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Shigeto Nakamura[a]; Kenichi Akiba[a]
[a] Research Institute of Mineral Dressing and Metallurgy Tohoku University, Sendai, Japan

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Transport of Europium through Supported Liquid Membrane Containing Dihexyl-*N,N*-diethylcarbamoylmethylphosphonate

SHIGETO NAKAMURA and KENICHI AKIBA

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

Abstract

The transport of europium has been studied through a supported liquid membrane (SLM) impregnated with dihexyl-*N,N*-diethylcarbamoylmethylphosphonate (CMP). Europium was effectively extracted from the perchlorate solution into SLM, but was insufficiently stripped to a dilute acid solution. The addition of 1-decanol improved the stripping process, and quantitative transport of europium was achieved. By the combination of two SLM systems consisting of diisodecylphosphoric acid and CMP, europium was transported from the feed solution (0.1 *M* HNO_3) through the intermediate solution (1 *M* $HClO_4$ + 4 *M* $NaClO_4$) to the product solution (0.1 *M* HNO_3) and effectively concentrated by a factor of about 20.

INTRODUCTION

Selective transport of metal ions across a supported liquid membrane (SLM) containing a mobile carrier has been studied for applications to separation and concentration techniques. The combination of different SLMs containing selective carriers has been proposed as a further advanced procedure. The double liquid membrane systems consisting of the first membrane with a carbamoylmethylphosphine oxide derivative (CMPO) and the second membrane with a long chain primary amine

were employed for the recovery of actinoids and lanthanoids from acidic nuclear wastes (*1, 2*); the second SLM served for the selective removal of nitric acid transported together with metals through the first SLM. The successive permeation of metals has been performed through a series of SLMs as an effective separation of metals that are difficult to separate by a single-stage SLM. The composite SLM system containing di(2-ethylhexyl)phosphoric acid (DEHPA) and CMPO was employed for the mutual separation of americium and europium (*3*); europium was preferentially transported from 0.01 *M* (*M* = mol/dm^3) hydrochloric acid through the first SLM of DEHPA and through the second SLM of CMPO into 0.01 *M* hydrochloric acid. Since the composition of the final solution was the same as that of the initial solution, the multistage transport was also attempted by arranging a large number of composite SLMs (*4*).

In the present study the transport of europium by dihexyl-*N,N*-diethylcarbamoylmethylphosphonate (CMP) was investigated in order to combine this CMP-SLM system to the diisodecylphosphoric acid (DIDPA)-SLM system studied previously (*5*). Since CMP is a powerful extractant from a high acidic solution (*6, 7*), europium is expected to be transported through CMP-SLM from acidic solutions corresponding to the stripping solution in the DIDPA-SLM system. The optimum conditions for europium transport with CMP-SLM were examined, and the transport of europium was performed by combining DIDPA-SLM and CMP-SLM.

EXPERIMENTAL

Materials

Radioisotopes ^{152,154}Eu were obtained from the Radiochemical Centre (England) and diluted with a nitric acid solution. Dihexyl-*N,N*-diethylcarbamoylmethylphosphonate (CMP) was obtained from Tokyo Chemical Industry Co., Ltd. The other chemicals used here were of guaranteed reagent grade. The flat-sheet support used here was a polytetrafluoroethylene film (Fluoropore FP-045, Sumitomo Electric Ind., Ltd.) with a thickness of 80 μm, a porosity of 74%, and an average pore size of 0.45 μm. Kerosene was used as a diluent since it wetted the support film and formed a stable liquid membrane.

Procedure

Transport experiments through the supported liquid membrane were similar to those described previously (*8*). SLM was prepared by impregnating a microporous sheet with a kerosene solution containing 0.1 *M* CMP and 10% 1-decanol. A nitrate or perchlorate solution (100 cm^3), initially containing europium spiked with $^{152,154}Eu$, was taken as the feed solution, and a dilute nitric acid solution (10 cm^3) was used as the product solution for stripping. The assembled apparatus was shaken at 120 strokes per minute at 25°C. At appropriate time intervals the concentrations of europium in the feed and product solutions were determined by counting the radioactivity with a NaI(Tl) scintillation detector.

