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journal or publication title	Solvent Extraction Research and Development
volume	14
page range	97-104
year	2007-01-01
URL	http://hdl.handle.net/2297/7036

Enhancement of the Extraction of Lanthanide(III) with 2-Thenoyltrifluoroacetone in the Presence of Foreign Metal(III) Ions: Coextraction of Light Lanthanide(III) with Al^{3+}, Sc^{3+} and Fe^{3+}

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Enhancement of the extraction, or coextraction of lanthanide(III) (Ln) with metal(III) ions (M^{3+}) such as Al^{3+}, Sc^{3+}, and Fe^{3+} was found in a typical chelate extraction system of 2-thenoyltrifluoroacetone (Htta)-benzene.   The distribution ratio of La^{3+} was enhanced by a factor of 6 with 3.0×10^{-2} M Al^{3+}, while that of Lu^{3+} was not affected at all.   The magnitude of the coextraction decreased with the atomic number of Ln.   Equilibrium analysis and spectroscopic studies indicated that the coextraction was ascribed to the formation of the 1:1 adduct between $Ln(tta)_3$ and $M(tta)_3$ extracted into the organic phase. The overall equilibrium of the coextraction was expressed as

$$Ln^{3+} + M^{3+} + 6\ Htta_{org} \rightleftharpoons Ln(tta)_3(M(tta)_3)_{org} + 6\ H^+.$$

1. Introduction

Coextraction phenomena have been found in various solvent extraction systems, especially in ion-association systems, and these have been comprehensively reviewed by Bagreev et al [1].   The mechanism of the coextractions reported so far can be classified as follows:

(1) Ion association between the cationic and the anionic complexes with the same ligands; e.g., Zn(II) was co-extracted with Fe(III) into isopentyl alcohol due to the formation of an ion-association complex, $[ZnCl]^+[FeCl_4]^-$ [1].

(2) Ion association between the cationic and the anionic complexes with different ligands; e.g., coextraction of Tc(VII) with U(VI) in the n-octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide (CMPO) system has been reported [2].   The equilibrium was proposed as follows:

$$UO_2(NO_3)_2 \cdot nCMPO_{org} + TcO_4^-{}_{aq} \rightleftharpoons UO_2NO_3 \cdot TcO_4 \cdot nCMPO_{org} + NO_3^-{}_{aq}.$$
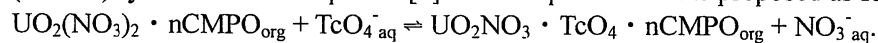
(3) Ion association between anionic complexes and cationic chelates, or anionic chelates and cations; e.g., Ca(II) was co-extracted with Sc(III) or Nd(III) as $Ca[REA_4]_2$ in which REA_4^- is the anionic rare earth(III) β-diketonate [1].   Dyrssen has described the coextraction of the ion association complex between Na^+ and anionic chelates of the 4-isopropyltropolone of Ni(II) or Zn(II) [3].

(4) Formation of a binuclear complex composed of the same ligand; e.g., Fe(II) was co-extracted with Sn(II) when these metals were extracted by dimethylglyoxime (H_2A) as the result of the formation of $FeSn_x(HA)_y$ [1].

(5)Alkylphosphoric acid, naphthenic acid, and carboxylic acids extraction systems; the mechanisms of these coextraction systems are complex, and have not been completely clarified [1].

Most of the mechanisms proposed for the coextraction related to the formation of ion-association complexes.   Very few detailed studies on fundamental chelate extraction systems such as β-diketone-non-polar solvent systems have been reported.

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In a series of studies on novel synergism, the remarkable enhancement of the extraction of Ln with a β-diketone such as acetylacetone, hexafluoroacetylacetone, and 2-thenoyltrifluoroacetone (Htta) has been found in the presence of tris(acetylacetonato)-chromium(III) [4] and -cobalt(III) [5-8], tris(8-quinolinolato)cobalt(III) [9] or tris(4-isopropyltropolonato)cobalt(III) [8, 10] in the organic phase. This phenomenon was attributed to adduct formation between Ln-β-diketone chelates and the inert Cr(III) or Co(III) chelates in the organic phase. These results reveal that the coordinately saturated metal(III) chelates of Cr(III) and Co(III) act as a complex ligand toward the coordinately unsaturated chelates of Ln-β-diketones and that adduct formation occurs between both chelates even with the same ligand.

