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# Transport of Europium(III) through Supported Liquid Membrane Containing Diisodecylphosphoric Acid

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**Abstract**

Carrier mediated transport of europium has been investigated by the use of a flat-sheet membrane impregnated with diisodecylphosphoric acid (DIDPA). The addition of 1-octanol to the membrane improves the stripping process, and hence europium can be quantitatively transported from the feed solution of 0.1 *M* $HNO_3$ into the product solution of 5 *M* $HNO_3$. Its concentration in the feed solution decreases as $[Eu]_{f,t} = [Eu]_{f,0} \exp(-k_{obs}t)$. The apparent rate constant ($k_{obs}$) increases with increasing carrier concentration and becomes nearly constant above 0.05 *M* DIDPA. The europium flux is proportional to initial europium concentrations less than $10^{-3}$ *M*, and becomes constant at high concentrations.

## INTRODUCTION

A supported liquid membrane (SLM) containing a mobile carrier continuously transports a metal ion against its concentration gradient. This is very attractive for separation and concentration of metal ions from dilute solutions; the amount of reagent used is considerably reduced and separation procedures will be advanced by employing a variety of solid supports such as hollow fibers (*1*). The utility of this convenient method is potentially large in the recovery of radionuclides for analytical and process separations.



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The effectiveness of SLM has been demonstrated for the selective recovery of radionuclides including transuranium elements from nuclear waste solutions by the use of SLM containing a variety of mobile carriers including bifunctional organophosphorus extractants (*2–4*). Di(2-ethylhexyl)phosphoric acid (DEHPA) has also been used as a carirer for applications to the recovery of trivalent lanthanoid and actinoid ions (*5–7*). For the selection of a mobile carrier, a extractant of low solubility in aqueous solutions would be desirable to maintain a stable liquid membrane.

In the present study we employed diisodecylphosphoric acid (DIDPA) as a mobile carrier for the transport of europium(III) from dilute nitric acid solutions. The hydrophobicity of DIDPA seems to be higher owing to its high molecular weight; further, its extractability for lanthanoids was found to be larger than that of DEHPA (*8*). In the liquid membrane systems, the stripping process in addition to the extraction process is particularly important for the quantitative transport of metals without remaining in the membrane phase. The effect of 1-octanol on europium stripping has also been investigated, and optimum conditions have been ascertained.

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## EXPERIMENTAL

### Materials

Radioisotopes $^{152,154}$Eu were obtained from the Radiochemical Centre (England) as a hydrochloric acid solution and diluted with a $HNO_3$ solution. The purity of DIDPA (Daihachi Chemical Industry Co.) was checked to be 91.4% by potentiometric titration with a glass electrode in 80% v/v ethanol–water solution. The other chemicals used here were of guaranteed reagent grade. A microporous polytetrafluoroethylene film (Fluoropore FP-045, Sumitomo Electric Ind.) was used as a solid support. It is 80 μm thick, 74% porous, and has an average pore size of 0.45 μm.

### Extraction of Europium

The nitric acid solution containing europium(III) spiked with $^{152,154}$Eu was shaken with an equal volume of the kerosene solution of DIDPA over 1 h at 25°C. After centrifugation, aliquots of both phases were taken

and then their radioactivities were measured with a NaI(Tl) scintillation detector connected with a single channel analyzer.

### Transport of Europium

Experimental procedures were essentially the same as those described previously (*9*). An apparatus used for transport experiments consists of inner and outer polypropylene vessels corresponding to extraction and stripping compartments, respectively. The microporous support sheet was impregnated with the kerosene solution of DIDPA and 10% v/v 1-octanol and was attached to the bottom of the inner vessel. The feed solution (100 $cm^3$) of 0.01–1 *M* (*M* = $mol/dm^3$) $HNO_3$ initially containing europium(III) spiked with $^{152,154}Eu$ was poured into the outer vessel, and 10 $cm^3$ of 1–10 *M* $HNO_3$ as a stripping solution (product solution) was poured into the inner vessel. The apparatus was shaken at 120 strokes per minute in a water bath kept at 25°C. At time intervals the concentrations of europium in the feed and product solutions were determined by measuring the radioactivity.

