This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Separation Science and Technology

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

Extraction Kinetics of Rare Earth Metals with 2-Ethylhexyl Phosphonic Acid Mono-2-ethylhexyl Ester Using a Hollow Fiber Membrane Extractor

Fukiko Kubota[a]; Masahiro Goto[a]; Fumiyuki Nakashio[a]; Tadashi Hano[b]
[a] DEPARTMENT OF CHEMICAL SCIENCE & TECHNOLOGY, KYUSHU UNIVERSITY, HAKOZAKI, FUKUOKA, JAPAN [b] DEPARTMENT OF APPLIED CHEMISTRY, OITA UNIVERSITY, OITA, JAPAN

To cite this Article Kubota, Fukiko , Goto, Masahiro , Nakashio, Fumiyuki and Hano, Tadashi(1995) 'Extraction Kinetics of Rare Earth Metals with 2-Ethylhexyl Phosphonic Acid Mono-2-ethylhexyl Ester Using a Hollow Fiber Membrane Extractor', Separation Science and Technology, 30: 5, 777 — 792

To link to this Article: DOI: 10.1080/01496399508013891

URL: http://dx.doi.org/10.1080/01496399508013891

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SEPARATION SCIENCE AND TECHNOLOGY, 30(5), pp. 777–792, 1995

Extraction Kinetics of Rare Earth Metals with 2-Ethylhexyl Phosphonic Acid Mono-2-ethylhexyl Ester Using a Hollow Fiber Membrane Extractor

FUKIKO KUBOTA, MASAHIRO GOTO,
and FUMIYUKI NAKASHIO*
DEPARTMENT OF CHEMICAL SCIENCE & TECHNOLOGY
KYUSHU UNIVERSITY
HAKOZAKI, FUKUOKA 812, JAPAN

TADASHI HANO
DEPARTMENT OF APPLIED CHEMISTRY
OITA UNIVERSITY
OITA 870-11, JAPAN

ABSTRACT

A kinetic study concerning chemical complexation-based solvent extraction of rare earth metals with 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester dissolved as an extractant in *n*-heptane was carried out using a microporous hydrophobic hollow fiber membrane extractor. The effects of concentration of chemical species in aqueous and organic feed solutions on the apparent permeabilities of metal species for extraction and stripping, respectively, were investigated to clarify the permeation mechanism. From the experimental results it was predicted that the permeation rate is controlled by diffusion of the chemical species in aqueous and organic phases and by interfacial chemical reaction. The experimental data were analyzed by the diffusion model accompanied with an interfacial reaction, taking into account the velocity distributions of the aqueous and organic phases through the inner and outer sides of the hollow fiber.

INTRODUCTION

There has been increasing interest in the development of new advanced materials by utilizing rare earth metals in a highly-purified state. Mul-

---

* To whom correspondence should be addressed.

tistage solvent extraction is known as the most effective method for the separation and purification of rare earth metals on an industrial scale. However, the similarity of the chemical and physical properties of rare earth elements complicates the processes used to produce metals of high-purity from raw materials, even in solvent extraction (1).

A membrane-based solvent extraction process was recently shown to be an effective alternative to conventional solvent extraction technology. A supported liquid membrane (SLM) is one way to realize this new technology (2). The use of SLMs eliminates the problems caused by the mixing of aqueous and organic phases in conventional solvent extraction processes, e.g., loading, flooding, and emulsification. In addition, a membrane module of the hollow fiber type offers a very large interfacial area per unit equipment volume. Owing to these attractive advantages, hollow fiber modules have been used to study the recovery of various metal ions (3–8) and the extraction of organic compounds (9–13).

The success of separation with SLMs depends on selective permeation through the membrane. In a number of studies concerning the permeation of metal ions through SLMs, it has been suggested that the interfacial chemical reaction plays a predominant role in extraction kinetics (8, 14–21). If a sufficient difference between permeation rates is obtained under a nonequilibrium state for neighboring metals, a hollow fiber membrane can be applied to the separation and purification of rare earth metals.

The extraction equilibrium of rare earth metals was investigated with 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (commercial name, PC-88A, henceforth abbreviated HR) in a previous paper (22). In this study the extraction and stripping of rare earth metals with PC-88A were carried out by using a membrane extractor which consisted of a single hollow fiber in order to obtain more detailed information on the permeation mechanism of rare earth metals.

EXPERIMENTAL

Reagents

PC-88A was from Daihachi Chemical Industry Co. Ltd. (Lot No. N10102) and used without further purification. *n*-Heptane of commercial GR grade was used as the organic solvent without further purification. All other inorganic reagents used were GR grade.

The metal complexes of PC-88A, MR_3, were prepared by adding an aqueous solution of the chloride salt of a rare earth metal to a methanol solution of PC-88A at about 333 K, adjusting the pH of the solution with aqueous ammonia solution. The resulting complexes were purified by recrystallization in a mixture of methanol and chloroform to obtain solids. These were analyzed by elementary analysis.

Analysis: Calculated for $C_{48}H_{102}P_3O_9Y(H_2O)$: C, 56.70; H, 10.20%. Found: C, 56.35; H, 10.25%.

Analysis: Calculated for $C_{48}H_{102}P_3O_9Ho(H_2O)$: C, 52.35; H, 9.33%. Found: C, 52.45; H, 9.54%.

