Extraction Behavior of Europium with Thenoyltrifluoroacetone (TTA)

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The distribution ratios of europium(III) were determined between chloroform containing thenoyltrifluoroacetone (TTA) and 0.1M aqueous perchlorate solution at 25°C, the TTA concentration in the organic phase and the hydrogen ion concentration in the aqueous phase being varied $10^{-4}\sim 10^{-1}$ M and $10^{-3}\sim 10^{-7}$ M, respectively. The distribution behavior was explained as the extraction of the tris chelate complex into the organic phase and as the formation of the chelate complexes, EuA^{2+} , EuA_2^+ and EuA_3 (A=anion of TTA) in the aqueous phase. The following equilibrium constants were obtained graphically for the respective equilibrium reactions.

Distribution of Eu (II) was also studied. The distribution ratios for Eu (II) were smaller than those for Eu (III). It was suggested that the separation of Eu (II) from Eu (III) may be possible at pH 4.2~4.8.

1. Introduction

Thenoyltrifluoroacetone (TTA) in various organic solvents has been widely used for the extraction of rare earth elements in aqueous solutions^{(1)~(7)}. Especially, the extraction behavior of europium (III) has attracted much attention in connection with the phenomena of the synergism and adduct formation.^{(4), (5), (7)} In this paper, the extraction behavior of europium with TTA in chloroform in the pH range of 3.0~7.0 is elucidated in terms of the extraction equilibrium and the chelate complex formation with TTA anion in the aqueous phase.

Furthermore, separation of europium (II) from europium (III) by TTA extraction is investigated.

2. Experimental

2.1 Reagents

$^{152}, ^{154}\text{Eu}$ or ^{159}Eu was used in 0.1M perchloric acid solution as the tracer. Inactive europium solution in 0.1M perchloric acid was prepared from europium oxide of 99.9% purity made by Yamada Chemical Co., Ltd. The solution was labelled with a few drops

of the above mentioned radioactive europium. The europium concentration of this solution was 6.6×10^{-6} M. Thenoyltrifluoroacetone was supplied from Dojindo Co., Ltd. All of the other reagents used were of the reagent grade and used without any further purification.

2.2 Procedures

All equilibrations were carried out at $25 \pm 1^\circ\text{C}$. In a 50 ml separatory funnel, 9.9 ml of a 0.1M sodium perchlorate—perchloric acid solution of various pH from a burette and 10 ml of a $10^{-1}\sim 10^{-4}$ M chloroform solution of TTA were taken, and then 0.1 ml of the labelled europium solution ($0.1 \mu\text{g}$ Eu) was added. The solutions in the separatory funnel were shaken vigorously by a mechanical shaker for more than 1 hr and then centrifuged at 3000 rpm for 2 min. Five ml portion of each was then pipetted from each phase and transferred into a small polyethylene counting tube. The γ -activity of each solution was measured by a well-type NaI(Tl) scintillation counter. The hydrogen ion concentration in the aqueous phase was measured by transferring its small portion onto a small glass electrode of a pH-meter.

In some experiments, back-extraction of europium from the organic phase was carried out with the equal volume of an aqueous solution. The activity of each phase and pH of the aqueous phase were measured in the same way.

The extraction of europium(II) was carried out after reducing europium(III) with zinc amalgam. The procedures were similar to those for europium(III) with some exceptions as follows: The amount of europium carrier added was 300 μg . The amalgam reduction of europium(III) was carried out in the nitrogen atmosphere, and the chloroform solution of TTA was deaerated by passing nitrogen in a 3-necked reduction separatory funnel. The equilibration was also carried out under constant passing of nitrogen. The volume of each phase was usually 4.0 ml, and 2.0 ml aliquot of each was taken for γ -counting.

3. Results and Discussion

3.1 Treatment of the distribution data

The distribution equilibrium of europium (III) between an aqueous phase and an immiscible organic phase with an organophilic chelating acid, HA (HA=HTTA in the present case), may be described as follows:

