

**EXTRACTION AND SEPARATION OF HEAVY RARE EARTH METALS  
IN THE PRESENCE OF DIETHYLENETRIAMINEPENTAACETIC ACID**

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The extraction and separation of heavy rare earth metals (Y/Er and Yb/Lu) by liquid-liquid extraction with 2-ethyl-2-methylheptanoic acid (VA-10) in the presence of diethylenetriaminepentaacetic acid (DTPA) has been investigated. The extraction equilibrium for each heavy rare earth metal with VA-10 is established up to high loading ratios. In the presence of DTPA, the distribution ratios of each metal are decreased by the masking effect. In the Y/Er system, the order of the extractabilities of Y and Er is reversed and the selective extraction of Y is enhanced especially at high pH values, while the separation is little improved in the Yb/Lu system.

### **1. Introduction**

Liquid-liquid extraction in the presence of water-soluble complexing agents has been investigated for the effective separation of rare earth metals. There are two methods, equilibrium<sup>1,2</sup> and non-equilibrium,<sup>3-5</sup> for improving separation by the addition of water-soluble complexing agents. In the case of equilibrium separation, the combined effect of the extractant and the complexing agent is very small for acidic extractants,

because the extraction equilibrium constants of rare earth metals increase with increasing atomic number while the complex formation constants of most complexing agents show similar increase. However, the separation of heavy rare earth metals is expected to be improved by adding DTPA, because the complex formation constants from Dy to Lu decrease with increasing atomic number.<sup>6</sup>

In the present work, the extraction and separation of combinations of heavy rare earth metals (Y/Er and Yb/Lu) with 2-ethyl-2-methylheptanoic acid (VA-10) in the presence of a water-soluble complexing agent (DTPA) was investigated. The extraction equilibria of the metals up to high loading ratios in single metal and binary metal systems were investigated. The complex formation reaction with DTPA was then combined with the extraction reaction and the effect of the addition of DTPA was investigated.

## 2. Experimental

2-Ethyl-2-methylheptanoic acid (VA-10, marketed by Shell Chemical Co.) was used as received. All the inorganic chemicals were supplied by Wako Pure Chemical Industries as analytical reagents grade. The water-soluble complexing agents, diethylenetriaminepentaacetic acid (DTPA) and ethylenediaminetetraacetic acid (EDTA), were supplied by Dojin Chemical Industries. The procedure for measuring the degree of extraction of the metals was identical to that in previous work.<sup>7</sup> It has been reported that the VA-10 exists mainly as a dimer in nonpolar diluents such as kerosene.<sup>8</sup> The loading ratio is thus defined as the concentration of the rare earth metal extracted to that of the feed extractant dimer.

## 3. Results and Discussion

### 3.1 Extraction Equilibrium Formulations.

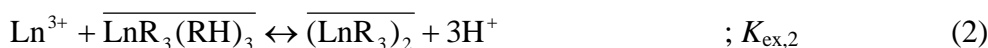
The extraction equilibrium of heavy rare earth metals (Y, Er, Lu, and Yb) at low loadings is formulated as eq 1 by using the slope analysis method.



**Table 1.** Extraction equilibrium constants for rare earth metals.

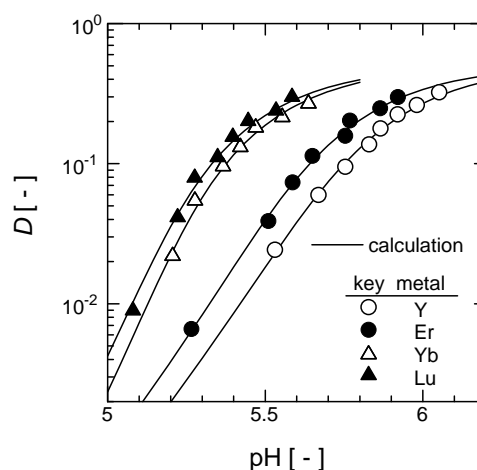
	Y	Er	Yb	Lu
$K_{ex,1}$	$2.92 \times 10^{-14}$	$5.30 \times 10^{-14}$	$5.11 \times 10^{-14}$	$9.09 \times 10^{-14}$
$K_{ex,2}$	$1.84 \times 10^{-16}$	$4.59 \times 10^{-16}$	$1.85 \times 10^{-14}$	$1.95 \times 10^{-14}$

