

# Equilibrium extraction of light rare earth metals with PC-88A as extractant

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## PC-88Aを抽出剤とした軽希土類金属の平衡抽出

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軽希土類金属としてランタン及びセリウム，抽出剤としてPC-88A，希釈剤としてSolvesso150または灯油を用い，金属濃度、原料水溶液相中のpHを変化させて液液平衡抽出を測定した。両金属イオンは溶媒相中に抽出され，ランタンに比較してセリウムの抽出率は高く，溶媒抽出によりセリウムとランタンを分離できることを確認した。水溶液相中のpHの増加および抽出溶媒相中の未反応の抽出剤濃度の増加とともに，金属の抽出溶媒相への分配比は増加した。Solvesso150に比較して灯油を溶媒とした場合，両金属の分配比は大きかったが，分離係数は同程度であった。抽出溶媒相中の未反応抽出剤濃度が高い条件を除いて抽出平衡は報告されている反応式に従った。

### 1. Introduction

Rare earth (RE) metals which possess physically and chemically specific properties are applied in many fields of advanced technology such as magnets, ceramics, electronics, nuclear technology and so on. [1] It is difficult to separate RE metals, since RE metals has the similar chemical nature because of same electric configuration of outermost husks, and all RE metals generally form trivalent cations.

In recent years, demand of RE metals is increasing with development of a high-tech industry. However, supply of RE metals depends strongly on limited area, it is difficult to maintain a stable RE metals supply and price of RE metals are increasing. On the other hand, RE metal deposits are very common, but mineral deposits of RE metals in another area have not been exploited. To maintain a stable RE metals supply, in the present, the Japanese government pushed exploitation of mineral deposits of RE metals in another area and establishment of enrichment plant of RE metals is estimated.

Solvent extraction is presently one of the major techniques on industrial scale for the separation of RE metals. 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) is an acidic organophosphorus extractant and has been widely used in solvent extraction of lanthanides industry for the separation and purification of the metal ions.

In separation process of RE metals, most of the RE metals are separated by solvent extraction and only cerium (Ce) is recovered by precipitation. The extraction equilibrium of Ce is not fully studied relative to other RE metals.

A number of fundamental studies of RE solvent extraction have been carried out under low metal concentrations and relatively low extractant concentration. However, practical metal extraction on a commercial scale is usually conducted under high concentrations of metal extractant. There are not many studies on extraction equilibrium analysis of RE metals in high metal concentration and high extractant concentration. Nakamura used lanthanum (La) hydroxide,  $\text{La}(\text{OH})_3$ , as a solute and measured that the

effect of extractant concentration on extraction equilibrium. [2] Mori et al. reported that in the region of high extractant concentration, the extraction reaction was quite different from those in the region of relatively low extractant concentration. [3]

In this study, La and Ce were selected from the RE metals. La is neighboring element of Ce in periodic table and well-studied elements in solvent extraction of RE metals. The extraction equilibrium of La and Ce with PC-88A were studied under various conditions.

### 2. Experimental

**Table 1** shows the experimental conditions of solvent extraction of La and Ce by PC-88A.  $\text{La}(\text{NO}_3)_3$ ,  $\text{La}(\text{OH})_3$  and  $\text{Ce}(\text{NO}_3)_3$  were used as sources of metal ions. Solvesso150 or kerosene was used as a diluent. Solvesso150 is one of the petroleum fractions and contains a high proportion of aromatic hydrocarbons. Kerosene is one of the petroleum fractions and contains a high proportion of alkane. To adjust the pH, solutions of NaOH and  $\text{HNO}_3$  were added to the extraction system. The initial concentrations of metal and extractant were changed.

Same volumes (20ml) of the organic and aqueous solution were poured into a 50ml conical flask with screw cop, and stirred with magnetic stirrer for 24h at  $298 \pm 3\text{K}$  to attain equilibrium. The two phases were then separated by a separating funnel and RE metal concentrations of the aqueous solutions were analyzed by ICP-AES. The metal complex concentration of organic solutions was calculated by material balance. The pH values of the aqueous solutions were measured by pH meter. In this study, the effect of ionic strength of the aqueous solutions on the extraction equilibrium was not considered.

