

# Solvent Extraction of Rare Earth Metals by a Continuous Stirred Vessel

Student Number: 13M18184 Name: Takehiko YAZAKI Supervisor: Ryuichi EGASHIRA

## 連続式攪拌槽を用いた希土類金属の溶媒抽出

矢崎 健彦

まずPC-88Aを抽出剤として塩酸水溶液-ケロシン間におけるネオジウム、ジスプロシウム、鉄の液液平衡を実測し、これらの抽出平衡定数を求めた。ついで同様の物質系において原料水相を連続相、溶媒油相を分散相として標準型の攪拌槽による金属の連続抽出を行った。攪拌速度の増加や水相流量の減少に伴い液液接触界面積は増加し、抽出速度も増加した。また各金属の物質移動係数を求め、分配比が大きい条件では水相(連続相)側の物質移動抵抗が支配的であることを確認した。

### 1.Introduction

Rare earth metals are industrially useful and applied to advanced technologies in many fields. Since these metals are found in resource as a mixture, they should be separated into each other. Solvent extraction is presently one of the commercialized techniques for the separation, and a number of fundamental studies of solvent extraction for rare earth metal separation have been conducted, in which the reaction equilibrium of respective rare earth metals with various kinds of extractants were mainly discussed. For the practical use of this method on industrial scale, the multi-stage stirred vessel is commonly utilized as a contacting equipment. So the information of extraction rate is necessary for effective operation, however, only few studies of the extraction rate of rare earth metals using continuous stirred vessel have been reported.

In this work, the extraction rates of metal ions by stirring vessel were studied, in which neodymium (Nd), dysprosium (Dy) and iron (Fe) were selected as model metals of light rare earth, heavy rare earth and impurity metals occurring in separation process of rare earth metals respectively. Firstly the extraction equilibrium of metals was confirmed in a batch-wise run. In the second, the continuous extractions of metals with stirred vessel were carried out under various experimental conditions, and the effects of these conditions on liquid-liquid dispersion, extraction rate and yield were studied. Finally, the mass transfer coefficients of the metal ions were estimated based on these experimental results, and the contribution of the local mass transfer resistances to the overall resistance was studied.

### 2.Experimental

#### 2.1.Extraction equilibrium

The material systems and experimental conditions are shown in Tables 1 and 2. Chloride hexahydrate of Nd, Dy and Fe were used as a metal ion sources. 2-Ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) was used as an extractant, without further purification. This extractant was diluted by kerosene to be an organic phase. Hydrochloric acid was used to adjust pH in the aqueous feed solution.

In batch-wise extraction, the specified amounts of feed and solvent phases in a flask of  $5.0 \times 10^{-5} \text{ m}^3$  were shaken in a constant temperature bath at 298 K for 12 hours to be equilibrated and these liquid phases were separated by separating funnel. The metal concentrations and pH in the aqueous phases were

determined by ICP-AES (SPS7800, SII Nano Technology) and pH meter (Horiba, F-52), respectively.

#### 2.2.Continuous extraction

The experimental conditions of the continuous extraction with stirred vessel are listed in Table 3. The material systems were the same as used in the extraction equilibrium measurements as Table 1.

An experimental apparatus of the continuous extraction operation is schematically shown in Fig.1. A standard type stirred vessel of 0.08 m inner diameter and height with baffles was used as a contactor. A six flat blade paddle impeller of 0.05 m diameter was equipped at the center of the vessel. The volume as a reactor inside the vessel is  $V = 3.85 \times 10^{-6} \text{ m}^3$ . The stirred vessel was immersed in the constant temperature bath to keep the temperature of the liquids in the vessel constant. After the aqueous feed phase was provided to fill up the vessel, the supply of the organic solvent phase and the stirring were started to begin the continuous run with oil in water (O/W) type dispersion. While the feed and solvent phases separately entered through the inlets at the bottom of the vessel, the raffinate and extract phases after the extraction was obtained together through the top outlet. The flow rates of the feed and solvent phases were monitored by rotameters, and adjusted to proper values by valves. The flow rates at exit were estimated by measuring the volumes of the phases over the defined period. The obtained raffinate solutions were analyzed in the same way as used in the measurements of extraction equilibrium to determine the metal concentrations and pH.