Analysis: Calculated for $C_{48}H_{102}P_3O_9Er(H_2O)$: C, 51.93; H, 9.28%. Found: C, 52.34; H, 9.51%.

Organic solutions were prepared by dissolving PC-88A or/and metal complexes in *n*-heptane. Aqueous solutions containing rare earth metals were prepared by dissolving chloride salt hexahydrates of rare earth metals in nitric acid solutions and adjusting the pHs and ionic strengths of solutions with sodium acetate–nitric acid solution or sodium nitrate–nitric acid solution. Nitric acid solution was used for stripping.

Measurement of Extraction and Stripping Rates

The extraction and stripping rates were measured at 303 K with the membrane extractor shown schematically in Fig. 1. The extractor is com-

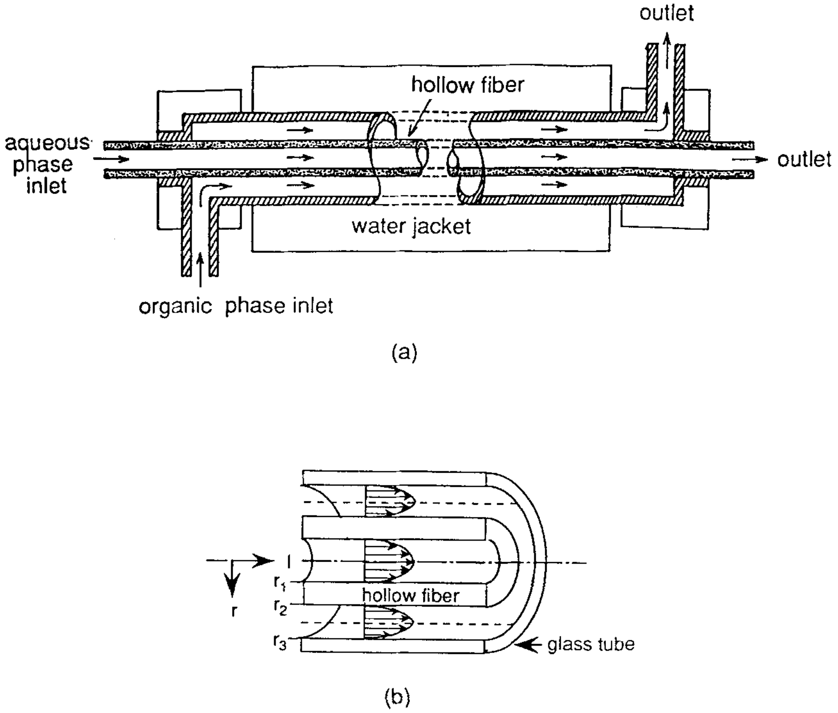

FIG. 1 (a) Schematic diagram of the hollow fiber membrane extractor. (b) Flow pattern of each phase in the membrane extractor.

posed of a glass tube and a microporous hollow fiber made of polytetrafluoroethylene (Japan Gore-tex Inc.). The characteristics of the hollow fiber were measured and are shown in Table 1. The aqueous and organic solutions were fed cocurrently along the inner and outer sides of the hollow fiber, respectively, by a microtube pump (Tokyo Rika MP1001). Since the fiber is hydrophobic, the pores of the membrane are filled with the organic solution containing extractant. At the steady state, the concentrations of rare earth metals and metal complexes in effluent solutions were measured by ICP-atomic emission spectroscopy (Seiko SPS-1200VR).

To discuss the extraction results, the apparent permeabilities for the extraction and stripping of rare earth metal, P_M and P'_M, respectively, were defined as follows:

$$P_M \ (= J_M/C_{M0}) = EQ_{aq}/(2\pi r_1 L) \tag{1}$$

$$P'_M \ (= J'_M/C_{MR33HR0}) = E'Q_{org}/(2\pi r_1 L) \tag{2}$$

where J_M and J'_M are the average extraction and stripping rates, Q_{aq} and Q_{org} are the volumetric flow rates of the aqueous and organic solutions, and E and E' are the extents of metal extracted and stripped, respectively.

RESULTS AND DISCUSSION

Extraction and Stripping Rates of Rare Earth Metals

Figure 2 shows the relation between P_M and pH of the feed solution. The slopes of the correlation for each metal in the low pH range were almost 3, while P_M was not affected in the high pH range. Figure 3 shows the relation between P_M of middle rare earth metals and the concentration of metal in the feed solution, C_{M0}. P_M was not affected by C_{M0} under the

TABLE 1
Specifications of Membrane Extractor

Material	Polytetrafluoroethylene (made in Japan by Gore-Tex Inc.)	
Hollow fiber type	A	B
Inner diameter, $2r_1$ (m)	9.38×10^{-4}	1.02×10^{-3}
Outer diameter, $2r_2$ (m)	1.84×10^{-3}	1.86×10^{-3}
Porosity, ϵ (—)	0.45	0.43
Tortuosity factor, τ (—)	1.60	1.14
Inner diameter of extractor, $2r_3$ (m)	2.4×10^{-3}	
Length, L (m)	0.25	

