

## Synergic Extraction of Lanthanoids(III) with 2-Thenoyltrifluoroacetone and Nitrogen-Containing Polydentate Ligands

著者	Satake S., Tsukahara S., Suzuki N.
journal or publication title	CYRIC annual report
volume	1993
page range	81-86
year	1993
URL	<a href="http://hdl.handle.net/10097/49751">http://hdl.handle.net/10097/49751</a>

## II. 1. Synergic Extraction of Lanthanoids(III) with 2-Thenoyltrifluoroacetone and Nitrogen-Containing Polydentate Ligands

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### Introduction

The synergic effect has been a well-known phenomenon in solvent extraction, which involves an enhancement of the extractability of a metal ion with an acidic chelating agent (HA) by the addition of a neutral ligand (S). The authors have conducted systematic studies<sup>1-5)</sup> concerning synergic extraction using various nitrogen-containing bidentate ligands, such as ethylenediamine (en) and 1,10-phenanthroline, finding that synergic extraction provides a new possibility for improving the separation efficiency among lanthanoids(III) (Ln). These results are never expected in the conventional synergic extraction system using a monodentate ligand, such as tributyl phosphate.

In the present extraction study, we paid the special attention to the synergic effect of polydentate ligands other than the bidentate type, *i.e.*, diethylenetriamine (dien) and triethylenetetramine (trien), in order to understand the synergic effect on the separation efficiency. We examined the synergic extraction of several Ln (III) (La, Sm, Tb and Lu) with 2-thenoyltrifluoroacetone (Htta) in the presence of such a neutral polydentate amine.

### Experimental

#### MATERIALS

The radioisotopes, <sup>140</sup>La, <sup>153</sup>Sm, <sup>160</sup>Tb and <sup>177</sup>Lu, which were used as tracers, were produced by neutron irradiation of metal nitrate in the JRR-4 nuclear reactor of the Japan Atomic Research Institute at a thermal neutron flux  $5.5 \times 10^{13}$  n cm<sup>-2</sup>s<sup>-1</sup> for 12 h. A radioactive solution of Ln was prepared by dissolving a known amount of the irradiated sample in 0.1 M (1 M=1 mol/dm<sup>3</sup>) nitric acid.

Htta was purified by vacuum sublimation. Polydentate amines were purified by recrystallization of their hydrochloride. Benzene was stirred with concentrated sulfuric acid, washed with water and distilled after drying. Other reagents were of analytical reagent grade.

## PARTITION COEFFICIENT OF POLYDENTATE AMINE

An aqueous solution containing 0.2 M polydentate amine (S) at pH 12-13 was shaken for 30 min with benzene. After phase separation by centrifuging, the distributed amine in the benzene phase was back-extracted into a  $1 \times 10^{-3}$  M HCl solution. The amine concentration was determined spectrophotometrically with *p*-chloranil<sup>6</sup>).

## EXTRACTION OF LN(III)

An aqueous solution ( $5 \text{ cm}^3$ ) containing  $1 \times 10^{-5}$  M Ln(III) labeled with its radioisotope,  $1 \times 10^{-4}$ - $1 \times 10^{-1}$  M dien-3HCl or  $3 \times 10^{-5}$ - $3 \times 10^{-3}$  M trien-4HCl, and  $1 \times 10^{-2}$  M sodium citrate to prevent hydrolysis, were placed in a centrifuge tube. The pH of the aqueous phase was adjusted with  $1 \times 10^{-3}$ - $1 \times 10^{-2}$  M piperazine-*N,N'*-bis(2-ethanesulfonic acid) or *N*-tris(hydroxymethyl)methyl-3-aminopropanesulfonic acid, and a sodium hydroxide solution. The ionic strength was adjusted to 0.1 with sodium chloride. A benzene solution ( $5 \text{ cm}^3$ ) containing  $1 \times 10^{-4}$ - $1 \times 10^{-2}$  M Htta was added, shaken for 1 h at 25 °C and centrifuged. The  $\gamma$ -activity of an aliquot ( $3 \text{ cm}^3$ ) of each phase was measured with an NaI(Tl) well-type scintillation counter, and the distribution ratio of Ln(III) was calculated as the radioactivity ratio. The pH of the equilibrated aqueous phase was measured immediately with a glass electrode after phase separation.