The liquid-liquid dispersion in the stirred vessel, which should affect mass transfer, was also studied in terms of the drop size and the holdup of the dispersed phase. The drop diameters of the organic dispersed phase were measured as follows: a portion of O/W type liquid-liquid dispersion in the vessel was sampled during the run into an appropriate aqueous hydrophilic surfactant solution prepared in a pipette to avoid the coalescence of the organic phase drops; this surfactant solution containing the drops was microphotographed; and the numbers of the drops of the respective diameter ranges were counted from among the 200 ~ 300 drops on the photograph to estimate the mean diameter and the distribution. At the end of the experimental run, the valves at the inlets of the vessel were closed simultaneously and the volumes of the liquid phases retained in the vessel were measured. From these

volumes, the holdup of the dispersed phase, the volume ratio of dispersed phase relative to total liquid in the vessel, was determined.

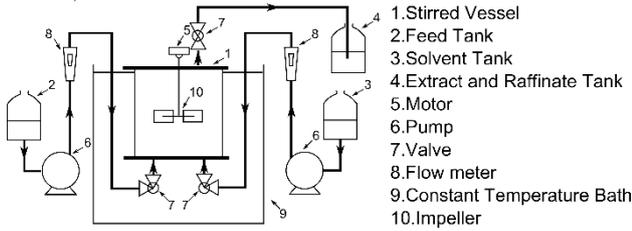


Fig.1 Schematic diagram of experimental system for continuous extraction

Table 1 Material system

Solute in aqueous phase	NdCl <sub>3</sub> 6H <sub>2</sub> O DyCl <sub>3</sub> 6H <sub>2</sub> O FeCl <sub>3</sub> 6H <sub>2</sub> O
Extractant	PC-88A
Aqueous phase	Aqueous solution of HCl
Organic phase	Kerosene solution of PC-88A

Table 2 Experimental conditions of batch-wise extraction

Concentration of metal in initial aqueous phase, $C_{M,eq,0}$ [kmol/m <sup>3</sup> ]	$5.0 \times 10^{-3}$
Concentration of PC-88A in initial organic phase, $C_{RH_2,org,0}$ [kmol/m <sup>3</sup> ]	0.25
pH of initial aqueous phase, $pH_0$	0.1~3.0 (Nd) -0.3~3.0 (Dy) -0.3~0.6 (Fe)
Temperature, $T$ [K]	298
Volume of aqueous phase, $V_{aq}$ [m <sup>3</sup> ]	$2.0 \times 10^{-6}$
Volume of organic phase, $V_{org}$ [m <sup>3</sup> ]	$2.0 \times 10^{-6}$

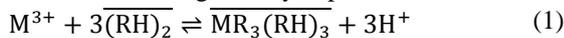
Table 3 Experimental conditions of continuous extraction

Concentration of metal in aqueous feed, $C_{M,aq,in}$ [kmol/m <sup>3</sup> ]	$5.0 \times 10^{-3}$
Concentration of PC-88A in organic solvent, $C_{RH_2,org,in}$ [kmol/m <sup>3</sup> ]	0.25
pH of aqueous feed, $pH_{in}$	1.2~2.5 (Nd) 0.6~1.8 (Dy) 0.3 (Fe)
Temperature, $T$ [K]	298
Volume flow rate of aqueous feed, $Q_{aq,in}$ [m <sup>3</sup> /h]	$6.3 \times 10^{-3} \sim 13.0 \times 10^{-3}$
Volume flow rate of organic solvent, $Q_{org,in}$ [m <sup>3</sup> /h]	$3.0 \times 10^{-6}$
Stirring velocity, $n$ [1/h]	$1.8 \times 10^4 \sim 5.7 \times 10^4$

### 3. Results and Discussion

#### 3.1. Extraction equilibrium

The extraction reaction of trivalent lanthanides and iron ion with PC-88A is generally expressed as



where  $M^{3+}$  and  $(RH)_2$  represent the metal ion and PC-88A dimer, respectively, and symbols with overbar express species in organic phase. The reaction equilibrium constant,  $K_{ex,M}$ , is thus, described as,

$$K_{ex,M} = \frac{C_{M,org,eq} C_{H^+,aq,eq}^3}{C_{M,aq,eq} C_{RH_2,org,eq}^3} = m_M \frac{C_{H^+,aq,eq}^3}{C_{RH_2,org,eq}^3} \quad (2)$$