In this paper, the effect of labile metal ions (M^{3+}) such as Al^{3+}, Sc^{3+}, and Fe^{3+} on the extraction of Ln with Htta in benzene was studied to reveal the evidence of coextraction in this typical chelate extraction system. To prove adduct formation between the tta chelates, the extraction of Ln with Htta in the presence of inert $Co(tta)_3$ instead of the labile metal tta chelates was also studied. The equilibrium and mechanism of the coextraction were investigated by not only equilibrium analysis but also spectroscopic studies such as electronic absorption and IR.

2. Experimental

2.1 Reagents

Ln stock solutions were prepared by dissolving high purity Ln oxides (Aldrich, 99.99%) in nitric acid, evaporating to dryness, and redissolving in dilute perchloric acid. Stock solutions of Al^{3+}, Sc^{3+}, and Fe^{3+} were prepared by dissolving the corresponding nitrate or chloride (Wako) in a perchloric acid solution. Htta was obtained from Dojindo Lab. and purified by vacuum sublimation. Trihydrated tris(2-thenoyl-trifluoroacetonato)europium(III) ($Eu(tta)_3(H_2O)_3$) was synthesized in the same manner as described in a previous paper [6]. Tris(2-thenoyltrifluoroacetonato)cobalt(III) ($Co(tta)_3$) was synthesized using sodium tris(carbonato)cobaltate(III) prepared by the usual method [11] and Htta in acetone-water. Purification of $Co(tta)_3$ was performed in the similar manner as reported previously [9]. The purity was confirmed by elemental analysis (Found : C, 39.59; H, 1.84 %. Calculated for $Co(C_8H_4O_2F_3S)_3$: C, 39.90; H, 1.67 %). From ^1H-NMR of $Co(tta)_3$ in $CDCl_3$, it was ascertained to be a single geometric meridional isomer. Other reagents used were of analytical reagent grade.

2.2 Extraction procedure

An aqueous solution containing 1.0×10^{-5} M Ln and 2.5×10^{-3}-3.0×10^{-2} M Al^{3+}, Sc^{3+}, or Fe^{3+} was shaken with an equal volume of a benzene solution of 3.0×10^{-1} - 4.0×10^{-1} M Htta for 3-24 h at 25 °C. After centrifugation, Ln and M^{3+} in the aqueous phase were determined by ICP-AES (Nippon Jarrell Ash ICAP-575). An aliquot of the organic phase was shaken with 0.1 M perchloric acid for 1 h to strip Ln and M^{3+} into the aqueous solution, which was then subjected to the ICP-AES determination. In the case of Al^{3+} and Fe^{3+}, the stripping was done using 6 M hydrochloric acid for 3-24 h. The distribution ratios of Ln and M^{3+} were calculated from the concentrations in the organic and the aqueous phases. The equilibrium pH was measured just after phase separation with a Radiometer PHM93 pH meter with a combination glass electrode. From the equilibrium analysis almost all M^{3+} was extracted into the organic phase as $M(tta)_3$. Therefore, the ionic strength of the aqueous phase could be maintained at 0.15 M by using sodium perchlorate.
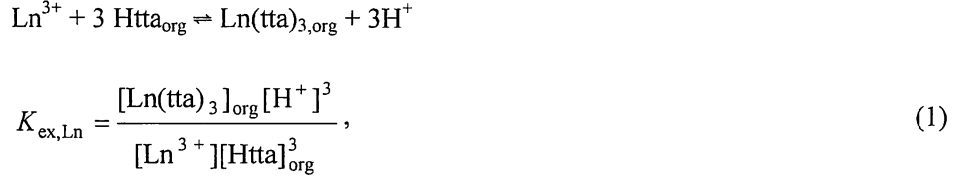
2.3 Spectroscopic measurements

A sample solution containing $Ln(tta)_3$ and $Co(tta)_3$ for the measurement of the electronic absorption spectra was prepared by mixing the $Co(tta)_3$ solution with the $Ln(tta)_3$ solution prepared by the solvent extraction of 1.0×10^{-2} M Ln with 1.0×10^{-1} M Htta in benzene at pH 5.7-6.3. Electronic absorption spectra for 2.0×10^{-3} M $Co(tta)_3$ were measured in the presence of varying concentrations of $Ln(tta)_3$ (Ln: La, Eu, and Lu) at 500-700 nm with a JASCO V-560 UV/VIS spectrophotometer.