## Results and Discussion

### PARTITION COEFFICIENT OF POLYDENTATE AMINE

In the region where the pH is high, the amount of the protonated amine,  $\text{H}_i\text{S}^{i+}$ , is negligible. Hence, the distribution ratio of S is equal to the partition coefficient of amine ( $P_S = \overline{[S]}/[S]$ ). The upper-bar denotes in the organic phase. The stepwise acid dissociation constants ( $K_{\text{H}_i\text{S}}$ ) of the protonated amine ( $\text{H}_i\text{S}^{i+}$ ) were reported as:  $pK_{\text{H}_3\text{S}}=4.23$ ,  $pK_{\text{H}_2\text{S}}=9.02$  and  $pK_{\text{H}\text{S}}=9.847$ ) for dien;  $pK_{\text{H}_4\text{S}}=3.27$ ,  $pK_{\text{H}_3\text{S}}=6.59$ ,  $pK_{\text{H}_2\text{S}}=9.07$  and  $pK_{\text{H}\text{S}}=9.747$ ) for trien.  $P_S$  determined at pH 12-13 are  $10^{-4.41}$  and  $10^{-4.64}$  for dien and trien, respectively.

## EXTRACTION OF LN(III)

By considering the small  $P_S$  value of dien and trien, a noticeable synergic effect can be expected at a high pH region. Therefore,  $1 \times 10^{-2}$  M citric acid ( $\text{H}_3\text{cit}$ ) was added to prevent the hydrolysis of  $\text{Ln}^{3+}$  in the following extraction.

At first, the extraction of  $\text{Ln}^{3+}$  with HA was carried out in the absence of polydentate amines. When  $\text{Ln}^{3+}$  quantitatively exists as complexes with  $\text{cit}^{3-}$ ,  $\text{Ln}(\text{cit})_j^{(3-3j)+}$  in the aqueous phase, the distribution ratio ( $D_o$ ) of  $\text{Ln}^{3+}$  can be expressed as:

$$D_o = \frac{[\overline{\text{LnA}_3}]}{\sum_j [\text{Ln}(\text{cit})_j^{(3-3j)+}]} = K_{\text{ex}}' P_{\text{HA}}^3 [\text{A}^-]^3 / K_{\text{HA}}^3 \quad (1)$$

where  $K_{\text{ex}}'$  is the conditional extraction constant in the presence of 0.01 M citrate ion,  $P_{\text{HA}}$  and  $K_{\text{HA}}$  being the partition coefficient and acid-dissociation constant of HA, respectively.

The plots of  $\log D_o$  vs.  $\log [\text{tta}^-]$  give straight lines with a slope of 3.0 for each Ln(III), and thus the extracted species is  $\text{Ln}(\text{tta})_3$ . The equilibrium  $\text{tta}^-$  concentration in the aqueous phase was calculated using,

$$[\text{tta}^-] = C_{\text{HA}} / \{ (P_{\text{HA}} + 1)[\text{H}^+] / K_{\text{HA}} + 1 \} \quad (2)$$

where  $C_{\text{HA}}$  denotes the initial Htta concentration. The literature values of  $K_{\text{HA}}$  ( $10^{-6.23}$ )<sup>8</sup> and  $P_{\text{HA}}$  ( $10^{1.62}$ )<sup>9</sup> were used. The  $K_{\text{ex}}'$  values calculated using Eq. (1) are listed in Table 1.

