Solvent Extraction of Anionic Chelate Complexes of Lanthanum(III), Europium(III), Lutetium(III), Scandium(III), and Indium(III) with 2-Thenoyltrifluoroacetone as Ion-Pairs with Tetrabutylammonium Ions

Junji Noro† and Tatsuya Sekine*
Department of Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162
†Research Department, Nissan ARC Ltd., Natsushima-cho, Yokosuka-shi, Kanagawa 237

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The solvent extraction of lanthanum(III), europium(III), lutetium(III), scandium(III), and indium(III) in 0.1 mol dm^{-3} sodium nitrate solutions with 2-thenoyltrifluoroacetone (Htta) in the absence and presence of tetrabutylammonium ions (tba$^+$) into carbon tetrachloride was measured. The extraction of lanthanum(III), europium(III), and lutetium(III) was greatly enhanced by the addition of tba$^+$; this could be explained in terms of the extraction of a ternary complex, M(tta)$_4^-$tba$^+$. However, the extractions of scandium(III) and indium(III) were nearly the same when tba$^+$ was added. The data were treated on the basis of the formation equilibrium of the ternary complex from the neutral chelate, M(tta)$_3$, with the extracted ion-pairs of the reagents, tta$^-$tba$^+$, in the organic phase. It was concluded that the degree of association of M(tta)$_3$ with the ion-pair, tta$^-$tba$^+$, is greater in the order La(tta)$_3$≈Eu(tta)$_3$>Lu(tta)$_3$, or that the stability of the ternary complex in the organic phase is higher in the order La(tta)$_4^-$tba$^+$≈Eu(tta)$_4^-$tba$^+$>Lu(tta)$_4^-$tba$^+$. This is similar to those of adduct metal chelates of Htta with tributylphosphate (TBP) in synergistic extraction systems.

It was pointed out in a previous paper[1)] that the solvent extraction of europium(III) in aqueous solutions with benzoyltrifluoroacetone (Hbfa, 1-phenyl-4,4,4-trifluoro-1,3-butanedione) into carbon tetrachloride is greatly enhanced by the addition of tetrabutylammonium ions (tba$^+$). This could be explained in terms of the extraction of the anionic benzoyltrifluoroacetonate chelate of europium(III) as ion-pairs with tba$^+$; the enhancement was explained by the fact that the extractability of the ion-pair, Eu(bfa)$_4^-$tba$^+$, was much higher than that of the neutral complex, Eu(bfa)$_3$. Furthermore, the present authors statistically treated the solvent extraction equilibrium of this Eu(bfa)$_4^-$tba$^+$ complex as the overall equilibrium of the extraction of the neutral complex, Eu(bfa)$_3$, and the formation of the anionic complex from this extracted species by association with the bfa$^-$tba$^+$ species in the organic phase.

In the present study the solvent extraction of lanthanum(III), europium(III), lutetium(III), scandium(III), and indium(III) with 2-thenoyltrifluoroacetone (Htta, 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione, which is denoted by HA) into carbon tetrachloride in the absence and presence of tba$^+$ was measured. The β-diketone, Htta, was chosen because a series of work had been carried out regarding the solvent extraction of several metal ions with this reagent in both the absence and presence of a neutral ligand, such as tributylphosphate (TBP), in the organic phase. This caused a synergistic effect upon extraction.[2)] The data were statistically analyzed in the same manner as in the previous study. From the results a similarity was found regarding the enhancement due to the extraction of ternary complexes, MA$_4^-$tba$^+$, and with that due to the extraction of adduct chelates, such as MA$_3$L$_2$, where L is a unidentate organophilic ligand, such as TBP.

Statistical

In the present paper any chemical species in the organic phase is denoted by subscript "org"; that in the aqueous phase is shown without any subscript. The volume of the two liquid phases was assumed to be the same.

The two-phase distribution and acid dissociation equilibrium of HA can be written as follows:

$$\mathrm{HA} \rightleftarrows \mathrm{HA}_{(\mathrm{org})};\ K_\mathrm{d}=[\mathrm{HA}]_\mathrm{org}[\mathrm{HA}]^{-1} \qquad (1)$$

and

$$\mathrm{HA} \rightleftarrows \mathrm{H}^+ + \mathrm{A}^-;\ K_\mathrm{a}=[\mathrm{H}^+][\mathrm{A}^-][\mathrm{HA}]^{-1}. \qquad (2)$$

From these equations it can be seen that the concentration of the extractant anion, A$^-$, can be calculated using

$$[\mathrm{A}^-]=[\mathrm{HA}]_\mathrm{initial}/(1+(K_\mathrm{d}+1)[\mathrm{H}^+]K_\mathrm{a}^{-1}). \qquad (3)$$

The equilibrium for the extraction of M^{3+} with HA in the organic phase can be written as

$$\mathrm{M}^{3+}+3\mathrm{HA}_{(\mathrm{org})} \rightleftarrows \mathrm{MA}_{3(\mathrm{org})}+3\mathrm{H}^+$$

and

$$K_{\mathrm{ex}3,0}{}^*=[\mathrm{MA}_3]_\mathrm{org}[\mathrm{H}^+]^3[\mathrm{M}^{3+}]^{-1}[\mathrm{HA}]_\mathrm{org}{}^{-3}. \qquad (4)$$

