EXTRACTION RATE OF PRASEODYMIUM AND NEODYMIUM WITH PHOSPHONIC ACID MONO ESTER

Yasushige MORI, Takafumi HAMADA, Eiichiro KORESAWA
AND THE LATE Wataru EGUCHI

*Department of Chemical Engineering, Kyoto University, Kyoto 606*

Recently, interest has increased in the practical application of solvent extraction technology for the mutual separation and purification of rare earth metals. 2-Ethylhexyl phosphonic acid mono-2-ethylhexyl ester (henceforth EHPNA) has recently been developed, and was found to have high capability of lanthanoid extraction.

This paper reports the extraction rate of praseodymium and neodymium with EHPNA in toluene from hydrochloric acid solution by use of a stirred transfer cell of Lewis type at 298 K. The experimental results suggested the existence of chemical reaction resistance at the interface at low extractant concentration and high pH value in the forward extraction, in addition to the film mass transfer resistances in the aqueous and the organic phases. The time course change of the extraction from mixed lanthanoid aqueous solution was satisfactorily predicted by the extraction model presented.

Introduction

Recently, interest has increased in the practical application of solvent extraction technology for the mutual separation and purification of rare earth metals, which is a difficult process because of the similarity in their chemical nature. Many acidic organophosphorus extractants have been developed and were found to have high capability of mutual separation of lanthanoids. Typical extractants of this nature are *di*(2-ethylhexyl) phosphoric acid (henceforth D2EHPA) and 2-ethylhexyl phosphonic acid *mono* 2-ethylhexyl ester (henceforth EHPNA).

In the previous work,[8] the authors made a quantitative investigation of the extraction equilibrium of cerium, praseodymium and neodymium from hydrochloric acid solution with D2EHPA or EHPNA in toluene at 298 K. These metal (Ln) ions are extracted according to the following equation.

$$\mathrm{Ln^{3+}} + 3\overline{\mathrm{(HR)_2}} \rightleftharpoons \overline{\mathrm{LnR_3(HR)_3}} + 3\mathrm{H^+} \qquad (1)$$
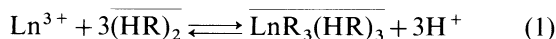
$$K_{ex} = \frac{[\overline{\mathrm{LnR_3(HR)_3}}][\mathrm{H^+}]^3}{[\mathrm{Ln^{3+}}][\overline{\mathrm{(HR)_2}}]^3} \qquad (2)$$

where $\overline{\mathrm{(HR)_2}}$ stands for the dimer of the extractant in the organic phase, as it is reported that D2EHPA and its analogs, like EHPNA, in aromatic diluent are present as dimer.[2] Our result is the same as the extraction equilibrium by D2EHPA in aromatic diluent reported by Peppard *et al.*[11] and many other

researchers.[3,7,10,13,15] But in the case of EHPNA, our experimental results[8] indicated the existence of an additional complex in the region of high EHPNA concentration.

$$\overline{\mathrm{LnR_3(HR)_3}} + \overline{\mathrm{(HR)_2}} \rightleftharpoons \overline{\mathrm{LnR_3(HR)_5}} \qquad (3)$$
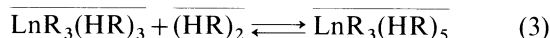
$$K_c = \frac{[\overline{\mathrm{LnR_3(HR)_5}}]}{[\overline{\mathrm{LnR_3(HR)_3}}][\overline{\mathrm{(HR)_2}}]} \qquad (4)$$

On the other hand, studies of the extraction rate of lanthanides with D2EHPA are rather few. Most of the published papers[4,6,9] on the kinetics conclude that the mass transfer rate of lanthanides is controlled by chemical reactions. But Danesi *et al.*[1] conclude that two alternative models can interpret the extraction rate behavior. The first assumes that interfacial chemical reactions are the rate-determining process, while the second is that the rate is controlled by interfacial film diffusion with a fast chemical reaction.

In the case of EHPNA, the extraction rate of lanthanides also may be fast. Teramoto *et al.*[14] assume the interfacial reaction process can be considered one of the controlled steps, based on a study of liquid surfactant membranes with EHPNA.