### SYNERGIC EXTRACTION OF LN(III)

In the synergic extraction of  $\text{Ln}^{3+}$  with HA and a polydentate amine S, the distribution ratio (D) of  $\text{Ln}^{3+}$  is expressed as:

$$\begin{aligned} D &= \{ \overline{[\text{LnA}_3]} + \sum_n \overline{[\text{LnA}_3\text{S}_n]} \} / \sum_j [\text{Ln}(\text{cit})_j^{(3-3j)+}] \\ &= \overline{[\text{LnA}_3]} (1 + \sum_n \beta_{s,n} \overline{[\text{S}]^n}) / \sum_j [\text{Ln}(\text{cit})_j^{(3-3j)+}] \\ &= (1 + \sum_n \beta_{s,n} \overline{[\text{S}]^n}) K_{\text{ex}}' P_{\text{HA}}^3 [\text{A}^-]^3 / K_{\text{HA}}^3 \end{aligned} \quad (3)$$

where  $\beta_{s,n}$  is the adduct formation constant in the organic phase corresponding to the following equilibrium:



According to Eq. (3), it is expected that D depends on the third power of  $[\text{A}^-]$ . From Eqs. (1) and (3), the following simple relationship is obtained:

$$D/D_o = 1 + \sum_n \beta_{s,n} \overline{[\text{S}]^n} \quad (5)$$

If  $\text{LnA}_3\text{S}_n$  is the dominant species in the organic phase,  $D/D_o$  depends on the n-th power of the free amine concentration in the organic phase. The conditional synergic extraction constant ( $K_{\text{ex},s,n}'$ ) in the presence of the citrate is obtained by

$$K_{\text{ex},s,n}' = K_{\text{ex}}' \cdot \beta_{s,n} \quad (6)$$

The plots of  $\log D$  vs.  $\log [\text{tta}^-]$  give straight lines with a slope of 3.0 for each Ln(III) (La, Sm, Tb and Lu) in the Htta-dien and Htta-trien systems. Therefore, three  $\text{tta}^-$  also participate in these cases.

The plots of  $\log (D/D_o)$  against  $\log \overline{[\text{S}]}$  with  $1 \times 10^{-4}$ - $1 \times 10^{-2}$  M Htta and  $3 \times 10^{-5}$ -

$1 \times 10^{-2}$  M dien are shown in Fig. 1.  $\overline{[S]}$  of dien (and trien) was calculated as:

$$\overline{[S]} = \frac{C_S}{1 + \{1 + \sum_i [H^+]^i / (K_{H_iS} K_{H(i-1)S} \cdots K_{HS})\} / P_S} \quad (7)$$

where  $C_S$  denotes the initial concentration of S.  $D_o$  values were calculated from Eq. (1) using the  $K_{ex}$ ' values. As shown in Fig. 1, the plots for each Ln give straight lines with a slope of 1.0. This indicates that the  $Ln(tta)_3S$  forms in the organic phase. The similar relation was observed for La, Sm and Tb in the Htta-trien system, although an enhancement of D of Lu was not clearly observed even upon the addition of  $3 \times 10^{-3}$  M trien.

The  $\beta_{s,1}$  and  $K_{ex,s,1}'$  values calculated from Eq.(5) and Eq.(6), respectively, are summarized in Table 1. The  $\beta_{s,1}$  for dien is about  $10^5$ -times larger than that for another tridentate amine, 2,2':6',2''-terpyridine ( $pK_{H_2S}=3.45$ ;  $pK_{HS}=4.55^{16}$ ), and  $\log \beta_{s,1}=7.16$ (La); 6.97(Sm); 4.75(Lu)<sup>13</sup>). These differences can be explained by the general understanding that a neutral ligand with higher basicity produces higher synergic effect. The  $\beta_{s,1}$  for a series of amines, en,<sup>4</sup>) dien, and trien, show a marked variation, that is,  $\beta_{s,1}$  for La(III) increase in the order: en < dien < trien, although three amines seem to be nearly the same level in basicity,  $pK_{HS}=9.89$  (en); 9.84 (dien); 9.74 (trien)<sup>7</sup>). This result means that the polydentate amine, having a greater number of nitrogen atoms, shows larger synergic effect as a usual tendency observed in general complex formation. This relation is recognized for light lanthanoids with a larger ionic radius, e.g., La(III); however, for Lu(III) with a smaller ionic radius,  $\beta_{s,1}$  for trien is smaller than those for en and dien, due to an insufficient coordination containing the steric hindrance of the four nitrogens of trien. The  $\beta_{s,1}$  values are plotted against the atomic numbers of Ln(III) for en, dien and trien in Fig. 2. Although  $\beta_{s,1}$  values for the bidentate en increase simply with increasing atomic number, it tends to decrease with increasing atomic number for the tridentate dien;  $\beta_{s,1}$  values decrease abruptly for the quadridentate trien.