The distribution ratio,  $m_M$ , was defined as,

$$m_M = \frac{C_{M,org,eq}}{C_{M,aq,eq}} \quad (3)$$

The arrangement of this equation leads to,

$$\log m_M - 3 \log C_{RH_2,org,eq} = 3pH_{eq} + \log K_{ex,M} \quad (4)$$

The metal and extractant concentrations in the organic phases were estimated by the material balance relationships with the metal concentration in the aqueous phase. Figure 2 shows the plots of the left side in Eq. (4)

against  $pH_{eq}$ . The values of the left side in Eq. (4) increased in the order of Nd, Dy and Fe. The plots for each metal ion increased linearly with  $pH_{eq}$  with slope 3. In these measurement ranges, the extraction reaction followed Eq. (1). Then  $K_{ex,M}$  of each metal ion was estimated by the intercept of the lines, drawn in Fig. 2 as solid lines, and these values are listed in Table 2. That of Fe was the largest, that is, Fe should be extracted most, followed by Dy and Nd.

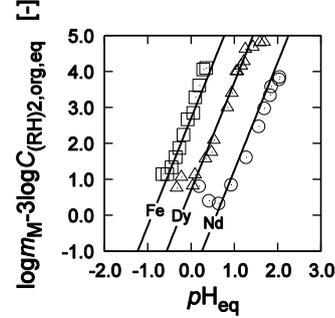


Fig. 2 Relation among pH of aqueous raffinate, distribution ratio and concentration of extractant of organic extractant.

Table 5 Experimental extraction equilibrium constants,  $K_{ex,M}$

Metal	Extraction equilibrium constant, $K_{ex,M}$
Neodymium (Nd)	$1.8 \times 10^{-2}$
Dysprosium (Dy)	1.9
Iron (Fe)	$5.0 \times 10^2$

#### 3.2. Continuous extraction

##### 3.2.1. Liquid-liquid dispersion

In all experiments of continuous extraction, the system attained the steady state within 5 minutes and the liquid-liquid extraction could be stably operated. The volume flow rates of inlet and outlet solutions were same in all cases, and the volume flow rates of aqueous and organic phases could be represented as  $Q_{aq} = Q_{aq,in} = Q_{aq,out}$  and  $Q_{org} = Q_{org,in} = Q_{org,out}$ , respectively.

The holdup of the dispersed phase to the total volume,  $\phi$ , sauter mean diameter of the dispersed drops,  $d_{32}$ , and the specific interfacial area,  $a$ , were estimated as,

$$\phi = V_d/V \quad (5)$$

$$d_{32} = \sum_l l d^3 / l d^2 \quad (6)$$

$$a = 6\phi/d_{32} \quad (7)$$

where  $V_d$ ,  $V$  and  $d$  represent the volume of dispersed phase, total volume, and diameter of dispersed drops. Figure 3 shows the effects of stirring velocity,  $n$ , and  $Q_{aq}$  on  $\phi$ . The  $\phi$  increased as  $n$  increased and  $Q_{aq}$  decreased. In the lower range of  $n$ , the mixing was insufficient to cause low  $\phi$ . As  $n$  increased, the flow pattern in the vessel approached to the perfect mixing condition and  $\phi$  attained the ratio of the organic flow rate relative to the total flow rate: 0.25 ( $=Q_{org}/(Q_{aq} + Q_{org})$ ). Figure 4 shows the effects of  $n$  and  $Q_{aq}$  on sauter mean diameter of dispersed phase,  $d_{32}$  at fixed  $Q_{aq}$ . The  $d_{32}$  decreased as  $n$  or  $Q_{aq}$  increased. These tendencies were reported in the previous studies of liquid-liquid dispersion [1]. Figure 5 shows the effects of  $n$  and  $Q_{aq}$  on  $a$ . The  $a$  increased as  $n$  increased, and was less influenced by  $Q_{aq}$ , since  $d_{32}$  decreased as  $n$  and  $Q_{aq}$  increased, but  $\phi$  decreased as  $Q_{aq}$  increased. The metal species or  $pH$  in the aqueous solution had little effect on  $\phi$ ,  $d_{32}$  and  $a$ .