In this paper we report the results of a study of the extraction rate of praseodymium and neodymium with EHPNA in the same system as for the previous equilibrium experiments, and discuss the contribution of the interrfacial chemical reaction. The possibility of the mutual separation of lanthanoid elements by utilizing the difference in extraction rate is also investigated.

1. Experimental

1.1 Reagents

EHPNA was purified by washing the commercial extractant PC88A, kindly supplied by Daihachi Chemical industry Co., Ltd., Japan, with a $6 \, kmol/m^3$ hydrochloric acid solution, and then with deionized water several times. Toluene of guaranteed grade was used as the diluent without further purification. The organic solutions were prepared by diluting a desired amount of extractant with toluene.

The aqueous solution was prepared by dissolving the desired amount of lanthanoid chloride into deionized water. The ionic strength and the pH value of the aqueous solution were adjusted to $0.2 \, kmol/m^3$ and a desired level, respectively, by using lithium chloride and hydrochloric acid.

In the case of back extraction experiments, the organic solution used contained the extractant and the extractant-lanthanoid complex in known concentrations. An aqueous solution free from lanthanoid ion with $0.2 \, kmol/m^3$ ionic strength at a desired level of pH value was used as the stripping solution. The initial loading ratio, defined as the ratio of the total metal concentration in the organic phase to the dimer EHPNA concentration, was less than 5%.

1.2 Experimental procedure

A stirred transfer cell of Lewis type made of glass, shown in **Fig. 1**, was used in the present work. The vessel, whose inner diameter is 53.6 mm, was equipped with four glass baffles of 7.5 mm width and a water jacket. The shape of the interface between the aqueous and the organic phases is like a ring, with an area of $7.54 \, cm^2$. The aqueous solution was first fed into the lower compartment of the cell and circulated through the flow cells of the pH meter and of the spectrophotometer with the help of a microtube pump. The total volume of the aqueous solution was $87 \, cm^3$. The organic phase, whose volume was $67 \, cm^3$, was carefully filled into the upper compartment of the cell in such a manner as not to disturb the interface. This was taken as the experimental time, $t = 0$.

Stirring in both compartments was carried out in the same direction at a constant speed of 100 r.p.m., using a turbine impeller with four flat blades. The diameter of the impeller is 28 mm, and the width is 6 mm.

The concentration of the lanthanoid ion and the pH value in the aqueous phase were continually measured by spectrophotometer and pH meter, respectively.

2. Results and Discussion

2.1 Measurement of initial extraction rate

Figure 2 shows the time course changes of the total neodymium concentration and the pH value in the
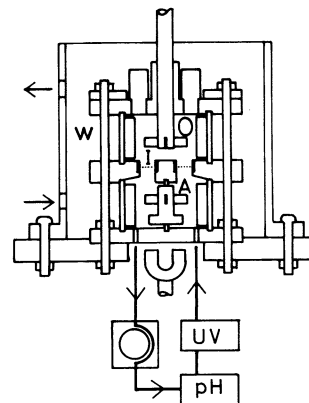

Fig. 1. Schematic diagram of experimental apparatus (O: organic phase; A: aqueous phase; I: interface; W: water jacket)
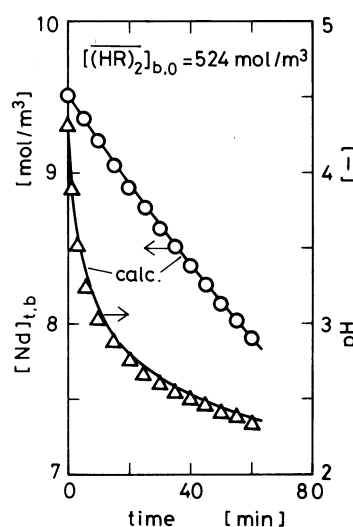

Fig. 2. Time course change of concentrations of neodymium and hydrogen ions

forward extraction. The initial mass transfer flux of the lanthanoids, calculated from the initial slope of the concentration change, was proportional to the initial lanthanoids concentration. **Figures 3** and **4** show the relationship between the initial mass transfer flux, i.e. extraction rate, of neodymium and the initial pH value with the extractant concentrations as the parameter, in the case of forward and back extraction, respectively.