The equilibrium constant for this reaction is;

$$K_0 = [\text{EuA}_3]_{\text{org}} [\text{H}^+]^3 / [\text{Eu}^{3+}] [\text{HA}]_{\text{org}}^3 \quad (2)$$

where the subscript "org" stands for the species or concentrations in the organic phase, whereas terms without subscript denote those in the aqueous phase. The distribution ratio, D , is defined as;

$$D = [\text{Eu(II)}]_{\text{total,org}} / [\text{Eu(II)}]_{\text{total}} \quad (3)$$

where $[\text{Eu(II)}]_{\text{total}}$ stands for the total concentration of trivalent europium, regardless of its chemical state. By assuming that (i) europium exists in the aqueous phase as $\text{EuA}_n^{(3-n)+}$ ($n = 0, 1, 2, \dots, N$) and that (ii) europium exists in the organic phase only in the form of the neutral tris chelate complex, EuA_3 , the equation (3) is written as;

$$D = [\text{EuA}_3]_{\text{org}} / ([\text{Eu}^{3+}] + [\text{EuA}_2^+] + [\text{EuA}_2^+] + \dots + [\text{EuA}_N^{(3-N)+}]) \quad (4)$$

where N is the maximum coordination number of Eu(III) for ligand A. For the complex formation reaction of

the stability constant, β_n , is defined as follows:

$$\beta_n = [\text{EuA}_n^{(3-n)+}] / [\text{Eu}^{3+}] [\text{A}^-]^n \quad (6)$$

By introducing β_n in Eq. (4),

$$D = [\text{EuA}_3]_{\text{org}} / [\text{Eu}^{3+}] \{1 + \beta_1 [\text{A}^-] + \beta_2 [\text{A}^-]^2 + \dots + \beta_N [\text{A}^-]^N\} \quad (7)$$

From Eq. (2),

$$[\text{EuA}_3]_{\text{org}} = K_0 [\text{Eu}^{3+}] [\text{HA}]_{\text{org}}^3 / [\text{H}^+]^3 \quad (8)$$

therefore,

$$D = K_0 [\text{HA}]_{\text{org}}^3 / [\text{H}^+]^3 \{1 + \beta_1 [\text{A}^-] + \beta_2 [\text{A}^-]^2 + \dots + \beta_N [\text{A}^-]^N\} \quad (9)$$

$$K_0 / D [\text{H}^+]^3 [\text{HA}]_{\text{org}}^{-3} = 1 + \beta_1 [\text{A}^-] + \beta_2 [\text{A}^-]^2 + \dots + \beta_N [\text{A}^-]^N \quad (10)$$

The distribution coefficient of the chelating acid between the two phases, K_D , is expressed as follows:

$$K_D = [\text{HA}]_{\text{org}} / [\text{HA}] \quad (11)$$

The dissociation constant of the chelating acid for the reaction

in the aqueous phase, K_a , is;

$$K_a = [\text{H}^+] [\text{A}^-] / [\text{HA}] \quad (12)$$

The concentrations $[\text{HA}]_{\text{org}}$ and $[\text{A}^-]$ can be calculated from the initial chelating acid concentration in the organic phase, $[\text{HA}]_{\text{org, initial}}$, and the observed values of D and $[\text{H}^+]$ according to Eqs. (13) and (14), respectively.

$$\begin{aligned} [\text{HA}]_{\text{org}} &= [\text{HA}]_{\text{org, initial}} - [\text{HA}] - [\text{A}^-] \\ &= [\text{HA}]_{\text{org, initial}} - K_D^{-1} [\text{HA}]_{\text{org}} \\ &\quad - K_D^{-1} K_a [\text{HA}]_{\text{org}} [\text{H}^+]^{-1} \\ &= [\text{HA}]_{\text{org, initial}} / (1 + K_D^{-1} \\ &\quad + K_D^{-1} K_a [\text{H}^+]^{-1}) \end{aligned} \quad (13)$$

$$\begin{aligned} [\text{A}^-] &= [\text{HA}]_{\text{org, initial}} - [\text{HA}] - [\text{HA}]_{\text{org}} \\ &= [\text{HA}]_{\text{org, initial}} - K_a^{-1} [\text{H}^+] [\text{A}^-] \\ &\quad - K_D K_a^{-1} [\text{H}^+] [\text{A}^-] \\ &= [\text{HA}]_{\text{org, initial}} / (1 + K_a^{-1} [\text{H}^+] \\ &\quad + K_D K_a^{-1} [\text{H}^+]) \end{aligned} \quad (14)$$

Further, the value of K_0 in Eq. (10) is obtained

from the equilibrium data in the low pH region, where the concentrations of the chelate complexes EuA^{2+} , EuA_2^+ , $\dots$ in the aqueous phase are sufficiently low, and $\beta_1[\text{A}^-]$, $\beta_2[\text{A}^-]^2$, $\dots$ can be neglected. Then,

$$K_0 = D[\text{H}^+]^3[\text{HA}]_{\text{org}}^{-3} \quad (15)$$

In Eq. (10), when the terms of $\beta_i[\text{A}^-]^i$ with the i -values higher than 3 can be neglected, the equation becomes;

$$B = \beta_1 + \beta_2[\text{A}^-] \quad (16)$$

where

$$B = \frac{1}{[\text{A}^-]} \left(\frac{K_0}{D[\text{H}^+]^3[\text{HA}]_{\text{org}}^{-3}} - 1 \right) \quad (17)$$

This condition is satisfied when only chelate complex formation reactions take place, and in the pH region where the $\log D$ vs. pH plot gives the slope of 3~1. The values of β_1 and β_2 are readily obtained on the graph of B vs. $[\text{A}^-]$ by measuring the intercept on the ordinate and the slope, respectively.

