and int represent the external and the internal aqueous phases, respectively.

*Extraction of Uranium.* The (w/o) emulsions containing LIX 63 were stirred with ten times as much as the volume of uranium solution (pH 3—4.5) containing $^{237}$U as a tracer. The initial concentration of uranium was usually $10^{-5}$ mol $\text{dm}^{-3}$. After stirring at 300 $\text{min}^{-1}$, aliquots of the external aqueous solution were pipetted off for analysis at selected time intervals and their uranium concentrations were determined by measuring γ-radioactivities of $^{237}$U with a NaI scintillation detector. The quantity of uranium moved into emulsion globules was evaluated from the difference between the concentrations in the external aqueous phase before and after stirring.

All experiments were carried out at 25 °C.

## Results and Discussion

*Emulsion Stability.* When the (w/o) emulsion is dispersed by stirring in the continuous aqueous solution, the emulsion must be sufficiently stable in order to extract metal ions into the internal aqueous droplets. The emulsion breakdown will result in a lowering of extraction efficiency and loss of the extracted species. For the recovery of extracted metals, on the contrary, the emulsion must be readily broken by the use of demulsification techniques such as electrostatic means.11)

The several factors governing the emulsion stability have been examined in order to prepare the optimum emulsion liquid membranes suited for these conflicting requirements.

Figure 1 shows the effect of the surfactant concentration on the emulsion breakdown after stirring at 300 min$^{-1}$. The distilled water was stirred with emulsions consisting of equal volumes of the organic phase free from carriers and the sulfuric acid solution. The emulsion breakdown was less than 0.5% at Span 80 concentrations above 2 (w/v)%, indicating that the membrane was sufficiently stable, while the emulsion stability steeply decreased with a decrease in the surfactant concentrations less than 2%. No emulsion was formed at low Span 80 concentrations below 0.25% owing to a lack of the surfactant adsorbing the organic-aqueous interface. Though high concentrations of surfactant seem to be suitable for the stable emulsion, they would cause difficulties in demulsification. On the basis of the data, 2 (w/v)% of Span 80 was selected in the subsequent experiments.

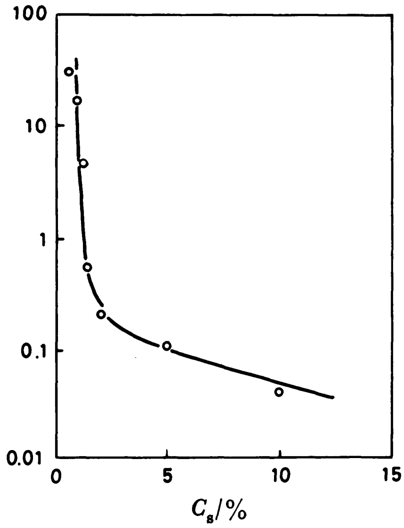

Fig. 1. Effect of Span 80 concentration on the emulsion breakdown after stirring at 300 min$^{-1}$ for 40 min. $V_{em}$: 10 cm$^3$; $V_{ext}$: 100 cm$^3$.

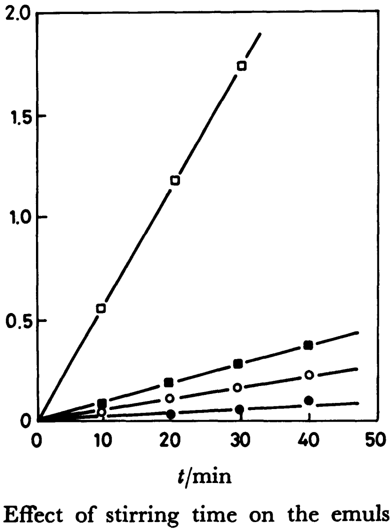

Fig. 2. Effect of stirring time on the emulsion breakdown. 2(w/v)% Span 80; $V_{org}/V_{int}$: □ 0.50, ■ 1.0, ○ 1.5, ● 2.0.

As shown in Fig. 2, the emulsion breakdown increased linearly with stirring time at 300 min$^{-1}$. This trend is marked with the emulsion of the low contents of the organic phase. The emulsion with the ratio ($V_{org}/V_{int}$) of 1 was found to be its optimum composition.