### 3. Results and Discussion

#### 3.1 Precipitation of solid phase and oxidization of Ce

**Figure 1** shows the photographs of the organic and aqueous solutions in separating funnels. When  $\text{La}(\text{OH})_3$  was used with relatively high metal

Table 1 Experimental condition of solvent extraction of La and Ce by PC-88A

Aqueous feed phase		Aqueous solution of La(NO <sub>3</sub> ) <sub>3</sub> , La(OH) <sub>3</sub> , Ce(NO <sub>3</sub> ) <sub>3</sub>	
Volume of aqueous feed phase	$V_{aq}$ [m <sup>3</sup> ]		$2.0 \times 10^{-3}$
Concentration of metal in aqueous feed phase	$[M^{3+}]_0$ [kmol·m <sup>-3</sup> ]	$2.5 \times 10^{-4}$ -0.215	
Initial pH (Adjusting by HNO <sub>3</sub> or NaOH)	$pH_0$ [-]		1 – 13
Organic solvent phase PC-88A diluted by Solvesso150 or kerosene			
Volume of organic solvent phase	$V_{org}$ [m <sup>3</sup> ]		$2.0 \times 10^{-5}$
Concentration of PC-88A in organic solvent phase	$[(RH)_2]_0$ [kmol·m <sup>-3</sup> ]		0.06-0.5
Stirring time	$t$ [h]		24
Temperature	$T$ [K]		$298 \pm 3$

concentration, the solid particles were precipitated in the organic phase to be turbid. [4] When La(NO<sub>3</sub>)<sub>3</sub> or Ce(NO<sub>3</sub>)<sub>3</sub> was used, the solid phase didn't appeared in all cases. When NaOH solution was used to adjust pH in cases with Ce(NO<sub>3</sub>)<sub>3</sub>, the color of both phase changed from colorless to yellow. Since the colors of the solutions containing trivalent and tetravalent Ce are colorless and yellow, respectively, increasing pH made Ce oxidized from trivalent to tetravalent. To prevent oxidization of trivalent Ce, NaOH solution was added to extraction system at contact of solvent phase and aqueous phase. Therefore, it was considered that quantity of oxidized Ce was small and tetravalent Ce wasn't considered.

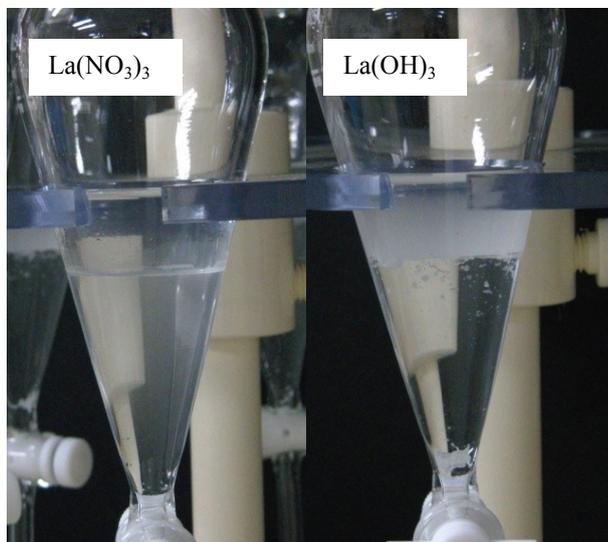


Fig. 1 Photographs of the organic and aqueous solutions in separating funnel

### 3.2 Distribution ratio

In previous studies, the cation exchange reaction has been reported by: [5] (M= RE metal)



$$K_1 = \frac{[MR_3(RH)_3][H^+]^3}{[M^{3+}][(RH)_2]^3} \quad (2)$$

Distribution ratio,  $D$ , is defined by:

$$D = \frac{[MR_3(RH)_3]}{[M^{3+}]} \quad (3)$$

Figures 2 and 3 show that the effect of pH on  $D$  of La and Ce, respectively. RE metals were extracted to the solvent phase and  $D$  of Ce was higher than that of La. Ion radius decreases with an increase of atomic number in lanthanide, and the metal ion of smaller ion radius is easy to make a metal complex because of increase of charge density in the ion[6]. Then Ce was more preferably extracted than La.  $D$  of RE metal increased with pH.