A sample solution for IR measurement was prepared by the same manner except that 3.0×10^{-2} M Htta which was equivalent to the total concentration of Ln was used to decrease a free Htta in the sample solution. The concentration of the remaining Htta was reduced to less than 9×10^{-4} M. The water content in the sample solutions was kept constant at 2.0×10^{-2} M using benzene saturated with water and anhydrous benzene. In the IR experiments, synthesized $Eu(tta)_3(H_2O)_3$ was also used in anhydrous benzene. The IR spectra of free water and water coordinated to 6.0×10^{-3} M $Ln(tta)_3$ (Ln : Eu and Lu) in benzene were measured in the presence of varying concentrations of $Co(tta)_3$ at 3000-4000 cm^{-1} with a Shimadzu-8200A FT-IR spectrophotometer. A demountable liquid cell with calcium fluoride windows was used and the path length was adjusted to 1 mm.

3. Results and Discussion

3.1 Effect of metal(III) ions on the extraction of lanthanide(III)

The extraction of La^{3+}, Eu^{3+}, and Lu^{3+} was carried out with 4.0×10^{-1} M Htta in benzene in the presence of 3.0×10^{-2} M Al^{3+}, Sc^{3+}, or Fe^{3+} at various pH values (Fig.1). The extraction equilibrium of Ln was studied to quantitatively evaluate the effect of the metal ions. The extraction of Ln with Htta is expressed as,

$$Ln^{3+} + 3\, Htta_{org} \rightleftharpoons Ln(tta)_{3,org} + 3H^+$$

$$K_{ex,Ln} = \frac{[Ln(tta)_3]_{org}[H^+]^3}{[Ln^{3+}][Htta]_{org}^3},$$
(1)

where the subscript org indicates the species in the organic phase, and $K_{ex,Ln}$ is the extraction constant of Ln. The distribution ratio of Ln under the present conditions is given as,

$$D_0 = \frac{[Ln(tta)_3]_{org}}{[Ln^{3+}] + \sum_n [Ln(tta)]_n^{(3-n)+}} \approx \frac{[Ln(tta)_3]_{org}}{[Ln^{3+}]}.$$
(2)

From Eqs.(1) and (2), following relation is derived,

$$\log D_0 = \log K_{ex,Ln} + 3\, pH + 3 \log [Htta]_{org}.$$
(3)

The equilibrium concentration of Htta in the organic phase was calculated from the total concentration (C_{HA}) of Htta and pH as follows:
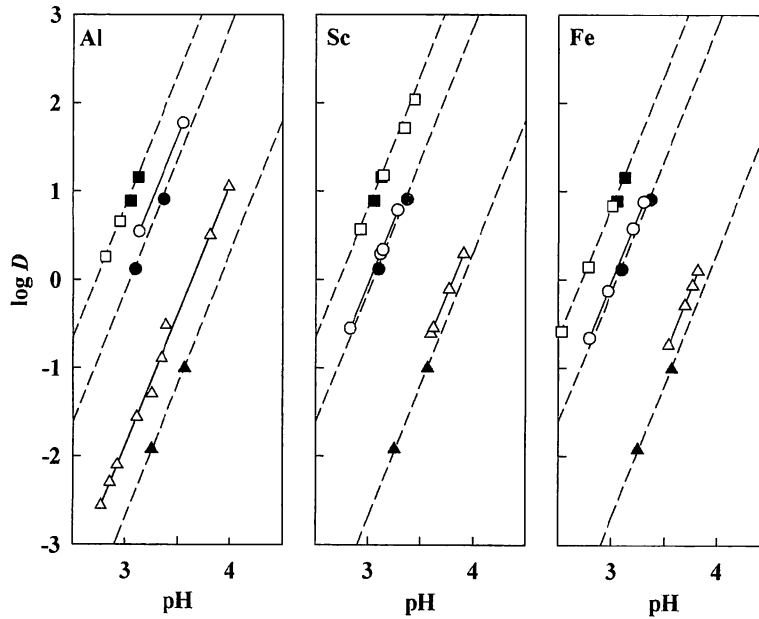