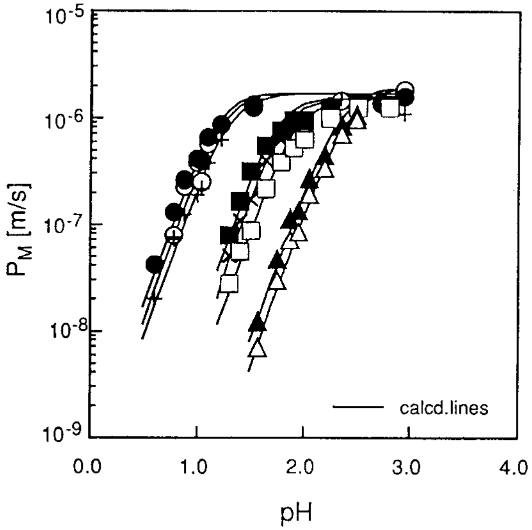

FIG. 2 Relation between P_M and pH of feed aqueous solution. C_{Mi0} = 0.5 mol/m^3, $C_{(HR)20}$ = 23.6 mol/m^3; (△) Pr and (▲) Nd, hollow fiber type A; (□) Sm, (×) Eu, (■) Gd, (+) Ho, (○) Y, and (●) Er, hollow fiber type B.

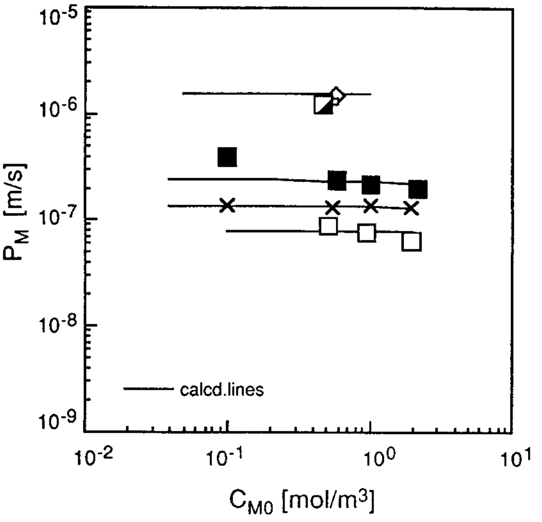

FIG. 3 Relation between P_M of middle rare earth metals and feed concentration of metal ions. $C_{(HR)20}$ = 23.6 mol/m^3, type B; (□) Sm, (×) Eu, and (■) Gd, pH 1.5; (◩) Sm, (✢) Eu, and (◇) Gd, pH 2.5.

present experimental condition; that is, the extraction rate was proportional to C_{M0}. Figure 4 shows the relation between P_M and the concentration of the dimeric extractant in the feed organic solution, $C_{(HR)20}$. P_M increased with $C_{(HR)20}$ in the low pH and $C_{(HR)20}$ range whereas it was scarcely affected by $C_{(HR)20}$ in the high pH and $C_{(HR)20}$ range.

Figure 5 shows the relation between P'_M and the activity of hydrogen ion of the feed aqueous solution, a_{H0}. P'_M increased with a_{H0} at low a_{H0} and approached a constant at high a_{H0}. Figure 6 shows the relation between P'_M of light rare earth metals and the concentration of metal complex, $C_{MR33HR0}$, in the feed organic solution. P'_M was not affected by C_{MR33HR} under the experimental condition, hence the stripping rate was proportional to $C_{MR33HR0}$. Figure 7 shows the relation between P'_M and the feed concentration of dimeric extractant, $C_{(HR)20}$. At high acid concentration, P'_M was scarcely affected by $C_{(HR)20}$, while at low acid concentration P'_M decreased with increasing $C_{(HR)20}$.

Analysis of Extraction and Stripping Rates

The experimental results suggest that the extraction and stripping rates of rare earth metals are controlled by the interfacial reaction and/or by

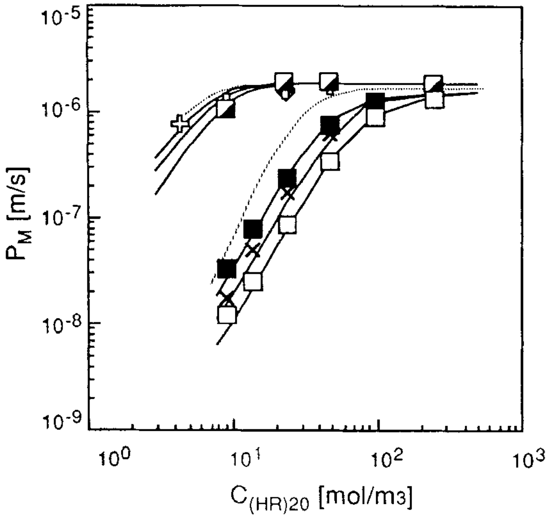

FIG. 4 Relation between P_M of middle rare earth metals and feed concentration of dimeric PC-88A. C_{Mi0} = 0.5 mol/m^3; (□) Sm, (×) Eu, and (■) Gd, pH 1.5, type B; (◪) Sm, (✚) Eu, and (◇) Gd, pH 2.5, type A; (——) calculated lines; (- - -) calculated lines for Gd assuming that diffusion was the rate-controlling step.