The magnitude of the  $K_{ex,s,1}'$  is governed by  $\beta_{s,1}$  as indicated by Eq. (6).  $K_{ex,s,1}'$  is directly related to the extraction efficiency of Ln(III). The  $K_{ex,s,1}'$  values are plotted against the atomic number of Ln(III) in Fig. 3. For the Htta-en system,  $K_{ex,s,1}'$  values increase with increasing atomic number. For Htta-dien,  $K_{ex,s,1}'$  shows the maximum at Tb, and for Htta-trien they decrease with increasing atomic number. These results suggest that there is a possibility regarding an improvement in the extraction selectivity to choose the nitrogen-containing neutral ligands.

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Table 1. Conditional extraction constants ( $K_{ex}$ '), adduct formation constants ( $\beta_{s,1}$ ) and conditional synergic extraction constants ( $K_{ex,s,1}$ ') in the Ln(III)-Htta-S-benzene systems.

S	Ln(III)	$\log K_{ex}'^a)$	$\log \beta_{s,1}$	$\log K_{ex,s,1}'^a)$
Dien	La	-16.89	12.22	-4.67
	Sm	-15.74	11.86	-3.88
	Tb	-15.16	11.61	-3.55
	Lu	-15.35	9.82	-5.53
Trien	La	-16.89	13.64	-3.25
	Sm	-15.74	12.08	-3.66
	Tb	-15.16	10.86	-4.30
	Lu	-15.35	<8.5	<-6.9

a) In the presence of 0.01 M citrate ion.

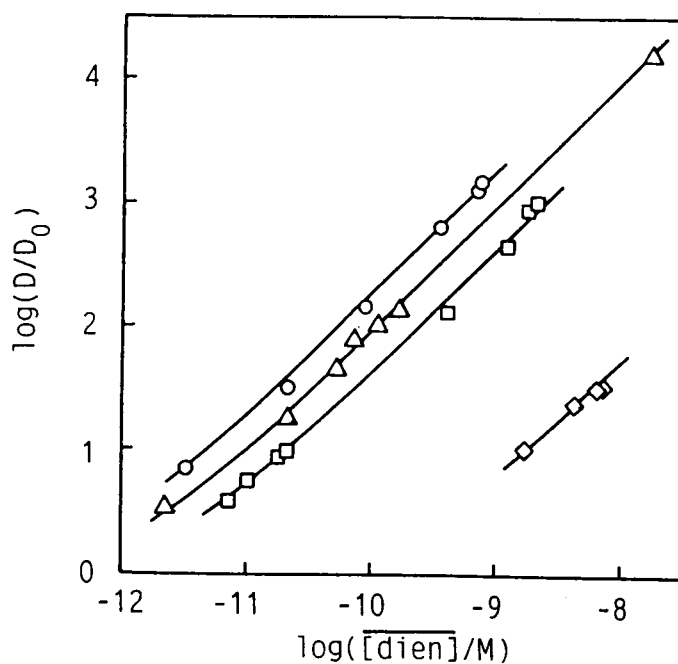


Fig. 1. Dependence of  $D/D_0$  on the concentration of dien in the benzene phase.  $[Htta]_{ini} = 1 \times 10^{-4} - 1 \times 10^{-2}$  M.  $\circ$ La,  $\Delta$ Sm,  $\square$ Tb,  $\diamond$ Lu