This formulation is consistent with that reported previously.<sup>9</sup> The high loadings of the extractant were brought about by increasing the feed metal concentration and by raising the equilibrium pH value. The maximum loading ratios approach about 0.66, suggesting that a complex containing the metal and the dimeric extractant with a mole ratio of 2 : 3 is likely to be formed at the extreme conditions of maximum loading ratios of the extractant. Therefore, the formation of aggregated species,  $\overline{(\text{LnR}_3)_2}$ , in the organic phase is assumed, as shown in eq 2.



The extraction equilibrium constants are determined by the nonlinear least square method,<sup>7</sup> and are summarized in **Table 1**. The distribution ratios are then predicted with these constants and by using the mass balance equations for the concentration of rare earth metal in the organic phase and the feed concentration of the dimeric extractant.<sup>7</sup> The experimental distribution ratios are plotted in **Figure 1**, together with the predicted lines. The extraction behavior of these rare earth metals in single metal systems can be expressed up to high loadings by the proposed extraction scheme.

The results obtained in single metal systems are extended to the extraction in Y/Er and Yb/Lu binary systems. The experimental distribution ratios of each metal in each binary system are plotted in **Figure 2(a)**. If the interaction between the two metals is

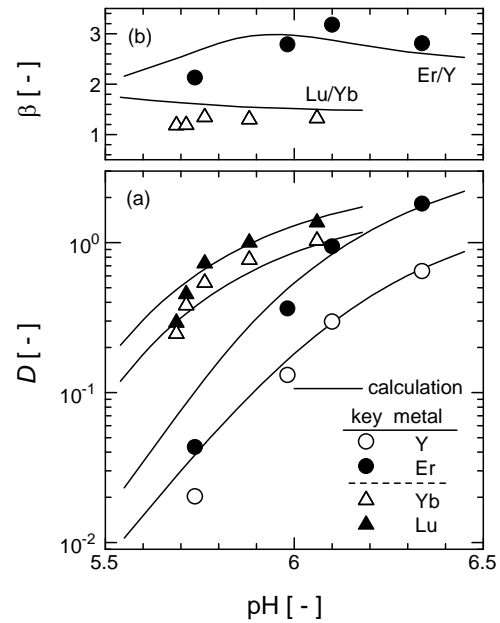


**Figure 1.** Effect of equilibrium pH values on the distribution ratios in single metal systems. Comparison of observed data with prediction shown by solid lines.  $[(\text{RH})_2]_{\text{feed}} = 0.025$  mol/l and  $[\text{Ln}]_{\text{feed}} = 0.05$  mol/l.

negligible, the distribution ratios of each metal can be calculated using the extraction equilibrium constants determined in the single metal systems. The predicted distribution ratios are shown in Figure 2(a) by solid lines. The experimental data except for the low loading region are seen to cluster on the predicted values, indicating that the extraction scheme obtained in the single metal system also describes the binary metal system. The deviation between the experimental and predicted values at low loadings may be due to limitations of the ICP-AES analytical, caused by the interaction between the two metals during analysis. The experimental and predicted separation factors, defined as the ratio of distribution ratios, are also shown in Figure 2(b). In the case of the Y/Er system, the ratio of  $K_{ex,2}$  for the two metals is larger than the ratio of  $K_{ex,1}$ , thus enhancing the separation factor with increasing loading ratio. In the case of the Yb/Lu system, however, the separation factor is almost independent of the loading ratio, because the ratio of  $K_{ex,2}$  for the two metals is slightly lower than the ratio of  $K_{ex,1}$ .

