

# Effect of operating condition on solvent extraction of La with PC-88A

Student Number: 08\_18048 Name: Kazuma NAKAMURA Supervisor: Ryuichi EGASHIRA, Hiroaki HABAKI

## 1. Introduction

Rare earth metals are mainly used as raw materials for high purity individual rare earth chemicals. Lanthanide elements have major applications in magnets, ceramics, electronics, nuclear technology and so on [1].

Solvent extraction is well known as an effective method for separation of lanthanides on the industrial scale. Due to the growing demand of high purity metals with the developing high-technology industry, establishing the more effective operating condition of solvent extraction is needed. 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) is an acidic organophosphorus extractant. PC-88A has been widely used in solvent extraction of lanthanides industry for the separation and purification of the metal ions. However in the previous studies the concentration ranges of rare-earth metals and extractant were much lower than those used in the industrial scale. The rare-earth metal concentrations were so low relative to those of extractant in organic phases that it was assumed that the free extractant concentration could not be affected by the metal extraction. Nishihama et al. [2] reported that in the high concentration region, the extraction reaction was quite different from those in the low concentration ranges.

In the present work, solvent extraction of La with PC-88A is studied. La was selected from the rare-earth metals and the extraction equilibrium of La between the organic phases of PC88A and the aqueous phases in which the proton concentration was adjusted. Moreover the effects of La concentration in the system on the extraction equilibrium were also studied.

## 2. Experimental

Table1 shows the experimental conditions for distribution equilibrium measurements. The organic solutions were prepared by diluting PC-88A with solvesso150. Solvesso150 is one of the petroleum fractions, rich in aromatic hydrocarbons. The aqueous solution of nitric acid was used as the aqueous phases. La hydroxide was used as La source.

The solute, aqueous and organic phases were put into 50ml conical flasks with screw cop, and stirred with magnetic stirrer for 24h. The two phases were then separated with a separating funnel and the obtained aqueous solutions were analyzed by ICP-AES.

Table1 Experimental condition of La hydroxide extraction

Solute	La(OH) <sub>3</sub>	
Aqueous phase	Aqueous solution of HNO <sub>3</sub>	
Organic phase	Organic solution (solvesso150) of PC-88A	
Mole load relative to aqueous phase	$C_{La,org,0}$ [kmol/m <sup>3</sup> ]	0, 0.1, 0.05, 0.025
Concentration of nitric acid in aqueous phase .	$C_{NA,org,0}$ [kmol/m <sup>3</sup> ]	0~0.175
Concentration of PC-88A in organic phase	$C_{RH,org,0}$ [kmol/m <sup>3</sup> ]	0.5, 1.0
Volume of aqueous phase	$V_{aq}$ [m <sup>3</sup> ]	$2.0 \times 10^{-4}$
Volume of organic phase	$V_{org}$ [m <sup>3</sup> ]	$2.0 \times 10^{-4}$
Stirring time	$t$ [h]	24
Stirring speed	$v$ [h <sup>-1</sup> ]	60,000

## 3. Results and Discussion

### 3.1 Solvent extraction of La hydroxide

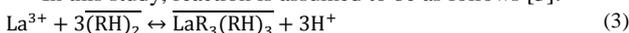
The extraction degree,  $E$ , is given by:

$$E = \frac{C_{La,org}}{C_{La,org} + C_{La,org,0}} = \frac{D}{1+D} \quad (1)$$

Distribution ratio,  $D$ , is defined by:

$$D = \frac{C_{La,org}}{C_{La,org,0}} \quad (2)$$

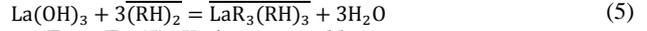
In this study, reaction is assumed to be as follows [3]:



where  $(RH)_2$  is extractant dimer, and  $\overline{LaR_3(RH)_3}$  is extracted species.  $C_{RH,org}$  is an extractant concentration as dimer.