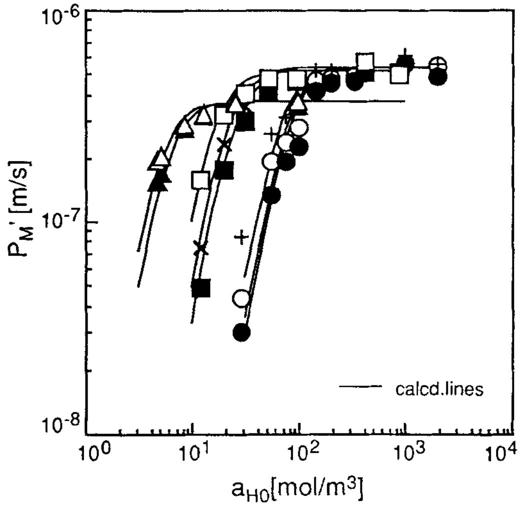

FIG. 5 Relation between P_M' and a_{H0} of feed aqueous solution, $C_{Mi0} = 0.5$ mol/m^3, $C_{(HR)20} = 23.6$ mol/m^3; (△) Pr and (▲) Nd, type A; (□) Sm, (×) Eu, (■) Gd, (+) Ho, (○) Y, and (●) Er, type B.

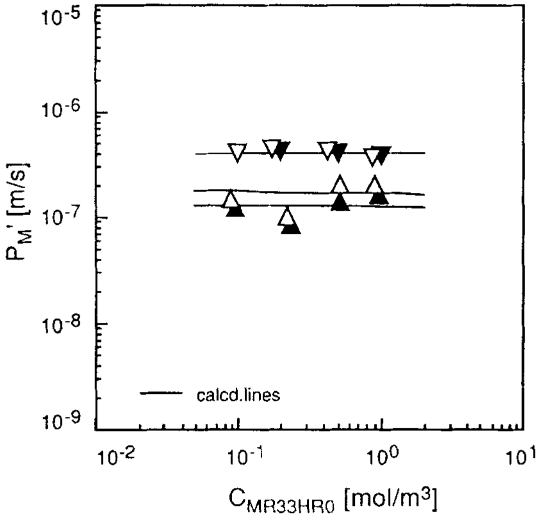

FIG. 6 Relation between P_M' of light rare earth metals and feed concentration of metal complexes. $C_{(HR)20} = 23.6$ mol/m^3, type A; (△) Pr and (▲) Nd, $a_{H0} = 5$ mol/m^3; (▽) Pr and (▼) Nd, $a_{H0} = 79$ mol/m^3.

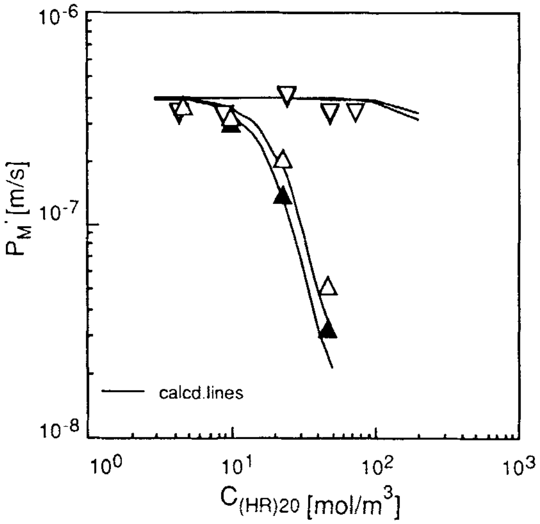

FIG. 7 Relation between P_M' of light rare earth metals and feed concentration of dimeric PC-88A. C_{Mi0} = 0.5 mol/m^3, type A; (△) Pr and (▲) Nd, a_{H0} = 5 mol/m^3; (▽) Pr and (▼) Nd, a_{H0} = 79 mol/m^3.

the diffusion of chemical species. That is, the metal ion in the aqueous phase diffuses from the bulk to the aqueous–organic interface at the inner surface of the hollow fiber. Then the metal ion reacts with the extractant at the aqueous–organic interface to form the metal complex, and the complex diffuses to the organic bulk phase through the membrane pore. Figure 8 shows the schematic concentration profile of the radial direction in a hollow fiber extractor for the extraction of rare earth metal.

The equilibrium study shows that the rare earth metal was extracted with the dimer of PC-88A, $(HR)_2$, as follows (22):

$$M^{3+}_{aq} + 3(HR)_{20,org} \rightleftharpoons MR_3 3HR_{org} + 3H^+_{aq} \qquad K_{ex} \qquad (3)$$

where the subscripts aq and org indicate the aqueous and organic species, respectively, and K_{ex} denotes the extraction equilibrium constant. On the basis of the experimental results mentioned above and previous studies on the adsorption equilibrium of PC-88A in n-heptane (19), the following interfacial reaction mechanism is suggested:

$$(HR)_{2org} \rightleftharpoons (HR)_{2ad}; \qquad K_{(HR)2} \qquad (4)$$

$$M^{3+}_{aq} + (HR)_{2ad} \rightleftharpoons MR^+_{2ad} + 2H^+_{aq}; \qquad K_1 \qquad (5)$$