Fig.1 Extraction of Ln^{3+} with Htta in benzene in the presence or absence of M^{3+} at $I = 0.15$. Open symbols: with 3.0×10^{-2} M M^{3+}; [Htta]$_{init}$ = 4.0×10^{-1} M; $\triangle$, La; $\bigcirc$, Eu; $\square$, Lu. Closed symbols: without M^{3+}; [Htta]$_{init}$ = 3.1×10^{-1} M; $\blacktriangle$, La; $\bullet$, Eu; $\blacksquare$, Lu. Each broken line was calculated from the $K_{ex,Ln}$ value of Ln and the corrected concentration (3.1×10^{-1} M) of Htta.

$$[\text{Htta}]_{\text{org}} = \frac{C_{\text{HA}}}{1 + (K_{\text{HA}} + [\text{H}^+])/[\text{H}^+]P_{\text{HA}}} \ , \tag{4}$$

where K_{HA} and P_{HA} are the acid-dissociation constant and the partition coefficient of Htta respectively. To obtain the equilibrium concentration of Htta, the total concentration of Htta free from extracted M^{3+} must be used because a part of Htta is consumed as $M(\text{tta})_3$ in the organic phase. Since M^{3+} was quantitatively extracted into the organic phase at pH 2.8 – 4.0, the total concentration of Htta was calculated to be 3.1×10^{-1} M. The extraction of Ln with 3.1×10^{-1} M Htta was also carried out in the absence of M^{3+} at $I = 0.15$. Figure 1 shows that the experimental plots (closed symbols) are consistent with the calculated values (broken lines) which were obtained by Eq.(3) using $K_{\text{ex,Ln}}$ ($=10^{-10.14}$ (La), $10^{-7.64}$ (Eu), $10^{-6.66}$ (Lu)) [4], $K_{\text{HA}}(=10^{-6.23})$ [12], and $P_{\text{HA}}(=10^{1.62})$ [13] at $I = 0.10$. This result suggests that the difference in the distribution ratio of Ln between $I = 0.10$ and 0.15 is negligible under the given conditions. Therefore, the calculated values of D_0 for Ln can be adopted.

The enhancement of the extraction, i.e., coextraction, of La and Eu is observed in Fig.1 when $M(\text{tta})_3$ was extracted into the organic phase. Particularly the coextraction of La^{3+} with Al^{3+} is remarkably large. The distribution ratio of La^{3+} and Eu^{3+} increased by a factor of 6 and 2.4 respectively in the presence of 3.0×10^{-2} M $Al(\text{tta})_3$ in the organic phase. On the other hand, no phenomenon of coextraction was observed for Lu^{3+}. The enhancement of the extraction of La^{3+} and Eu^{3+} with Sc^{3+} or Fe^{3+} was also observed when Sc^{3+} and Fe^{3+} were extracted into the organic phase as $Sc(\text{tta})_3$ and $Fe(\text{tta})_3$ respectively. However, the magnitude of the enhancement effect of Sc^{3+} and Fe^{3+} was smaller that that of Al^{3+}.

Since the enhancement of the extraction of Ln was observed when labile M^{3+} was extracted into the organic phase as coordinately saturated chelates, $M(\text{tta})_3$, the distribution ratio of Ln in the presence of M^{3+} can be expressed as follows,

$$D = \frac{[\text{Ln(tta)}_3]_{\text{org}} + \sum[\text{Ln(tta)}_3(\text{M(tta)}_3)_m]_{\text{org}}}{[\text{Ln}^{3+}] + \sum[\text{Ln(tta)}_n^{(3-n)+}]} \approx \frac{[\text{Ln(tta)}_3]_{\text{org}} + \sum[\text{Ln(tta)}_3(\text{M(tta)}_3)_m]_{\text{org}}}{[\text{Ln}^{3+}]} \tag{5}$$