RESULTS AND DISCUSSION

Transport from Nitrate Solution

The transport of europium through the membrane with diisodecylphosphoric acid (DIDPA) was previously performed from dilute nitric acid of ~0.1 *M* to a stripping solution of 5 *M* nitric acid (*5*). In order to create a separation process by the combination of this DIDPA-SLM, the transport of europium across the membrane was examined by employing CMP as the mobile carrier. The extraction equilibrium of europium with CMP from nitrate solutions has been reported as follows (*6*):

$$Eu^{3+}_{aq} + 3NO^{-}_{3,aq} + 3CMP_{org} \rightleftharpoons Eu(NO_3)_3(CMP)_{3,org} \quad (1)$$

The driving force for europium transport must be the concentration gradient for nitrate ion across the membrane. Figure 1 illustrates the time-dependent transport of europium through the membrane with 0.1 *M* CMP from the nitrate solutions. Europium was not entirely extracted from 5 *M* nitric acid alone, and only a small portion of europium was transported from a dilute concentration (0.01–0.1 *M*) of nitric acid while keeping the total concentration of nitrate ion at 5 *M* by the addition of sodium nitrate. This low transport can be attributed to the decrease in the

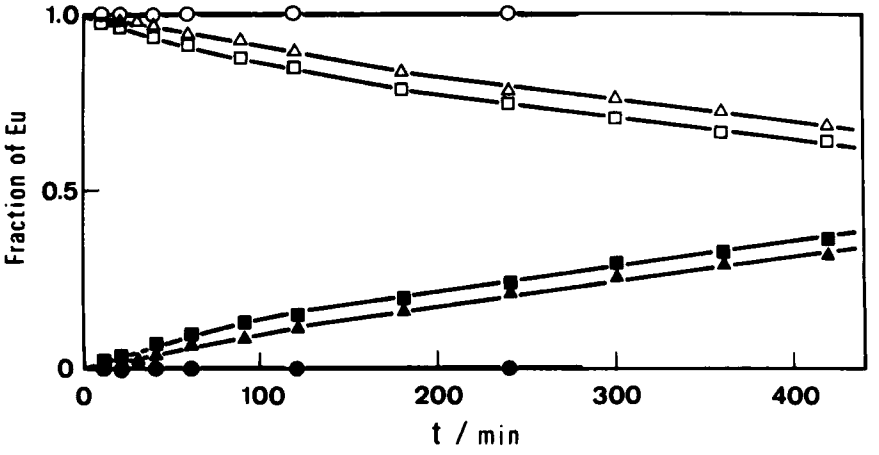

FIG. 1. Transport of europium from nitrate solutions. Feed: (○, ●) 5 *M* HNO_3, (△, ▲) 0.1 *M* HNO_3 + 4.9 *M* $NaNO_3$, (□, ■) 0.01 *M* HNO_3 + 5 *M* HNO_3, 100 cm^3; product: 0.1 *M* HNO_3, 10 cm^3; SLM: 0.1 *M* CMP in kerosene. Open and closed symbols indicate the feed and product solutions, respectively.

concentration of free CMP owing to its interaction with nitric acid (*9, 10*).

$$CMP_{org} + HNO_{3,aq} \rightleftharpoons CMP \cdot HNO_{3,org} \quad (2)$$

Although the transport of europium was found to be promoted by a further increase of CMP concentration in SLM, only a half of the europium was transported through SLM with 1 *M* CMP, and quantitative transport was not achieved.

Transport from Perchlorate Solution

The extraction of europium from the perchlorate medium is more effective than that from the nitrate medium (*11*). Figure 2 shows the europium transport across the membrane from perchlorate solutions. Europium was only slightly transported from 5 *M* perchloric acid but was more effectively transported from 1 *M* perchloric acid in the presence of 4 *M* sodium