*Equilibrium in Liquid-Liquid Extraction.* Extraction equilibrium of uranium(VI) by LIX 63 (HR) can be expressed by,[9]

$$\mathrm{UO_2^{2+}} + 2\mathrm{HR_{org}} \overset{K_{ex}}{\rightleftharpoons} \mathrm{UO_2R_{2,org}} + 2\mathrm{H^+}. \tag{1}$$

The subscript org represents the organic phase, which corresponds to the membrane phase in the liquid membrane system. The extraction constants were obtained as $\log K_{ex} = -2.11$ and $-3.32$ for 0.1 mol dm$^{-3}$ perchlorate and sulfate media, respectively. Based on these data, the hydrogen ion concentrations on both sides of the membrane can be adjusted so as to enhance the extraction in the external aqueous phase and the stripping in the internal aqueous phase. The overall processes promote the transport of the uranyl ion from the external to the internal aqueous phases through the liquid membrane and the transport of the hydrogen ion in the opposite direction.

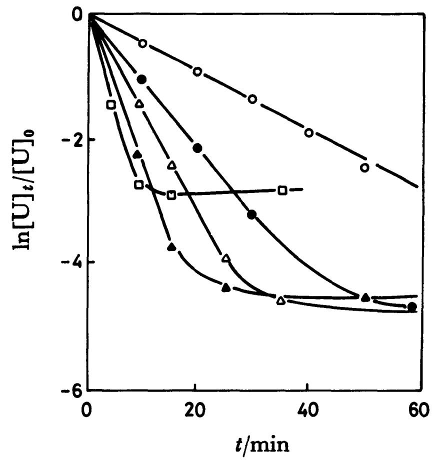

Fig. 3. Effect of stirring speed on the extraction of uranium(VI) by the emulsion liquid membrane. $5\times10^{-3}$ mol dm$^{-3}$ LIX 63; pH$_{ext}$ 4.20; pH$_{int}$ 2.06; Stirring speed/min$^{-1}$: ○ 200, ● 300, △ 400, ▲ 500, □ 800.

*Extraction by Emulsion Liquid Membrane.* Effect of stirring on the extraction of uranium(VI) by the emulsion liquid membrane containing LIX 63 is shown in Fig. 3. The uranium solution at pH 4.2 was stirred with the emulsion having the volume ratio ($V_{org}/V_{int}$) of 1. The uranium concentrations in the external aqueous phase decreased with stirring time and then approached equilibrium. The rate of extraction increased with an increase in stirring speed, while the limiting value at equilibrium was approximately constant about 0.5% of the initial concentration irrespective of stirring speed under 500 min$^{-1}$, and little pH drop, *e.g.*, from 4.2 to 4.1, was observed at 500 min$^{-1}$ for 1 h stirring. However, the external uranium concentration no longer decreased as above cases at higher speed of stirring, and the pH drop became large, *e.g.*, from 4.2 to 3.7 at 800 $\text{min}^{-1}$ for 40 min stirring. This anomalous behavior could be attributable to the high degree of emulsion breaking. Subsequent experiments were carried out at 300 $\text{min}^{-1}$ where the emulsion breakdown during extraction was negligibly small.

*Effect of Carrier Concentration.* The rates of extraction were examined by varying carrier concentrations at 2 (w/v)% of Span 80 (Fig. 4). Plots of ln $[\text{U}]_t/[\text{U}]_0$ against time yielded a series of straight lines,

$$\ln\frac{[\text{U}]_t}{[\text{U}]_o} = -k_{\text{obsd}}t, \tag{2}$$

where $[\text{U}]_t$ and $[\text{U}]_0$ are the concentrations in the external aqueous phase at time $t$ and initial one, respectively. The slope of the line gives the apparent rate constant, $k_{\text{obsd}}$. The plots of log ($k_{\text{obsd}}/\text{s}^{-1}$) *vs.* log ([LIX 63]/mol $\text{dm}^{-3}$) yielded the straight line with a slope of 0.61 (Fig. 5). Under these experimental conditions, about 99.5% of uranium in the external solution was extracted into the emulsion globules at equilibrium.