$D$  was larger with kerosene than that with Solvesso150.  $D$  with La(NO<sub>3</sub>)<sub>3</sub> was approximately equal to  $D$  with La(OH)<sub>3</sub> except for the case that solid phase was precipitated. When the system contained both of Ce and La,  $D$  with binary metal system was approximately equal to that with single metal system.

Solute	Diluent	
M(NO <sub>3</sub> ) <sub>3</sub>	Solvesso150	▲
M(NO <sub>3</sub> ) <sub>3</sub>	Kerosene	◆
M(OH) <sub>3</sub>	Solvesso150	▲
La(NO <sub>3</sub> ) <sub>3</sub> + Ce(NO <sub>3</sub> ) <sub>3</sub>	Solvesso150	▲

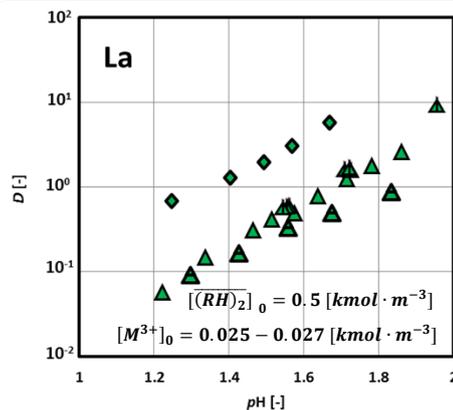


Fig. 2 Effect of pH on the distribution ratio of La

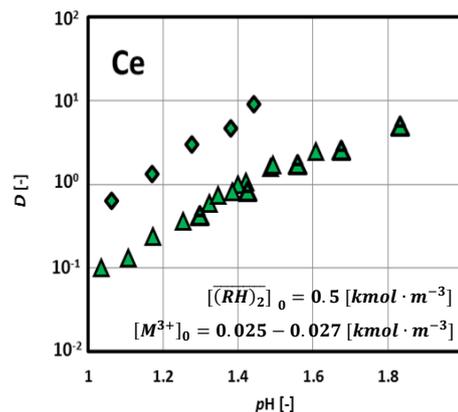


Fig. 3 Effect of pH on the distribution ratio of Ce

From Eq. (2) and Eq. (3),  $D$  is expressed by:

$$D = K_1 \frac{[(RH)_2]^3}{[H^+]^3} \quad (4)$$

Figures 4 and 5 show that the effects of pH on  $D$ s of La and Ce, respectively.  $D$  decreased with an increase in initial metal concentration. With the results in which the initial extractant concentrations were fixed as  $0.5 \text{ kmol} \cdot \text{m}^{-3}$ , the unreacted extractant concentration

decreased with the initial metal concentration at same pH value. Accordingly  $D$  increased with the unreacted extractant concentration, as expressed in Eq.(4).

Solute	$[M^{3+}]_0$ [kmol·m <sup>-3</sup> ]	
M(NO <sub>3</sub> ) <sub>3</sub>	2.5 × 10 <sup>-4</sup>	▲
M(NO <sub>3</sub> ) <sub>3</sub>	0.005	▲
M(NO <sub>3</sub> ) <sub>3</sub>	0.027	▲
M(NO <sub>3</sub> ) <sub>3</sub>	0.055	▲
M(NO <sub>3</sub> ) <sub>3</sub>	0.11	▲
M(NO <sub>3</sub> ) <sub>3</sub>	0.215	▲
M(OH) <sub>3</sub>	0.025	▲
La(NO <sub>3</sub> ) <sub>3</sub> + Ce(NO <sub>3</sub> ) <sub>3</sub>	0.027(respectively)	▲