The adduct formation in the organic phase is expressed as follows,

$$\text{Ln(tta)}_{3,\text{org}} + m\ \text{M(tta)}_{3,\text{org}} \rightleftharpoons \text{Ln(tta)}_3(\text{M(tta)}_3)_{m,\text{org}}, \tag{6}$$
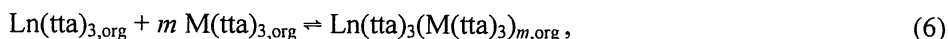
$$\beta_{\text{s},m} = \frac{[\text{Ln(tta)}_3(\text{M(tta)}_3)_m]_{\text{org}}}{[\text{Ln(tta)}_3]_{\text{org}}[\text{M(tta)}_3]_{\text{org}}^m} \ . \tag{7}$$

The following relationship can be derived from Eqs.(2), (5), and (7):

$$D / D_0 = 1 + \Sigma \beta_{\text{s},m} [\text{M(tta)}_3]_{\text{org}}^m \ . \tag{8}$$

To support this equilibrium analysis, the extraction of Ln with Htta was carried out in the presence of $Co(\text{tta})_3$ which is an inert complex. Figure 2 shows the relationship between $\log(D/D_0)$ and $\log[Co(\text{tta})_3]_{\text{org}}$ or $\log[Al(\text{tta})_3]_{\text{org}}$. The D/D_0 values of La^{3+} increase with increase in the $Co(\text{tta})_3$ and $Al(\text{tta})_3$ concentrations. These plots approach straight lines with a slope of unity. Therefore, the formation of the 1:1 adduct between $La(\text{tta})_3$ and $Co(\text{tta})_3$ or $Al(\text{tta})_3$ in the organic phase can be considered. In our previous papers, it has been reported that $Ln(\text{tta})_3$ formed only 1:1 adducts with various tris-M(III) chelates (M(III) : Cr(III) and Co(III)) in the organic phase [4-10].

In the Eu^{3+}-Al^{3+} system, although the plots do not approach straight lines with a slope of unity, the formation of the 1:1 adduct can be assumed by considering the previous work described above. The $\beta_{\text{s},1}$ values were determined by a nonlinear least-squares method for the plots based on Eq.(8), and are listed in Table 1. The lines in Fig.2 calculated by using the $\beta_{\text{s},1}$ values obtained are in good agreement with the experimental plots for all cases. The $\beta_{\text{s},1}$ values in all M^{3+} cases decrease with increasing atomic number of Ln. Moreover, the $\beta_{\text{s},1}$ values of each Ln are influenced by the central metals (M^{n+}) of $M(\text{tta})_3$.
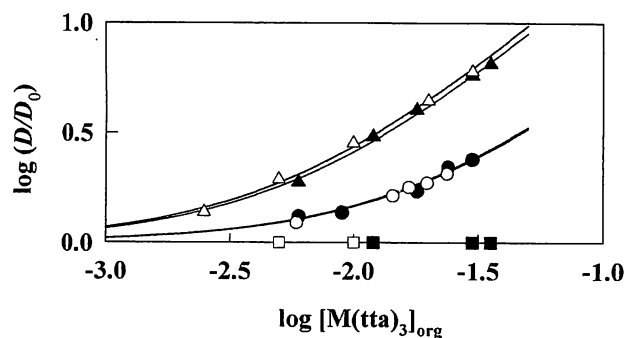
Fig.2 Effect of the concentration of $M(tta)_3$ extracted into the organic phase on the extraction of Ln^{3+} with 3.0×10^{-1} M Htta at pH = 2.3-3.5 (I = 0.15). Open symbols, $Al(tta)_3$; Closed symbols, $Co(tta)_3$. $\triangle\blacktriangle$, La; $\bigcirc\bullet$, Eu; $\square\blacksquare$, Lu.

Table 1 Adduct formation constants of $Ln(tta)_3(M(tta)_3)$
in benzene at $25°C$

Ln	M(tta)$_3$	log $\beta_{s,1}$
La	Al(tta)$_3$	2.24 ± 0.01
	Sc(tta)$_3$	1.49 ± 0.03
	Fe(tta)$_3$	1.60 ± 0.02
	Co(tta)$_3$	2.21 ± 0.01
Eu	Al(tta)$_3$	1.67 ± 0.01
	Sc(tta)$_3$	1.12 ± 0.01
	Fe(tta)$_3$	1.19 ± 0.02
	Co(tta)$_3$	1.66 ± 0.02

Numerical values after ±show the standard error.

