

Liquid-Liquid Equilibria of Terbium and Dysprosium with PC-88A as Extractant

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1. Introduction

Rare earth elements (REEs) are used in various industrial products, such as, the electric vehicles and air conditioners, in which Ne-Fe-B magnets containing neodymium, terbium (Tb) and dysprosium (Dy) are used^{[1][2]}. Since the REEs coexist in the ores and the industrial products usually contain multiple REEs, the separation of REEs in the ore or the recovery of them from industrial product wastes must be important technology.

The solvent extraction is commercially used as a method to separate REEs. Although a number of works on the separation of REEs by solvent extraction have been reported, there are only few studies focusing on the equilibria in the single element system of Tb or in the binary element system of Tb and Dy, whose chemical properties are quite similar, making separation difficult.

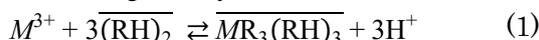
In this work, the extraction equilibria were studied in the single element system of Tb or Dy, and the binary element system of Tb and Dy, using PC-88A as an extractant.

2. Experimental

Chloride salts of Tb and Dy in analytical grade were used as metal ion sources. PC-88A (2-Ethylhexyl-2-ethylhexylphosphonate) was used as an extractant. **Table 1** shows the experimental conditions for liquid-liquid equilibrium measurement. The feed solutions containing Tb or Dy for the single metal ion system, or Tb and Dy for the binary metal ion system were prepared. The initial molar concentrations of the metal ion in the aqueous phase and the extractant in the organic phase were fixed. The initial pH was adjusted using hydrochloric acid. Kerosene was used as a diluent to prepare the organic phase. The aqueous and organic phase of the same volumes were contacted each other in conical flask and shaken for 12 hours to reach equilibrium. Then, the aqueous phase at initial and equilibrium conditions were analyzed to determine the respective pHs and metal concentrations, using pH meter (F-74, Horiba) and ICP-AES (SPS7800, Hitachi High-Tech Science Corp.).

3. Results and Discussion

Reaction equilibrium of the trivalent rare earth metal ion between aqueous phase and organic phase with PC-88A, is generally described as,



where the overbar and $(\text{RH})_2$ stands for the compound in the organic phase and extractant in dimer, respectively. The material balance equation was expressed as,

$$V_{\text{aq},0}C_{M,\text{aq},0} = V_{\text{org,eq}}C_{M,\text{org,eq}} + V_{\text{aq,eq}}C_{M,\text{aq,eq}} \quad (2)$$

Table 1 Experimental conditions

Initial metal concentration	
$C_{M,\text{aq},0}$ ($M=\text{Tb, Dy}$)	
-Single element system	0.005 kmol m ⁻³
-Binary element system	0.005 kmol m ⁻³
	(for each)
Initial pH	
pH_0	0.0~2.0
Concentration of extractant	
$C_{\text{RH}_2,\text{org},0}$	0.25 kmol m ⁻³
Aqueous phase volume	
V_{aq}	2.0×10^{-5} m ³
Organic phase volume	
V_{org}	2.0×10^{-5} m ³
Extraction temperature	
	298 K
Extraction time	
	12 h

The metal concentration in the organic phase $C_{M,\text{org,eq}}$ at equilibrium was obtained using Eq. (2) with $C_{M,\text{aq},0}$ and $C_{M,\text{aq,eq}}$ directly measured. The concentration of extractant in the organic phase at equilibrium was calculated as,

$$C_{\text{RH}_2,\text{org,eq}} = C_{\text{RH}_2,\text{org},0} - 3C_{M,\text{org,eq}} \quad (3)$$

Using the equilibrium constant (K_M), Eq. (1) can be rewritten as Eq. (7), where D is the distribution coefficient, defined as,

$$D = C_{M,\text{org,eq}} / C_{M,\text{aq,eq}} \quad (4)$$

$$\log D - 3 \log C_{\text{RH}_2,\text{org,eq}} = 3\text{pH} + \log K_M \quad (5)$$

Fractional extraction of metal ion E_M and solvent free metal mol fraction in phase j , $x_{M,j}$ were defined as,

$$E_M = C_{M,\text{org,eq}} / C_{M,\text{aq},0} \quad (6)$$

$$x_{M,j} = C_{M,j,\text{eq}} / (C_{\text{Dy},j,\text{eq}} + C_{\text{Tb},j,\text{eq}}) \quad (7)$$

where j stands for aq or org.

Single element system

In all cases, the pH at equilibrium became lower than that at initial condition since hydrogen of the extractant was released by the extraction of metal ions.

The plots of E_M in the single systems against the equilibrium pH are shown in **Fig. 2**. In the range of low pH, both REEs were little extracted into the organic phase. In the range of pH of 0 to 0.5, both elements started to be extracted. Change of fractional extraction was significant in the range of pH of 0 to 1, and over 90% of REEs were extracted when pH was higher than 1.

The terms of the left hand of Eq. (5) were plotted against the pH at equilibrium in the case of the single metal ion systems, as shown in **Fig. 2**. According to Eq.

