Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Permeation Behavior of Europium through Versatic Acid Liquid Membrane

Shigeto Nakamura[a]; Shinichi Ohashi[a]; Kenichi Akiba[a]
[a] RESEARCH INSTITUTE OF MINERAL DRESSING AND METALLURGY TOHOKU UNIVERSITY, SENDAI, JAPAN

To cite this Article Nakamura, Shigeto , Ohashi, Shinichi and Akiba, Kenichi(1992) 'Permeation Behavior of Europium through Versatic Acid Liquid Membrane', Separation Science and Technology, 27: 6, 741 — 752
To link to this Article: DOI: 10.1080/01496399208019721
URL: http://dx.doi.org/10.1080/01496399208019721

SEPARATION SCIENCE AND TECHNOLOGY, **27**(6), pp. 741–752, 1992

Permeation Behavior of Europium through Versatic Acid Liquid Membrane

SHIGETO NAKAMURA, SHINICHI OHASHI,
and KENICHI AKIBA
RESEARCH INSTITUTE OF MINERAL DRESSING AND METALLURGY
TOHOKU UNIVERSITY
KATAHIRA, SENDAI 980, JAPAN

Abstract

The permeation behavior of europium(III) was examined by using a supported liquid membrane impregnated with Versatic 10 (VA10) diluted in kerosene. Europium was quantitatively transported through the liquid membrane even with a high concentration of VA10, and it was concentrated in the product solution of dilute nitric acid. The permeation rate increased with the feed pH and the carrier concentration, and then eventually approached a constant value. The permeation behavior is discussed in connection with the liquid–liquid extraction behavior of europium.

INTRODUCTION

Facilitated transport through an organic liquid membrane containing a mobile carrier has been studied as a promising method for the separation and concentration of metals from dilute aqueous solutions. Metal ions in a feed solution are extracted into the liquid membrane and then stripped in a product solution. The selection of a suitable carrier and appropriate conditions of these feed and product solutions are important for efficient transport of metals. Many acidic organophosphorus extractants, such as di(2-ethylhexyl)phosphoric acid (DEHPA) (*1–3*), 2-ethylhexyl 2-ethylhexylphosphonic acid (EHEHPA) (*4*), and diisodecylphosphoric acid (*5*), have been used as mobile carriers for the transport of lanthanoid ions. When these carriers with high extractability have been employed, a high concentration of acid is required for sufficient stripping of metals.

Versatic acids, kinds of monocarboxylic acids with long alkyl chains, have been used for extraction and separation of metals, such as copper, nickel, and cobalt, in the field of hydrometallurgy. Their extractability for lanthanoids (*6*) is relatively lower than that of dialkylphosphoric acids such as DEHPA; this is favorable for membrane transport. That is, optimum conditions of the feed and product solutions can be adjusted in a moderate pH region, and carriers in a much higher concentration can be used for a high transport rate and a high flux of metal species. This study is concerned with the transport of europium(III) through a supported liquid membrane (SLM) containing Versatic 10 (VA10). Further, the permeation behavior is discussed in connection with the liquid–liquid extraction equilibria.

EXPERIMENTAL

Materials

Radioisotopes ^{152,154}Eu (The Radiochemical Centre, England) were diluted with the nitric acid solution. Versatic 10 (VA10) was donated by Shell Chemical Co., and its purity was checked to be 97.1% by potentiometric titration in ethanol with a sodium hydroxide solution. The microporous support used here was a polytetrafluoroethylene film (Fluoropore FP-045, Sumitomo Electric Ind.) with a thickness of 80 μm, a porosity of 74%, and an average pore size of 0.45 μm.

Extraction of Europium

An aqueous solution containing 10^{-5} *M* (*M* = mol/dm^3) europium(III) spiked with ^{152,154}Eu was equilibrated with an equal volume of a kerosene solution of VA10 for over 1 h at 25°C. After phase separation by centrifugation, the radioactivities of both phases were measured with a NaI(Tl) scintillation counter. The pH in the aqueous phase was adjusted with a mixture of 0.01 *M* acetic acid and its sodium salt solutions.

