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Effect of Complexing Agent on Transport of Lanthanoid Elements across Versatic Acid Liquid Membrane

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Abstract

Transport of several trivalent lanthanoids (La, Nd, Sm, Eu, Tb, Tm, and Lu) was examined across a supported liquid membrane (SLM) containing Versatic 10 (VA10) in kerosene. Lanthanoids in the feed solution can be effectively transported and concentrated into the product solution. Separation factors obtained from the transport rates for lighter lanthanoids were larger than those for heavier lanthanoids, in agreement with the result on the distribution ratios in liquid–liquid extraction. The separation factors for heavier lanthanoids were enhanced by the addition of citrate to the feed solution. The transport rate was controlled by the extraction process from the feed solution to the SLM and the diffusion process of lanthanoid-VA10 complexes in SLM.

INTRODUCTION

A variety of extractants have been employed as mobile carriers for transport of metals through a liquid membrane. In liquid–liquid extraction, extractants having high extractability and selectivity are usually desirable; however, in membrane transport involving the stripping process of metals, the high extracting ability of mobile carriers is not always preferable for quantitative stripping of metals from the liquid membrane.

Transports of lanthanoids across liquid membranes of di(2-ethylhexyl)phosphoric acid (DEHPA) (*1–3*) and diisodecylphosphoric acid (DIDPA) (*4*) have been accomplished using relatively higher acidic solutions for complete stripping. In a previous study (*5*) the permeation behavior of europium(III) through a Versatic 10 (VA10) liquid membrane was examined, and europium was quantitatively transported in the product solutions at a relatively higher concentration of the mobile carrier.

The present paper deals with the transport of representative lanthanoid(III) elements through the VA10 liquid membrane in connection with the separation factor of lanthanoids. The effect of complexing agents was investigated to improve the separation of heavier lanthanoids.

EXPERIMENTAL

Materials

Radioisotopes ^{140}La, ^{147}Nd, ^{153}Sm, ^{160}Tb, ^{170}Tm, and ^{177}Lu, used as tracers, were produced by neutron irradiation of each oxide at a thermal neutron flux of 5.5×10^{13} n/cm^2·s for 6 h in a nuclear reactor (JRR-4) of the Japan Atomic Research Institute. Radioactive solutions were prepared by dissolving the irradiated samples in nitric acid. ^{152,154}Eu were obtained from Radiochemical Centre in England. Versatic 10 (VA10, Shell Chemical Co.) was diluted in kerosene. The pH in the feed solution was controlled with a buffer solution containing 0.01 *M* acetic acid or piperazine-*N*,*N*'-bis(2-ethanesulfonic acid). A polytetrafluoroethylene membrane (Fluoropore FP-045, Sumitomo Electric Ind.) of 80 μm thickness, 74% porous, and of 0.45 μm average pore size was used as an inert support.

Extraction of Lanthanoids

An aqueous solution containing 10^{-5} *M* (*M* = mol/dm^3) lanthanoid(III) was shaken with an equal volume of a VA10 solution over 1 h at 25°C. After centrifugation, aliquots of both phases were taken and then the concentration of lanthanoid in each phase was determined by measuring the radioactivity with a NaI(Tl) scintillation detector or inductively coupled plasma atomic emission spectrometry (ICP-AES). In the ICP-AES method, the lanthanoid concentration in the aqueous phase was determined after matching matrix components by the addition of a large excess of (H,Na)NO_3. The concentration in the kerosene phase was also determined by comparison with a reference solution prepared by extraction of lanthanoid at higher pH.

Transport of Lanthanoids

Experimental procedures adopted here for the transport of lanthanoid(III) were essentially same as those described previously (*6*). The apparatus consisted of inner and outer polypropylene vessels that correspond to extraction and stripping compartments, respectively. The microporous support sheet attached to the bottom of the inner vessel was impregnated with a kerosene solution of VA10. A feed solution (100 cm^3)

initially containing 10^{-5} M lanthanoid spiked with each radioisotope and a product solution (10 cm^3) of 10^{-3} to 10^{-2} M HNO_3 were placed in the outer and inner vessels, respectively. The apparatus was shaken at 120 strokes per minute (spm) in a water bath kept at 25°C. At time intervals, the concentrations of lanthanoid in the feed and product solutions were determined by measuring the radioactivity.

RESULTS AND DISCUSSION

Extraction of Lanthanoids

The extraction behavior of some lanthanoids(III) by VA10 in kerosene was examined. The distribution ratios D of La, Nd, Tb, and Lu as a function of pH are shown in Fig. 1. These plots are a series of straight lines with a slope of about 3; they are almost parallel in the order of atomic number.