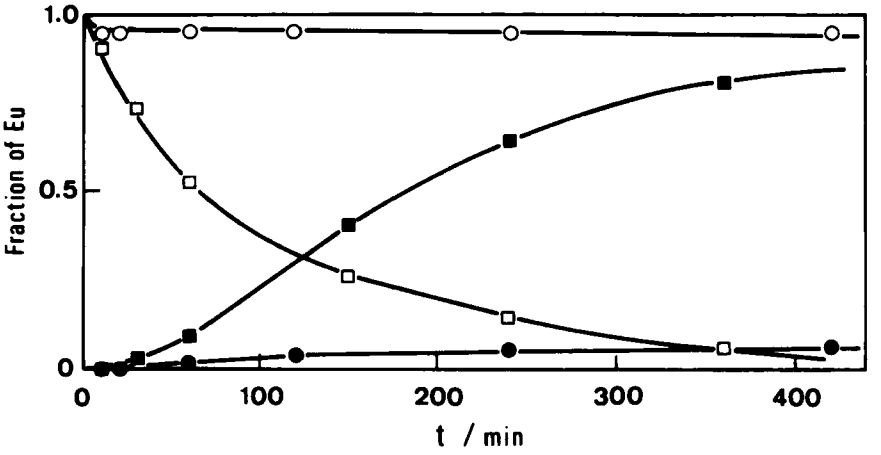

FIG. 2. Transport of europium from perchlorate solutions. Feed: (○, ●) 5 *M* $HClO_4$, (□, ■) 1 *M* $HClO_4$ + 4 *M* $NaClO_4$, 100 cm^3; product: 0.1 *M* HNO_3, 10 cm^3; SLM: 0.1 *M* CMP in kerosene.

perchlorate. However, curves of europium fractions in the feed and product solutions are unsymmetrical; that is, europium can be effectively extracted into SLM, but insufficiently stripped to the product solution, and a part of europium remains in SLM.

In solvent extraction experiments with 0.1 *M* CMP from 1 *M* perchloric acid and 4 *M* sodium perchlorate solution, a third phase was observed, probably owing to the interaction between CMP and perchloric acid, and most of the europium was extracted into this phase. A similar phenomenon may occur in the feed side of SLM; a portion of europium may be extracted into the third phase separating from the organic solution in SLM, so that the transfer of europium complex through SLM will become lower.

Effect of 1-Decanol

The formation of the third phase could be avoided in the presence of a long chain alcohol in the organic phase, so the addition of 1-decanol to

the membrane phase was attempted to prevent third-phase formation. The transport of europium in the presence of 1-decanol is shown in Fig. 3. The europium fractions in the feed and product solutions varied almost symmetrically, that is, the stripping process was improved by the addition of 1-decanol. Europium was quantitatively transported through SLM containing 10% 1-decanol after about 7 h, but any further increase in 1-decanol content lowered the europium transport.

Since the time lag between the decrement of the europium fraction in the feed solution and the increment in the product solution is negligibly small in this thin membrane, the decreasing rate in the feed side is regarded as the transport rate. The apparent rate constant k_{obs} is defined as follows (5):

$$\ln \frac{[\mathrm{Eu}]_{f,t}}{[\mathrm{Eu}]_{f,0}} = -k_{obs} \cdot t \tag{3}$$

where $[\mathrm{Eu}]_{f,t}$ and $[\mathrm{Eu}]_{f,0}$ denote the concentrations of europium in the feed solution at time t and initially, respectively.

Figure 4 shows the effect of 1-decanol concentration on the k_{obs} value. The k_{obs} value is nearly constant up to 10% 1-decanol and decreases with a