The high content of Span 80 resulted in a decrease in the extraction rate and further caused the extraction of small amounts of uranium by Span 80 alone. These findings together with the emulsion stability suggest that the optimum concentration of Span 80 lies in the 2% range. The uranium extraction by this 2% surfactant was negligibly small.

*Effect of pH.* It is important to maintain an appreciable pH gradient between the external and the internal aqueous phases, because this pH gradient provides an effective driving force of the active transport of uranium across the membrane.

Plots of log ($k_{\text{obsd}}/\text{s}^{-1}$) *vs.*$\text{pH}_{\text{ext}}$ of the external aqueous phase gave the straight lines with slopes of about 1.3 at different concentrations of stripping acid (Fig. 6). As long as the internal acid concentrations were maintained high enough to strip uranium, the extraction rate increased with an increase in the external pH values.

The effect of stripping acid concentration on the extraction rate is illustrated in Fig. 7. Plots of log $k_{\text{obsd}}$ *vs.* $\text{pH}_{\text{int}}$ gave the linear lines with small negative slopes around −0.2 at different $\text{pH}_{\text{ext}}$. Varying the internal pH values over a fairly wide range has only a minor effect on the extraction rate.

From these findings, the extraction reaction into the membrane layers rather than the stripping reaction into

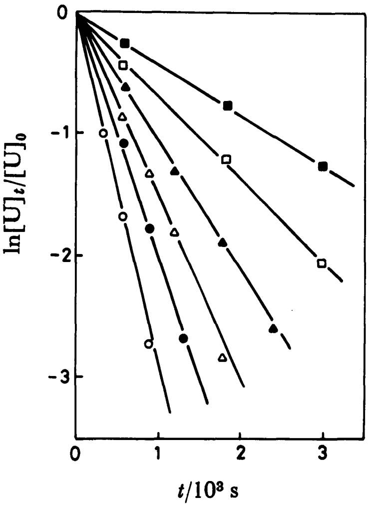

Fig. 4. Rate of uranium extraction by the emulsion liquid membrane. $\text{pH}_{\text{ext}}$ 4.25; $\text{pH}_{\text{int}}$ 2.48; [LIX 63]/mol $\text{dm}^{-3}$: ○ $2\times10^{-2}$, ● $10^{-2}$, △ $5\times10^{-3}$, ▲ $2.5\times10^{-3}$, □ $1.25\times10^{-3}$, ■ $6.25\times10^{-4}$.

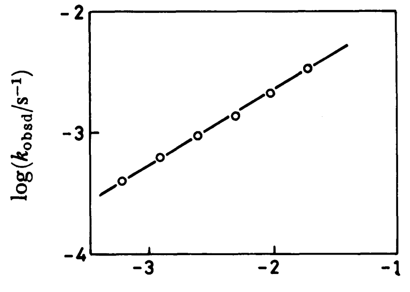

Fig. 5. Effect of the carrier concentration on the apparent rate constant.

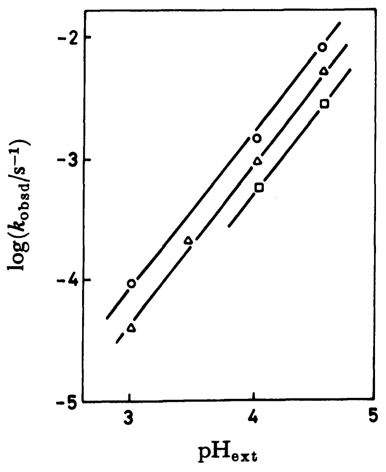

Fig. 6. Effect of pH of the external aqueous phase on the apparent rate constant. $5\times10^{-3}$ mol $\text{dm}^{-3}$ LIX 63; $\text{pH}_{\text{int}}$: ○ 0.93, △ 2.38, □ 3.52.