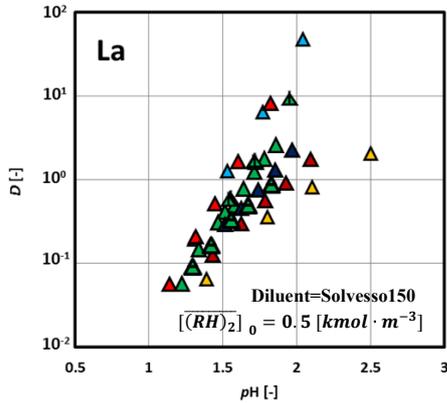


Fig. 4 Effect of pH on the distribution ratio of La

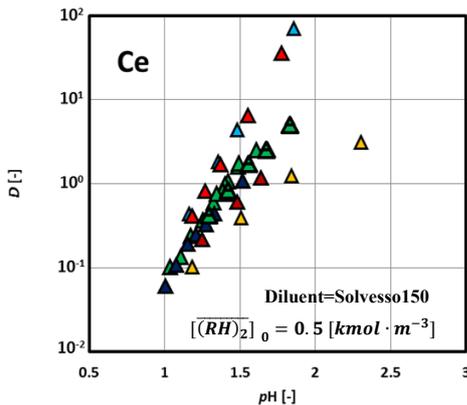


Fig. 5 Effect of pH on the distribution ratio of Ce

### 3.3 Effect of Na on the extraction of La and Ce

PC-88A makes metal complexes with wide variety of metals. The effect of sodium (Na) on the extraction of La and Ce were investigated. The distribution ratio of sodium,  $D$  of Na, is defined by:

$$D = \frac{[NaR(RH)]}{[Na^+]} \quad (5)$$

Figure 6 shows that the effect of pH on  $D$  of Na. Sodium formed metal complexes with PC-88A in the pH range more than 5[7]. The extraction of La and Ce were measured in the pH range from 1 to 2.5.  $D$  of Na is very small in the pH range, and the effects of Na on the extraction of La and Ce might to be small.

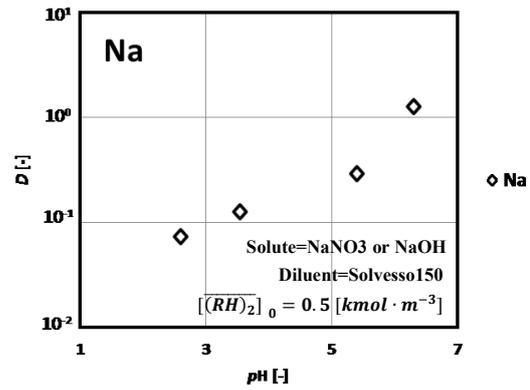


Fig. 6 Effect of pH on the distribution ratio of Na

### 3.4 Effect of $[(HR)_2]$ on $D \cdot [H^+]^3$

Eq. (2) is expressed as below:

$$D \cdot [H^+]^3 = K_1 \cdot [(RH)_2]^3 \quad (6)$$

If the extraction reaction should follow the reaction of Eq. (1),  $D \cdot [H^+]^3$  is proportional to the third power of unreacted extractant concentration. Figures 7 and 8 show that the effect of unreacted extractant concentration on  $D \cdot [H^+]^3$  of La and Ce, respectively. Plots in relatively low unreacted extractant concentration agreed with the line whose slope was 3, but the plots in high unreacted extractant concentration were deviated from the line. This indicated that the extraction reaction should not follow the reaction of Eq. (1) and the additional reaction might occur. It has been reported that in the higher range of extractant concentration, the reaction should require the dimeric species of extractant more than 3 to form complex in the organic phase[3]. In this study, the extraction reaction was not fully clarified in high extractant concentration region.

Solute	$[M^{3+}]_0$ [kmol·m <sup>-3</sup> ]	$[(RH)_2]_0$ [kmol·m <sup>-3</sup> ]	
M(NO <sub>3</sub> ) <sub>3</sub>	2.5 × 10 <sup>-4</sup>	0.5	▲
M(NO <sub>3</sub> ) <sub>3</sub>	0.005	0.5	▲
M(NO <sub>3</sub> ) <sub>3</sub>	0.027	0.5	▲
M(NO <sub>3</sub> ) <sub>3</sub>	0.055	0.5	▲
M(NO <sub>3</sub> ) <sub>3</sub>	0.11	0.5	▲
M(NO <sub>3</sub> ) <sub>3</sub>	0.215	0.5	▲
M(OH) <sub>3</sub>	0.025	0.5	▲
La(NO <sub>3</sub> ) <sub>3</sub> + Ce(NO <sub>3</sub> ) <sub>3</sub>	0.027(respectively)	0.5	▲
M(NO <sub>3</sub> ) <sub>2</sub>	0.055	0.06, 0.08, 0.1, 0.3	■