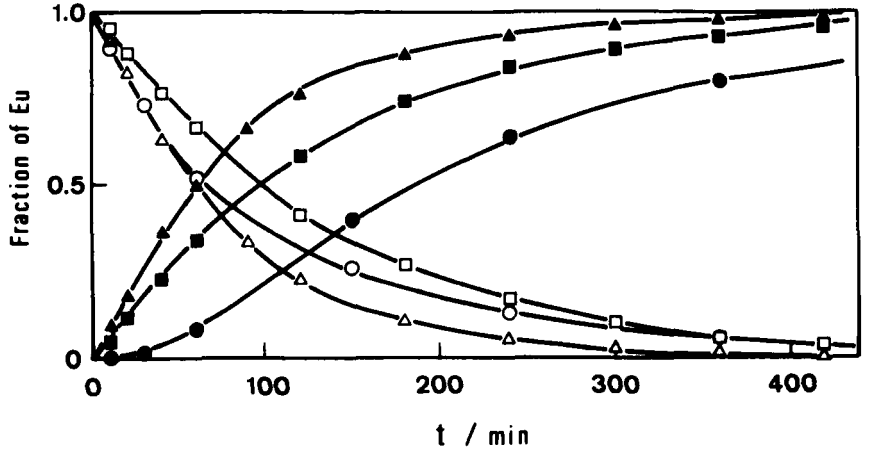

FIG. 3. Transport of europium in the presence of 1-decanol. Feed: 1 *M* $HClO_4$ + 4 *M* $NaClO_4$, 100 cm^3; product: 0.1 *M* HNO_3, 10 cm^3; SLM: 0.1 *M* CMP in kerosene, 1-decanol (○,●) 0%, (△, ▲) 10%, (□, ■) 20%.

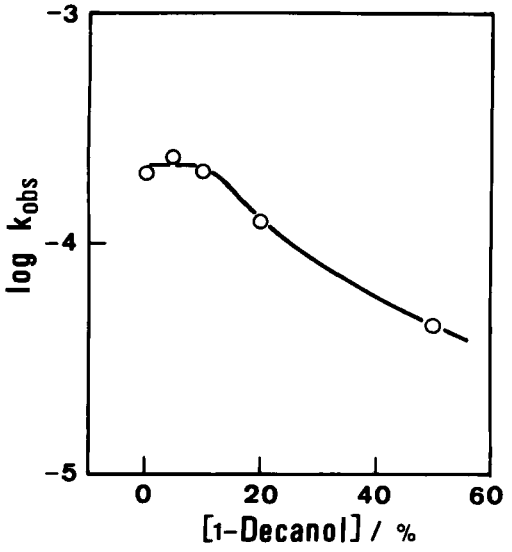

FIG. 4. Effect of 1-decanol concentration on k_{obs}. Feed: 1 *M* $HClO_4$ + 4 *M* $NaClO_4$, 100 cm^3; product: 0.1 *M* HNO_3, 10 cm^3; SLM: 0.1 *M* CMP + 1-decanol in kerosene.

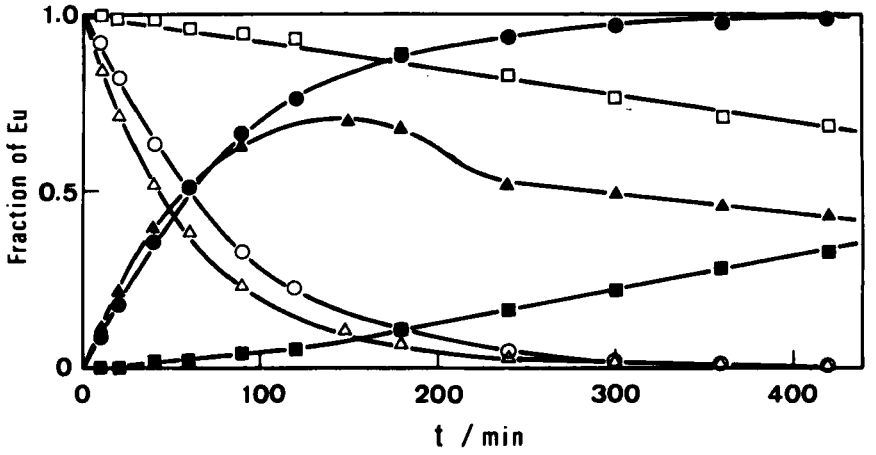

FIG. 5. Effect of CMP concentration in SLM. Feed: 1 *M* $HClO_4$ + 4 *M* $NaClO_4$, 100 cm^3; product: 0.1 *M* HNO_3, 10 cm^3; SLM: 10% 1-decanol, CMP in kerosene (△, ▲) 0.5 *M*, (○, ●) 0.1 *M*, (□, ■) 0.02 *M*.

further increase in 1-decanol content because of an appreciable decrease in the distribution ratio of europium.