Dissolution of La hydroxide in water is written as follows:  
 $La(OH)_3 = La^{3+} + 3OH^- \quad (4)$

From Eqs (3) and (4), we have Eq (5):



From Eq (5),  $K_{ex}$  is expressed by:

$$K_{ex} = \frac{C_{La,org} \times C_{H,org}^3}{C_{La,org,0} \times C_{RH,org}^3} = D \times \frac{C_{H,org}^3}{C_{RH,org}^3} \quad (6)$$

From Eq (3), concentration of free extractant,  $C_{RH,org}$ , expressed by:

$$C_{RH,org} = C_{RH,org,0} - 3C_{La,org} \quad (7)$$

The effect of initial and equilibrium  $H^+$  concentration,  $C_{H,org}$ , on the extraction degree,  $E$ , is shown in Fig.1. Fig.2 shows the effect of nitric acid concentration,  $C_{NA,org}$ , on the extraction degree. All La hydroxide was extracted with aqueous solution of no nitric acid and the organic phase of  $C_{RH,org,0}=0.5\text{kmol/m}^3$  could extract all La in case of  $C_{La,org,0}=0.1\text{kmol/m}^3$ .

$C_{H,org}$  increased after the extraction but Eq(5) means that  $C_{H,org}$  isn't change before and after the extraction. This change may be because of PC-88A dissolved in aqueous phase. The effect of organic phase contact with water is shown in Table2. This result means that  $C_{H,org}$  is decrease without extraction.

Table2 The effect of PC-88A dissolution in  $2.0 \times 10^{-4} \text{m}^3$  water

Organic phase	$C_{H,org}$
PC-88A $0.02(\text{kmol/m}^3)$	2.77
PC-88A $0.02(\text{kmol/m}^3)$ + solvesso150 ( $2.0 \times 10^{-4} \text{m}^3$ )	2.84

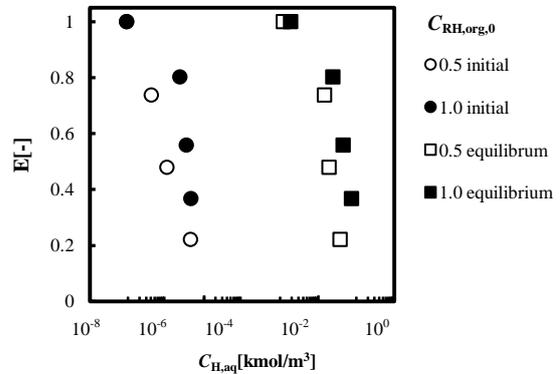


Fig.1 Effect of initial and equilibrium  $C_{H,org}$  on the extraction degree.  $C_{La,org,0}=0.1 \text{ kmol/m}^3$ ,  $C_{RH,org,0}=0.5, 1.0 \text{ kmol/m}^3$

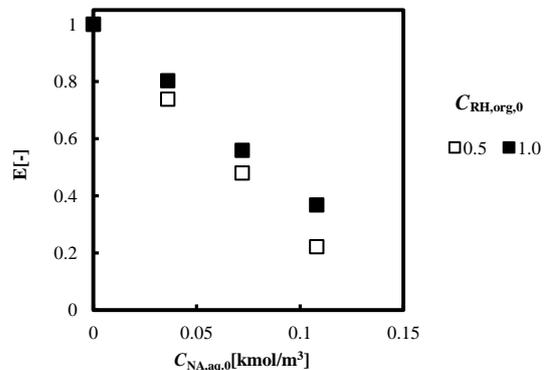


Fig.2 Effect of nitric acid concentration on the Extraction degree.  $C_{La,org,0}=0.1 \text{ kmol/m}^3$ ,  $C_{RH,org,0}=0.5, 1.0\text{kmol/m}^3$

### 3.2 Measurement of extraction equilibrium constant

**Fig.3** shows the effect of free extractant concentration on  $K_{ex}$ . When the free extractant concentration was lower than  $0.3\text{ kmol/m}^3$ ,  $K_{ex}$  was not constant. In the range of  $C_{RH,org} > 0.3\text{ kmol/m}^3$ ,  $K_{ex}$  was almost constant but the value was affected by La concentration.