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## RESULTS AND DISCUSSION

### Extraction of Europium

The solvent extraction of europium(III) with DIDPA from nitric acid solutions was carried out as a guide to the selection of appropriate conditions for membrane transport. Typical extraction curves are shown in Fig. 1. The distribution ratio (*D*) decreased with an increase in nitric acid concentration, reached a minimum at around 5 *M* $HNO_3$, and subsequently increased with further increase in acid concentrations. The plots gave almost linear relations with slopes of about −3.5 below 2 *M* $HNO_3$; these results are approximately similar to those for extraction of neodymium by DIDPA (*8*). At the same time, this increase in acid cocnentration is accompanied by an increase in the ionic strength. When the ionic strength was kept at 0.1 by the addition of $NaNO_3$, the data indicated by the filled circles are adequately fitted by a line with a slope of 3, as is expected from the +3 charge of europium.

The effect of extractant concentrations on the distribution ratios of europium is illustrated in Fig. 2. Here, we used the concentration of dimer

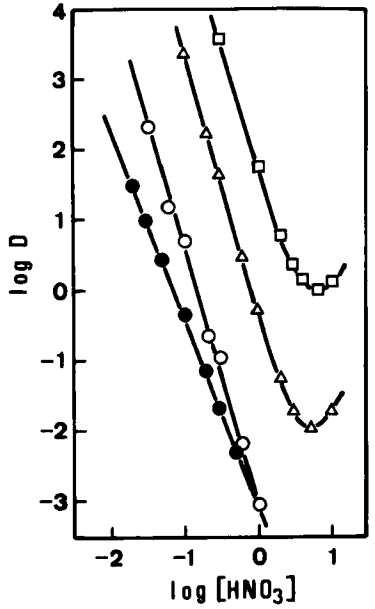


FIG. 1. Effect of $HNO_3$ concentration on the distribution ratio of europium with DIDPA in kerosene. $(DIDPA)_2$ (□) 0.5 *M*, (△) 0.05 *M*, (○) 0.005 *M*, (●) 0.005 *M* at 0.1 *M* (H,Na)$NO_3$.

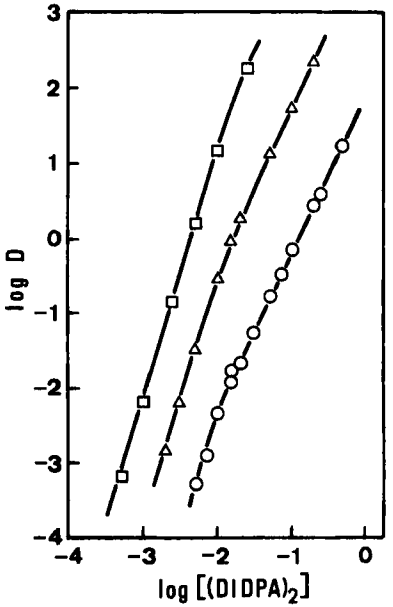


FIG. 2. Effect of DIDPA concentration on the distribution ratio of europium. $HNO_3$ (○) 1 *M*, (△) 0.3 *M*, (□) 0.1 *M*.

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as the abscissa, since DIDPA seems to be dimerized in a nonpolar organic solution. The slopes of the plots are about 3 in DIDPA concentrations below $10^{-2}$ *M*, but they become slightly smaller at high concentrations.

The extraction of lanthanoid ($M^{3+}$) with dialkylphosphoric acid (HA) is usually expressed by (*10*)

$$M^{3+}_{aq} + 3(HA)_{2,org} \rightleftharpoons M(HA_2)_{3,org} + 3H^{+}_{aq} \quad (1)$$

In DIDPA systems this reaction is appropriate in the regions of low acid and extractant cocnentrations. Other extraction equilibria may, however, participate at higher acidities; e.g., the formation of a ternary complex with $NO_3^-$.