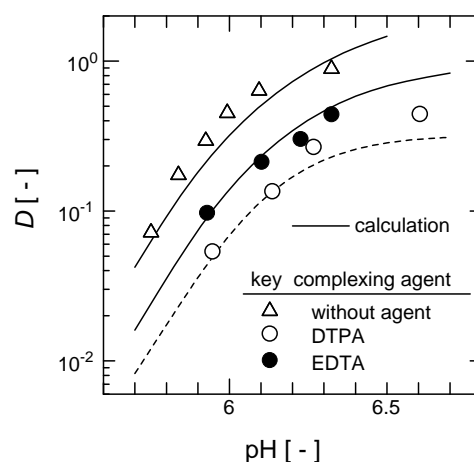
### 3.2 Effect of Addition of DTPA into the Extraction System.

The presence of a water-soluble complexing agent, such as DTPA ( $H_5L$ ) and EDTA ( $H_4L$ ), in the extraction system, which complexes with the rare earth metals causes the rare earth metals to be masked from the extraction, and, thus, the distribution ratios of the metals are decreased. It is generally known that a rare earth metal forms a 1 : 1 complex with the dissociated ligand of DTPA ( $L^{5-}$ ) or EDTA ( $L^{4-}$ ) as shown in eq 3 (the charge of each element is abbreviated).



**Figure 2.** Effect of equilibrium pH values on (a) distribution ratios and (b) separation factor in binary systems (Y/Er and Yb/Lu). Comparison of observed data with prediction shown by solid lines.  $[(RH)_2]_{feed} = 0.02 \text{ mol/l}$  and  $[Ln]_{feed} = 0.01 \text{ mol/l}$ .

The literature values of the complex formation constants of DTPA,  $K_f$ , for Y, Er, Yb, and Lu are  $10^{22.05}$ ,  $10^{22.74}$ ,  $10^{22.62}$ , and  $10^{22.44}$ , respectively, and that of EDTA for Y is  $10^{18.08}$ .<sup>6</sup> **Figure 3** shows the distribution ratios of Y in the presence of DTPA or EDTA. In the presence of the complexing agent, the distribution ratios become lower than those in the absence of the agent as expected. The distribution ratios in the presence of the complexing agent are predicted by combining the extraction equilibrium expression and the complex formation reaction between the agent and rare earth

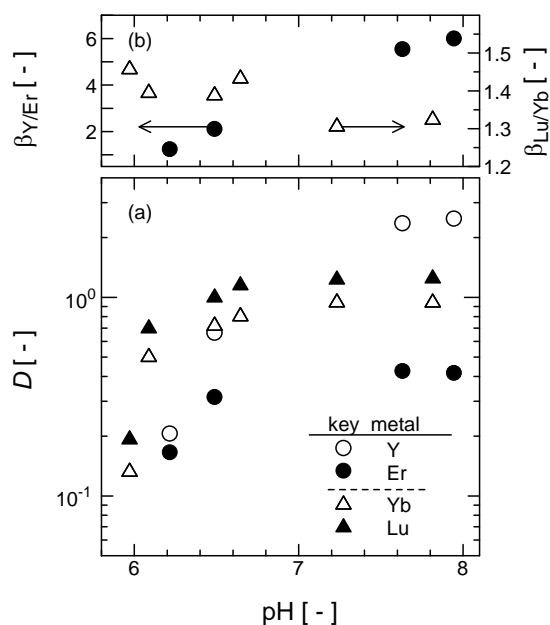


metals in the aqueous phase. The predicted distribution ratios are also shown as lines in Figure 3. In the EDTA system, the experimental data are seen to cluster on the predicted values based on the assumption of a 1 : 1 complex. In the DTPA system, however, the experimental values are lower than those predicted based on the assumption of a 1 : 1 complex. The predicted values for the DTPA system should be equal to those for the EDTA system, because both complexing agents are completely dissociated and form a 1 : 1 complex with rare earth metals in this pH region. The deviation of experimental values from predicted values in the DTPA system may be caused by a change in the molar ratio of rare earth metal and DTPA in the complex. Several calculation runs were carried out assuming various molar ratios of rare earth/DTPA in the complex. The predicted values based on the molar ratio of rare earth to DTPA of 1.5 are shown in Figure 3 by the dotted line. The experimental data are seen to cluster on the predicted line based on a 1.5 : 1 complex at  $\text{pH} < 6.15$ , but are located between the predicted lines based on the ratios of 1 : 1 and 1.5 : 1 at  $\text{pH} > 6.15$ .