The initial forward rate becomes constant in the high range of pH_0 above 3, as can be seen from Fig. 3. The initial forward rate in this region is not proportional to the extractant concentration but becomes constant, as shown in **Fig. 5**. This indicates that the rate is governed by the diffusion of lanthanoid ion in the aqueous phase, in the case of high pH value and high EHPNA concentration.

On the other hand, the initial back extraction rate becomes constant in the low pH_0 region, as shown in Fig. 4. The diffusion of the extractant-lanthanoid
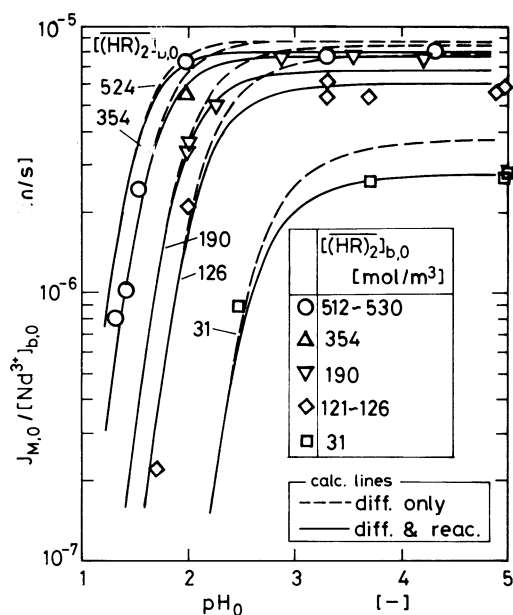
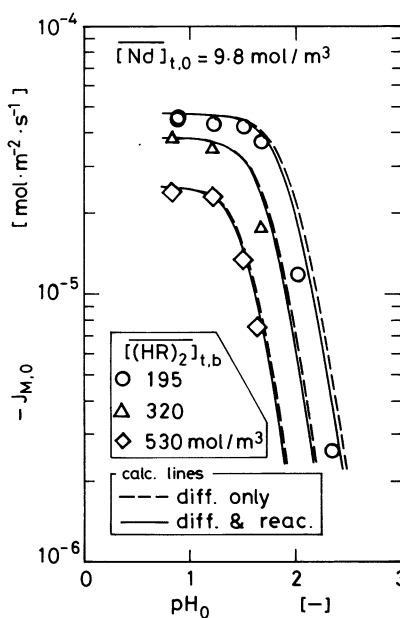**Fig. 3.** Effect of hydrogen ion concentration on initial forward extraction rate

Fig. 5. Effect of extractant concentration on initial forward extraction rate

Fig. 4. Effect of hydrogen ion concentration on initial back extraction rate
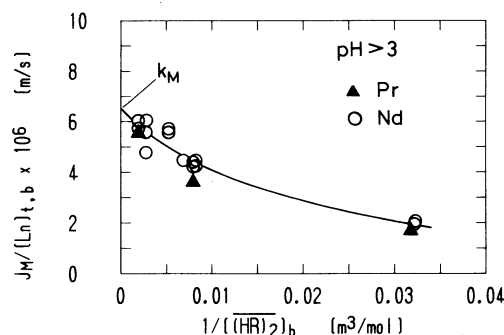
Fig. 6. Determination of mass transfer coefficient of lanthanoids ion in aqueous phase

complex in the organic phase is considered to control the back extraction rate in this region.

2.2 Mass transfer coefficient

When the extraction kinetics or mechanism is to be discussed from the experimental results using a transfer cell of Lewis type, it is very important to estimate the values of the mass transfer coefficient of the chemical species involved. In the present case, we need six mass transfer coefficients, that is, hydrogen ion, lanthanoid ion and lanthanoid-chloro complex ion in the aqueous phase and EHPNA, EHPNA-lanthanoid complex and additional complex in the
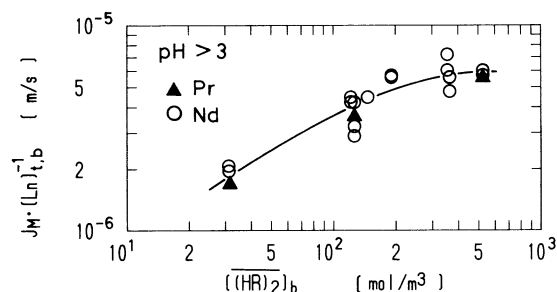
organic phase.