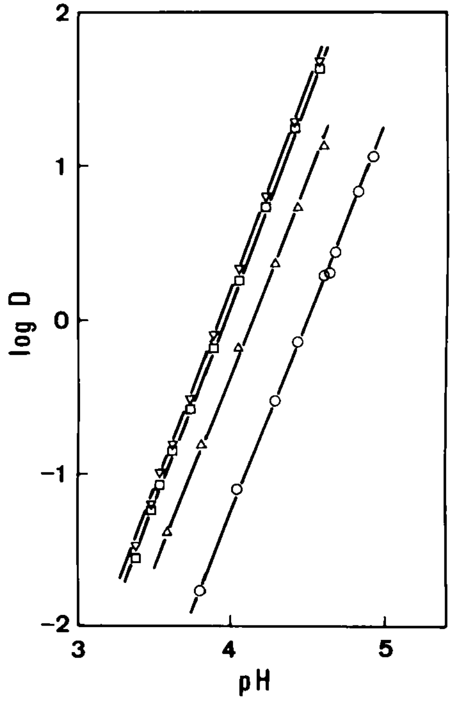

FIG. 1. Extraction of lanthanoids with 1 M $(VA10)_2$ in kerosene. (○) La, (△) Nd, (□) Tb, (▽) Lu.

TABLE 1
Extraction Constants and Separation Factors

M(III)	log K_{ex}	α_D[a]	α_T[b]
La	−13.44		
		10	10
Nd	−12.42		
		2.3	2.0
Sm	−12.06		
		1.6	1.3
Eu	−11.86		
		1.0	1.1
Tb	−11.85		
		1.0	1.1
Tm	−11.86		
		1.2	1.3
Lu	−11.78		

[a] $\alpha_D = K_{ex,2}/K_{ex,1}$.
[b] $\alpha_T = k_{obs,2}/k_{obs,1}$.

The extraction of lanthanoid M^{3+} can be expressed by

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

where $(HA)_2$ represents the dimer of VA10. The extraction constants K_{ex} given in Table 1 increased with increasing atomic number from lanthanum to europium, but those of heavier lanthanoids are close to each other. The separation factors α_D evaluated from the extraction constants are listed in Table 1. The α_D values for the lighter lanthanoids are larger than those of heavier lanthanoids. The distribution ratios of lanthanoids with DEHPA have been known to increase almost linearly with atomic number even for heavier lanthanoids, yielding an average separation factor of about 2.5 (*7*, *8*). The value of α_D between lanthanum and neodymium in the VA10 system is slightly larger than 8.4 in the DEHPA system (*8*). This extraction system may be accessible for mutual separation of lighter lanthanoids or group separation of a mixture of heavier lanthanoids.

Transport of Lanthanoids

Based on the extraction behavior, the transport of lanthanoids was carried out through SLM with 1 *M* $(VA10)_2$ in kerosene. Figure 2 shows the transport of La, Nd, and Lu at the fixed conditions of the feed and product solutions. The fractions in the feed side decreased with shaking time, and

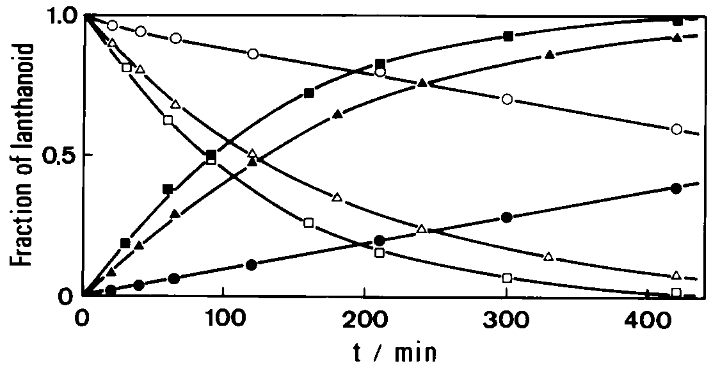

FIG. 2. Transport of lanthanoids through SLM containing 1 M $(VA10)_2$ in kerosene. Feed: pH 4.4, 100 cm^3, (○, ●) La, (△, ▲) Nd, (□, ■) Lu; product: 0.01 M HNO_3, 10 cm^3. Shaking speed: 120 spm. Open and closed symbols indicate the feed and the product fractions, respectively.

those in the product side symmetrically increased; each lanthanoid was transported and concentrated in the product solution without remaining in the SLM layer. The lanthanoid fraction in the feed solution decreased according to

$$\ln([M]_{f,t}/[M]_{init}) = -k_{obs}t \tag{2}$$

where $[M]_{f,t}$ and $[M]_{init}$ denote the concentration of lanthanoid at time t and the initial concentration in the feed solution, respectively, and k_{obs} (s^{-1}) is the apparent rate constant. Figure 3 shows the effect of pH in the feed solution on the k_{obs} values of individual lanthanoids. The k_{obs} value increased with pH and became almost constant in a higher pH region. In a lower pH region, the separation factors α_T given by the ratio of the k_{obs} values between lanthanoids are also listed in Table 1. The value of α_T is close to the α_D value for each pair of lanthanoids.

