Synergic Extraction of Lanthanoids (III) with Thenoyltrifluoroacetone and Terpyridine

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Introduction

In the solvent extraction of metal ion (M^{n+}), the synergic extraction using acidic chelating extractant (HA) and neutral ligand (S) have been studied. The synergic extraction is built up two processes; (1) M^{n+} is extracted into the organic phase as a metal complex, MA_n, and (2) the MA_n and m molecules of S form an adduct, MA_nS_m, in the organic phase. The apparent equilibrium constant of the first process is known as the extraction constant, K_{ex}, and that of the second is the adduct formation constant in the organic phase, $ß_{s,m}$. As a neutral ligand, unidentate ligands such as tributyl phosphate (tbp) or trioctylphosphine oxide (topo) possessing an oxygen to coordinate have been widely used.

In the synergic extraction of lanthanoids using ß-diketone as HA, it was observed that two molecules of tbp or topo coordinates to MA_3, and $ß_{s,2}$ decreased monotonically with increasing in the atomic number (Z) of lanthanoids. In these systems, the extractabilities of metal is highly improved compared with the extraction system using HA only, but the separation efficiency among lanthanoids become poor. But recently, a new trend was found in the synergic extraction with neutral bidentate ligands having nitrogens as coordinating atom, such as 1,10-phenanthroline (phen) or 2,2'-bipyridine (bpy) [1-4]. In these systems, $ß_{s,1}$ increased with increasing in Z, and this suggest a new possibility that the synergic extraction improve both the extractability and the separation efficiency. So the detailed study of the synergic extraction involving multidentate heterocyclic amine is important.

In this paper, the synergic extraction of lanthanoids with 2-thenoyltrifluoroacetone (Htta) and 2,2':6',2''-terpyridine (tpy), which has three nitrogens to coordinate, is performed.

Theoretical

In the extraction system with HA, the logarithmic distribution ratio (D_o) of metal is written as

$$\log D_o = \log(K_{ex}P_{HA}^n/K_{HA}^n) + n\cdot\log[A^-] \qquad (1),$$

where K_{ex} is the extraction constant ($= [\overline{MA_n}]\cdot[H^+]^n/[M^{n+}]/[\overline{HA}]^n$), P_{HA} the partition coefficient of HA, K_{HA} the acid-dissociation constant of HA and A^- the dissociated anion of HA. Upper bar donates the organic phase.

In a synergic extraction with HA and S, the logarithmic distribution ratio (D) is written as

$$\log D = \log\{K_{ex}P_{HA}^n(1 + \Sigma\beta_{s,m}[\overline{S}]^m)/K_{HA}^n\} + n\cdot\log[A^-] \quad (2),$$

where $\beta_{s,m}$ is the overall adduct formation constant in the organic phase ($= [\overline{MA_nS_m}]/[\overline{MA_n}]/[\overline{S}]^m$). From Eqns. 1 and 2,

$$\log(D/D_o) = \log(1+\Sigma\beta_{s,m}[S]^m) \quad (3).$$

The synergic extraction constant, $K_{ex,s,m}$, ($= [\overline{MA_nS_m}]\cdot[H^+]^n/[M^{n+}]/[\overline{HA}]^n/[\overline{S}]^m$) is simply obtained as

$$K_{ex,s,m} = K_{ex}\cdot\beta_{s,m} \quad (4).$$

Experimental

Htta and tpy were purified by vacuum sublimation. Radioisotopes, ^{140}La, ^{147}Nd, ^{153}Sm, ^{175}Yb and ^{177}Lu were produced by the neutron irradiation of these metal oxides or nitrates in a nuclear reactor (JRR-2 or JRR-4) of the Japan Atomic Research Institute. ^{152}Eu was purchased. The radioactive solution of lanthanoid Ln(III) was prepared by dissolving a known amount of the irradiated target in nitric acid, evaporating to dryness and redissolving in 10^{-3} M perchloric acid or hydrochloric acid solution.