**Fig.4** shows the slope analysis method to determine  $K_{ex}$  at each La concentration.  $K_{ex}$  could be obtained by the intercepts of the line of which slope is 3 and pass the all plot. In **Fig.4**, Eq(3) was assumed to be able to apply each conditions where  $K_{ex}$  are constant. The obtained  $K_{ex}$  are listed in **Table3**.

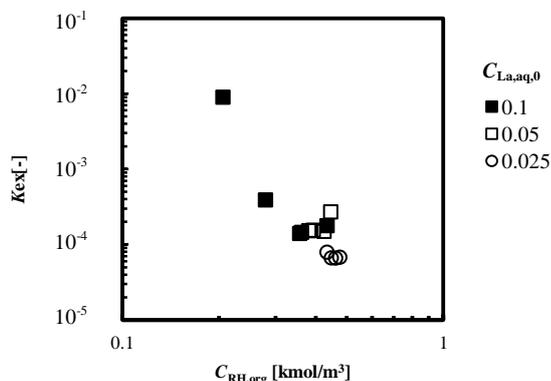


Fig.3 Effect of free extractant concentration on the extract equilibrium constant.  $C_{RH,org,0} = 0.5\text{ kmol/m}^3$ ,  $C_{La,aq,0} = 0.1, 0.05, 0.025\text{ kmol/m}^3$

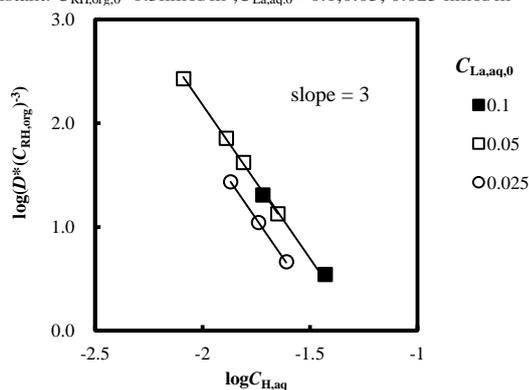


Fig.4 Determination of  $K_{ex}$  by using of slope analysis method.  $C_{RH,org,0} = 0.5\text{ kmol/m}^3$ ,  $C_{La,aq,0} = 0.1, 0.05, 0.025\text{ kmol/m}^3$

Table3

Extraction equilibrium constants at each feed La concentration

$C_{La,aq,0}$ [kmol/m <sup>3</sup> ]	intercepts	$K_{ex}$ [-]
0.1	3.81	$1.55 \times 10^{-4}$
0.05	3.83	$1.48 \times 10^{-4}$
0.025	4.18	$6.61 \times 10^{-4}$

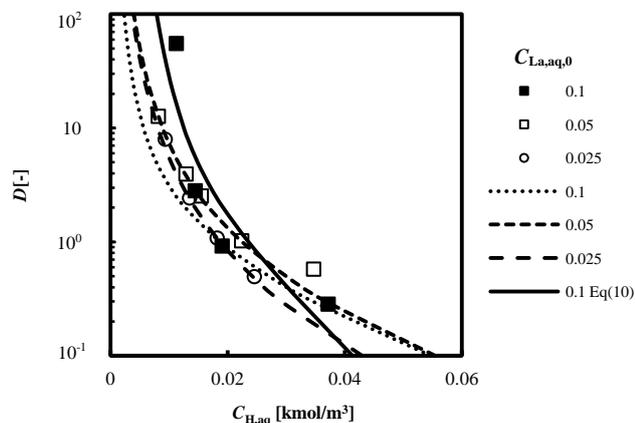


Fig.5 Effect of hydrogen ion concentration on the distribution ratio. The comparison of observed distribution ratio (plot) with predicted distribution ratio (broken and dotted line).