3.2 Spectroscopic studies of adduct formation

To prove adduct formation between $Ln(tta)_3$ and $M(tta)_3$ in the organic phase, spectroscopic studies such as electronic and IR absorption were carried out by using inert $Co(tta)_3$ instead of labile $M(tta)_3$. Electronic absorption spectra for 2.0×10^{-3} M $Co(tta)_3$ were measured in the presence of varying concentrations (5.0×10^{-4}-8.0×10^{-3} M) of $Ln(tta)_3$. The absorption band for the d-d transition of $Co(tta)_3$ with a maximum absorbance at 611 nm did not shift. However, the molar absorptivity of $Co(tta)_3$ slightly increased with increase in the concentration of $Ln(tta)_3$ except for Lu. The same trend has been observed in the adduct formation between $Ln(tta)_3$ and tris(acetylacetonato)cobalt(III) $(Co(acac)_3)$ [5]. The enhancement of the molar absorptivity is probably ascribed to the vibrational distortion because some of the coordinating oxygen atoms of $Co(tta)_3$ are participated in the adduct formation with $Ln(tta)_3$. Figure 3 shows the relationship between the apparent molar absorptivity (ε_{app}) of $Co(tta)_3$ and the molar ratio of $Ln(tta)_3$ to $Co(tta)_3$. The $\beta_{s,1}$ values were calculated by least squares fitting for these plots on the basis of the following Eq.(9), which was derived with respect to the apparent absorbance (A_{app}) of $Co(tta)_3$:

$$A_{app} = \varepsilon_{add,Co}[Ln(tta)_3(Co(tta)_3)]_{org} + \varepsilon_{Co}[Co(tta)_3]_{org,}$$

$$= (\varepsilon_{add,Co} - \varepsilon_{Co}) \frac{(\beta_{s,1}C_{Ln} + \beta_{s,1}C_{Co} + 1) - \sqrt{(\beta_{s,1}C_{Ln} + \beta_{s,1}C_{Co} + 1)^2 - 4\beta_{s,1}^2 C_{Ln}C_{Co}}}{2\beta_{s,1}} + \varepsilon_{Co}C_{Co}, \tag{9}$$

where $\varepsilon_{add,Co}$ and ε_{Co} denote the molar absorptivity of complexed Co(tta)$_3$ in the adduct and free Co(tta)$_3$ respectively, and C_{Co} and C_{Ln} are the total concentrations of Co(tta)$_3$ and Ln(tta)$_3$ respectively. The log $\beta_{s,1}$ values determined are 2.60±0.21 and 2.05±0.25 for La and Eu respectively. The broken lines in Fig.3 indicate the values calculated by using the $\beta_{s,1}$ values, and are in good agreement with the experimental plots. The $\beta_{s,1}$ values are reasonably consistent with those in Table 1 within experimental error for the spectrophotometric method. As described in the previous papers [4,6,10], the difference in $\beta_{s,1}$ is due to the difference in the water content of the benzene solution in both methods. The adduct formation should compete with the hydration of Ln(tta)$_3$ as well as Co(tta)$_3$ as shown below.

Figure 4 shows the IR absorption spectrum of 6.0×10^{-3} M Eu(tta)$_3$(H$_2$O)$_3$ in anhydrous benzene as well as those in the presence of different concentrations of Co(tta)$_3$. The percentages of complexed Eu(tta)$_3$ with Co(tta)$_3$ were calculated to be 50% and 61% for (b) and (c) in Fig.4 respectively using the $\beta_{s,1}$ values.