In the previous study, (5), the k_{obs} for europium transport through SLM containing VA10 was expressed by

$$k_{obs} = \frac{1}{\dfrac{\delta_a}{D_a} + \dfrac{\delta_0}{D_0}\dfrac{1}{D}}\frac{S}{V} \tag{3}$$

where δ_a and D_a denote the thickness of the feed–SLM boundary layer and the diffusion coefficient of the lanthanoid ion, respectively, and δ_0 and D_0,

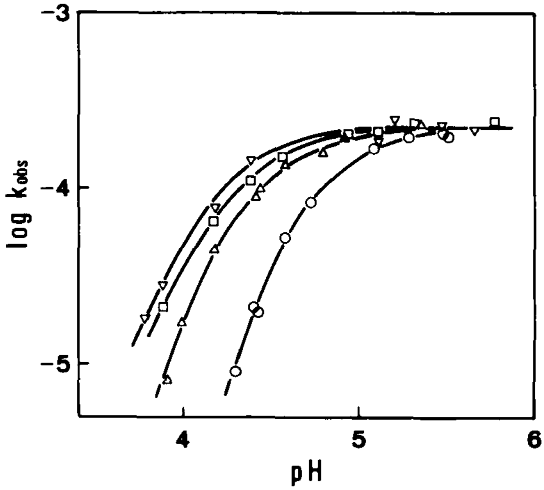

FIG. 3. Effect of pH of the feed solution on k_{obs}. (○) La, (△) Nd, (□) Tb, (▽) Lu.

the thickness of SLM and the diffusion coefficient of the lanthanoid complex, respectively. S is the membrane area, V is the feed volume, and D is the distribution ratio of lanthanoid between SLM and the feed solution. Figure 4 shows the plots of log k_{obs} against log D determined by liquid–liquid extraction. The k_{obs} value increased proportionally with increasing

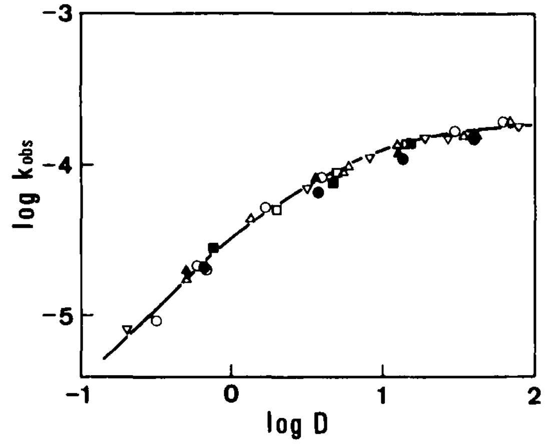

FIG. 4. Relation between k_{obs} and the distribution ratio of lanthanoid. (○) La, (△) Nd, (□) Sm, (▽) Eu, (●) Tb, (▲) Tm, (■) Lu.

distribution ratio and became asymptotic to a plateau at a higher distribution ratio. These plots are almost situated on the same curved line, suggesting that the values of D_a and D_0 are almost unchanged for lanthanoids. At low distribution ratios, the term of δ_a/D_a becomes negligibly small compared with $\delta_0/(D_0D)$, and Eq. (3) is simplified to

$$k_{\mathrm{obs}} = \frac{D_0}{\delta_0}\frac{S}{V}D \tag{4}$$

Since S, V, and δ_0 are the constants fixed by the experimental conditions, k_{obs} is directly proportional to D for each lanthanoid. Thus, the α_T values are nearly equal to the α_D values as seen in Table 1, and the separation ability in the membrane transport can be predicted from the extraction behavior.

