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Kenichi Akiba[a]; Takuji Kanno[a]
[a] RESEARCH INSTITUTE OF MINERAL DRESSING AND METTALLURGY TOHOKU UNIVERSITY, SENDAI, JAPAN

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Transport of Uranium(VI) through a Supported Liquid Membrane Containing LIX 63

KENICHI AKIBA and TAKUJI KANNO

RESEARCH INSTITUTE OF MINERAL DRESSING AND METTALLURGY
TOHOKU UNIVERSITY
KATAHIRA, SENDAI, JAPAN

Abstract

The carrier transport of U(VI) has been studied by means of the liquid membrane of LIX 63 (HR) held on a porous support. U was effectively transported from the dilute feed solution (pH = 4–5) to the product solution of 0.1 M H_2SO_4. Its concentration in the feed decreased according to $[U]_{f,t} = [U]_{f,0} \exp(-k_{obs}t)$. The apparent rate constant (k_{obs}) increased with an increase in carrier concentration up to 0.05 M, but it became nearly constant in the range of [HR] = 0.05–0.2 M. The rate of transport was inversely proportional to the feed volume. More than 99% of U was recovered and the final concentration ratio in the product to the feed ($[U]_p/[U]_f$) exceeded 10^3.

INTRODUCTION

Liquid membranes containing extractants have been proposed as a new separation method (*1–3*). This simultaneous extraction and stripping operation is very attractive because it can move metal ions from a low concentration range to a high concentration range. Two types of liquid membranes, i.e., a liquid surfactant membrane and a supported liquid membrane, have been developed by employing several extractants as mobile carriers (*4–10*).

From the practical point of view, a supported liquid membrane (SLM) consisting of two aqueous phases separated by a solid support could be very useful for recovering metal ions in concentration from dilute aqueous solutions, because it reduces extractant usage and the product can be obtained in a one-step operation. For the application of this method, it is important to select suitable carriers and hydrophobic porous supports.

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Recovery of uranium from acidic solution has been accomplished by the use of SLM of TBP (*11*), DEHPA/TOPO (*12*) and Alamine 336 (*13*); U was effectively transported against its concentration gradient, but its transport rate was rather slow (*11–13*).

In a previous study, LIX 63 (5,8-diethyl-7-hydroxy-dodecan-6-one oxime) was found to be a very powerful reagent for uranium extraction (*14*), therefore it could be expected to be a suitable carrier. The present paper deals with parameters affecting the transport and concentration of U in the LIX 63 liquid membrane system.

EXPERIMENTAL

Materials

An extractant LIX 63 (Henkel), used as a mobile carrier, was diluted with kerosene. Uranium-237 ($t_{1/2} = 6.75$ d) was prepared on $^{238}U(\gamma, n)^{237}U$ reaction with bremsstrahlung from LINAC in the Laboratory of Nuclear Science, Tohoku University, and was purified by an extraction method as mentioned previously (*15*). The other chemicals used here were of reagent grade. A hydrophobic porous sheet of polyolefin Cell Pore NWO1 (Sekisui) was used as a support. It is 0.15 mm thick, has 70% porosity, and an average pore size of 1.0 μm.

Preparation of SLM

The apparatus for the transport experiment is illustrated in Fig. 1. The support sheet was clamped on the bottom of inner vessel (polyethylene ware), and its geometric area was 26 cm^2. This microporous support was impregnated with LIX 63 dissolved in kerosene, and excess extractant solution was removed by wiping with a filter paper. The LIX 63 solution incorporated in the support (26 cm^2) was estimated to be about 0.3 cm^3 by weighing the membrane before and after impregnation.

Procedure

The feed solution, initially containing uranyl ion (10^{-5} *M* otherwise noted below), was poured into the outer vessel (Fig. 1). Its pH was adjusted to 4–5 with 10^{-2} *M* acetate buffer solution to favor uranium extraction. An acid

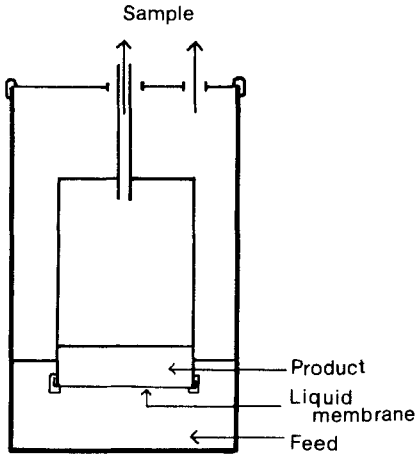

FIG. 1. Experimental apparatus of SLM.

solution was poured into the inner vessel to liberate UO_2^{2+} in the product. These feed and product solutions should be completely separated by SLM without leakage. The support was stable in the present system and had minimal expansion in a short time (<6 h), but a little swelling was observed after a long shaking time (>10 h).