Transport of Europium

Experiments of the membrane transport were carried out in a manner similar to those described previously (*7*). The apparatus was composed of inner and outer polypropylene vessels. A microporous film (26 cm^2) was attached to the bottom of the inner vessel and impregnated with a kerosene solution of VA10. The feed solution (100 cm^3) initially containing 10^{-5} *M* europium(III) spiked with ^{152,154}Eu was poured into the outer vessel, and the product solution (10 cm^3) of dilute nitric acid was poured into the inner vessel. The apparatus was shaken at 120 strokes per minute (spm) in a water bath kept at 25°C. Portions of the feed and product solutions were periodically taken and their radioactivities were counted; they were returned to each vessel after measurement.

RESULTS AND DISCUSSION

Extraction Equilibrium

The extraction behavior of europium was investigated with VA10 (dialkylphosphoric acid, HA) in kerosene for the selection of optimum conditions for membrane transport. Since VA10 is considered to exist as a dimeric species in nonpolar diluents, its concentration is expressed as a dimer. The effect of pH on the distribution ratio *D* of europium is shown in Fig. 1. The plots are straight lines with a slope of 2.8. The slope of a logarithmic plot of *D* against $[(HA)_2]$ was found to be 3.0, as illustrated in Fig. 2. The extraction of europium can be expressed by

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

The extraction constant K_{ex} for the above reaction was evaluated to be 1.3×10^{-12}. This value is considerably lower than 0.41 for EHEHPA in kerosene (*8*) and 300 for DEHPA in dodecane (*9*). This lower extractability will be favorable to strip metal species from the membrane layer by a dilute acid solution.

Transport of Europium

The membrane transport can be performed by continuous extraction and stripping of metals on each side of an SLM; in particular, quantitative recovery of metals may be affected by the conditions of the stripping side.

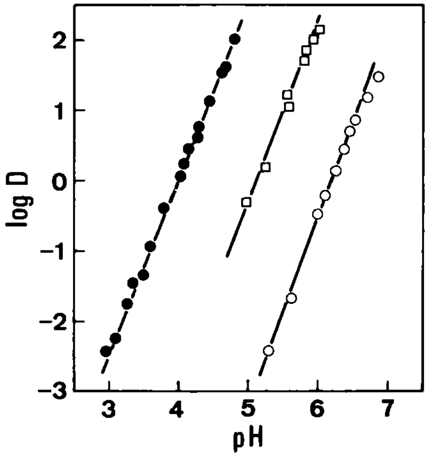

FIG. 1. Distribution ratio of europium as a function of pH. (○) 0.01 *M*, (□) 0.1 *M*, (●) 1 *M* $(HA)_2$ in kerosene.

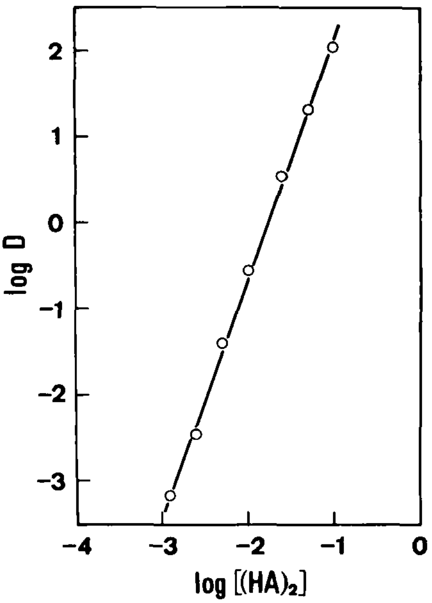

FIG. 2. Effect of VA10 concentration on the distribution ratio of europium at pH 6.0.