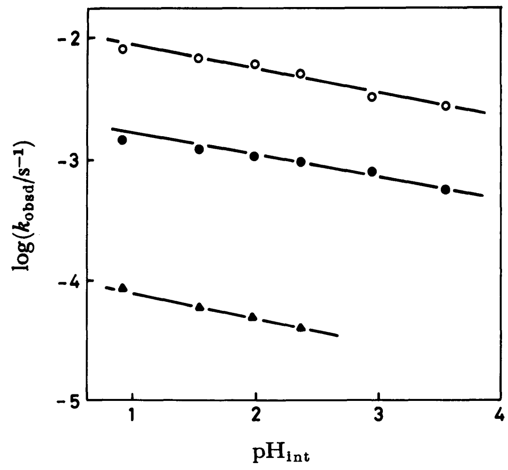

Fig. 7. Effect of pH of the internal aqueous phase on the apparent rate constant. $5\times10^{-3}$ mol $\text{dm}^{-3}$ LIX 63; $\text{pH}_{\text{ext}}$: ○ 4.58, ● 4.05, ▲ 3.03.

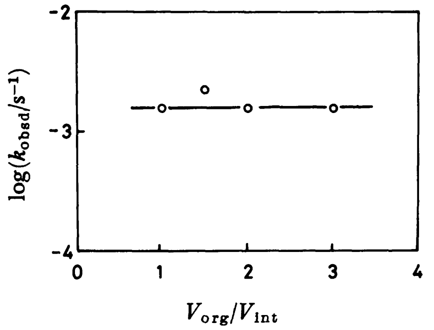

Fig. 8. Effect of the emulsion composition on the apparent rate constant. $5\times10^{-3}$ mol dm$^{-3}$ LIX 63; pH$_{ext}$ 4.34; pH$_{int}$ 1.98.

the internal aqueous phase probably contributes to the rate determining process. If the stripping reaction was the rate determining step, the content of the internal phase would also affect the extraction rate, but the $k_{obsd}$ values at different compositions of emulsion, were nearly constant as seen in Fig. 8. This indicates that the stripping reaction is not of importance in the rate determining process.

The most significant factor for the carrier-mediated transport appears to control the external pH value maintaining the pH gradient against internal pH. The final concentration of external uranium was observed to decrease greatly under the large pH gradient; the uranium remaining in the external solution dropped to $10^{-3}$ of its initial concentration under the conditions of pH$_{ext}$ 4.6 and pH$_{int}$ 2.0.

Furthermore, wide variations in the initial uranium concentration ranging from $10^{-7}$ to $10^{-4}$ mol dm$^{-3}$ gave no effect on the extraction efficiency and the extraction rate. The reagent LIX 63 in the membrane acts as an ion carrier from the outer to the inner solutions, rather than a metal storage phase in liquid-liquid extraction. Thus, uranium could be efficiently concentrated into small encapsulated droplets with the concentration factor of $V_{ext}/V_{int}$ given by the volume ratio of the external to the internal aqueous phases.

## References

1) N. N. Li, "Recent Development in Separation Science," CRC Press, Florida, (1981), Vol. VI.

2) J. Strzelbicki and W. Charewicz, *J. Inorg. Nucl. Chem.*, **40**, 1415 (1978).

3) K. H. Lee, D. F. Evans, and E. L. Cussler, *AIChE J.*, **24**, 860 (1978).

4) J. W. Frankenfeld, R. P. Cahn, and N. N. Li, *Sep. Sci. Technol.*, **16**, 385 (1981).

5) S. Sifniades, T. Largman, A. A. Tunick, and F. W. Koff, *Hydrometallurgy*,**7**, 201 (1981).

6) W. C. Babcock, R. W. Baker, D. J. Kelly, and E. D. LaChapell, Proc. Int. Solvent Extrn. Conf. (1980), Vol. II.

7) K. Akiba and T. Kanno, *Proc. Sym. Solvent Extraction*, **1983**, p. 63.

8) J. Bock and P. L. Valiant, Jr., *Ind. Eng. Chem., Fundam.*, **21**, 417 (1982).

9) K. Akiba and T. Kanno, *Solvent Extrn. Ion Exchange*, **1**, 729 (1983).

10) K. Akiba and T. Kanno, *Sep. Sci. Technol.*, **18**, 831 (1983).

11) H. Ino, N. Imaishi, M. Hozawa, and K. Fujinawa, *Kagaku Kogaku Ronbunshu*, **9**, 263 (1983).