The apparatus, consisting of two vessels, was shaken in an incubator thermostatted at 25 °C. Samples of the feed and product solutions were pipetted off at time intervals. U concentrations in two aqueous solutions were determined by measuring the γ-radioactivity of ^{237}U with a NaI scintillation counter. After measurements, the two phases were returned to each vessel. A shaking speed of 150 strokes/min was employed after confirming the transport rate was almost independent of shaking speed in the range of 130 to 170 strokes/min.

RESULTS AND DISCUSSION

Uranium Extraction Equilibrium

The extraction equilibrium of U(VI) from perchlorate ($I = 0.1$) solution with LIX 63 is represented by

$$UO_2^{2+} + 2HR_{org} \overset{K_{ex}}{\rightleftharpoons} UO_2R_{2,org} + 2H^+ \quad (1)$$

and its extraction constant is $\log K_{ex} = -2.11$ (*14*). The subscript "org" represents the organic phase, which corresponds to the membrane layer in the liquid membrane system. Extraction from sulfate media ($I = 0.1$) was also confirmed to follow Eq. (1), and its extraction constant was rather low ($\log K_{ex} = -3.32$).

These equilibrium data are useful guides to choosing the experimental pH values for both sides of the membrane. For example, when SLM containing 0.1 *M* LIX 63 is employed, U(VI) could be entirely extracted at pH > 4 in the feed side, while it could be readily stripped with mineral acids around pH 1 in the product side.

Active Transport of U

In order to ensure active transport against a concentration gradient, the experiment with a LIX 63 liquid membrane was carried out by starting at equal concentrations of U(VI) in two aqueous compartments. As Fig. 2 shows, U concentration in the feed (pH = 4.7) gradually decreased from its

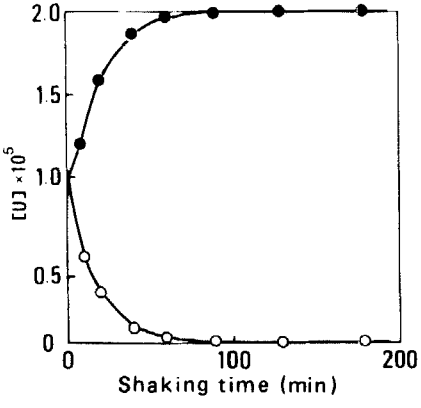

FIG. 2. Active transport of U(VI) across SLM containing 0.1 *M* LIX 63. (○) feed: pH 4.7 with 10^{-2} *M* acetate buffer, 40 cm^3; (●) product: 0.1 *M* H_2SO_4, 40 cm^3.

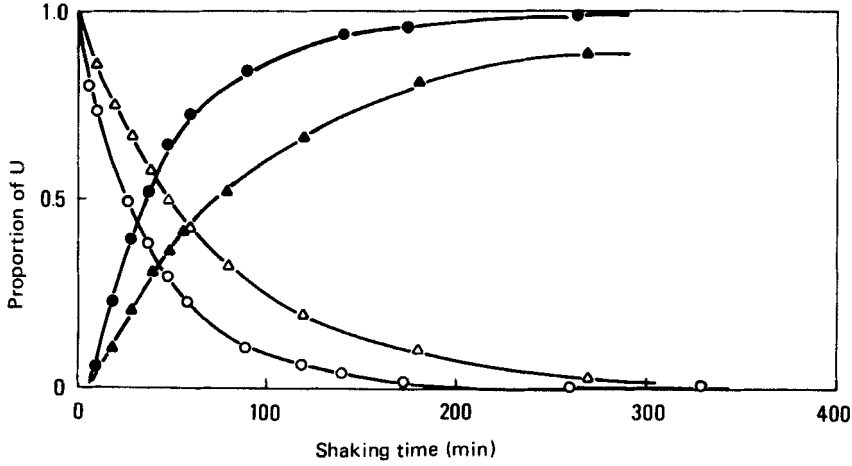

FIG. 3. Concentration of U(VI) across SLM of 0.1 *M* LIX 63. Feed: 100 cm^3 of 10^{-5} *M* UO_2^{2+}, pH 4.7 (○, ●) and 3.65 (△, ▲); open and closed symbols indicate feed and product, respectively. Product: 10 cm^3 of 0.1 *M* H_2SO_4.