Effect of CMP Concentration

The transport of europium across SLM containing different concentrations of CMP in the presence of 10% 1-decanol is illustrated in Fig. 5. With a low concentration of 0.02 *M* CMP in SLM, only a small fraction of europium was transported due to the low distribution ratio. Quantitative transport was accomplished by using 0.1 *M* CMP-SLM, yielding almost symmetrical fraction curves of each side as represented by the circles in Fig. 5. As for 0.5 *M* CMP-SLM, europium in the feed side smoothly decreased, but europium concentration in the product side has a maximum at around 150 min and gradually decreases with time. This seems to be due to insufficient stripping from the SLM containing the high concentration of CMP. Further, the cotransport of acid from the feed to the product solution results in an increase in acid concentration in the product side, and this may cause europium extraction into SLM from the product solution in the reverse direction. The optimum concentration of CMP is thus around 0.1 *M*, taking into account complete stripping from SLM.

Effect of Acid Concentrations

The driving force for this transport is provided by the concentration gradient for perchlorate ion between the feed and product sides. For the purpose of europium transport from higher acidity to lower acidity, it is significant to investigate the effect of acid concentration.

The effects of perchloric acid concentration in the feed solution for 0.1 *M* CMP-SLM are summarized in Table 1. Here, the concentrations of perchlorate ion were kept at 5 *M* with sodium perchlorate. Variations in perchloric acid concentrations of less than 3 *M* have practically no effect on the transport rate, but k_{obs} values sharply decrease with a further increase in acidity due to appreciable interaction between CMP and perchloric acid.

The effects of nitric acid concentration on the product solution are also given in Table 1. The k_{obs} values were nearly constant in the concentration

TABLE 1
The Effect of Acid Concentration on the Transport of Eu(III)[a]

Feed $[HClO_4]$ (M)	Product $[HNO_3]$ (M)	k_{obs} (s^{-1})	Eu (% at 7 h) Feed	Eu (% at 7 h) Product
0.1	0.1	1.9×10^{-4}	0.8	99.2
0.3	0.1	2.0×10^{-4}	0.5	99.5
1	0.1	2.3×10^{-4}	0.6	99.4
3	0.1	1.8×10^{-4}	2.0	97.8
5	0.1	6.0×10^{-5}	15.8	83.2
1	0.01	2.0×10^{-4}	1.0	98.2
1	0.05	2.0×10^{-4}	1.3	98.2
1	0.3	2.4×10^{-4}	0.5	99.2
1	1	2.1×10^{-4}	0.5	99.5

[a]Feed: 5 M (H,Na)ClO_4, 100 cm^3; SLM: 0.1 M CMP and 10% 1-decanol in kerosene; product: 10 cm^3.

region from 0.01 to 1 M nitric acid, and sufficient stripping was achieved.

Thus europium in the feed solution below 3 M perchloric acid decreased to less than 1% of its initial value at 7 h, and more than 99% of initial content was recovered into the product solution containing 0.01 to 1 M nitric acid unless remaining SLM only with a few exceptions.

Effect of Europium Concentration

Figure 6 shows the effect of the initial concentration of europium on the europium flux through SLM with 0.1 M CMP. The flux (J, mol · cm^{-2} · s^{-1}) is given by (5)

$$J = \left(\frac{d[\mathrm{Eu}]_{f,t}}{dt}\right)_{t=0} \cdot \frac{V_f}{S} \tag{4}$$

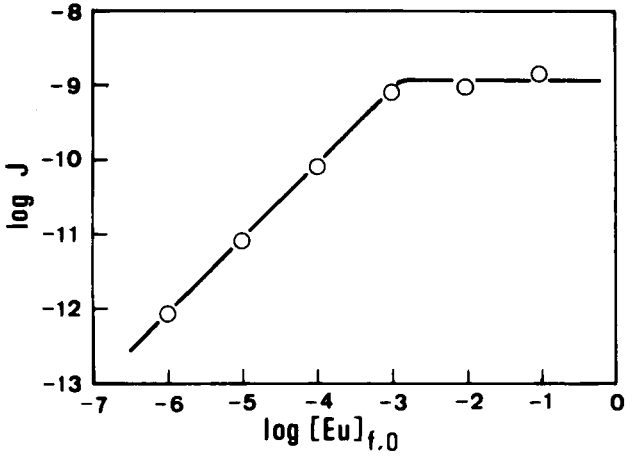

FIG. 6. Effect of europium concentration on the flux. Feed: 1 *M* $HClO_4$ + 4 *M* $NaClO_4$, 100 cm^3; product: 0.1 *M* HNO_3, 10 cm^3; SLM: 0.1 *M* CMP + 10% 1-decanol in kerosene.

where V_f denotes the volume of the feed solution (100 cm^3) and S is the geometric area of the support (26 cm^2).