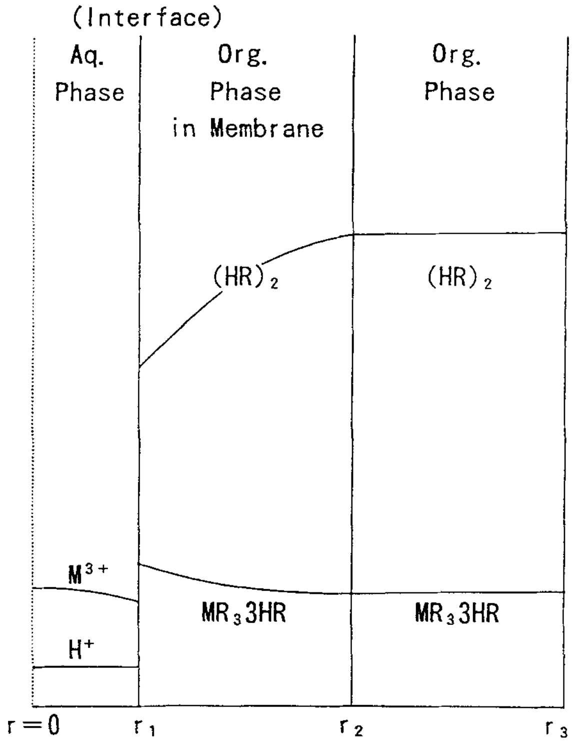

FIG. 8 Schematic concentration profile of the radial direction in a hollow fiber extractor.

$$MR_{2ad}^{+} + (HR)_{2org} \rightleftharpoons MR_3HR_{ad} + H_{aq}^{+}; \qquad K_2 \qquad (6)$$

$$MR_3HR_{ad} + (HR)_{2org} \rightleftharpoons MR_33HR_{org}; \qquad K_3\ (= k_f'/k_r) \qquad (7)$$

where $K_{(HR)2}$ is the adsorption equilibrium constant of the dimeric PC-88A and K_1, K_2, and K_3 are the equilibrium constants of Eqs. (5), (6), and (7), respectively. In Eq. (7), k_f' and k_r are the forward and backward reaction rate constants, respectively. The subscript ad denotes the adsorbed state at the interface. From the fact that the apparent order of P_M is almost 3 with respect to pH at low pH values and more than 2 with respect to the dimeric concentration of PC-88A in low $C_{(HR)20}$, the reaction of Eq. (7) is considered to be the rate-controlling step in the interfacial reactions. Therefore the interfacial reaction rate is expressed as follows:

$$R = k_f' C_{MR3HRad} C_{(HR)2org} - k_r C_{MR33HRorg} \qquad (8)$$

By using the Langmuir adsorption isotherm for the adsorbed species and assuming that the interfacial area occupied by the unit mole of each adsorbed species is equal to that of $(HR)_2$, $S_{(HR)2}$, R is ultimately written as follows:

$$R = \frac{k_f' K_1 K_2 \dfrac{K_{(HR)2}}{S_{(HR)2}} \cdot \dfrac{C_M C^3_{(HR)2}}{a^3_H} - k_r C_{MR33HR}}{1 + \left(1 + \dfrac{K_a}{a_H}\right) K_{HR} C_{HR} + K_{(HR)2} C_{(HR)2} + K_1 K_{(HR)2} \dfrac{C_M C_{(HR)2}}{a^2_H} + K_1 K_2 K_{(HR)2} \dfrac{C_M C^2_{(HR)2}}{a^3_H}} \tag{9}$$

where K_a and K_{HR} are the dissociation constant of PC-88A and the adsorption equilibrium constant of monomer species, respectively. The forth and fifth terms in the denominator, which represent the extent of intermediate complexes adsorbed at the interface, MR^+_{2ad} and MR_3HR_{ad}, are considered to be negligible under the present experimental conditions since the concentration of extractant is fairly higher than those of the complexes.

Hence the interfacial extraction and stripping rates of rare earth metal are simplified as follows:

$$R = k_f (C_M C^3_{(HR)2} / a^3_H - C_{MR33HR} / K_{ex}) / \sigma \tag{10}$$

$$R' = k_r (C_{MR33HR} - K_{ex} C_M C^3_{(HR)2} / a^3_H) / \sigma \tag{11}$$

where

$$k_f = k_f' K_1 K_2 (K_{(HR)2} / S_{(HR)2}) \tag{12}$$

and

$$\sigma = 1 + (1 + K_a / a_H) K_{HR} C_{HR} + K_{(HR)2} C_{(HR)2} \tag{13}$$

In laminar flow, the linear velocities of the aqueous and organic solutions in a tubular extractor, $u_{aq}(r)$ and $u_{org}(r)$ shown in Fig. 1, are expressed as follows:

$$u_{aq}(r) = \frac{2Q_{aq}}{\pi r_1^2} \{1 - (r/r_1)^2\} \tag{14}$$

$$u_{org}(r) = \frac{2Q_{org}}{\pi r_1^2} \times \frac{(r_3/r_1)^2 - (r/r_1)^2 + \dfrac{(r_3/r_1)^2 - (r_2/r_1)^2}{\ln(r_3/r_2)} \ln(r/r_3)}{(r_3/r_1)^4 - (r_2/r_1)^4 - \dfrac{\{(r_3/r_1)^2 - (r_2/r_1)^2\}^2}{\ln(r_3/r_2)}} \tag{15}$$

