

Synergic Extraction of Rare Earth Elements with Thenoyltrifluoroacetone and Neutral Bidentate Ligands

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II. 2 Synergic Extraction of Rare Earth Elements with Thenoyltrifluoroacetone and Neutral Bidentate Ligands

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Synergic extraction of a metal ion with an acidic chelating agent and a neutral unidentate ligand, such as tributylphosphate (tbp) and trioctylphosphine oxide (topo), has been extensively studied.¹⁾ But quite a few studies on the synergic extraction system involving a neutral bidentate ligand have been made.

In the present work, the synergic extraction of rare earth element(III), RE(III), with 2-thenoyltrifluoroacetone (Htta) and a neutral bidentate ligand, such as 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen) and 2,9-dimethyl-1,10-phenanthroline (dmp), in benzene is investigated.

Radioactive tracers such as ¹⁴⁰La, ¹⁴¹Ce, ¹⁴⁷Nd, ¹⁵³Sm, ¹⁵³Gd, ¹⁶⁰Tb, ¹⁶⁹Yb and ¹⁷⁷Lu were produced by neutron irradiation of each oxide (99.99% purity) in the nuclear reactor (JRR-4) of the Japan Atomic Energy Research Institute. ¹⁶⁸Tm was produced by bremsstrahlung irradiation of the oxide with a linear electron accelerator of Tohoku University. A radioactive RE(III) solution was prepared by dissolving a known amount of the irradiated sample in hydrochloric acid, evaporating to dryness, and redissolving in 10⁻³M perchloric acid. The γ -activity was measured with an NaI(Tl) well-type scintillation detector connected with a single-channel analyzer.

An aqueous solution containing 10⁻⁷-10⁻⁵M radioactive RE(III) and 10⁻¹M sodium perchlorate was shaken with the equal volume of benzene solution containing 10⁻⁴-10⁻²M Htta and 10⁻⁵-10⁻²M S for 1-3 hours at 25°C. An aliquot was taken from each phase and the γ -activity was measured. The distribution ratio (D) of RE(III) was obtained as the radioactivity ratio.

The extraction of a trivalent rare earth metal ion (M³⁺) with a chelating extractant (HA) can be expressed as follows;



$$K_{ex} = \frac{[\overline{MA_3}] [H^+]^3}{[M^{3+}] [\overline{HA}]^3} \quad (2)$$

where the bar denotes the organic phase, K_{ex} , the extraction constant and $\overline{MA_3}$, the extracted neutral chelate. The distribution ratio of the metal (D_o) is written as follows;

$$D_o = \frac{[\overline{MA_3}]}{[M^{3+}] + \Sigma [MA_n^{3-n}]} = \left(\frac{P_{HA}}{K_{HA}}\right)^3 \cdot K_{ex} \cdot \frac{[A^-]^3}{1 + \Sigma \beta_n [A^-]^n} \quad (3)$$

where P_{HA} and K_{HA} are the partition coefficient and the acid dissociation constant of HA, respectively, and β_n , the stability constant of MA_n^{3-n} in the aqueous phase. In a region where the concentration of A^- is very low, $\Sigma \beta_n [A^-]^n$ is negligibly small, hence D_o depends on the third power of $[A^-]$. The extraction of RE(III) with 10^{-3} - 10^{-2} M Htta in benzen from various pH aqueous solution was carried out and the plots of $\log D_o$ of RE(III) against $\log [tta^-]$ are shown in Fig. 1. The equilibrium concentration of tta^- in the aqueous phase was calculated by using $K_{HA}^{2)}$ and $P_{HA}^{3)}$ of Htta from the initial concentration of Htta and the equilibrium pH value. The plots for each RE(III) give a straight line with a slope of 3.0 as expected for the formation of $RE(tta)_3$. The extraction constant, K_{ex} , was calculated experimentally and listed in Table 1.