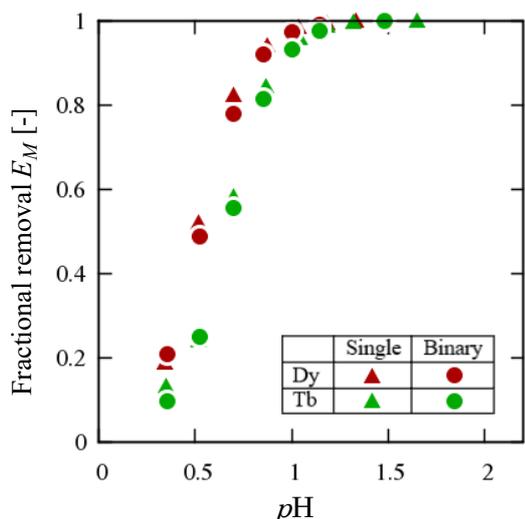


Fig. 1 Fractional removal vs. pH at equilibrium in single or binary element system

(5), the slope of the line of the plots with each metal ion should be 3, and it was found that both reactions of Tb and Dy with PC-88A in the single systems followed Eq. (1). Then, the reaction equilibrium constants of K_{Tb} and K_{Dy} were estimated as 1.34 and 2.99, respectively. The Dy ion was extracted more than Tb because the heavier REEs should be generally extracted more than the lighter ones.

The separation factor between Tb and Dy were obtained as $\beta_{Dy,Tb} = K_{Dy} / K_{Tb} = 2.2$. Then, $\beta_{Dy,Tb}$ was relatively low and the separation between Tb and Dy was found to be relatively difficult by the solvent extraction.

Binary element system

pH change was also observed in the binary element system and the decrease was more significant than that in the single element system because the larger amount of REE was extracted.

The plots of E_M in the binary systems against the equilibrium pH are shown in Fig. 2. Trend of extraction was similar to that in the single system.

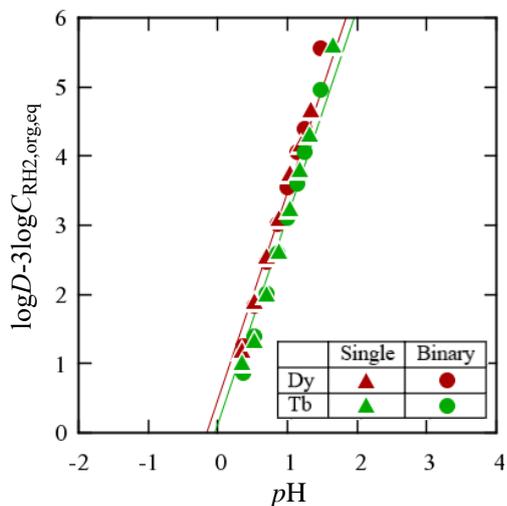


Fig. 2 Slope analysis of terbium and dysprosium in single and binary system

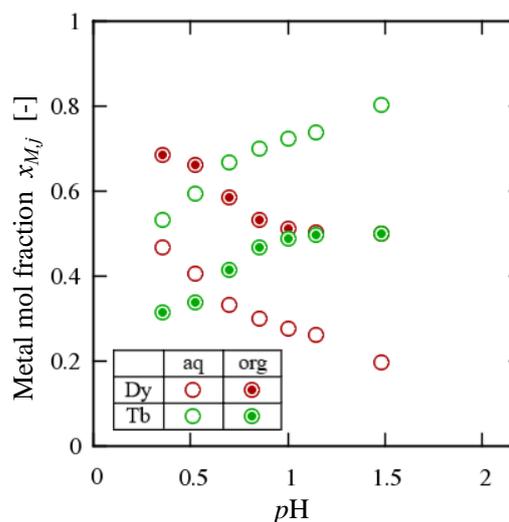


Fig. 3 Mol fraction of each REE in each phase

The extraction equilibria with the binary system containing both Tb and Dy ions are shown in Fig. 2, together with those with the single systems. The results with the binary system were approximately the same as those for the respective metal ions with the single systems, and no effects of the coexisting metal ions were found in this measurement range.

Plots on **Fig. 3** show the mol fraction of each metal in organic phase. Mol fraction of Dy was higher than Tb at the lower pH while almost same mol fraction was obtained at the higher pH . From this result, purification can be obtained when pH is low, but as Fig. 3 shows, REEs are not extracted into organic phase at the lower pH , such as less than 0.5, so the concentrations of both elements should be low.

The mol fraction of each metal in aqueous phase is also shown on Fig. 3. In contrast to the result in organic phase, mol fraction of Tb is higher than that of Dy and the higher pH made the larger difference of mol fraction. When pH is higher than 1, although the difference of mol fraction between the 2 elements was relatively wide, over 90% of elements were extracted into organic phase. From the results shown on Fig. 1, it is declared that batch separation or purification is not enough in this condition, and for the further separation, multistage process should be considered.

4. Conclusions

From the experiment on the single element system, extraction coefficient of terbium and dysprosium and the separation factor were estimated; $K_{Dy} = 2.99$, $K_{Tb} = 1.34$, $\beta_{Dy,Tb} = 2.2$. From the experiment on the binary element system, extraction trends were clarified.

5. Reference

- [1] Y. Arai *et al.*, 廃棄物資源循環学会誌, Vol. 22, No. 1, p. 41-49 (2011)
- [2] S. Ishihara *et al.*, Chishitsu News, No. 609, p. 4-18 (2005)