In the case of binary systems (Y/Er and Yb/Lu), most of experimental data also fall between the predicted values with the ratios of 1 : 1 and 1.5 : 1, suggesting that the average

**Figure 3.** Effect of equilibrium pH values on the distribution ratios of Y in a single metal system in the presence of DTPA or EDTA. Comparison of observed data with prediction shown by lines. Solid line: based on 1 : 1 complex, dotted line: based on 1.5 : 1 complex.  $[(\text{RH})_2]_{\text{feed}} = 0.02 \text{ mol/l}$ ,  $[\text{Y}]_{\text{feed}} = 0.02 \text{ mol/l}$ , and  $[\text{complexing agent}] = 0.01 \text{ mol/l}$ .

of the molar ratio of rare earth to DTPA in the extraction system with DTPA varies between 1 and 1.5. **Figure 4** shows the distribution ratios of each rare earth metal in the binary systems (Y/Er and Yb/Lu) in the presence of DTPA. In the case of the Y/Er system, the order of extraction between Y and Er is reversed by the masking effect with DTPA. The effect increases with increase in the equilibrium pH value, making the distribution ratio of Er decrease, and thus improves the selective extraction of Y. In the case of the Yb/Lu system, however, the separation is hardly changed by the presence of DTPA, although this is expected by the masking of Yb, which is the less extractable component. This is due to the fact that the ratio of rare earth metal and DTPA changes from 1 : 1 to 1.5 : 1. In this system, thus, the masking effect with DTPA is hardly expected, and the separation factor decreases with increase in the loading ratios.



**Figure 4.** Effect of equilibrium pH on (a) distribution ratios and (b) separation factor in binary systems (Y/Er and Yb/Lu) in the presence of DTPA.  $[(\text{RH})_2]_{\text{feed}} = 0.02 \text{ mol/l}$ ,  $[\text{Ln}_i]_{\text{feed}} = 0.01 \text{ mol/l}$ , and  $[\text{DTPA}] = 0.01 \text{ mol/l}$ .

#### 4. Conclusion

The extraction and separation of heavy rare earth metals (Y/Er and Yb/Lu) in the presence of a water-soluble complexing agent (DTPA) has been investigated, with the following results.

(1) The extraction equilibrium for heavy rare earth metals with VA-10 is determined.  $\overline{\text{LnR}_3(\text{RH})_3}$  is formed at low loading ratios and then an aggregated species,  $\overline{(\text{LnR}_3)_2}$  appears at increasing loading ratios. The extraction equilibrium formulations determined can represent the extraction behavior in both single and binary metal systems up to high

loading ratios.

(2) In the presence of DTPA, the distribution ratios of each metal are decreased by the masking effect. In the Y/Er system, the order of the extractabilities of Y and Er is reversed and the selective extraction of Y is improved especially at high pH values, while the separation is little changed in the Yb/Lu system. The ratio of rare earth metal and DTPA in the rare earth-DTPA complex is not 1 : 1, but varies between 1 : 1 and 1.5 : 1 in the extraction system.

### Acknowledgement

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### Nomenclature

$D$	= distribution ratio	[ - ]
$K_{\text{ex}}$	= extraction equilibrium constant	
$K_{\text{f}}$	= complex formation constant	
L	= dissociate ligand of DTPA or EDTA	
Ln	= rare earth metal	
(RH) <sub>2</sub>	= dimeric species of VA-10	
$\beta$	= separation factor	[ - ]
[ ]	= concentration of the species in the bracket	[mol/l]
Subscript		
i	= component (Y, Er, Yb, or Lu)	
feed	= aqueous or organic feed solution	
Superscripts		
—	= organic phase species	

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