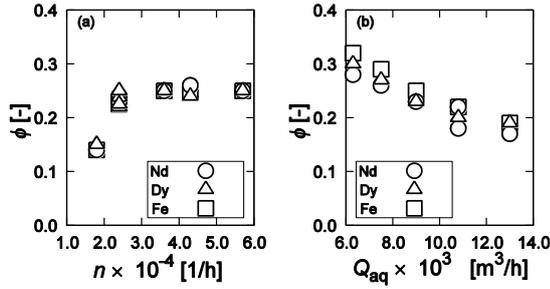


Fig. 3 (a) The effect of stirring velocity on holdup. Conditions:  $Q_{aq}=9.0 \times 10^{-3} \text{ m}^3/\text{h}$ ,  $pH_{in}=2.0$  (Nd),  $pH_{in}=1.0$  (Dy),  $pH_{in}=0.3$  (Fe). (b) The effect of volume flow rate of aqueous phase on holdup. Conditions:  $n=2.4 \times 10^4 \text{ 1/h}$  (Nd,Dy),  $n=3.6 \times 10^4 \text{ 1/h}$  (Fe),  $pH_{in}=1.2 \sim 2.0$  (Nd),  $pH_{in}=0.6 \sim 1.8$  (Dy),  $pH_{in}=0.3$  (Fe)

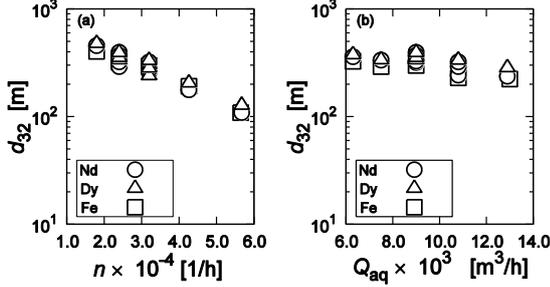


Fig. 4 (a) The effect of stirring velocity on the mean drop diameter of dispersed phase. Conditions:  $Q_{aq}=9.0 \times 10^{-3} \text{ m}^3/\text{h}$ ,  $pH_{in}=1.2 \sim 2.0$  (Nd),  $pH_{in}=0.6 \sim 1.8$  (Dy),  $pH_{in}=0.3$  (Fe). (b) The effect of volume flow rate of aqueous phase on the mean drop diameter of dispersed phase. Conditions:  $n=2.4 \times 10^4 \text{ 1/h}$  (Nd,Dy),  $n=3.6 \times 10^4 \text{ 1/h}$  (Fe),  $pH_{in}=1.2 \sim 2.0$  (Nd),  $pH_{in}=0.6 \sim 1.8$  (Dy),  $pH_{in}=0.3$  (Fe)

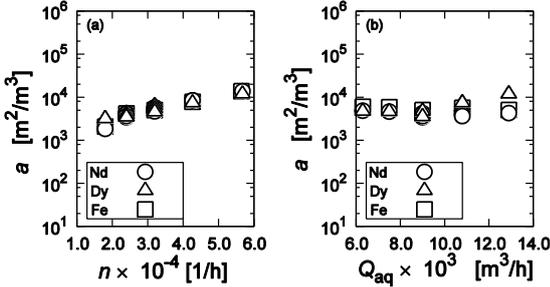


Fig. 5 (a) The effect of stirring velocity on the specific interfacial area. Conditions:  $Q_{aq}=9.0 \times 10^{-3} \text{ m}^3/\text{h}$ ,  $pH_{in}=1.2 \sim 2.0$  (Nd),  $pH_{in}=0.6 \sim 1.8$  (Dy),  $pH_{in}=0.3$  (Fe). (b) The effect of volume flow rate of aqueous phase on the specific interfacial area. Conditions:  $n=2.4 \times 10^4 \text{ 1/h}$  (Nd,Dy),  $n=3.6 \times 10^4 \text{ 1/h}$  (Fe),  $pH_{in}=1.2 \sim 2.0$  (Nd),  $pH_{in}=0.6 \sim 1.8$  (Dy),  $pH_{in}=0.3$  (Fe)