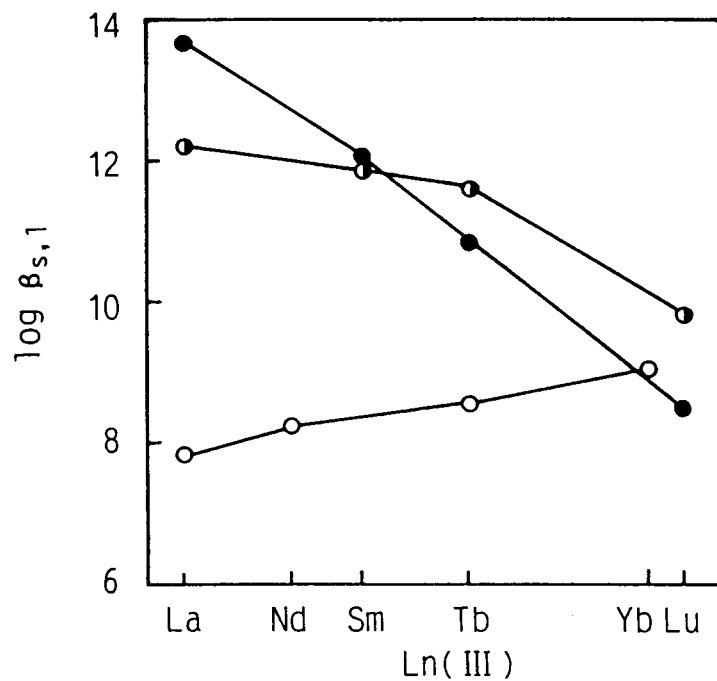


Fig. 2. Plots of  $\beta_{s,1}$  in the Ln(III)-Htta-S-benzene systems in order of atomic number. S; Oen<sup>4</sup>, ◐ dien, ● trien.

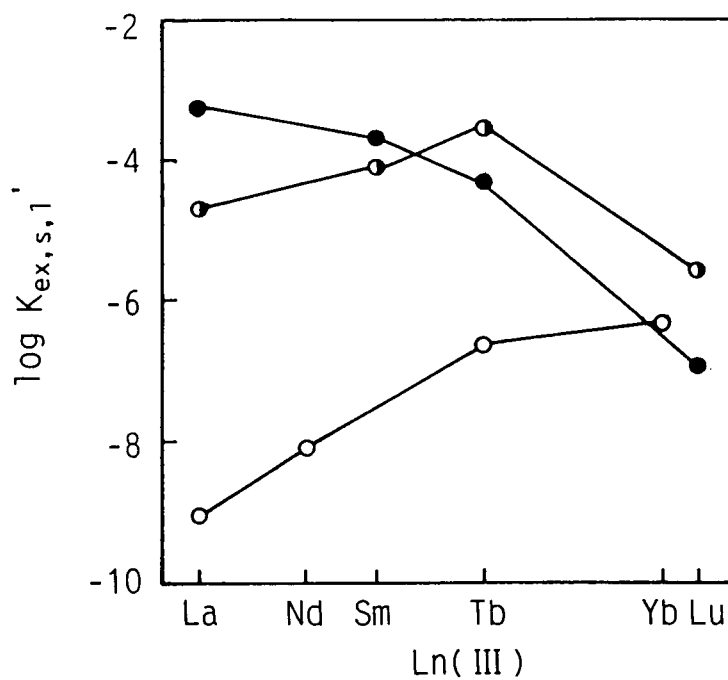


Fig. 3. Plots of  $K_{ex,s,1}$  in the Ln(III)-Htta-S-benzene systems in order of atomic number. S; Oen<sup>4</sup>, ◐ dien, ● trien.