The aqueous solution containing 10^{-6}-10^{-5} M of Ln(III) labelled with radioactive traces, 10^{-3} M of sulfanilic acid (pK_a=3.23) for pH buffer, 0.1 M electrolyte for adjusting the ionic strength was shaken with the equivolume (5 cm^3) of benzene solution containing 10^{-3}-10^{-1} M Htta and 10^{-6}-10^{-2} M tpy for 1 h. Perchloric acid and sodium perchlorate were used to adjust the ionic strength, but hydrochloric acid and sodium chloride were used in some cases of the extraction of Lu. After phase separation by centrifugation, 3 cm^3 of the benzene and the aqueous phase were pipetted and the radioactivities were measured with a NaI(Tl) well-type scintillation counter. The distribution ratio of Ln was obtained as the radioactivity ratio of the benzene and the aqueous phases, and the equilibrium pH of the aqueous phase was measured with a glass electrode. All experiments were performed in a thermostated room at 25 ± 1 °C.

Results and Discussion

The distribution ratios of tpy between the benzene and the aqueous phase were examined in the pH range 1-3. From these data and the acid dissociation constants of the conjugated acids of tpy, K_{HS} for $Htpy^+$ and K_{H2S} for H_2tpy^{2+}, the partition coefficient of tpy, P_s was obtained as 1445 ± 3 (n = 5). The equilibrium concentration of tpy in the organic phase, $[\overline{tpy}]$, can be calculated from Eqn. 5.

$$[\overline{tpy}] = \frac{C_S \cdot P_S}{1+[H^+]/K_{HS}+[H^+]^2/K_{H2S}/K_{HS}+P_S}, \qquad (5)$$

where C_S is the initial concentration of tpy in the benzene phase.

Distribution ratio of Ln with Htta (D_o) was examined in the pH range 3.4-5.6 at a constant initial concentration of Htta, C_{HA}. Log D_o is plotted against log [tta^-] as shown in Fig. 1. In these plots, [tta^-] was calculated from Eqn. 6,

$$[tta^-] = \frac{C_{HA}}{1+(1+P_{HA})[H^+]/K_{HA}} \qquad (6)$$

All the data for every lanthanoids are located on the line of slope three. From these plots, Ln are thought to be extracted as $Ln(tta)_3$ from Eqn. 1, and K_{ex} is obtained as summarized in Table 1. Small value of K_{ex} shows that Ln can not be practically extracted Htta only.

As shown in Fig. 1, an addition of a small amount of tpy causes an enhancement of distribution ratio of Ln by 10^2-10^4 times. In the present systems, the slopes of the plots of log D against log [tta^-] are almost three. These facts indicate Ln(III) are extracted with three tta^- anions even in the presence of tpy. In the synergic extraction of Lu, when the ionic strength was adjusted with perchlorate as usual, the slope of the plots was 2.67. This is smaller than the expected value of three, but when the ionic strength was adjusted with chloride, the slope is 2.91 and close to three as shown in Fig. 1.

According to Eqn. 3, the coordinated molecule number of tpy, m, in the extracted species is estimated. Log(D/D_o) is plotted against log $[\overline{tpy}]$ calculated from Eqn. 5. D_o at the same condition is calculated from Eqn. 1. The slopes are almost one as shown in Fig. 2. These results indicate the coordinated molecule number of tpy, m, is 1 for all Ln's.

As a result, Ln(III) is extracted as $Ln(tta)_3(tpy)$. $ß_{s,1}$ and $K_{ex,s,1}$, are calculated using Eqns. 3 and 4 as summarized in Table 1. $ß_{s,1}$ decreases with increasing in the atomic number, on the other hand, $K_{ex,s,1}$ shows a clear increase from La to Nd and then seems to be similar order of magnitude for higher Ln's.