initial value of 10^{-5} *M*, whereas that in an equal volume of the product (0.1 *M* H_2SO_4) increased with shaking time and eventually approached twice the initial value. After shaking for 100 min, more than 99% of the uranium initially present in the feed was transported across the liquid membrane against the concentration gradient, and the concentration in the product side was about 200 times higher than that in the feed.

Concentration of U

The degree of concentration of U is governed by the volume ratio of the feed to product, V_f/V_p. Figure 3 shows the concentration of U through SLM of 0.1 *M* LIX 63 from 100 cm^3 of the feed solution initially containing 10^{-5} *M* U to 10 cm^3 of the product solution initially free from U. The ordinate indicates the proportion of U in each aqueous solution to total uranium. U was effectively concentrated into the small volume of product by continuous permeation, resulting in a final concentration 10 times higher than its initial feed concentration.

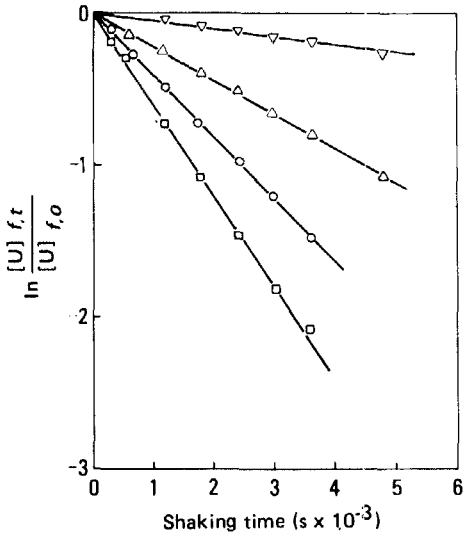

FIG. 4. Rate of uranium transport from feeds of different pH. (□) pH 5.05, (○) 4.70, (△) 3.65, (▽) 3.02. Experimental conditions in Figs. 4 and 5 are same as those in Fig. 3.

Rate of Transport

A plot of the logarithm of the concentration ratio at time t to the initial value in the feed, $[U]_{f,t}/[U]_{f,0}$, against t gave a series of straight lines, indicating first order with respect to U, as shown in Fig. 4. The initial rate of transport is given by

$$\ln \frac{[U]_{f,t}}{[U]_{f,0}} = -k_{obs}t \tag{2}$$

The slopes of these linear plots give the apparent rate constants of uranium transport, k_{obs}.

Effect of pH of the Feed on k_{obs}

The log k_{obs} values are plotted against the pH values of the feed in Fig. 5. They increased with increasing pH below 4, while a small difference in the transport rate was detected in the region of pH > 4. A change in the concentration of acetate ion from 5×10^{-3} to 1.5×10^{-2} M had a minor

effect on k_{obs} values, and therefore subsequent runs were performed around pH 4.7, adjusted with 10^{-2} M acetate buffer solution.

Effect of Carrier Concentration

The logarithmic dependence of k_{obs} on the carrier concentration is shown in Fig. 6. The transport rate increased with increasing LIX 63 concentration when that value was less than 0.05 M, but little difference in them was observed in the range of 0.05 to 0.2 M. In the liquid–liquid extraction system, a large amount of extractant is in general preferred for complete extraction, whereas an appreciably high concentration of carrier is not always required in the liquid membrane system, because the extractant in the membrane is not an agent for metal loading but a carrier to move the metal species from one side of the membrane to the other side. On the contrary, a further increase in carrier concentration beyond an appropriate value might result in a lowering of transport owing to the difficulty of releasing U into the product.

From the above findings together with the effect of pH, the transport rate might not be controlled by the chemical reaction between LIX 63 and UO_2^{2+} in the region of constant k_{obs} values, but it seems to be controlled by the diffusion of the complex into the membrane layer. Only in the low pH and low [HR] region is the extraction process considered to be the rate-controlling step.