Based on the extraction equilibrium, the stripping of europium will be accomplished by an acidic product solution below pH 3 from an SLM containing a high carrier concentration, 1 *M* $(VA10)_2$. Figure 3 shows the effect of HNO_3 concentration for stripping on the transport of europium. The europium fraction in the feed side decreased with the shaking time in

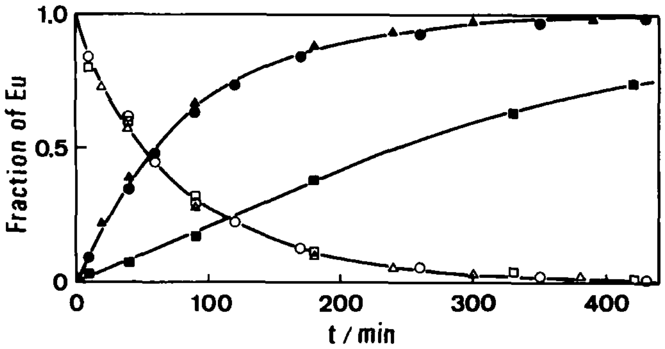

FIG. 3. Effect of HNO_3 concentration in the product solution on the transport of europium through SLM with 1 *M* $(HA)_2$ in kerosene. Feed: pH 5.1, 100 cm^3. Product: (○, ●) 0.003 *M*, (△, ▲) 0.01 *M*, (□, ■) 0.1 *M* HNO_3, 10 cm^3. Shaking speed: 120 spm. Open and closed symbols indicate the feed and the product solutions, respectively.

a manner similar under a given HNO_3 concentration, and those in the product side increased in an almost symmetrical curve except for 0.1 *M* HNO_3. A large lag in the europium increment was observed in the product side for 0.1 *M* HNO_3; this is difficult to explain from the liquid–liquid extraction data. In subsequent experiments, 10^{-3}–10^{-2} *M* HNO_3 was employed as the product solution in order to obtain sufficient stripping.

As seen in Fig. 4, the time-dependent fractions in the feed and product sides at various feed pH values are approximately symmetrical, indicating little remaining europium in the SLM. The curves above pH are very close, and europium was quantitatively transported into the product side after 7 h.

The europium fraction in the feed solution was found to decrease according to

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

where $[\mathrm{Eu}]_{f,t}$ and $[\mathrm{Eu}]_{\mathrm{init}}$ denote the concentration of europium at time t and the initial concentration, respectively, and k_{obs} (s^{-1}) denotes the apparent rate constant. The effect of pH in the feed solution of k_{obs} is shown in Fig. 5. The k_{obs} value increased with pH up to 5, and a further increase of pH had little effect on the k_{obs} value.

The k_{obs} values for different carrier concentrations are listed in Table 1. The transport rate increased with the pH of the feed solution and was larger for higher concentrations of the carrier. The effect of carrier concentration in the SLM on k_{obs} is shown in Fig. 6 at a fixed pH of 5.1 in the feed solution. The k_{obs} value increased with the VA10 concentration and

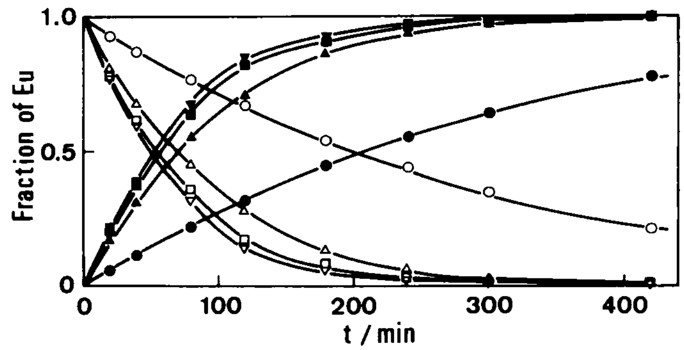

FIG. 4. Effect of pH of the feed solution on the transport of europium. Feed: (○, ●) pH 4.2, (△, ▲) pH 4.6, (□, ■) pH 5.1, (▽, ▼) pH 5.3, 100 cm^3. Product: 0.01 *M* HNO_3, 10 cm^3. SLM: 1 *M* $(HA)_2$ in kerosene.