It is interesting to compare $ß_{s,1}$ of tpy with that of relative heterocyclic amines such as pyridine (py) and bipyridine (bpy).[3] $ß_{s,1}$ of tpy and bpy is higher than $ß_{s,2}$ of unidentate ligand py for all Ln's, but tpy and bpy show opposite trend each other, for example $ß_{s,1}$ of

tpy is 100 times larger than that of bpy for light lanthanoid La, but 100 times smaller for heavy lanthanoid Lu.

It is reported that tpy in the ternary crystal $Eu(dpm)_3(tpy)$ (dpm = dipivaloylmethanate), where dpm is one of ß-diketones, coordinates as a tridentate ligand.[5] In the synergic extraction system of Ln with Htta and phenanthroline (phen), which is bidentate neutral ligand, the adduct formation of $Ln(tta)_3$ with two molecules of phen is observed for lighter lanthanoids.[1-2] From these results, in the present study, tridentate tpy is able to coordinate to the metal chelate of light lanthanoids, and $ß_{s,1}$ for tpy is larger than that for bidentate bpy, but tpy can not fulfil its function as a tridentate ligand for metal chelate of heavy lanthanoids with smaller ionic size and play as a bidentate ligand, in other words the coordination of tpy with lager molecular size than bpy is highly interfered by a steric hindrance in a crowded surroundings of metal chelate, hence $ß_{s,1}$ of tpy for heavy lanthanoids may be smaller than that of bpy.

The characteristic trend observed in the synergic extraction involving multidentate neutral ligand may suggest a new possibility to improve the separation efficiency in the synergic extraction.

References

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Table 1.
Equilibrium constants of Ln(III) in Htta-benzene and Htta-tpy-benzene system.

Ln(III)	log K_{ex}	log $ß_{s,1}$	log $K_{ex,s,1}$
La	- 10.19	7.16	- 3.03
Nd	- 8.64	7.26	- 1.38
Sm	- 7.80	6.97	- 0.83
Eu	- 7.72	6.78	- 0.94
Ho[a]	- 7.09	5.86	- 1.23
Yb	- 6.61	5.03	- 1.58
Lu[b]	- 6.56	4.75	- 1.81

a) Reference 4
b) Ionic strength 0.1M(H^+,Na^+)Cl^-.