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## Transport of Europium through SLM

On the basis of extraction data, the acid concentrations of both sides of the membrane were adjusted to give an appropriate concentration gradient. Figure 3 represents the time-dependent fractions of europium transport through SLM containing various concentrations of DIDPA from 0.1 *M* $HNO_3$ solution into 5 *M* $HNO_3$ solution. The europium fraction in the feed solution decreased with shaking time, while that in the product solution gradually increased. In the case of SLM with 0.2 *M* $(DIDPA)_2$, europium was quantitatively transported after 6 h, yielding a maximum concentration factor of 10, since the volume of the product solution was one-tenth that of the feed solution. The plots of europium fractions for both sides are approximately symmetrical for 0.2 *M* $(DIDPA)_2$-SLM, but they are unsymmetrical for SLM with low concentrations of DIDPA. This indicates that europium extracted in SLM is incompletely released into the product solution, and partially remains in SLM.

## Addition of 1-Octanol

In the previous study on uranium transport through DEHPA-SLM, symmetrical curves of uranium fraction were obtained in the presence of 1-octanol in SLM (*11*). We attempted the addition of 1-octanol to the membrane in order to favor complete stripping of europium from the liquid membrane. The effect of 1-octanol on the distribution ratio of europium is shown in Fig. 4; the distribution ratio sharply decreased with

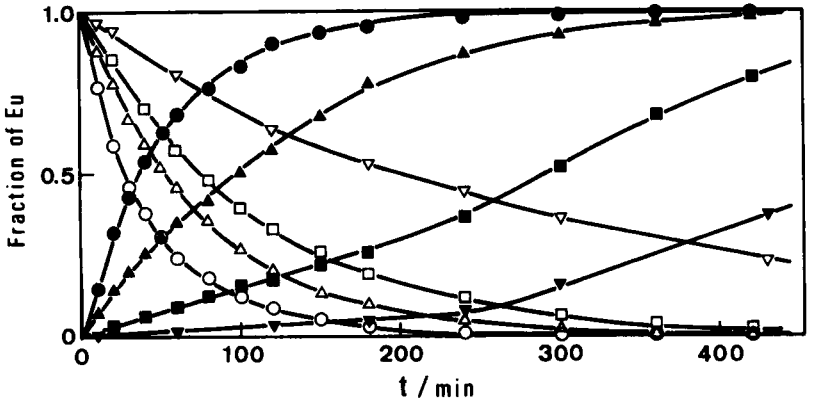


FIG. 3. Transport of europium through SLM. Feed: 0.1 *M* $HNO_3$, 100 $cm^3$; product: 5 *M* $HNO_3$, 10 $cm^3$; SLM: $(DIDPA)_2$ in kerosene (○, ●) 0.2 *M*, (△, ▲) 0.02 *M*, (□, ■) 0.01 *M*, (▽, ▼) 0.005 *M*. Open and closed symbols indicate the feed and product solutions, respectively.

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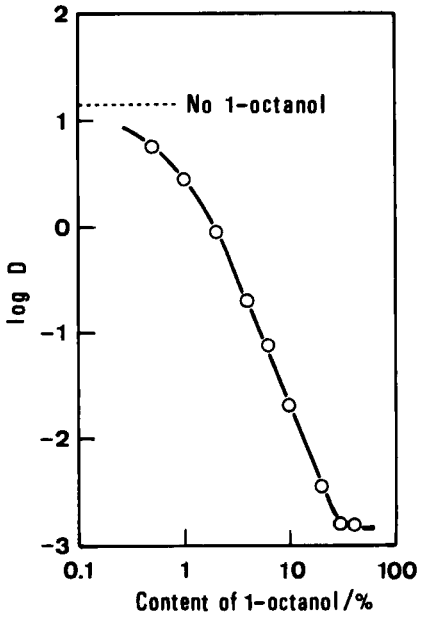