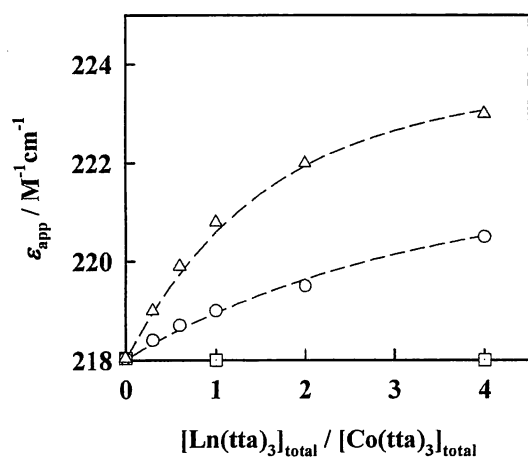Fig.3 Relationship between the molar absorptivity of Co(tta)$_3$ at 611 nm and the molar ratio of Ln(tta)$_3$ to Co(tta)$_3$. Total concentration of Co(tta)$_3$ was 2.0×10^{-3} M. Total concentration of Ln(tta)$_3$ ranged from 5.0×10^{-4} to 8.0×10^{-3} M. △, La; ○, Eu; □, Lu.
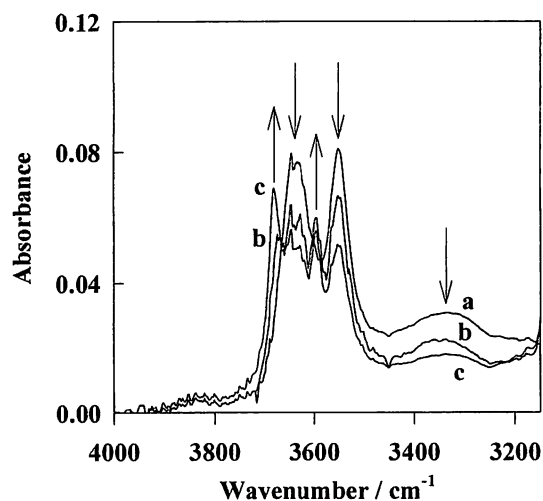
Fig. 4 IR spectra for 6.0×10^{-3} M Eu(tta)$_3$(H$_2$O)$_3$ in the presence or absence of Co(tta)$_3$ in benzene. (a) free Eu(tta)$_3$(H$_2$O)$_3$; (b) [Co(tta)$_3$]$_{total}$ / [Eu(tta)$_3$(H$_2$O)$_3$]$_{total}$ = 2.0; (c) [Co(tta)$_3$] $_{total}$ / [Eu(tta)$_3$(H$_2$O)$_3$]$_{total}$ = 3.0.

Two narrow bands at 3552 and 3649 cm^{-1} and a broad band at 3335 cm^{-1} for (a) in Fig.4 correspond to the coordinated water molecules of $Eu(tta)_3(H_2O)_3$ [6]. The absorbance of those three bands decreases with increasing $Co(tta)_3$ concentration, while two intense peaks appeared at 3600 cm^{-1} and 3680 cm^{-1} corresponding to free water. These spectral changes demonstrated that the coordinated water molecules of $Eu(tta)_3(H_2O)_3$ were displaced by $Co(tta)_3$ and released into anhydrous benzene as free water. Therefore, $Co(tta)_3$ directly coordinates to the central Eu ion through the coordinating oxygen atoms of the tta ligands.

Since the adduct formation constant of $Ln(tta)_3(Al(tta)_3)$ is comparable to that of $Ln(tta)_3(Co(tta)_3)$, these adducts are expected to have a similar structure. The difference in the $\beta_{s,1}$ value between La and Eu in all $M(tta)_3$ cases probably reflects the difference in the steric repulsion between those Ln chelates and $M(tta)_3$. $M(tta)_3$ is able to enter the inner-coordination sphere of $La(tta)_3$ more easily because the ionic radius of La^{3+} is larger than that of Eu^{3+}. Similar differences in the $\beta_{s,1}$ values have been observed in the adduct formation between $Ln(tta)_3$ and various tris-M(III) chelates [4-10].

The IR spectrum of the coordinated water of $Lu(tta)_3(H_2O)_n$ did not change on addition of $Co(tta)_3$. In a previous paper, the adduct of $Lu(tta)_3$ with $Co(acac)_3$ is formed by hydrogen bonding between the coordinated water molecules of $Lu(tta)_3$ and $Co(acac)_3$ since the latter cannot enter the inner-coordination sphere of Lu^{3+} [6]. In the present study, it was difficult for $Co(tta)_3$ to hydrogen-bond with the coordinated water of the $Lu(tta)_3$ owing to the lower basicity of $Co(tta)_3$ because the tta ligand has a strong electron withdrawing trifluoromethyl group. In fact, the hydrogen-bond accepting power of $Co(tta)_3$ was much weaker than that of $Co(acac)_3$, i.e., the formation constants of 1:1 hydrogen bond complexes of $Co(acac)_3$ and $Co(tta)_3$ with 3,5-dichlorophenol as a proton donor in CCl_4 are $10^{3.14}$ and $10^{0.96}$ respectively. Consequently, the coextraction of Lu with M^{3+} was not observed.