In the pH region where the slope of the $\log D$ vs. pH plot changes smoothly to less than 1, Eq. (10) may be written as:

$$B = \beta_1 + \beta_2[\text{A}^-] + \beta_3[\text{A}^-]^2 \quad (18)$$

The value of β_1 may be obtained as mentioned above in the low $[\text{A}^-]$ region. Then the following equation analogous to Eq. (16) may be derived;

$$B' = \beta_2 + \beta_3[\text{A}^-] \quad (19)$$

where

$$B' = (B - \beta_1)/[\text{A}^-] \quad (20)$$

Thus, the intercept on the ordinate and the slope of the graph of B' vs. $[\text{A}^-]$ give β_2 and β_3 , respectively.

3.2 Extraction data and analyses of them

The preliminary experiments showed that the values of D obtained both by the extraction and the back-extraction agreed well with each other within the experimental error, revealing the attainment of the distribution equilibrium under the present experimental conditions.

The results of the measurement of the distribution ratio using 0.1 M chloroform solution of TTA at the various pH values are shown in Fig. 1. The dependence of the distribution

Fig. 1 Distribution ratio at the various pH at 25°C.
Aqueous phase: Eu(III) in 0.1M $(\text{Na}, \text{H})\text{ClO}_4$, organic phase: 0.1M TTA in CHCl_3

Fig. 2a The relation between distribution ratio and the initial concentration of TTA in CHCl_3 at pH 3.5.

Fig. 2b The relation between distribution ratio and the initial concentration of TTA in CHCl_3 at pH 6.8.

ratio on the concentration of TTA at pH 3.5 and pH 6.8 is shown in Figs. 2a and 2b respectively. It is revealed that the pH ranges which allow Eqs. (16) and (19) to hold good are 4.0 ~6.0, and up to ~7.0, respectively.

These experimental data are then subjected to the analyses according to Eqs. (16) and (19). The values of K_a and K_D are already measured to be 6×10^{-7} and 69.2 at 25°C , respectively^{(8), (9)}. By using these data, the concentrations $[\text{HA}]_{\text{org}}$ and $[\text{A}^-]$ are readily calculated according to Eqs. (13) and (14), respectively, and K_0 according to Eq. (15). The value of B is then calculated and plotted vs. $[\text{A}^-]$. The results are shown in Fig. 3a. The linear relation between B and $[\text{A}^-]$ indicates that Eq. (16) holds good in this extraction system. The values of β_1 and β_2 thus obtained are shown in Table 1. The value of B' is in turn calculated by using the numerical value of β_1 . Fig. 3b shows the relation between B'

Fig. 3a Relation between B and $[\text{A}^-]$.

Fig. 3b Relation between B' and $[\text{A}^-]$.

and $[\text{A}^-]$, revealing that Eq. (19) is also valid. The values of β_2 and β_3 obtained on this graph are listed in Table 1.

Table 1 The value of stability constants

Species	Reaction	Stability constant
EuA^{2+}	$\text{Eu}^{3+} + \text{A}^- \rightleftharpoons \text{EuA}^{2+}$	$\beta_1 = 4.5 \times 10^4$
EuA_2^+	$\text{Eu}^{3+} + 2\text{A}^- \rightleftharpoons \text{EuA}_2^+$	$\beta_2 = \begin{cases} 4.7 \times 10^9 \text{ from Fig. 3a} \\ 4.7 \times 10^9 \text{ from Fig. 3b} \end{cases}$
EuA_3	$\text{Eu}^{3+} + 3\text{A}^- \rightleftharpoons \text{EuA}_3$	$\beta_3 = 1.1 \times 10^{12}$

The stepwise chelate formation constants K_1 , K_2 and K_3 which correspond to the following reactions are calculated as shown below right:

$$\begin{aligned} \text{Eu}^{3+} + \text{A}^- &\rightleftharpoons \text{EuA}^{2+} : K_1 = \beta_1 = 4.5 \times 10^4 \\ \text{EuA}^{2+} + \text{A}^- &\rightleftharpoons \text{EuA}_2^+ : K_2 = 1.0 \times 10^5 \\ \text{EuA}_2^+ + \text{A}^- &\rightleftharpoons \text{EuA}_3 : K_3 = 2.3 \times 10^2 \end{aligned}$$

The assumption (i) described in the foregoing section seems to be valid in the present extraction system, since the hydrolysis of europium in the aqueous phase may be neglected because of its low hydrolysis constant* and of the presence of the large excess of the chelating acid, and thence the mixed ligand complex formation with both OH^- and A^- is improbable. The formation of polynuclear complexes seems to be also improbable because of the very low total concentration of europium in the system.