The mass balance equations at steady state are derived as follows for each region of the membrane extractor. In the aqueous phase ($0 < r < r_1$),

$$U_{aq}(r)\frac{\partial C_M}{\partial l} = D_M\left(\frac{\partial^2 C_M}{\partial r^2} + \frac{1}{r}\cdot\frac{\partial C_M}{\partial r}\right) \tag{16}$$

$$U_{aq}(r)\frac{\partial a_H}{\partial l} = D_H\left(\frac{\partial^2 a_H}{\partial r^2} + \frac{1}{r}\cdot\frac{\partial a_H}{\partial r}\right) \tag{17}$$

In the organic phase of the outer side of the hollow fiber ($r_2 < r < r_3$),

$$U_{org}(r)\frac{\partial C_{(HR)2}}{\partial l} = D_{(HR)2}\left(\frac{\partial^2 C_{(HR)2}}{\partial r^2} + \frac{1}{r}\cdot\frac{\partial C_{(HR)2}}{\partial r}\right) \tag{18}$$

$$U_{org}(r)\frac{\partial C_{MR33HR}}{\partial l} = D_{MR33HR}\left(\frac{\partial^2 C_{MR33HR}}{\partial r^2} + \frac{1}{r}\cdot\frac{\partial C_{MR33HR}}{\partial r}\right) \tag{19}$$

In the porous membrane of the hollow fiber ($r_1 < r < r_2$)

$$D_{(HR)2}\frac{\epsilon}{\tau}\left(\frac{\partial^2 C_{(HR)2}}{\partial r^2} + \frac{1}{r}\cdot\frac{\partial C_{(HR)2}}{\partial r}\right) = 0 \tag{20}$$

$$D_{MR33HR}\frac{\epsilon}{\tau}\left(\frac{\partial^2 C_{MR33HR}}{\partial r^2} + \frac{1}{r}\cdot\frac{\partial C_{MR33HR}}{\partial r}\right) = 0 \tag{21}$$

The boundary conditions are expressed as follows:

$$l = 0,\ 0 < r < r_1; \qquad C_M = C_{M0},\ a_H = a_{H0} \tag{22}$$

$$l = 0,\ r_2 < r < r_3; \qquad C_{(HR)2} = C_{(HR)20},\ C_{MR33HR} = C_{MR33HR0} \tag{23}$$

$$l > 0,\ r = 0; \qquad D_M\frac{\partial C_M}{\partial r} = 0 \tag{24}$$

$$\begin{aligned} l > 0,\ r = r_1;\ -D_M\frac{\partial C_M}{\partial r} &= \frac{1}{3}D_H\frac{\partial a_H}{\partial r} = \frac{1}{3}D_{(HR)2}\frac{\epsilon}{\tau}\frac{\partial C_{(HR)2}}{\partial r} \\ &= -D_{MR33HR}\frac{\epsilon}{\tau}\frac{\partial C_{MR33HR}}{\partial r} = R\ (= R') \end{aligned} \tag{25}$$

$$\begin{aligned} l > 0,\ r = r_2;\ D_{(HR)2}\left.\frac{\partial C_{(HR)2}}{\partial r}\right|_{r_2-0} &= D_{(HR)2}\frac{\epsilon}{\tau}\left.\frac{\partial C_{(HR)2}}{\partial r}\right|_{r_2+0} \\ D_{MR33HR}\left.\frac{\partial C_{MR33HR}}{\partial r}\right|_{r_2-0} &= D_{MR33HR}\frac{\epsilon}{\tau}\left.\frac{\partial C_{MR33HR}}{\partial r}\right|_{r_2+0} \\ C_{(HR)2}|_{r_2-0} = C_{(HR)2}|_{r_2+0},\ C_{MR33HR}|_{r_2-0} & \\ = C_{MR33HR}|_{r_2+0} & \end{aligned} \tag{26}$$

$$t > 0,\ r = r_3; \qquad D_{(\mathrm{HR})2}\frac{\partial C_{(\mathrm{HR})2}}{\partial r} = D_{\mathrm{MR33HR}}\frac{\partial C_{\mathrm{MR33HR}}}{\partial r} = 0 \qquad (27)$$

where D_{M}, $D_{(\mathrm{HR})2}$, and D_{MR33HR} are the diffusivity of metal in the aqueous solution, dimeric PC-88A, and the complex in the organic solution, respectively.

The basic equations (16)–(21) were solved numerically by using the boundary conditions to obtain the concentration profiles in the extractor (16). The apparent permeability for the extraction and stripping, P_{M} or P'_{M}, were obtained from Eqs. (1) and (2) using E and E', which were calculated by the model mentioned above.

The values of K_{a}, K_{HR}, $K_{(\mathrm{HR})2}$, and K_{ex} for each metal were determined in previous papers (19, 22). The overall forward reaction rate constant, k_{f}, was evaluated with the trial-and-error method so as to minimize the standard deviation between the experimental and calculated permeabilities (17). The values of diffusivities, D_{M} and D_{MR33HR}, were also evaluated by analyzing the experimental data, whereas $D_{(\mathrm{HR})2}$ was estimated by the Wilke–Chang correlation (23). These values are listed in Table 2. The values of k_{f} for each metal are shown in Table 3, and the calculated results are shown in Figs. 2–4 as solid lines.