The distribution ratio (D) in the synergic extraction system with HA and the neutral bidentate ligand (S) is written as follows;

$$D = \frac{[\overline{MA_3}] + \Sigma [\overline{MA_3 S_m}]}{[M^{3+}] + \Sigma [MA_n^{3-n}]} = \left(\frac{P_{HA}}{K_{HA}}\right)^3 \cdot K_{ex} \cdot \frac{[A^-]^3 (1 + \Sigma \beta_{s,m} [\bar{S}]^m)}{1 + \Sigma \beta_n [A^-]^n} \quad (4)$$

where $MA_3 S_m$ is the adduct and $\beta_{s,m}$, the overall adduct formation constant for the equilibrium, $\overline{MA_3} + m \bar{S} \rightleftharpoons \overline{MA_3 S_m}$. From the equation (3) and (4), the following equation is given;

$$D/D_o = 1 + \Sigma \beta_{s,m} [\bar{S}]^m. \quad (5)$$

This equation can be rewritten as the next equation if only $MA_3 S_m$ is dominant species in the organic phase.

$$\log D/D_o = \log \beta_{s,m} + m \log [\bar{S}]. \quad (6)$$

The plots of $\log D/D_o$ against $\log [\bar{S}]$ may be a straight line with a slope of m. The synergic extraction of RE(III) with 10^{-3} M Htta and various concentration of S was carried out. As an example, the plots of $\log D/D_o$ against $\log [\overline{bpy}]$ are shown in Fig. 2. The equilibrium concentration of bpy in the organic phase was calculated by using the acid dissociation constant⁴⁾ and the partition coefficient⁴⁾ of bpy from the initial concentration and the pH value. These plots for RE(III) give the straight lines with the slope of 1.0, so that the 1:1 adduct as $RE(tta)_3 \text{bpy}$ is formed. This may be supported by the X-ray crystallographic study on the mixed ligand complex, $Nd(tta)_3 \text{bpy}$.⁵⁾

The values of $\beta_{s,1}$ in the bpy systems are listed in Table 1 together with

K_{ex} and $K_{ex,s,1}$, which is the synergic extraction constant and expressed as follows;

$$K_{ex,s,1} = \frac{[\overline{MA_3S}][H^+]^3}{[M^{3+}][\overline{HA}]^3[\overline{S}]} = K_{ex} \cdot \beta_{s,1} \quad (7)$$

The plots of their values against the atomic number of RE(III) are shown in Fig. 3. It is clearly observed that $\log \beta_{s,1}$ gradually increases with increasing of the atomic number of RE(III). This shows the reverse tendency in comparison with a tendency of the similar RE(III)-Htta systems involving unidentate ligands, such as tbp.⁶⁾ Consequently, the difference in $K_{ex,s,1}$ among RE(III) is larger than that in K_{ex} . This demonstrates that the extraction separation of RE(III) can be improved by synergic extraction with the neutral bidentate ligand.

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Table 1. Extraction constants in RE(III)-Htta-benzene systems and adduct formation constants and synergic extraction constants in RE(III)-Htta-bpy-benzene systems.

RE(III)	$\log K_{ex}$	$\log \beta_{s,1}$	$\log K_{ex,s,1}$
La	-10.35	5.36	-4.99
Ce	- 9.47	5.66	-3.81
Nd	- 8.70	5.95	-2.75
Sm	- 7.93	6.14	-1.79
Gd	- 7.76	6.38	-1.38
Tb	- 7.38	6.46	-0.92
Tm	- 6.84	6.58	-0.26
Yb	- 6.62	6.54	-0.08
Lu	- 6.65	6.51	-0.14