### 3.2.2. Extraction rate

Extraction rate of metal M,  $R_M$ , is expressed as,

$$R_M = Q_{org,out} C_{M,org,out} - Q_{org,in} C_{M,org,in} \quad (8)$$

Figure 6 shows the effect of  $n$  and  $Q_{aq}$  on  $R_M$ . The  $R_M$ s of Dy and Nd increased as  $n$  and  $Q_{aq}$ . As mentioned above,  $a$  increased with  $n$  to enhance the extraction. While  $Q_{aq}$  had little influence on  $a$ ,  $C_{M,org,out}$  increased with  $Q_{aq}$  to make  $C_{M,org,out}$  larger, as a consequence causing larger  $R_M$ . The  $R_M$  of Fe decreased as  $Q_{aq}$ . These results indicate that the extraction rates of Dy or Nd, and Fe were controlled by the diffusion and chemical reaction steps, respectively, as reported in the previous study[2,3]. Figure 7 shows the effect of  $pH$  in the aqueous feed,  $pH_{in}$ , on  $R_M$ . The  $R_M$ s of Dy and Nd increased with  $pH_{in}$  because the extraction reaction should be enhanced with an increase in  $pH_{in}$ , as shown in Fig. 2.

### 3.2.3. Yield

Yield of metal M,  $Y_M$  is defined as,

$$Y_M = \frac{Q_{org,out} C_{M,org,out}}{Q_{org,in} C_{M,org,in}} \quad (9)$$

Figures 8 and 9 show the effects of the operating conditions on  $Y_M$ .  $Y_M$  increased with an increase in  $n$  or  $pH_{in}$  because  $R_M$  increased as these values. The  $Y_M$  decreased as  $Q_{aq}$  increased because the residence time of solution decreased.

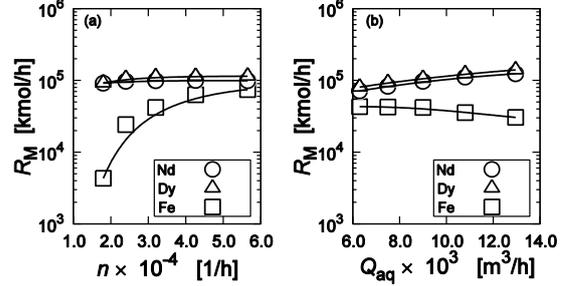


Fig. 6 (a) Effect of stirring velocity on the extraction rate. Conditions:  $Q_{aq}=9.0 \times 10^{-3} \text{ m}^3/\text{h}$ ,  $pH_{in}=2.0$  (Nd),  $pH_{in}=1.0$  (Dy),  $pH_{in}=0.3$  (Fe). (b) Effect of volume flow rate of aqueous solution on the extraction rate or yield of several metals. Conditions:  $n=2.4 \times 10^4 \text{ 1/h}$  (Nd,Dy),  $n=3.6 \times 10^4 \text{ 1/h}$  (Fe),  $pH_{in}=2.0$  (Nd),  $pH_{in}=1.0$  (Dy),  $pH_{in}=0.3$  (Fe)

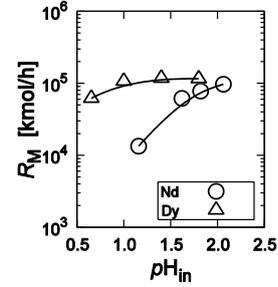


Fig. 7 Effect of  $pH$  in the aqueous feed on the extraction rate. Conditions:  $n=2.4 \times 10^4 \text{ 1/h}$ ,  $Q_{aq}=9.0 \times 10^{-3} \text{ m}^3/\text{h}$ .