The europium flux is linear to a europium concentration of less than 10^{-3} *M* and then becomes almost constant at high concentrations. Most of the CMP molecules in SLM participate in this region with the formation of a europium complex, and the diffusion of the europium complex in SLM may be the dominant process in determining the transport rate.

Feed	SLM(1)	Intermediate solution	SLM(2)	Product
0.1 M HNO_3	0.2 M $(DIDPA)_2$ + 10% DecOH	1 M $HClO_4$ + 4 M $NaClO_4$	0.1 M CMP + 10% DecOH	0.1 M HNO_3
100 cm^3	in kerosene	20 cm^3	in kerosene	5 cm^3

FIG. 7. Scheme of the successive transport through two SLM systems.

Transport through Double SLM

The combination of two liquid membranes containing DIDPA and CMP was attempted on the basis of the transport properties of the individual membranes. The transport scheme is illustrated in Fig. 7. The apparatus for this transport experiment consists of three polypropylene vessels corresponding to feed, intermediate, and product compartments. The feed solution was poured into the first vessel; and the second vessel, with DIDPA-SLM (26 cm^2) and containing the intermediate solution, was placed in the first vessel; the third stripping vessel, with CMP-SLM (7 cm^2), was placed in the second vessel. In the first transport step, experimental conditions were chosen mainly based on the results of the previous work for DIDPA-SLM (*5*). The intermediate solution containing 1 *M* perchloric acid and 4 *M* sodium perchlorate corresponded to the stripping solution for the first SLM. It was preliminarily confirmed that europium can be stripped with this intermediate perchlorate solution.

The experimental results are illustrated in Fig. 8. Europium was transported from the feed (100 cm^3) through the intermediate (20 cm^3) to the product solution (5 cm^3) and concentrated in the product solution.

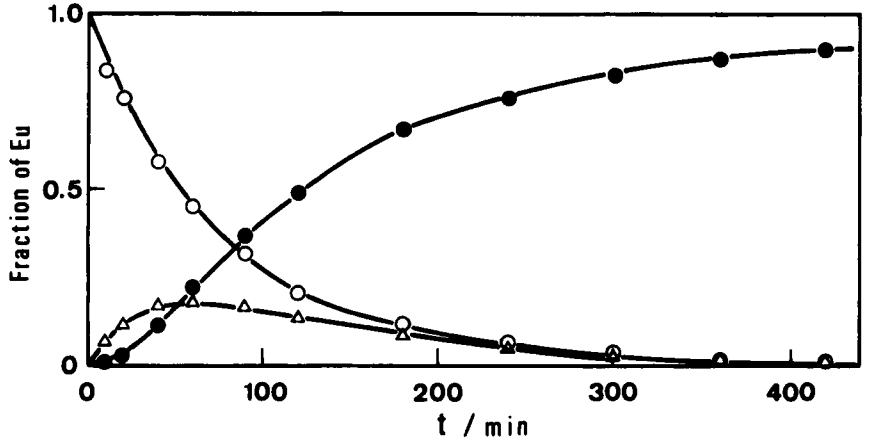

FIG. 8. Transport of europium through double SLM. (○) Feed: 0.1 *M* HNO_3, 100 cm^3; (△) intermediate solution: 1 *M* $HClO_4$ + 4 *M* $NaClO_4$, 20 cm^3; (●) product: 0.1 *M* HNO_3, 5 cm^3.

The concentration factor after 19 h was found to be close to 20. In this system the feed solution (0.1 *M* HNO_3) is the same as the product solution; thus it is possible to successively combine this product solution with another double SLM system to perform multistage separations and concentrations.

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