Effect of Complexing Agent

A small difference in the transport rate for heavier lanthanoids is insufficient to apply to their mutual separation. An addition of complexing agents forming water-soluble complexes with lanthanoids has been tested to enhance the separation factor of heavier lanthanoids. In the presence of ethylenediaminetetraacetic acid (EDTA), which gives a large difference in stability constants in a sequence of lanthanoid elements (*9*), the distribution ratio of lanthanoid sharply decreased with increasing EDTA concentration, but a small content of EDTA even at 5×10^{-6} M depressed the distribution ratio to about $1/10^4$ using a trace amount of europium. The complexing ability of EDTA was thus too large to employ for the transport of lanthanoid.

The addition of citric acid, which has a rather moderate complexing ability compared to EDTA, was attempted to improve the separation of lanthanoids based on differences in their stability constants (*10*). Figure 5 shows the distribution ratios of lanthanoid elements at a fixed pH. The distribution ratios without citrate increased with atomic number of the lighter lanthanoids from La to Eu, but became nearly constant for heavier lanthanoids. When citrate was added to the aqueous phase, the lanthanoid extraction was significantly depressed, and the distribution ratios only slightly increased for lighter lanthanoids, whereas those of heavier lanthanoids greatly decreased, owing to an increase in stability of aqueous-soluble citrate complexes with increasing atomic number.

This extraction system, including complex formation with different stabilities was applied to the transport of heavier lanthanoids. Figure 6 shows

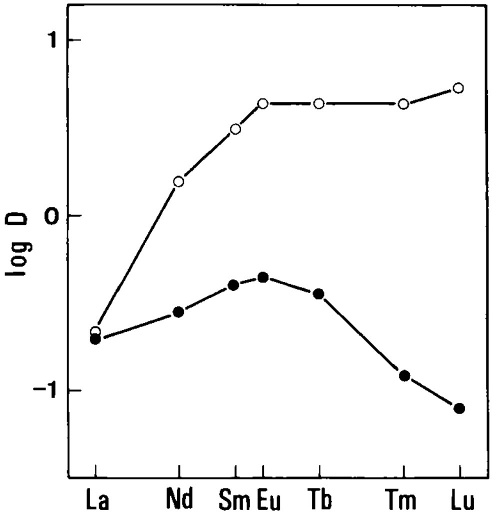

FIG. 5. Variation of distribution ratios of lanthanoids with 1 *M* $(VA10)_2$. (○) No citrate, pH 4.2; (●) 2.5×10^{-3} *M* citrate, pH 6.2.

the effect of pH of the feed solution on k_{obs} for each lanthanoid in the presence of 10^{-4} *M* citrate. The k_{obs} values were rather lower than those in the absence of citrate, and decreased with increasing atomic number, Eu > Tb > Tm > Lu.

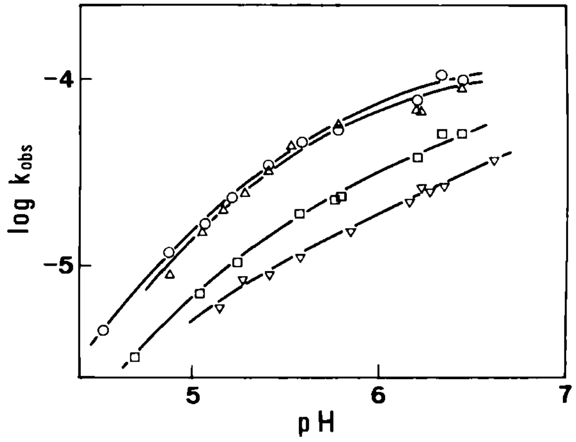

FIG. 6. Effect of pH of the feed solution on k_{obs} in the presence of 10^{-4} *M* citrate. (○) Eu, (△) Tb, (□) Tm, (▽) Lu.

The relation between k_{obs} and D obtained from liquid–liquid extraction is shown in Fig. 7. In the presence of citrate, the k_{obs} values decreased, especially in the higher D region, and these plots for lanthanoids appear as individual curved lines. These trends cannot be explained by Eq. (3) derived for the transport behavior in the citrate-free medium. Here, the following processes are considered for the transport of metals through SLM; (a) diffusion of lanthanoid citrate complexes in the aqueous boundary layer in the feed side, (b) extraction of lanthanoids into the membrane, and (c) diffusion of the lanthanoid complexes in SLM. Since lanthanoids seem to be present predominantly as citrate complexes in the feed solution, the lanthanoid flux j_a in the aqueous boundary layer is expressed by

$$J_a = \frac{D'_a}{\delta_a}([\text{M-Cit}]_f - [\text{M-Cit}]_i) \tag{5}$$

where D'_a denotes the diffusion coefficient of lanthanoid citrate, and [M-Cit]$_f$ and [M-Cit]$_i$ are the concentrations of lanthanoid citrate in the feed bulk and in the surface of SLM, respectively. The pseudo-first-order reaction is assumed in the extraction process, and the flux J_i is expressed by

$$J_i = k_1[\text{M-Cit}]_i - k_{-1}[\text{M}]_0 \tag{6}$$

where $[\text{M}]_0$ denotes the concentration of the extracted species $\text{M(HA}_2)_3$ and where k_1 and k_{-1} are the apparent rate constants of forward and