FIG. 4. Effect of 1-octanol contents on the distribution ratio of europium. Aqueous phase: 0.3 *M* $HNO_3$; organic phase: 0.05 *M* $(DIDPA)_2$ in kerosene.

increasing 1-octanol contents. It was confirmed that the plots of log $D$ vs log $[HNO_3]$ gave a slope of $-3.5$, comparable to that in the absence of 1-octanol, whereas the slopes of the log $D$ vs log $[(DIDPA)_2]$ plots in the presence of 10% v/v 1-octanol were found to be 4.3. Mason and coworkers showed that dialkylphosphoric acid is monomeric in alcohol and the distribution ratio of cation is lower than that in a nonpolar hydrocarbon (*12*, *13*). In the present extraction system, a part of DIDPA dimer would dissociate into monomer through the interaction with 1-octanol, and the extraction equilibrium may be represented as

$$Eu^{3+}_{aq} + 2(HA)_{2,org} + 2HA(ROH)_{n,org} \rightleftharpoons$$

$$Eu(HA_2)_{3,org} + 2nROH_{org} + 3H^{+}_{aq} \quad (2)$$

where ROH denotes 1-octanol. The addition of 1-octanol renders the extraction system more complex compared with the kerosene solution; it lowers the distribution ratio and will serve to release europium from the DIDPA-SLM.

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## DIDPA-SLM Containing 1-Octanol

The transport of europium through SLM impregnated with DIDPA and 10% 1-octanol is shown in Fig. 5. The curves for the feed and product solutions are almost symmetrical in each case, indicating that the diffusion time inside the membrane is negligibly small compared with the extraction time into the membrane. Europium was quantitatively transported across SLM with 0.05–0.4 $M$ $(DIDPA)_2$ after 6 h. Moreover, the presence of 1-octanol was favorable to stable liquid membranes, being effective about 8 h without leaching of the reagent.

On the assumption that the decreasing rate of europium in the feed solution is proportional to its concentration, the rate equation is given by a pseudo-first-order reaction, and the following equation is obtained:

$$\ln [Eu]_{f,t}/[Eu]_{f,0} = -k_{obs}t \quad (3)$$

where $k_{obs}$ denotes the apparent rate constant and $[Eu]_{f,t}$ and $[Eu]_{f,0}$ are the concentration of europium at time $t$ and the initial concentration, respectively. The plot of $\ln [Eu]_{f,t}/[Eu]_{f,0}$ against $t$ gave a straight line, and its slope corresponds to the $k_{obs}$ value. As can be seen in Fig. 5, the time lag between decreasing curves in the feed side and the corresponding increasing curves in the product side is considerably small, and hence

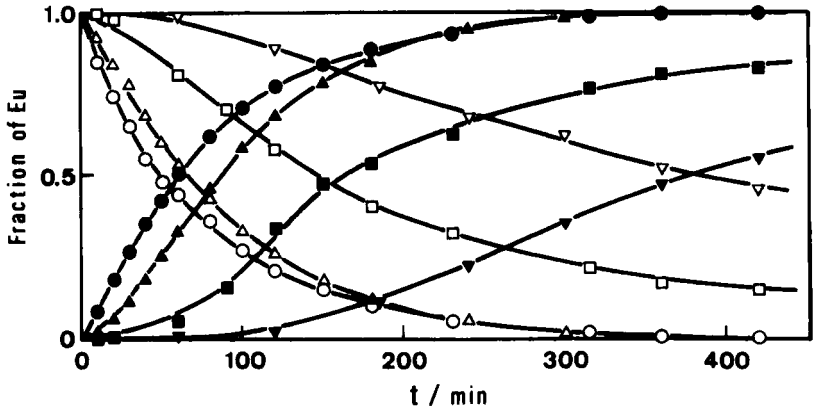


FIG. 5. Transport of europium through SLM in the presence of 10% 1-octanol. Feed: 0.1 *M* $HNO_3$, 100 $cm^3$; product: 5 *M* $HNO_3$, 10 $cm^3$; SLM: $(DIDPA)_2$ in kerosene (○, ●) 0.2 *M*, (△, ▲) 0.05 *M*, (□, ■) 0.02 *M*, (▽,▼) 0.01 *M*.