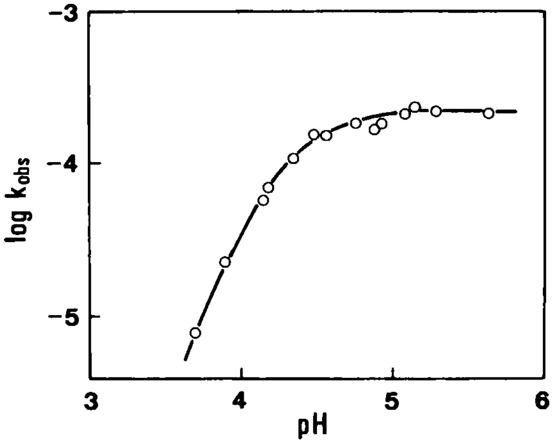

FIG. 5. Effect of pH of the feed solution on k_{obs}. Experimental conditions are the same as those in Fig. 4.

reached a plateau around 2.0×10^{-4} s^{-1}, which is close to the plateau in Fig. 5.

The large values of $[Eu]_p/[Eu]_f$ at 7 h listed in Table 1 indicate that europium can be transported against its concentration gradient. As is evident in the last column in Table 1, europium was concentrated in the product side to close to 10 times of its initial concentration in the feed side

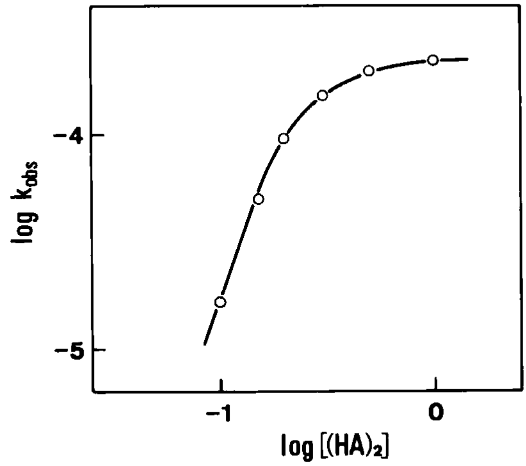

FIG. 6. Effect of VA10 concentration in SLM on k_{obs}. Feed: pH 5.1. Product: 0.01 *M* HNO_3.

TABLE 1
Transport of Europium with VA10 Liquid Membrane[a]

$[(HA)_2]$ (*M*)	pH of feed	k_{obs} (s^{-1})	$[Eu]_p/[Eu]_f$ at 7 h	$[Eu]_p/[Eu]_{init}$ at 7 h
0.1	5.1	1.7×10^{-5}	4.7	3.2
	5.3	4.2×10^{-5}	31	7.6
	5.5	8.7×10^{-5}	100	8.9
0.3	4.5	2.0×10^{-5}	6.1	3.7
	4.7	5.1×10^{-5}	20	6.7
	4.9	1.0×10^{-4}	310	9.7
	5.1	1.5×10^{-4}	440	9.8
1	4.2	5.6×10^{-5}	35	8.0
	4.6	1.5×10^{-4}	490	9.8
	5.1	2.2×10^{-4}	1700	9.9
	5.3	2.4×10^{-4}	2500	9.9

[a] Feed, 100 cm^3; product, 0.01 *M* HNO_3, 10 cm^3.

under the optimum conditions; the maximum enrichment factor becomes equal to the volume ratio of the feed to product solutions. Thus, relatively high concentrations of VA10 are acceptable for the transport and concentration of europium into a product solution of moderate acidity.