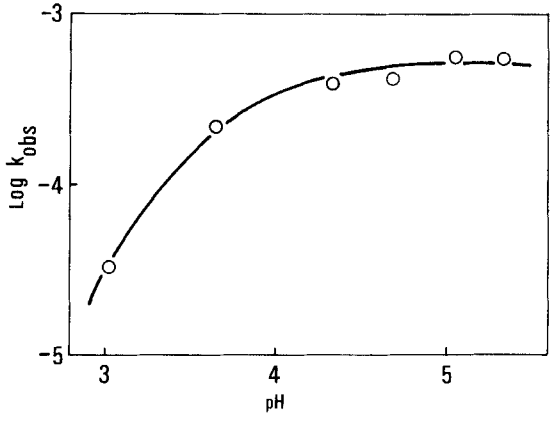

FIG. 5. Effect of feed pH on k_{obs}.

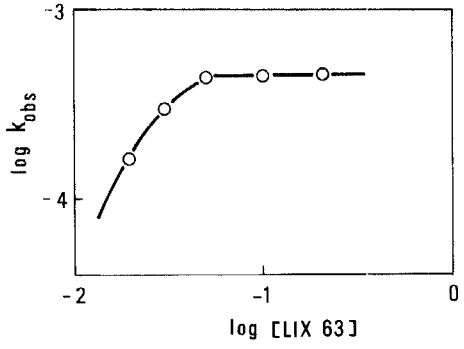

FIG. 6. Effect of carrier concentrations on k_{obs}. Feed: 10^{-5} M UO_2^{2+}, pH. 4.7, 100 cm^3; product: 0.1 M H_2SO_4, 10 cm^3.

Effect of Product Solution

A representative set of data on the effect of product solutions is given in Table 1 for the transport of U across the 0.1 M LIX 63 membrane from a feed with pH 4.7. When the acid concentration of the product is maintained high enough to strip U from SLM, the variation in H_2SO_4 concentration has only a minor effect on k_{obs} values. The volume change of the product (10-50 cm^3) has practically no effect on the transport rate. Other acids (HNO_3, HCl, and $HClO_4$) exerted effects similar to H_2SO_4, although k_{obs} values were slightly low.

TABLE 1
Effect of Acids on U Concentration by SLM of 0.1 M LIX 63 at 25°C

Product[a]					$[U]_p/[U]_f$		
Acid	(M)	k_{obs} (s^{-1})	$[U]_{f,5h}$[b] (M)	$[U]_{p,5h}$ (M)	5 h	20 h	U in SLM (%), 20 h
H_2SO_4	0.1	4.2×10^{-4}	5.0×10^{-8}	9.5×10^{-5}	1.9×10^3	8×10^3	0.5
	0.2	3.4×10^{-4}	1.0×10^{-7}	9.8×10^{-5}	9.8×10^2		0.5
	1.0	3.5×10^{-4}	6.2×10^{-8}	9.4×10^{-5}	1.5×10^3	5×10^3	
HNO_3	0.2	2.6×10^{-4}	1.0×10^{-7}	9.3×10^{-5}	9.3×10^2	5×10^3	0.3
HCl	0.2	3.1×10^{-4}	1.2×10^{-7}	9.7×10^{-5}	8.1×10^2	4×10^3	0.4
$HClO_4$	0.2	2.9×10^{-4}	1.1×10^{-7}	9.5×10^{-5}	8.6×10^2		

[a] $V_p = 10$ cm^3.
[b] $V_f = 100$ cm^3, $[U]_{f,\text{initial}} = 10^{-5}$ M.

As seen in Table 1, after 5 h of shaking the U concentration in the feed decreased by a factor of 1/100 of its initial value, and about 95% of U had moved into the product. The concentration ratio of the product to the feed, $[U]_p/[U]_f$, reached about 10^3. By operating up to 20 h, more than 99% of U was recovered in the product with a concentration ratio of several thousands, whereas the residues in SLM were about 0.5% and it could be recovered by washing with mineral acids.