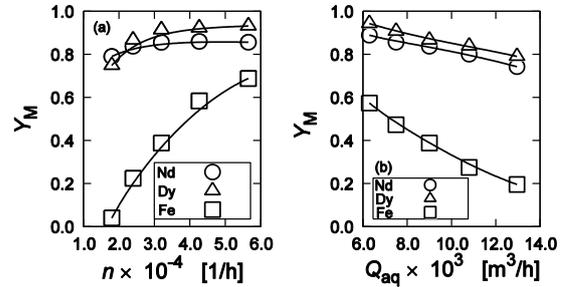


Fig. 8 (a) Effect of stirring velocity on the yield. Conditions:  $Q_{aq}=9.0 \times 10^{-3} \text{ m}^3/\text{h}$ ,  $pH_{in}=2.0$  (Nd),  $pH_{in}=1.0$  (Dy),  $pH_{in}=0.3$  (Fe). (b) Effect of volume flow rate of aqueous solution on the yield. Conditions:  $n=2.4 \times 10^4 \text{ 1/h}$  (Nd,Dy),  $n=3.6 \times 10^4 \text{ 1/h}$  (Fe),  $pH_{in}=2.0$  (Nd),  $pH_{in}=1.0$  (Dy),  $pH_{in}=0.3$  (Fe)

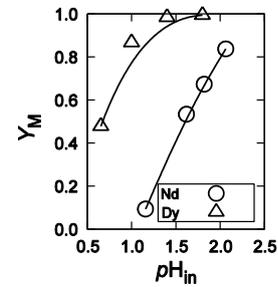


Fig. 9 Effect of  $pH$  in the aqueous feed on the yield. Conditions:  $n=2.4 \times 10^4 \text{ 1/h}$ ,  $Q_{aq}=9.0 \times 10^{-3} \text{ m}^3/\text{h}$ .

### 3.2.4. Experimental mass transfer coefficients

Overall mass transfer coefficients based on the aqueous phase,  $K_{M,aq}$ , was defined as,

$$R_M = K_{M,aq} (C_{M,org,out} - C_{M,org,in} / m_M) aV \quad (10)$$

Here  $m_M$  and  $K_{M,eq}$  were expressed as,

$$m_M = \frac{K_{ex,M} C_{RH2,org,out}^3}{C_{H+,aq,out}^3} \quad (11)$$

$$\frac{1}{K_{M,eq}} = \frac{1}{k_{M,eq}} + \frac{1}{m_M k_{M,org}} \quad (12)$$

where  $k_{M,eq}$  and  $k_{M,org}$  represent the local mass transfer coefficients in the aqueous and organic phase, respectively. Here it was assumed  $k_{M,eq}$  and  $k_{M,org}$  were constant and independent of the operating conditions and metal ion species. Then both coefficients were decided by fitting with all experimental results, and the obtained values were listed in Table 6. The effects of  $m_M$  on  $K_{M,eq}$  is shown in Fig. 10. The solid line is drawn by Eq. (12), and the dotted lines show  $K_{M,eq}$  when the mass transfer resistance lies only in either phase. In the range of large  $m_M$ , the diffusion in the aqueous phase was rate-determined, while in the range of small  $m_M$ , the diffusion in the organic phase was rate-determined.

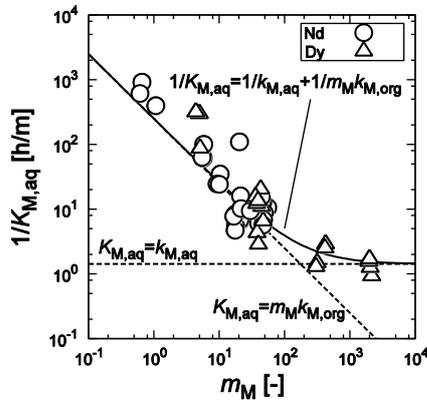


Fig. 10 Relation among distribution ratio and overall mass transfer coefficients based on aqueous phase

### 3.2.5. Theoretical mass transfer coefficients

The mass transfer coefficients in the dispersed drops and continuous phase were estimated by the following general simple models. The local mass transfer coefficients in the continuous and dispersed phases were estimated by the Ranz-Marshall [4] and penetration models [4], expressed as,

$$Sh = 2.0 + 0.6Re^{1/2}Sc^{1/3} \quad (13)$$

$$k_d = -\frac{d}{3t} \ln \left\{ \frac{6}{\pi^2} \sum_l \frac{1}{l^2} \exp \left( -\frac{l^2 \pi^2 D t}{d^2} \right) \right\} \quad (14)$$