Complexing Agent for Stripping

If we use a high concentration of acid as the product solution, a gradual decrease in the transport rate may be brought about by an increase in acidity of the feed solution through back-transport of the acid from the product solution. Here, the addition of a complexing agent to the product solution was tried in an attempt to enhance stripping from the membrane. Figure 7 shows the transport of europium from the feed solution at different pH values from 4 to 5 to the product solution containing 0.01 *M* ethylenediaminetetraacetic acid (EDTA) at pH 5.0. Europium was transported against its concentration gradient without remaining in the SLM. The transport rate of europium increased with the feed pH, and the plots for europium fractions in Fig. 7 are almost the same as those in Fig. 4 at the corresponding feed pH. Similar results were obtained by the addition of citric acid instead of EDTA. The extraction process into the liquid membrane was essentially similar to the case mentioned above, while the stripping process at higher pH was accomplished by the reaction of europium with the complexing agent.

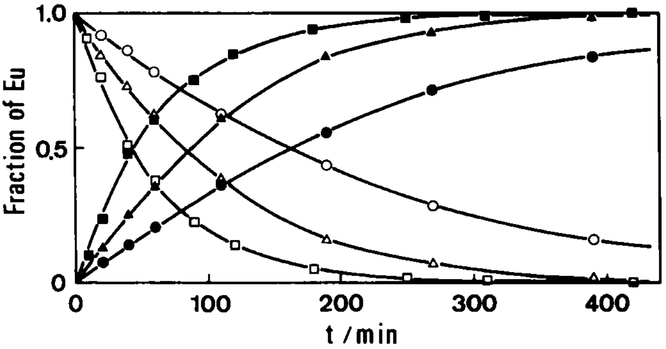

FIG. 7. Transport of europium through SLM to the EDTA solution. Feed: (○, ●) pH 4.2, (△, ▲) pH 4.4, (□, ■) pH 5.1. Product: 0.01 *M* EDTA, pH 5.0. SLM: 1 *M* $(HA)_2$ in kerosene.

Permeation Behavior through SLM

Permeation processes for the transport of europium are considered as described by Danesi et al. (*10*): (a) diffusion in the aqueous boundary layer to the surface of the membrane, (b) extraction reaction, (c) diffusion in SLM, (d) stripping reaction, and (e) diffusion to the product bulk. Under the conditions of this study, the following assumptions are made. (1) The carrier concentration in SLM remains constant in the presence of an excess concentration of VA10. (2) The variation in pH of the feed solution is slight. (3) The transfer rate in the stripping side is fast enough to neglect transport processes (d) and (e) in the rate-determining considerations because the transport rate was found to be independent of the composition of the product solution.

Processes (a), (b), and (c) are thus taken into consideration. The europium flux J_a through the aqueous boundary layer in the feed side is expressed by

$$J_a = \frac{D_a}{\delta_a}([\mathrm{M}]_f - [\mathrm{M}]_i) \tag{3}$$

where D_a is the diffusion coefficient in the boundary layer, δ_a is the thickness of this layer, and $[\mathrm{M}]_f$ and $[\mathrm{M}]_i$ are the concentrations of europium ion in the feed bulk and in the surface of SLM, respectively. In the extraction process a pseudo-first-order reaction is assumed, and the flux J_i of europium species is expressed by

$$J_i = k_1[\mathrm{M}]_i - k_{-1}[\mathrm{M}]_0 \tag{4}$$

where $[\mathrm{M}]_0$ is the concentration of the extracted species $\mathrm{Eu(HA_2)_3}$, and k_1 and k_{-1} are the apparent rate constants of the forward and backward extractions, respectively. The flux J_0 of the europium complex in SLM is

$$J_0 = \frac{D_0}{\delta_0}[\mathrm{M}]_0 \tag{5}$$

where D_0 is the diffusion coefficient of the europium complex in SLM and δ_0 is the thickness of the membrane.