The assumption (ii) seems also to be valid,

* It is reported $K = [\text{EuOH}^{2+}]/[\text{Eu}^{3+}][\text{OH}^-] = 10^{-8.49}$ by Frolova, *et al.*⁽¹⁰⁾

Table 2 Equilibrium constant for rare earth elements and TTA system at 25°C

Element	$\log K_0$	Aqueous phase	Organic solvent	References
Pr	-8.47	0.1M (NH ₄ , H)Cl	benzene	11)
Eu	-8.53	0.1M (Na, H)ClO ₄	CHCl ₃	this work
	-8.55*	"	CHCl ₃	4, 5)
	-8.13*	"	CCl ₄	4, 5)
Sc	-1.30	"	CHCl ₃	9)
	-0.77	—	benzene	12)

* The values are calculated from the value of $D[H^+]^3$ in the literature by multiplying the value of $[HA]_{org}^{-3}$.

since the third power dependence of D on the TTA concentration in lower pH region is obtained as shown in Fig. 2a and since no remarkable deviation on the plot is observed in Figs. 3a and 3b.

There are still very few data reported in the literature for the formation of TTA complexes in the aqueous phase¹⁴⁾. Sekine, Koizumi and Sakairi⁹⁾ studied the distribution of scandium (III) in the system of 0.1 M sodium perchlorate + perchloric acid solution and TTA in chloroform. They reported the value of $\log \beta_1$ for the reaction system of $Sc^{3+} + TTA^- \rightleftharpoons Sc(TTA)^{2+}$ as 7.1 at 25°C. As for the TTA complexes of europium(III), no stability constant has been hitherto reported.

The value of $\log K_0$ obtained is given in Table 2 together with the values for the systems of several rare earth elements and TTA reported in the literature. It is in very good accordance with that reported by Sekine, *et al.*^{4), 5)}

4. Extraction of bivalent europium

The values of $\log D$ obtained are plotted against pH in Fig. 4 together with the corresponding values for europium(III). The values obtained in the system of 0.1 M acetate buffer solution and 0.1 M TTA in carbon tetrachloride are also given. The slope of the curve for europium(II) is found to be about 1. Nachman and Lundin¹³⁾ reported a very fast oxidation of europium (II) to europium(III) in alkyl phosphoric acid extraction of europium of low concentration. It would still remain, therefore, some possibilities of oxidation of

Fig. 4 Distribution ratio for Eu(II) and Eu(III) at 25°C.

- I: 300 μ g Eu(II) in 0.1M perchlorate - 0.1M TTA in CHCl₃ system
- II: 0.1 μ g Eu(II) in " "
- III: 300 μ g Eu(II) in 0.1M acetate - 0.1 M TTA in CCl₄ system
- IV: 0.1 μ g Eu(III) in " "

europium (II) in the present experiment, although the whole procedures were done in the nitrogen atmosphere. At any rate, it seems that the values of D in Fig. 4 give the upper limit of the distribution ratio of europium (II).

From Fig. 4, it is likely to be said that separation of europium(II) from europium(III) may be achieved in the present system at pH 4.2~4.8.

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要 旨

TTA 抽出におけるユーロピウムの挙動

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3価のユーロピウムの溶媒抽出挙動をテノイルトリフルオロアセトン (TTA; HA) のクロロホルム溶液—0.1M 過塩素酸塩系でしらべた。有機相中の TTA 濃度を 10^{-4} ~ 10^{-1} M に変え, また水相中の水素イオン濃度を 10^{-3} ~ 10^{-7} M に変えたときの分配係数の変化は, EuA_3 の有機相への抽出と水相中での EuA^{2+} , EuA_2^+ および EuA_3 の生成として説明される。つぎの諸反応の平衡定数は以下のようである。

$$K_0 = 2.95 \times 10^{-9}$$

2価のユーロピウムの TTA 抽出の分配係数は対応する 3価のユーロピウムに比べて一般に小さく, pH 4.2~4.8 で両者の相互分離が可能であることが示された。