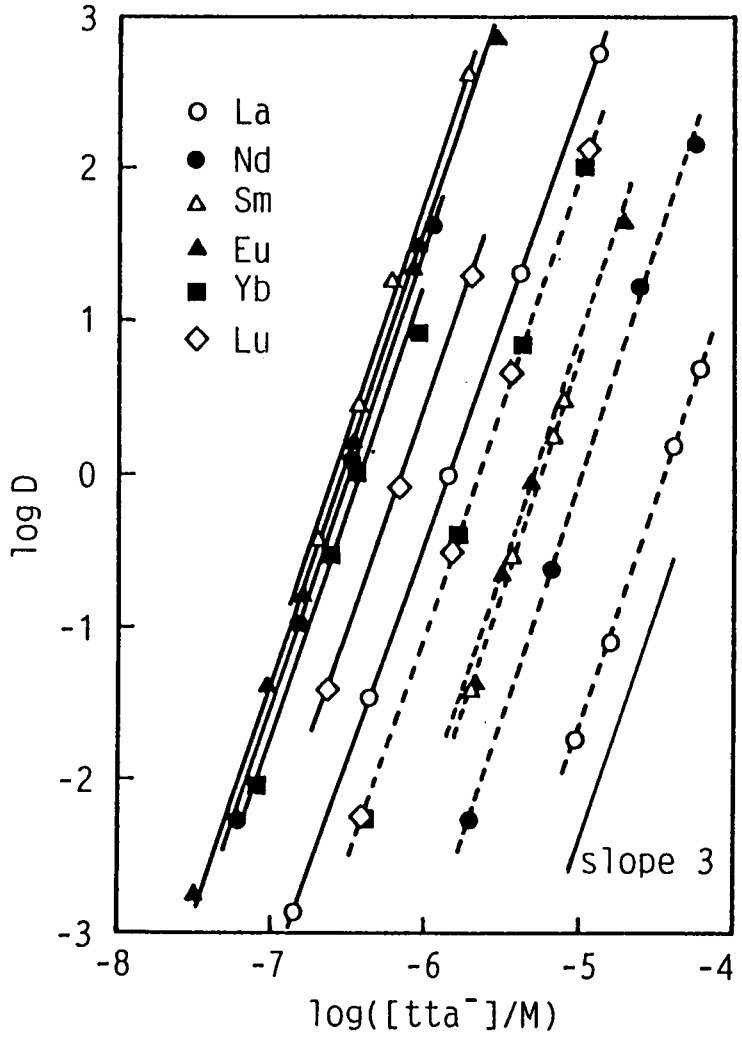

Fig. 1. Dependence of the distribution ratio of Ln on the equilibrium concentration of tta^- in the Htta-benzene system(- - - -) and in the Htta-tpy-benzene system(——).
$[\overline{tpy}] = 0.79 - 1.3 \times 10^{-3}M$

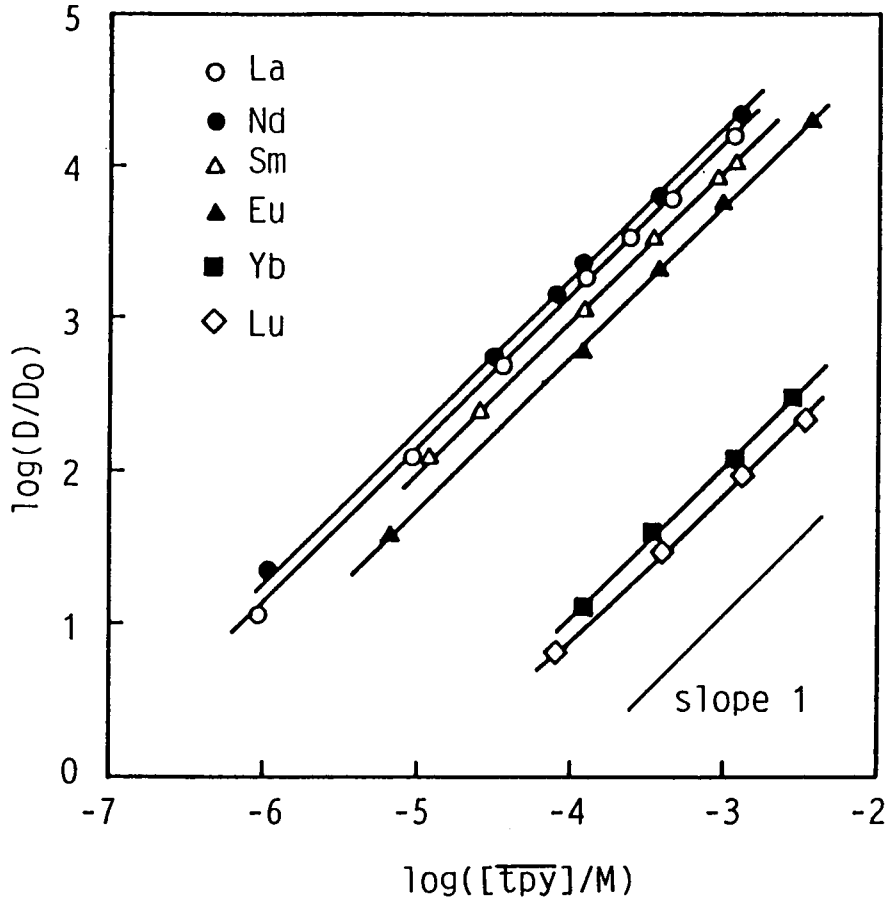

Fig. 2. Dependence of D/D_o on the equilibrium concentration of tpy in the benzene phase.