Moreover, the $\beta_{s,1}$ values for $Ln(tta)_3$ are obviously different among the four $M(tta)_3$ (M^{3+}:Al, Sc, Fe, and Co). This may be due to the difference in the Lewis basicity of those $M(tta)_3$. We have found that the complexing ability of tris(acetylacetonato)metals(III) ($M(acac)_3$) toward $Ln(tta)_3$ depends on basicity and steric factors [4]. The hydrogen-bond accepting power of $M(acac)_3$ toward 3,5-dichlorophenol, or the basicity of $M(acac)_3$ increases in the order of Sc < Fe < Al < Co [14], which agrees well with that of the $\beta_{s,1}$ values for $M(tta)_3$, Sc < Fe < Al, Co, in the present study.

3.3 Coextraction equilibrium

From the above equilibrium analysis and spectroscopic studies, the mechanism of the coextraction of Ln with M^{3+} in the Htta system can be expressed as shown in Fig.5. It was elucidated that coextraction occurred by adduct formation in the organic phase. The overall coextraction equilibrium is given as follows:

$$Ln^{3+} + M^{3+} + 6\ Htta_{org} \overset{K_{coex}}{\rightleftharpoons} Ln(tta)_3(M(tta)_3)_{org} + 6\ H^+, \tag{10}$$
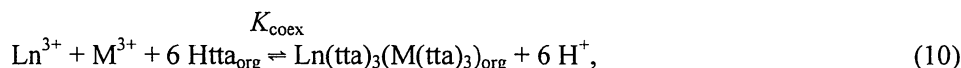
$$K_{coex} = K_{ex,Ln}K_{ex,M}\beta_{s,1} = K_{ex,s,1}K_{ex,M}, \tag{11}$$

where $K_{ex,M}$ ($= [M(tta)_3]_{org}[H^+]^3/[M^{3+}][Htta]_{org}^3$) and $K_{ex,s,1}$ ($= [Ln(tta)_3(M(tta)_3)]_{org}[H^+]^3/$ ($[Ln^{3+}][Htta]_{org}^3$ $[M(tta)_3]_{org}) = K_{ex,Ln}\beta_{s,1}$) are the extraction constants of M^{3+} and that of Ln in the presence of $M(tta)_3$
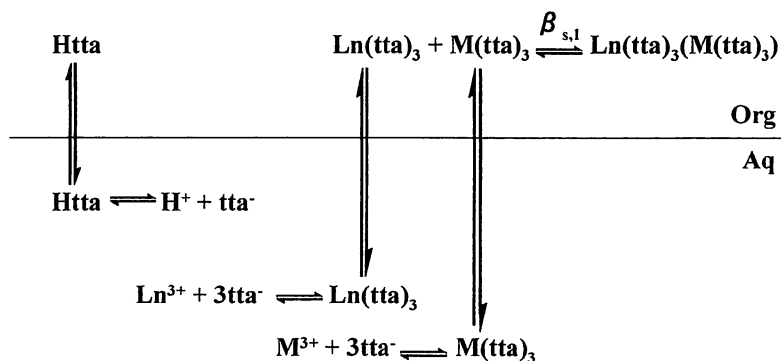

Fig. 5 Coextraction equilibrium of Ln^{3+} and M^{3+} in the Htta system.

respectively. The separation factors (α) between La^{3+} and Lu^{3+} in the presence or absence of M^{3+} are calculated from the extraction constants. The extraction constant ($K_{ex,s,1}$) of La^{3+} in the presence of M^{3+} were calculated to be $10^{-7.90}$ (Al^{3+}), $10^{-8.65}$ (Sc^{3+}), and $10^{-8.54}$ (Fe^{3+}). The α value obtained in the absence of M^{3+}, $10^{3.48}$, was significantly reduced to $10^{1.24}$, $10^{1.99}$ and $10^{1.88}$ in the presence of Al^{3+}, Sc^{3+} and Fe^{3+} respectively. The separation efficiency was significantly influenced by the coextraction. Coextraction in the well-known Htta-benzene chelate extraction system has been demonstrated for the first time, and the mechanism was elucidated in this work.

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