In the quasi-steady state, these fluxes are equal to the total flux J, so that the following equation is derived from Eqs. (3), (4), and (5);

$$J = \frac{k_1}{\dfrac{\delta_a}{D_a}k_1 + \dfrac{\delta_0}{D_0}k_{-1} + 1}[\mathrm{M}]_f \tag{6}$$

The apparent rate constant of transport, k_{obs}, is given by

$$k_{\mathrm{obs}} = \frac{J}{[\mathrm{M}]_f}\frac{S}{V} \tag{7}$$

where S and V denote the membrane area and the feed volume, respectively. The distribution ratio of europium in the extraction process is derived as

$$D = k_1/k_{-1} \tag{8}$$

Thus,

$$k_{\mathrm{obs}} = \frac{1}{\dfrac{\delta_a}{D_a} + \dfrac{1}{k_1} + \dfrac{\delta_0}{D_0}\dfrac{1}{D}}\frac{S}{V} \tag{9}$$

is obtained. Figure 8 shows the correlation between log k_{obs} and log D obtained from the liquid–liquid extraction by varying the $\mathrm{(HA)_2}$ concentration and the pH. The values of log k_{obs} increased proportionally with increasing log D and became asymptotic to the plateau at higher distribution ratios. Most of the data are situated on the same curved line. The rate constant of forward extraction is normally considered to be sensitive to the $\mathrm{(HA)_2}$ concentration and pH whereas the Fig. 8 plots give a regular trend under different conditions. The contribution of the term of $1/k_1$ to the transport rate may be negligibly small; that is, the extraction rate in the interface on the membrane is actually fast, and Eq. (9) is approximated to

$$k_{\mathrm{obs}} = \frac{1}{\dfrac{\delta_a}{D_a} + \dfrac{\delta_0}{D_0}\dfrac{1}{D}}\,\frac{S}{V} \tag{10}$$

Here, two limiting cases can be considered. In the lower region of D, the term δ_a/D_a has a negligibly small value compared to $\delta_0/(D_0D)$. Thus, Eq. (10) is simplified to

$$k_{\mathrm{obs}} = \frac{D_0}{\delta_0}\frac{S}{V}D \tag{11}$$

In this region the transport rate may be controlled by the diffusion process in the membrane phase and the k_{obs} value will be proportional to the distribution ratio. On the other hand, in the higher region of D, $\delta_a/D_a >> \delta_0/(D_0D)$ can be assumed; then Eq. (10) is approximated to

$$k_{\mathrm{obs}} = \frac{D_a}{\delta_a}\frac{S}{V} \tag{12}$$

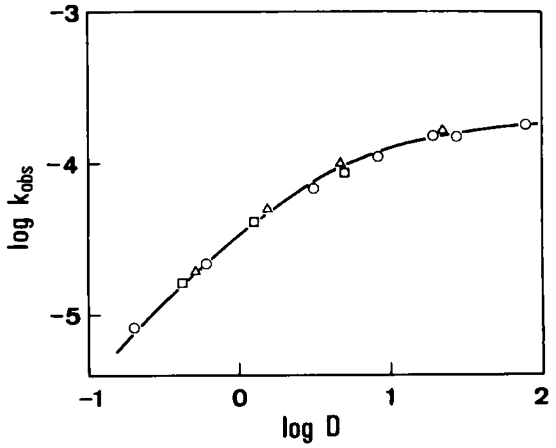

FIG. 8. Relation between k_{obs} and the distribution ratio of europium. (○) 1 M, (△) 0.3 M, (□) 0.1 M $(\mathrm{HA})_2$.

The transport rate may be mainly controlled by the diffusion process in the aqueous boundary layer, and the k_{obs} value will be independent of D. These limiting cases, expressed by Eqs. (11) and (12), are reflected by the plots in the lower and higher regions of D, respectively (Fig. 8). In order to support these considerations, the effect of the shaking speed was examined. As Fig. 9 shows, in the higher D region the k_{obs} value increases with increasing shaking speed, as illustrated by Curve (a); this is attributable to a decrease of δ_a in Eq. (12). On the other hand, in the lower D region the k_{obs} value is almost constant irrespective of the shaking speed, as indicated by Curve (b). This can be predicted from Eq. (11) which contains no parameters dependent on the shaking speed.