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$k_{obs}$ can be regarded as the apparent rate constant for the transport of europium. The effect of DIDPA concentration on $k_{obs}$ value is shown in Fig. 6. The $k_{obs}$ value increases with DIDPA concentration up to 0.05 *M*; a further increase in DIDPA concentration has little effect on $k_{obs}$ value. The transport rate is probably controlled by the extraction process only at low DIDPA concentrations.

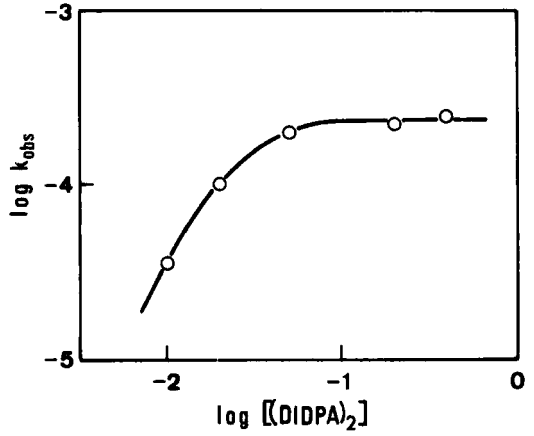


FIG. 6. Effect of carrier concentration on the apparent rate constant. Feed: 0.1 *M* $HNO_3$; product: 5 *M* $HNO_3$; SLM: 10% 1-octanol, DIDPA in kerosene.

## Effect of $HNO_3$ Concentration

The driving force for transport is provided by an appreciable gradient of acid concentrations between the extracting and stripping sides. The effects of the concentrations of nitric acid are summarized in Table 1. Here, the ionic strength in the feed solution was adjusted to 0.1 with sodium nitrate only in the low concentration region to minimize water permeation owing to a difference in the osmotic pressure. The value of $k_{obs}$ increased with increasing $HNO_3$ concentrations below 0.1 *M* in the feed side. However, increasing $HNO_3$ concentrations above 0.5 *M* caused a drop in the $k_{obs}$ value since it lowered the extraction in the feed side, and then the transport into the product solution became low.

As for the stripping solution, the rate of europium transport across the membrane almost remained unaffected up to 10 *M* $HNO_3$, although slightly insufficient stripping was observed with 1 *M* $HNO_3$.

The europium thus can be transported into product solutions against its large concentration gradient around 500–1000 as is evident from the values of $[Eu]_p/[Eu]_f$ at 7 h in the fourth column in Table 1. Based on these data, optimum conditions for transport across the membrane probably lie up to 0.3 *M* $HNO_3$ in the feed solution and in 5–10 *M* $HNO_3$ in the product solution. They would bring about almost quantitative transport with a reasonable transport rate ($k_{obs} > 2 \times 10^{-4}$ $s^{-1}$). That is, around 99% of the initial europium was recovered in the product side,

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TABLE 1
Effect of $HNO_3$ Concentration on Transport of Eu(III)[a]

| Feed $[HNO_3]$ (*M*) | Product $[HNO_3]$ (*M*) | $k_{obs}$ ($s^{-1}$) | $[Eu]_p/[Eu]_f$ (7 h) | Recovery (7 h) (%) |
|---|---|---|---|---|
| 0.01[b] | 5 | $>8 \times 10^{-4}$ | 760 | 98.7 |
| 0.03[b] | 5 | $>6 \times 10^{-4}$ | 700 | 97.8 |
| 0.05[b] | 5 | $3.4 \times 10^{-4}$ | 1300 | 99.1 |
| 0.3 | 5 | $2.1 \times 10^{-4}$ | 470 | 97.9 |
| 0.6 | 5 | $6.8 \times 10^{-5}$ | 34 | 78.1 |
| 1.0 | 5 | $2.0 \times 10^{-5}$ | 17 | 64.0 |
| 0.1 | 1 | $2.6 \times 10^{-4}$ | 1300 | 94.5 |
| 0.1 | 5 | $2.3 \times 10^{-4}$ | 1400 | 99.3 |
| 0.1 | 10 | $2.5 \times 10^{-4}$ | 490 | 98.0 |

[a]Feed: 100 $cm^3$, product: 10 $cm^3$. SLM: 0.2 *M* $(DIDPA)_2$ and 10% 1-octanol in kerosene.