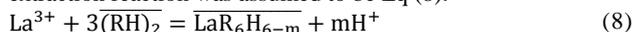
$C_{RH,org,0} = 0.5\text{ kmol/m}^3$ ,  $C_{La,aq,0} = 0.1, 0.05, 0.025\text{ kmol/m}^3$

From Eq (6) and (7), the distribution ratio at each hydroxide concentration, could be predicted by  $C_{La,aq,0}$  and  $C_{RH,org,0}$ .

The measured distribution ratios and the predicted distribution ratios obtained by using of the value of  $K_{ex}$  in **Table3** are shown in **Fig.5**.

The predicted distribution ratio could express the measured data well when  $C_{La,aq,0} = 0.05\text{ kmol/m}^3$  and  $0.025\text{ kmol/m}^3$ , but when  $C_{La,aq,0} = 0.1\text{ kmol/m}^3$ , it cannot express all distribution ratio.

To express the distribution ratio of  $C_{La,aq,0} = 0.1\text{ kmol/m}^3$ , the extraction reaction was assumed to be Eq (8).



**Fig.6** shows the slope analysis method to determine  $m$  and  $K_{ex}$  in Eq(8).

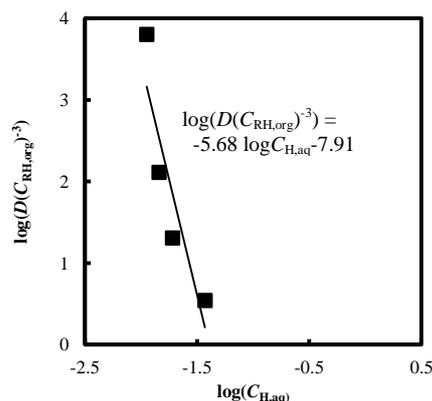


Fig.6 Determine of  $K_{ex}$  and  $m$  by using of the slope analysis method

$C_{La,aq,0} = 0.1\text{ kmol/m}^3$ ,  $C_{RH,org,0} = 1.0\text{ kmol/m}^3$

**Fig.6** shows that  $K_{ex}$  is  $10^{-7.91}$  and  $m = 5.68$ . The solid line in **Fig.5** compares the predicted obtained from **Fig.4** and **Fig.6** with measured data. **Fig.5** shows that the prediction line obtained from **Fig.6** (solid line) can express the measured plot better than that of from **Fig.4** (dotted line).

### 4. Conclusions

Extraction La hydroxide with PC-88A by using of solvent extraction was achieved.  $0.5\text{ kmol/m}^3$  PC-88A was appropriate to extract  $0.1\text{ kmol/m}^3$  feed La hydroxide and nitric acid for pH control was unnecessary.

The ratio of free extractant may have relation to the extraction reaction. And concentration of feed La has relation to the extraction equilibrium constant.

### Nomenclature

$C_i$	= concentration of $i$	[kmol/m <sup>3</sup> ]
$K_{ex}$	= extraction equilibrium constant	[-]
$E$	= extraction degree	[-]
$D$	= distribution ratio	[-]
$(\text{RH})_2$	= dimeric species of extractant	[kmol/m <sup>3</sup> ]
<Subscripts>		
0	= aqueous or organic feed solution	
aq	= aqueous phase	
org	= organic phase	
<Superscripts>		
—	= organic phase species	

### References

- [1] S. Radhika, B. Nagaphani Kumar, M. Lakshmi Kantam, B. Ramachandra Reddy, Liquid-Liquid extraction and separation possibilities of heavy and light rare-earth from phosphoric acid solutions with acidic organophosphorus reagents, Separation and Purification Technology 75(2010)295-302
- [2] Syouhei Nishihama, Takayuki Hirai, Isao Komasa, Design of Liquid-Liquid Extraction Process for Separation of Metal ions, KAGAKU KOGAKU RONBUNSHU, 26(2000)497-505
- [3] Hsiang-Chien Kao, Pei-Shin Yen, Ruey-Shin Juang, Solvent extraction of La(III) and Nd(III) from nitrate solutions with 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester, Chemical Engineering journal, 119(2006)167-174