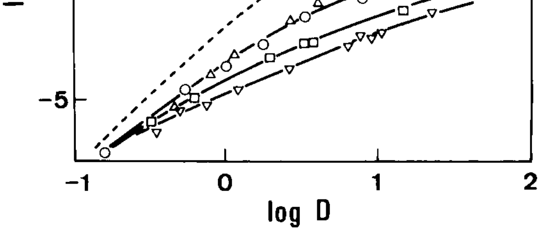

FIG. 7. Relation between k_{obs} and the distribution ratio of lanthanoid in the presence of citrate. (○) Eu, (△) Tb, (□) Tm, (▽) Lu. The broken line corresponds to the absence of citrate.

backward extraction, respectively. The flux J_0 of the lanthanoid complex in the SLM is

$$J_0 = \frac{D_0}{\delta_0}[\mathrm{M}]_0 \tag{7}$$

In the quasi-steady-state, these fluxes are equal to the total flux J, and hence the following equation is derived from Eqs. (5), (6), and (7):

$$J = \frac{k_1}{\frac{\delta_a}{D'_a}k_1 + \frac{\delta_0}{D_0}k_{-1} + 1}[\mathrm{M\text{-}Cit}]_f \tag{8}$$

k_{obs} can be written as

$$k_{\mathrm{obs}} = \frac{J}{[\mathrm{M\text{-}Cit}]_f}\frac{S}{V} = \frac{1}{\frac{\delta_a}{D'_a} + \frac{1}{k_1} + \frac{\delta_0}{D_0}\frac{1}{D}}\frac{S}{V} \tag{9}$$

where $D = k_1/k_{-1}$.

In a lower D region, Eq. (9) can also be simplified to Eq. (4), and the transport rate may be controlled by the diffusion process in the membrane. The plots of lanthanoid in Fig. 7 actually come close to each other and are asymptotic to a curved line for the citrate-free medium with decreasing D. Since the k_{obs} value is proportional to the distribution ratio, the separation factors α_T at pH 5.1 are close to α_D as given in Table 2.

On the other hand, in a higher region of D, Eq. (9) is approximated to

$$k_{\mathrm{obs}} = \frac{1}{\frac{\delta_a}{D'_a} + \frac{1}{k_1}}\frac{S}{V} \tag{10}$$

TABLE 2

Separation Factors in the Presence of 10^{-4} M Citrate

	pH 5.1		pH 6.3	
M_1/M_2	$\alpha_D{}^a$	$\alpha_T{}^b$	$\alpha_D{}^a$	$\alpha_T{}^b$
Eu/Tb	1.2	1.2	1.3	1.1
Tb/Tm	2.3	2.2	3.2	1.9
Tm/Lu	1.3	1.3	2.2	1.7

[a] $\alpha_D = D_1/D_2$.

[b] $\alpha_T = k_{\mathrm{obs},1}/k_{\mathrm{obs},2}$.

In this region, the k_{obs} values were experimentally found to be independent of the shaking speed, suggesting no contribution of a change in thickness of the boundary layer. Therefore, δ_a/D'_a seems to be negligibly small compared with $1/k_1$, and Eq. (10) can be simplified to

$$k_{\mathrm{obs}} = \frac{S}{V} k_1 \tag{11}$$

The rate-determining step may be the extraction process involving the ligand substitution reaction of the lanthanoid-citrate complex by VA10 in the feed–SLM boundary, and this rate appears to decrease with increasing atomic number as shown in Fig. 6. The separation factors at pH 6.3 are given in Table 2. The α_T value in this region corresponds to the ratio of the rate constants of the forward extraction of each lanthanoid and is substantially different from the α_D value composed of the rate constants of both forward and backward extraction. The values of α_T were found to be enhanced by the addition of citrate, though they were somewhat smaller than the α_D values.

In conclusion, VA10 having moderate extractability can be used as a mobile carrier of the liquid membrane transport of a series of lanthanoids and gives a higher separation factor for lighter lanthanoids. In the presence of citrate, the separation factors for heavier lanthanoids can be enhanced owing to decreasing distribution ratio and extraction rate with increasing atomic number.

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