Effect of Feed Volume

In order to concentrate U from dilute solution, a high volume ratio of feed to product is desirable, because it gives the concentration factor $[U]_p/[U]_{f,\text{initial}}$. The concentration of uranium was examined for different volumes of the feed containing 10^{-5} *M* U to a fixed volume (10 cm^3) of 0.1 *M* H_2SO_4. The k_{obs} values were inversely proportional to the feed volume (V_f) as shown in Fig. 7. The high volume ratio (V_f/V_p) might be expected for

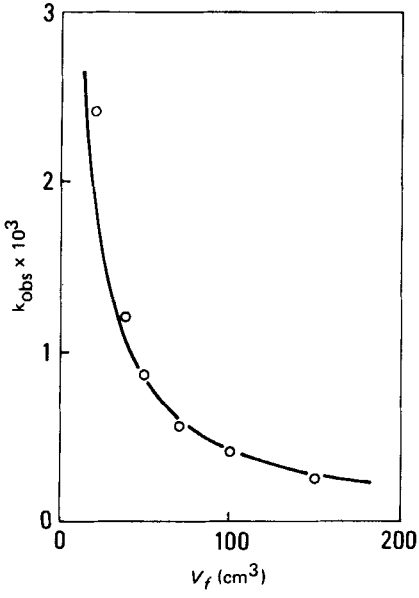

FIG. 7. Effect of feed volumes on k_{obs}. SLM: 0.1 *M* LIX 63; feed: 10^{-5} *M* UO_2^{2+}, pH 4.7; product: 0.1 *M* H_2SO_4, 10 cm^3.

effective concentration; however, a large volume of feed is not always desirable from the kinetic standpoint.

Effect of U(VI) Concentrations

The k_{obs} values given in Table 2 were almost independent of U concentrations in the range of 10^{-6} to 10^{-4} M, but they gradually decreased with an increasing concentration of U above 10^{-4} M. A membrane of 26 cm^2 contains about 0.3 cm^3 of 0.1 M LIX 63 solution, and this amount of carrier is estimated to be equivalent to about 1.5×10^{-4} M U(VI) solution (100 cm^3) owing to the stoichiometry of UO_2R_2. Transport rates seems to be unaffected by U concentrations below this value, whereas over this concentration range they decrease considerably because of a time-consuming process of back and force movement of carrier; that is,the carrier liberating uranyl ion into the product must return across the membrane to the feed side. Despite a lowering in rate constants, liquid membranes enable a large amount of U to move; for example, the quantity of U passed through SLM from 100 cm^3 of the 10^{-2} M U(VI) solution were several ten times as much as of LIX 63.

From the findings of the effect of feed volumes, the rate of transport can be expressed by

$$k_{obs} = P_U \frac{S}{V_f} \tag{3}$$

TABLE 2
Effect of Uranium(VI) Concentration and Permeability

$[U]_{f,initial}$ (M)	Temperature (°C)	k_{obs}[a] (s^{-1})	P_U[b] (cm/s)
10^{-6}	25	4.2×10^{-4}	1.6×10^{-3}
10^{-5}	25	4.2×10^{-4}	1.6×10^{-3}
10^{-4}	25	4.1×10^{-4}	1.6×10^{-3}
10^{-3}	25	1.2×10^{-4}	4.6×10^{-4}
10^{-2}	25	2×10^{-5}	8×10^{-5}
10^{-5}	15	3.1×10^{-4}	1.2×10^{-3}
10^{-5}	35	6.2×10^{-4}	2.4×10^{-3}

[a]Obtained at pH = 4.7/0.1 M LIX 63/0.1 M H_2SO_4 (10 cm^3).
[b]Evaluated by Eq. (3) for $S = 26$ cm^2 and $V_f = 100$ cm^3.

By combining Eqs. (2) and (3):

$$\ln \frac{[U]_{f,t}}{[U]_{f,0}} = -P_U \frac{S}{V_f} t \tag{4}$$

where P_U (cm/s) is the permeability of the membrane for uranium (*12*) and S is the SLM surface area, which is assumed to be equal to the geometric area of the support (26 cm^2).

The P_U values evaluated are given in the last column of Table 2, together with values obtained at different temperatures. The reported value, $P_U = 6.68 \times 10^{-5}$, of the DEHPA/TOPO membrane supported on Gore-Tex (0.15 mm thick) for 2000 ppm (8×10^{-3} *M*) U is close to the present results.

In order to enhance uranium transport, it is thus necessary not only to increase the surface area per unit volume, but also to maintain the U concentration in an appropriate range. Furthermore, increasing the temperature will appreciably promote transport as is seen in Table 2.

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