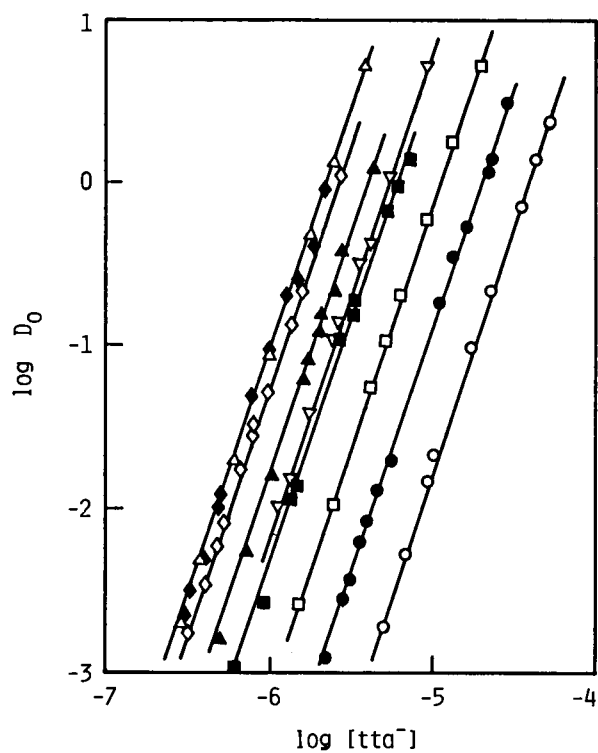


Fig. 1. The extraction of RE(III) with Htta in benzene.

○: La, ●: Ce, □: Nd, ■: Sm, ▽: Gd,
 ▲: Tb, ◇: Tm, △: Yb, ◆: Lu.

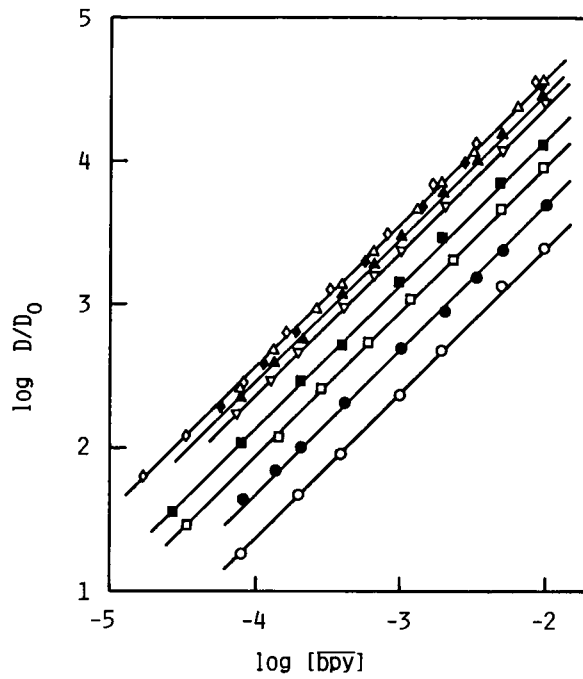


Fig. 2. The synergic extraction of RE(III) with Htta and bpy in benzene.

○: La, ●: Ce, □: Nd, ■: Sm, ▽: Gd,
▲: Tb, ◇: Tm, △: Yb, ◆: Lu.

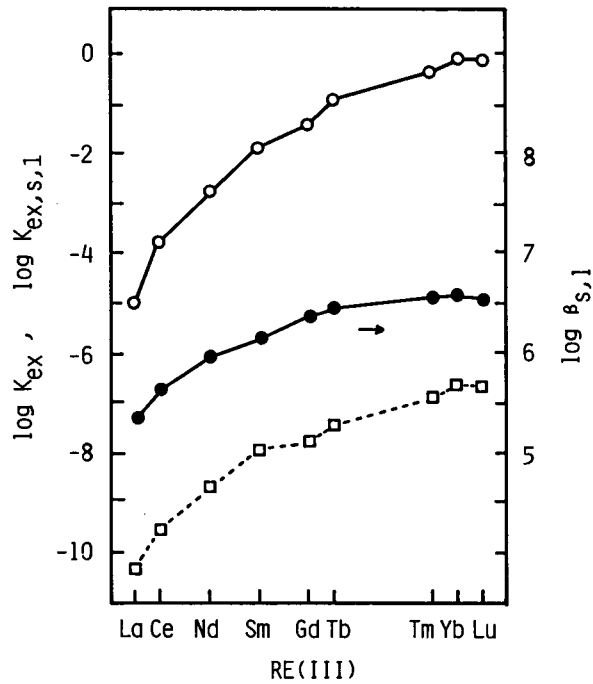


Fig. 3. Variation of the equilibrium constants in Htta-bpy-benzene systems with the atomic number of RE(III).

□: K_{ex} , ●: $\beta_{s,1}$, ○: $K_{ex,s,1}$.