[b]Ionic strength: 0.1 ($NaNO_3$).

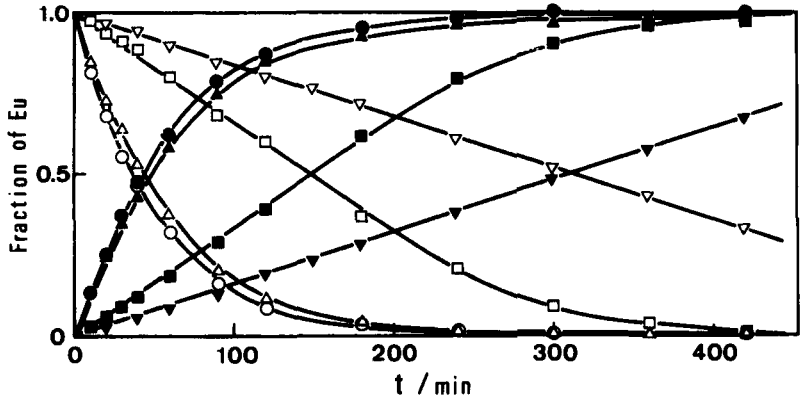


FIG. 7. Transport of europium of different initial concentrations through SLM. Feed: 0.1 $M$ $HNO_3$, europium (○, ●) $10^{-4}$ $M$, (△, ▲) $10^{-3}$ $M$, (□, ■) $10^{-2}$ $M$, (▽,▼) $3 \times 10^{-2}$ $M$, 100 $cm^3$; product: 5 $M$ $HNO_3$, 10 $cm^3$; SLM: 0.2 $M$ $(DIDPA)_2$, 10% 1-octanol in kerosene.

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and the europium remaining in SLM was less than 1% of its initial value.

## Effect of Europium Concentration

Figure 7 represents the effect of the initial concentration of europium on europium transport with 0.2 $M$ $(DIDPA)_2$-SLM. At low concentration regions below $10^{-3}$ $M$, we obtained similar fraction curves, but at high concentration regions the plots became almost linear until about 180 min, indicating that a constant amount of europium was transported independent of its concentration.

The initial europium flux through SLM ($J$) is expressed as

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

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

Plots of the flux against the initial europium concentration are shown in Fig. 8. The europium flux is proportional to the europium concentration at less than $10^{-3}$ $M$, while it becomes nearly constant above $3 \times 10^{-3}$ $M$ europium, probably owing to the saturation of the mobile carrier with europium.

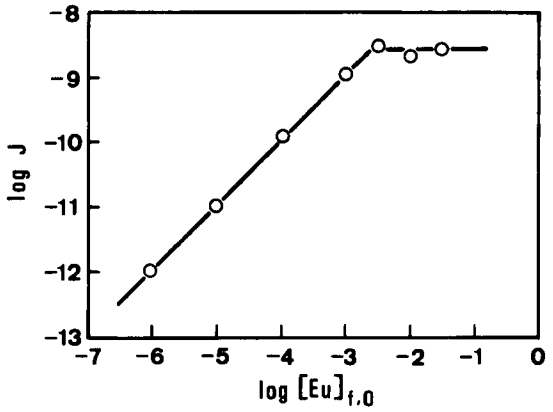


FIG. 8. Effect of europium concentration on the flux. Feed: 0.1 *M* $HNO_3$, 100 $cm^3$; product: 5 *M* $HNO_3$, 10 $cm^3$; SLM: 0.2 *M* $(DIDPA)_2$, 10% 1-octanol in kerosene.

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