Concerning the lanthanoid-chloro complexes in the aqueous phases, we assume that it is sufficient to consider the first stability constant,[8,12)] and that this equilibrium is realized everywhere in the aqueous phase.

$$Ln^{3+} + Cl^- \rightleftharpoons LnCl^{2+} \qquad (5)$$
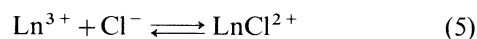
$$\beta_1 = \frac{[LnCl^{2+}]}{[Ln^{3+}][Cl^-]} \qquad (6)$$

As a result of this assumption, we can consider that the mass transfer coefficients of Ln^{3+} and $LnCl^{2+}$ in the aqueous phase are equal to each other. For the organic phase, the equilibrium state between $\overline{LnR_3(HR)_3}$ and $\overline{LnR_3(HR)_5}$ in Eq. (3) is assumed to be realized everywhere and the mass transfer coefficients of both species are the same.

First, the mass transfer coefficient of lanthanoids (chloro-complex) ion, k_M, was estimated from the experimental results in Fig. 5 at the conditions of high pH value and highest extractant concentration. **Figure 6** shows the relationship between the extraction rates and the reciprocals of the EHPNA concentration. k_M can be obtained from the value of the extraction rate when the abscissa approaches zero.

Second, the mass transfer coefficient of EHPNA-lanthanoid complex, k_M, is obtained from the back extraction experiments at low pH value. **Figure 7** shows that $\overline{k_M}$ depends on the viscosity of the organic
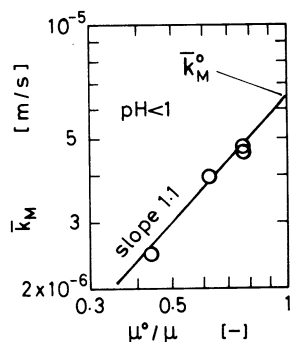
Fig. 7. Effect of visccosity in organic phase on mass transfer coefficient of lanthanoid-EHPNA complex

phase, that is, the concentration of EHPNA. The superscript $^{\circ}$ means the limit when the extractant concentration approaches zero. $\overline{k}_M$ can be calculated from Fig. 7, since the relationship between the extractant concentration and viscosity of the organic phase is given by experimental results using an Ostwald viscometer, as follows[5]:

$$\log \mu = 10^{\delta} - 1 \tag{7}$$

$$\delta = 0.3284([\overline{(HR)_2}] + n_i[\overline{C}]) - 0.3106 \tag{8}$$

$$[\overline{C}] = [\overline{LnR_3(HR)_3}] + [\overline{LnR_3(HR)_5}] \tag{9}$$

where the unit of viscosity is cent-poise, and the unit of the concentration of chemical species in the organic phase is $kmol/m^3$. n_i is the average coordination number of EHPNA dimer to lanthanoids in the organic phase.

$$n_i = (3[\overline{LnR_3(HR)_3}] + 4[\overline{LnR_3(HR)_5}])/[\overline{C}] \tag{10}$$

The relationship between the mass transfer coefficients and the diffusion coefficients were obtained experimentally, using the present transfer cell. The mass transfer coefficients of the hydrogen ion in the aqueous phase, k_H, and of the extractant in the organic phase, $\overline{k}_R$, can be estimated from the above relationship by using the diffusion coefficients of hydrogen ion, and of the extractant calculated by using the Wilke-Chang equation.[16]