The dashed lines in Fig. 4 were calculated for Gd assuming that the diffusion on both sides of the interface was a rate-controlling step. The deviation of the dashed lines from experimental data predicts the permeation at low pH and in the low $C_{(\mathrm{HR})20}$ region is controlled by the interfacial chemical reaction.

On the other hand, the experimental results for stripping were in excellent agreement with the lines calculated by assuming that the interfacial backward reaction was very fast and that the diffusion process was rate controlling, as shown in Figs. 5–7. Though P'_{M} was found to be slightly affected by chemical reaction at the high range of $a_{\mathrm{H}0}$ and $C_{(\mathrm{HR})20}$ in Fig. 7, it was difficult to estimate the backward reaction rate constants accurately since the influence of the interfacial reaction was observed at limited concentration range.

TABLE 2

Constants Used for Numerical Analysis

$K_{\mathrm{HR}} = 4.65^{(19)}$ (m^3/mol)
$K_{\mathrm{a}} = 4.79^{(19)}$ (mol/m^2)
$D_{\mathrm{M}} = 7.2 \times 10^{-10}$ (m^2/s)
$D_{\mathrm{MR33HR}} = 4.5 \times 10^{-10}$ (m^2/s)
$K_{(\mathrm{HR})2} = 1.80^{(19)}$ (m^3/mol)
$K_{\mathrm{D}} = 3.00^{(24)}$ (m^3/mol)
$D_{(\mathrm{HR})2} = 1.1 \times 10^{-9}$ (m^2/s)

TABLE 3
Rate Constants, Equilibrium Constants, and Separation Factors (303 K)

	Pr		Nd		Sm		Eu		Gd		Ho		Y		Er
$k_f \times 10^6$ (m/s)	0.86		1.6		16		27		57		1400		2000		3200
β_{Pij}		1.9		10		1.7		2.1		25		1.4		1.6	
K_{ex} (—)	0.052		0.082		1.0		2.4		3.6		94		150		180
β_{Dij}		1.6		12.5		2.4		1.5		26		1.5		1.2	

The results in Figs. 2, 3 and 5 were obtained by using two different hollow fiber membranes whose physical characteristics are shown in Table 1. The difference in the magnitude of permeabilities was observed in the region of approximately constant P'_M in Fig. 5.

By considering that the permeation for stripping in the high a_H range of Fig. 5 is controlled by the diffusion of metal complex in the organic phase of a membrane pore, the dependence of permeability on a_H can be approximately expressed as follows:

$$P'_M = \frac{\epsilon}{\tau} \frac{D_{MR33HR}}{\delta} \tag{28}$$

The approximated thickness of the organic side diffusion layer, δ, for the hollow fiber membranes used were determined by using Eq. (28) as 3.22×10^{-4}m and 3.04×10^{-4}m for types A and B, respectively. The ratio of these values are in reasonable agreement with that of membrane thickness.

In contrast, as shown in Figs. 2 and 3, the permeation rate of extraction at the range of approximately constant permeability was the same irrespective of the fibers used. This suggest that permeation was controlled by the diffusion of metal ion in the aqueous phase.

Separation Factors

The separation factors for neighboring members of rare earth metals are defined by the following equation and are listed in Table 3.

$$\beta_{Pij} = k_{fi}/k_{fj} \tag{29}$$

Compared with the separation factors reported in our previous paper (22), the efficiency of the mutual separation in the present hollow-fiber extractor, which is based on the difference of extraction rates, is nearly equal to that in the process based on the difference of extraction equilibria.

Relation between Extraction Rate Constants and Equilibrium Constants

The relation between k_f in the present study and K_{ex} in the previous study (22) obtained for the series of rare earth metals is shown in Fig. 9. It is found that k_f is proportional to K_{ex} in two kinds of solvent.

From Eq. (3) and Eqs. (4)–(7), K_{ex} is represented as follows:

$$K_{ex} = K_1 K_2 K_3 (K_{(HR)2}/S_{(HR)2}) \tag{30}$$

From a comparison of Eq. (30) with Eq. (12), the linear dependence between k_f and K_{ex} implies that the forward reaction rate constant and the equilibrium constant of the rate-controlling step shown by Eq. (7), k_f' and K_3 respectively, bear a linear relationship to each other. This suggests that the backward reaction rate constant, k_r, does not vary in the series of rare earth metals since the ratio of k_f to k_r is considered to be equal to K_{ex} for each metal.

A more detailed study is required to interpret the linear relationship in Fig. 9.

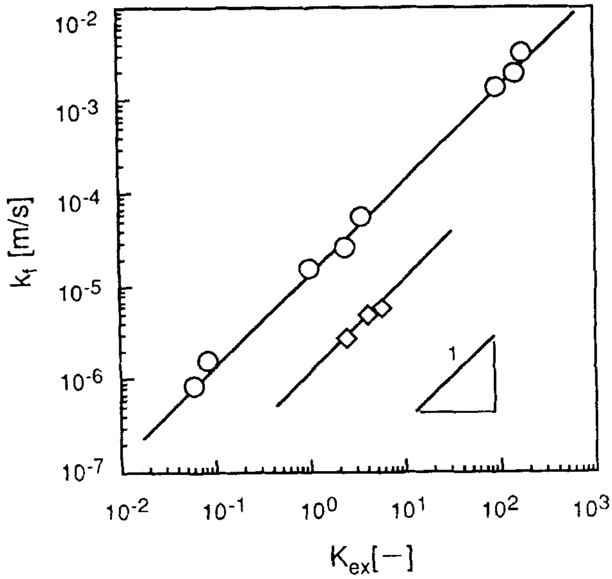

FIG. 9 Relation between k_f and K_{ex}. Solvents: (○) heptane, (◇) toluene (25).