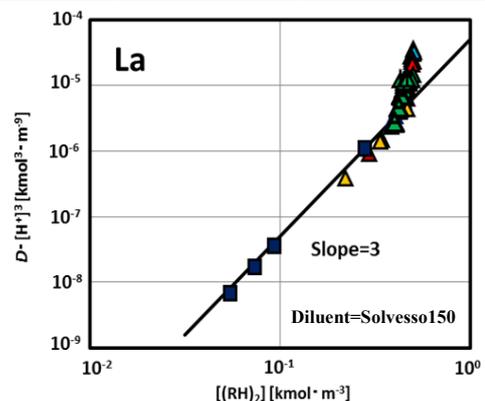


Fig. 7 Effect of  $[(HR)_2]$  on  $D \cdot [H^+]^3$  of La

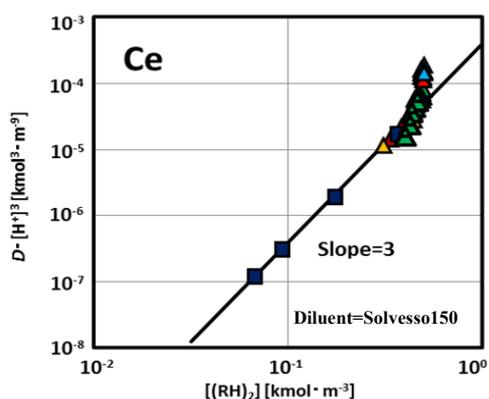


Fig. 8 Effect of  $[(RH)_2]$  on  $D \cdot [H^+]^3$  of Ce

### 3.5 Extraction equilibrium constant

Table 2 shows the extraction equilibrium constants of La and Ce.  $K_1$  could be obtained by the intercepts of the line whose slopes were 3 in Fig. 7 and Fig. 8.  $K_1$  of Ce was larger than that of La.  $K_1$  with kerosene was larger than that of Solvesso150.

Table 2  $K_1$  of La and Ce

Diluent	La	Ce
Solvesso150	$5.0 \times 10^{-5}$	$4.0 \times 10^{-4}$
Kerosene	$4.7 \times 10^{-4}$	$3.5 \times 10^{-3}$

### 3.6 Separation Factor

Separation Factor,  $\beta$ , is defined by:

$$\beta = \frac{D_{Ce}}{D_{La}} = \frac{K_{1,Ce}}{K_{1,La}} \quad (7)$$

Table 3 shows the separation factor.  $\beta$  is calculated by using  $K_1$  of La and Ce.  $\beta$  with Solvesso150 was approximately equal to that with kerosene.

Table 3 Separation factor,  $\beta$

Diluent	Separation factor, $\beta$
Solvesso150	7.94
Kerosene	7.59

## 4 Conclusion

Rare earth metals were extracted to the solvent phase and cerium was more preferable extracted than lanthanum. The distribution ratio increased with  $pH$  and unreacted extract concentration.

Effect of difference of diluent on the distribution ratio was observed, but effect of difference of diluent on the separation factor was not observed.

Effect of difference of anion ion of solute on the distribution ratio was not observed.

In the distribution ratio of both rare earth metals, the distribution ratio with binary metal system was approximately equal to distribution ratio with single metal system.

The extraction equilibrium was followed the reaction reported in previous studies except in high extractant concentration.

## Acknowledgement

PC-88A was supplied by daihachi chemical

industry corporation. .

## Nomenclature

$\beta$	=separation factor	[-]
$D$	=distribution ratio	[-]
$(RH)_2$	=dimeric species of extractant	[-]
[ ]	=molarity of the species in the bracket	[kmol · m <sup>-3</sup> ]
$K_1$	=extraction equilibrium constant	[-]
<Subscripts>		
0	=aqueous or organic feed solution	
aq	=aqueous phase	
org	=organic phase	
M	=Rare earth metal	
Na	=Sodium	
La	=Lanthanum	
Ce	=Cerium	
<Superscripts>		
—	=organic phase species	

## References

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