2.3 Evaluation of mass transfer and interface reaction resistance

With the above assumptions, the initial mass transfer flux, i.e. extractions rate, of lanthanoids can be expressed as

$$J_M = k_M([Ln]_b - [Ln]_i)$$
$$= k_H([H^+]_i - [H^+]_b)/3$$
$$= \overline{k}_M([\overline{C}]_i - [\overline{C}]_b)$$
$$= \overline{k}_R([\overline{(HR)_2}]_b - [\overline{(HR)_2}]_i)/n_i \tag{11}$$

$$[Ln] = [Ln^{3+}] + [LnCl^{2+}] \tag{12}$$

Here, the extraction progresses when the value of J_M

is positive, and J_M is negative in the back extraction. Now if the reaction rate at the interface is cosidered to be very fast, it is sufficient to consider the equilibrium of the extraction at the interface, as expressed by Eq. (2). The extraction rate can be calculated from Eqs. (2), (4), (6) and (9) to (12) with constants listed in **Table 1**. The broken lines in Figs. 3 and 4 are the calculated lines at $0.2\,kmol/m^3$ ionic strength. The calculated values agree approximately with the experimental values, except at the condition of high pH value in the forward extraction. This suggests that the reaction resistance at the interface cannot be neglected for the extraction mechanism in this region.

To introduce the interfacial reaction resistance, it is assumed that the reaction rate is expressed as

$$J_M = k_r([Ln^{3+}]_i[\overline{(HR)_2}]_i^{\xi}[H^+]_i^{\zeta}$$
$$- [\overline{LnR_3(HR)_3}]_i[\overline{(HR)_2}]_i^{\xi-3}[H^+]_i^{\zeta-3}/K_{ex}) \tag{13}$$

Here, ξ and ζ were assumed to take single values. Note that Eq. (13) satisfies the overall equilibrium relation. The reaction rate constant k_r and the power constants ξ and ζ were determined to fit the experimental data best. The solid lines in Figs. 3 and 4 are the calculated lines for neodymium by using Eq. (13) with $k_r = 2.0 \times 10^{-7}\,m^4\,mol^{-1}\,s^{-1}$, $\xi = 1$ and $\zeta = 0$. For praseodymium, the reaction rate constant was found to be $1.2 \times 10^{-7}\,m^4\,mol^{-1}\,s^{-1}$ with $\xi = 1$ and $\zeta = 0$. The fact that $\xi = 1$ and $\zeta = 0$ for both lanthanoids suggests that the rate-controlling step is the first complex formation reaction between the lanthanoid ion and EHPNA.

The solid lines in Fig. 2 are the calculated curves by using Eq. (13). The calculated concentrations of total neodymium and hydrogen ion agree with the experimental data.

The interfacial reaction resistance is at most 25% of the total resistance at high pH level and low extractant concentration in Fig. 3. If a smaller mass transfer coefficient of hydrogen ion is employed, the contribution of the reaction resistance becomes even smaller.

2.4 Extraction of mixed lanthanoids

Figure 8 shows the time course change of the concentrations of praseodymium and neodymium in the experiments for simultaneous extraction of the two lanthanoid metal ions. The solid lines are the

Table 1. Mass transfer coefficients

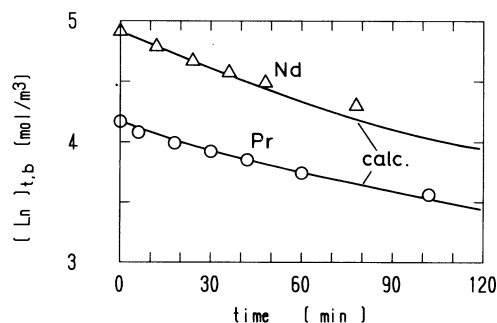| |
|---|
| $k_M = 6.5 \times 10^{-6}\,m/s$ |
| $k_H = 4.8 \times 10^{-5}\,m/s$ |
| $\overline{k}_M = 6.5 \times 10^{-6}\,(\mu^{\circ}/\mu)^{1.1}\,m/s$ |
| $\overline{k}_R = 1.3 \times 10^{-5}\,(\mu^{\circ}/\mu)^{1.1}\,m/s$ |

Fig. 8. Time course change of concentrations of neodymium and praseodymium in simultaneous extraction. (Initial concentration of EHPNA dimer $= 126\,\text{mol/m}^3$. Initial pH $= 5.8$)

calculated values when a reaction resistance exists. The calculated concentrations satisfactorily agree with the experimental values.