The solid curve in Fig. 8 has been calculated from Eq. (10) by using the following parameters: $S = 19$ cm^2, $V = 100$ cm^3, $D_a/\delta_a = 1.0 \times 10^{-3}$ cm/s, and $D_0/\delta_0 = 2.5 \times 10^{-4}$ cm/s. The curve is in good agreement with the experimental data in all regions. When the literature value $D_a = 6 \times 10^{-6}$ cm^2/s (*11*) is used, $\delta_a = 6 \times 10^{-3}$ cm is estimated at a shaking speed of 120 spm. This value is of the same order of magnitude as 1.4×10^{-3} cm (*1*) reported for the Eu–DEHPA transport system in spite of the different apparatus. $D_0 = 7.8 \times 10^{-6}$ cm^2/s is evaluated by using the mem-

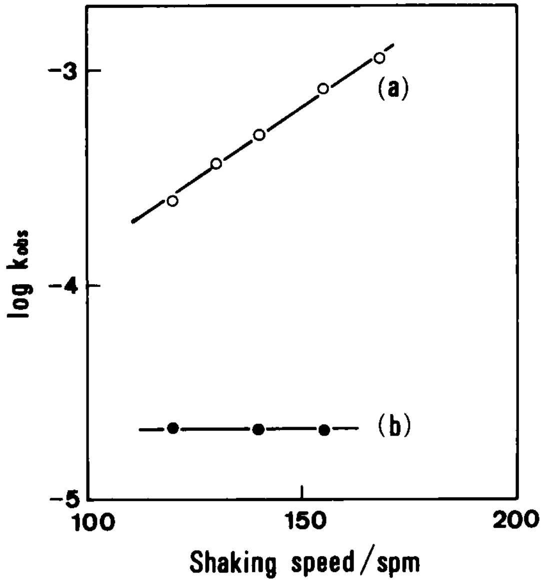

FIG. 9. Effect of shaking speed on k_{obs}. Feed: (a) pH 5.6, (b) pH 3.9. Product: 0.01 M HNO_3. SLM: 1 M $(HA)_2$ in kerosene.

brane thickness as δ_0; VA10 is preferable in D_0, which is rather larger than 2×10^{-7} cm^2/s when employing DEHPA in dodecane as the carrier (*1*).

The up-hill transport of europium through an SLM with VA10 can thus be achieved in a mildly acid aqueous solution, and its profile can be predicted by its relation to liquid–liquid extraction.

REFERENCES

1. P. R. Danesi, E. P. Horwitz, and P. Rickert, *Sep. Sci. Technol.*, *17*, 1183 (1982).
2. A. P. Novikov and B. F. Myasoedov, *Solv. Extr. Ion. Exch.*, *5*, 117 (1987).
3. T. Nishiki and R. G. Bautista, *Metall. Trans.*, *B*, *14*, 25 (1983).
4. M. Teramoto, T. Sakuramoto, T. Koyama, H. Matsuyama, and Y. Miyake, *Sep. Sci. Technol.*, *21*, 229 (1986).
5. S. Nakamura and K. Akiba, *Ibid.*, *24*, 673 (1989).
6. J. S. Preston, *Hydrometallurgy*, *14*, 171 (1985).
7. K. Akiba and T. Kanno, *Sep. Sci. Technol.*, *18*, 831 (1983).
8. K. Akiba, S. Sawai, S. Nakamura, and W. Murayama, *J. Liq. Chromatogr.*, *11*, 2517 (1988).
9. P. R. Danesi and G. F. Vandegrift, *J. Phys. Chem.*, *85*, 3646 (1981).
10. P. R. Danesi, E. P. Horwitz, G. F. Vandegrift, and R. Charizia, *Sep. Sci. Technol.*, *16*, 201 (1981).
11. E. P. Horwitz and C. A. A. Bloomquist, *J. Inorg. Nucl. Chem.*, *34*, 3851 (1972).

Received by editor April 10, 1991