CONCLUSION

A kinetic study on the solvent extraction of rare earth metals with PC-88A in *n*-heptane was carried out using a microporous hydrophobic hollow-fiber membrane extractor. The following results were obtained.

1. The interfacial reaction was composed of four steps expressed by Eqs. (4) to (7). The rate-determining step was the formation of a final complex between the intermediate complex, MR_3HR, at the interface and the extractant in the organic phase. The interfacial reaction rates are described by Eqs. (10) and (11).
2. The experimental results of extraction were analyzed by the diffusion model accompanied with a interfacial reaction, taking into account the velocity distributions of the aqueous and organic phases through the inner and outer sides of the hollow fiber, respectively. The model predicted satisfactorily the experimental results, and the forward reaction rate constants were determined. The experimental results of stripping were also explained by the same model with a fast interfacial reaction, that is, the reaction was in the equilibrium state.
3. The separation factors for neighboring members of rare earth metals in the present membrane extractor were nearly equal to those in extraction based on the difference of extraction equilibria. The interfacial forward reaction rate constants were proportional to the extraction equilibrium constant.

ACKNOWLEDGMENTS

We are grateful to Mr. Horiuchi of Kyushu University for his technical assistance in construction of the membrane extractor. This work was supported by a Grant-in-Aid for Scientific Research (No. 05453103) from the Ministry of Education, Science and Culture of Japan. The authors are grateful to Daihachi Chemical Industry Co., Ltd., and Japan Gore-tex Inc. for the supply of extractant PC-88A and hollow fiber membranes, respectively.

REFERENCES

1. C. G. Brown and L. G. Sherrington, *J. Chem. Tech. Biotechnol.*, *29*, 193 (1979).
2. J. D. Way, R. D. Noble, T. M. Flynn, and E. D. Sloan, *J. Membr. Sci.*, *12*, 239 (1984).
3. B. M. Kim, *Ibid.*, *21*, 5 (1984).
4. P. R. Danesi, *Sep. Sci. Technol.*, *19*, 857 (1984–85).
5. O. Loiacono, E. Drioli, and R. Morinari, *J. Membr. Sci.*, *28*, 123 (1986).

6. P. R. Alexander and R. W. Callahan, *Ibid.*, *35*, 57 (1987).
7. Y. Sato, K. Kondo, and F. Nakashio, *J. Chem. Eng. Jpn.*, *23*, 23 (1990).
8. C. H. Yun, R. Prasad, A. K. Guha, and K. K. Sirkar, *Ind. Eng. Chem. Res.*, *32*, 1186 (1993).
9. G. T. Frank and K. K. Sirkar, *Biotechnol. Bioeng. Symp.*, *15*, 612 (1985).
10. L. Dahuron and E. L. Cussler, *AIChE J.*, *34*, 130 (1988).
11. A. Sengupta, R. Basu, and K. K. Sirkar, *Ibid.*, *34*, 1698 (1988).
12. C. H. Yun, R. Prasad, and K. K. Sirkar, *Ind. Eng. Chem. Res.*, *31*, 1709 (1992).
13. H. B. Ding, P. W. Carr, and E. L. Cusslar, *AIChE J.*, *38*, 1493 (1992).
14. P. R. Danesi and C. Cianetti, *J. Membr. Sci.*, *14*, 175 (1983).
15. P. Plucinski and W. Nitsh, *Ibid.*, *39*, 43 (1988).
16. K. Yoshizuka, K. Kondo, and F. Nakashio, *J. Chem. Eng. Jpn.*, *19*, 312 (1986).
17. K. Yoshizuka, K. Kondo, and F. Nakashio, *Ibid.*, *19*, 396 (1986).
18. M. Matsumoto, H. Shimauchi, K. Kondo, and F. Nakashio, *Solv. Extr. Ion Exch.*, *5*, 301 (1987).
19. Y. Sato, Y. Akiyoshi, K. Kondo, and F. Nakashio, *J. Chem. Eng. Jpn.*, *22*, 182 (1989).
20. Y. Sato, K. Kondo, and F. Nakashio, *Ibid.*, *22*, 200 (1989).
21. Y. Sato, K. Kondo and F. Nakashio, *Ibid.*, *22*, 686 (1989).
22. F. Kubota, M. Goto, and F. Nakashio, *Solv. Extr. Ion Exch.*, *11*, 437 (1993).
23. C. R. Wilke and P. Chang, *AIChE J.*, *1*, 264 (1955).
24. F. Nakashio, K. Kondo, A. Murakami, and Y. Akiyoshi, *J. Chem. Eng. Jpn.*, *15*, 686 (1982).
25. M. Goto, F. Kubota, T. Miyata, and F. Nakashio, *J. Membr. Sci.*, *74*, 215 (1992).

Received by editor June 27, 1994