The separation factor is almost the same as that at equilibrium. It can be concluded that the effect of the difference in extraction rate on the separation factor is of minor importance.

Conclusion

The extraction rate of praseodymium and neo-dymium with 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester in toluene from hydrochloric acid solution was examined by using a stirred transfer cell of Lewis type at 298 K.

The following results were obtained:

1) The experimental results suggested the existence of a chemical reaction resistance at the interface at low extractant concentration and high pH value in the forward extraction, in addition to the film mass transfer resistances in the aqueous and the organic phases.

2) When the interfacial reaction rate could be expressed as in Eq. 13, the calculated values agreed with the data points of the initial extraction rates and the time course changes of the concentration of lanthanide and hydrogen ion in the aqueous phase.

3) The time course change of the extraction from mixed lanthanoids aqueous solution was satisfactorily predicted by the present extraction model.

Nomenclature

K_{ex}	= equilibrium constant of lanthanoids extraction	[—]
K_c	= equilibrium constant of additional complex formation in the organic phase, defined by Eq. (4)	$[\text{m}^3/\text{mol}]$
k	= mass transfer coefficient	[m/s]
k_r	= reaction rate constant at interface	$[\text{m}^4 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}]$
n_i	= average coordination number of EHPNA for lanthanoids in toluene	[—]
[ ]	= concentration of chemical species in square blankets	$[\text{mol/m}^3]$
β_1	= first stability constant of lanthanoid chloro complex	$[\text{m}^3/\text{mol}]$
μ	= viscosity of organic phase	$[\text{Pa} \cdot \text{s}]$

⟨Subscript⟩

b	= bulk
i	= interface
H	= hydrogen
R	= extractant
M	= lanthanoids or lanthanoid-extractant complex
0	= initial
t	= total

⟨Superscript⟩

—	= species in the organic phase
°	= limiting state when extractant concentration approaches zero in organic phase

Literature Cited

1) Danesi, P. R. and G. F. Vandegrift: *J. Phys. Chem.*, **85**, 3646 (1981).
2) Duyckaerts, G., P. Dreze and A. Simon: *J. Inorg. Nucl. Chem.*, **13**, 332 (1960).
3) Goto, T. and M. Smutz: *J. Inorg. Nucl. Chem.*, **27**, 1369 (1965).
4) Imai, M. and S. Furusaki: *Kagaku Kogaku Ronbunshu*, **13**, 355 (1987).
5) Kagaku Kogaku Benran, Maruzen, Tokyo, 1978, p. 55.
6) Kandil, A. T. and G. R. Choppin: *J. Inorg. Nucl. Chem.*, **37**, 1787 (1975).
7) Kolarik, Z., S. Drazanova and V. Chotivka: *J. Inorg. Nucl. Chem.*, **33**, 1125 (1971).
8) Mori, Y., H. Ohya, H. Ono and W. Eguchi: *J. Chem. Eng., Japan*, **21**, 86 (1988).
9) Novikov, A. P. and B. F. Myasoedov: *Solvent Extr. Ion Exch.*, **3**, 267 (1985).
10) Owens, T. C. and M. Smutz: *J. Inorg. Nucl. Chem.*, **30**, 1617 (1968).
11) Peppard, D. F., J. R. Farrado and G. W. Mason: *J. Inorg. Nucl. Chem.*, **4**, 371 (1957).
12) Robert, E.: *J. Am. Chem.. Soc.*, **73**, 1176 (1951).
13) Stary, J.: *Talanta*, **13**, 421 (1966).
14) Teramoto, M., T. Sakuramoto, T. Koyama, H. Matsuyama and Y. Miyake: *Sep. Sci. Technol.*, **21**, 229 (1986).
15) Weaver, B. and R. R. Shown: *J. Inorg. Nucl. Chem.*, **33**, 1909 (1971).
16) Wilke, C. R. and P. Chang: *AIChE J.*, **1**, 264 (1955).