where  $Sh$ ,  $Re$  and  $Sc$  are Sherwood, Reynolds and Schmidt numbers, and  $D$  is the diffusion coefficient in the organic phase, calculated by the Wilke-chang equation [4], respectively. The diffusion coefficient of lanthanum in the aqueous phase [5] and the properties of water at 298K are shown in Table 7. The relative velocity of the dispersed drops in the continuous phase was calculated as terminal velocity in gravity field [6]. The association parameter in Wilke-chang equation was set as 1~2, and molecular volume was  $322 \times 10^{-6} \text{ m}^3/\text{mol}$ , cited from the previous study [7]. The properties of the organic phase used for the estimation were listed in Table 8. The theoretical local mass transfer coefficients obtained by these equations were listed in Table 6 together with the results experimentally obtained. The respective  $k_{M,eq}$ s and  $k_{M,org}$ s experimentally and theoretically obtained were almost same as each other. Then the estimation could fully express the extraction rate of these rare earth metals in this

measurement range. This estimation method might be applicable for the design of the extraction vessel for the separation of rare earth metals.

Table 6 Local mass transfer coefficient

	$k_{M,eq}$	$k_{M,org}$
(a)Experimental	$7.0 \times 10^{-1}$	$4.0 \times 10^{-3}$
(b)Theoretical	$1.5 \times 10^{-1}$	$5.4 \times 10^{-3}$

Table 7 Material properties for calculation theoretical  $k_{M,eq}$

Density of aqueous phase, $\rho_{aq}$ [kg/m <sup>3</sup> ]	997
Viscosity of aqueous phase, $\mu_{aq}$ [mPa/s]	0.89
Diffusion coefficient in aqueous phase, $D_{aq}$ [m <sup>2</sup> /s]	$6.2 \times 10^{-10}$

Table 8 Material properties for calculation theoretical  $k_{M,org}$

	PC-88A	Kerosene
Molar weight [kg/mol]	0.31	0.28
Viscosity [mPa/s]	35	2.3

## 4. Conclusion

In the case of batch-wise extraction, metals were largely extracted in large  $pH$  of aqueous phase, and extraction equilibrium constant could be determined for each metals.

In the case of continuous extraction, interfacial area increased by increase of stirring velocity and decreased by increase of volume flow rate of aqueous solution. Rare earth metals largely extracted by increase of contact interfacial area and driving force for diffusion, on the other hand extraction of Fe could be accelerated by only increase of contact interfacial area. Extraction rate of rare earth metals is determined by diffusion in both aqueous and organic phase, while the extraction rate of Fe is seemed to be determined by chemical reaction. The experimental local mass transfer coefficients based on experimental results are almost good agreed with theoretical calculated values.

## Nomenclature

$C$ : concentration [kmol/m<sup>3</sup>],  $m$ : distribution ratio [-],  $V$ : volume  $n$ : stirring velocity [1/h],  $Q$ : volume flow rate [kmol/m<sup>3</sup>],  $R$ : extraction rate [kmol/h],  $Y$ : yield [-],  $K$ : overall mass transfer coefficient [m/h],  $k$  = local mass transfer coefficient [m/h],  $d_{32}$  =sauter mean diameter of dispersed phase [m],  $\Phi$ : dispersed phase holdup [-],  $a$ : specific interfacial area [m<sup>2</sup>/m<sup>3</sup>],  $K_{ex}$ : extraction equilibrium constant [-]

<Subscripts>

0: initial state, eq: equilibrium state, aq: aqueous phase, org: organic phase, in: inlet solution, out: outlet solution, d: dispersed phase, M: Metal, RH2: extractant as dimer, H+: hydrogen ion, Nd: Neodymium, Dy: Dysprosium, Fe: Iron

## References

- [1] Robert E. Treybal., LIQUID EXTRACTION 2nd edition, (1963)
- [2] K. Takahashi, et.al, *Chemical Engineering Science*, 57, 469 (2002)
- [3] Hideo Matsuyama, et.al, *Hydrometallurgy*, 24, 37 (1990)
- [4] 城塚 正, 化学技術者のための移動速度論, 275 (1966)
- [5] E.L. Clussler, *Diffusion* 3<sup>rd</sup> edition, 162 (2002)
- [6] 藤田 重文, 化学工学演習 第2版, 182 (1979)
- [7] Eiji Kamio et.al, *Chemical journal*, 139, 93 (2008)