It can also be written as

$$\mathrm{M}^{3+}+3\mathrm{A}^- \rightleftarrows \mathrm{MA}_{3(\mathrm{org})}$$

and

$$K_{\mathrm{ex}3,0}=[\mathrm{MA}_3]_\mathrm{org}[\mathrm{M}^{3+}]^{-1}[\mathrm{A}^-]^{-3}. \qquad (5)$$

When the anionic chelate, MA$_4^-$, is extracted as ion-pairs with tba$^+$, the equilibrium can be written as

$$\mathrm{M}^{3+}+4\mathrm{HA}_{(\mathrm{org})}+\mathrm{tba}^+ \rightleftarrows \mathrm{MA}_4{}^-\mathrm{tba}^+{}_{(\mathrm{org})}+4\mathrm{H}^+$$

and

$$K_{\mathrm{ex}4,1}{}^*=[\mathrm{MA}_4{}^-\mathrm{tba}^+]_\mathrm{org}[\mathrm{H}^+]^4[\mathrm{M}^{3+}]^{-1}[\mathrm{HA}]_\mathrm{org}{}^{-4}[\mathrm{tba}^+]^{-1}. \qquad (6)$$

It can also be written as

$$M^{3+}+4A^{-}+tba^{+} \rightleftarrows MA_4^{-}tba^{+}{}_{(org)}$$

and

$$K_{ex4,1}=[MA_4^{-}tba^{+}]_{org}[M^{3+}]^{-1}[A^{-}]^{-4}[tba^{+}]^{-1}. \quad (7)$$

However, this extraction of the ion-pairs can also be given in a form such that the extraction of the neutral chelate given by Eq. 5 occurs first, and then the addition of the ion-pairs of the reagents, $A^{-}tba^{+}$, on the neutral chelate follows in the organic phase. When the extraction equilibrium is written in this way, the following equations can be written:

$$MA_{3(org)}+A^{-}tba^{+}{}_{(org)} \rightleftarrows MA_4^{-}tba^{+}{}_{(org)}$$

and

$$K_{org}=[MA_4^{-}tba^{+}]_{org}[MA_3]_{org}^{-1}[A^{-}tba^{+}]_{org}^{-1}. \quad (8)$$

The anions of the chelating extractant, A^{-}, and the bulky cations, tba^{+}, should be extracted as ion-pairs, $A^{-}tba^{+}$. The following equations can be written for this extraction equilibrium:

$$A^{-}+tba^{+} \rightleftarrows A^{-}tba^{+}{}_{(org)}$$

and

$$K_{exAB}=[A^{-}tba^{+}]_{org}[A^{-}]^{-1}[tba^{+}]^{-1}. \quad (9)$$

It is possible that if A^{-} forms complexes in the aqueous phase, the distribution ratio should be written as

$$D_0=[MA_3]_{org}/([M^{3+}]+[MA^{2+}]+[MA_2^{+}]+\cdots) \quad (10)$$

$$=K_{ex3,0}[A^{-}]^3/(1+\beta_1[A^{-}]+\beta_2[A^{-}]^2+\cdots), \quad (11)$$

where β_n is the stability constant of the "nth" complex in the aqueous phase, which can be written as

$$\beta_n=[MA_n^{3-n}][M^{3+}]^{-1}[A^{-}]^{-n}. \quad (12)$$

For the same reason, the following general equations can be written when the bulky cation, tba^{+}, is added:

$$D=([MA_3]_{org}+[MA_4^{-}tba^{+}]_{org})/([M^{3+}]+[MA^{2+}]+[MA_2^{+}]+\cdots) \quad (13)$$

$$=(K_{ex3,0}[A^{-}]^3+K_{ex4,1}[A^{-}]^4[tba^{+}])/(1+\beta_1[A^{-}]+\beta_2[A^{-}]^2+\cdots). \quad (14)$$

When the concentration, $[A^{-}]$, is identical, the following equation can be introduced from Eqs. 5, 7, 8, 9, 11, and 14:

$$D/D_0=1+K_{ex4,1}K_{ex3,0}^{-1}[A^{-}][tba^{+}] \quad (15)$$

$$=1+K_{org}K_{exAB}[A^{-}][tba^{+}]. \quad (16)$$

However, in many cases, where $D \gg D_0$ Eqs. 13 and 14 may approximately be written as

$$D_f=[MA_4^{-}tba^{+}]_{org}/([M^{3+}]+[MA^{2+}]+[MA_2^{+}]+\cdots) \quad (17)$$

$$=K_{ex4,1}[A^{-}]^4[tba^{+}]/(1+\beta_1[A^{-}]+\beta_2[A^{-}]^2+\cdots). \quad (18)$$

In the presence of tba^{+} the free tba^{+} concentration can be obtained as

$$[tba^{+}]_{initial}=[tba^{+}]+[MA_4^{-}tba^{+}]_{org}+[A^{-}tba^{+}]_{org} \quad (19)$$

and

$$[tba^{+}]=([tba^{+}]_{initial}-[MA_4^{-}tba^{+}]_{org})/(1+K_{exAB}[A^{-}]). \quad (20)$$

When the concentration, $[A^{-}]$, is identical, the following equation can be introduced from Eqs. 5, 7, 8, 9, 11, and 18:

$$D_f/D_0=K_{ex4,1}K_{ex3,0}^{-1}[A^{-}][tba^{+}] \quad (21)$$

$$=K_{org}K_{exAB}[A^{-}][tba^{+}]. \quad (22)$$

As can be seen from Eq. 21, the enhancement of metal extraction by the addition of tba^{+} is dependent on the quantity $[A^{-}]$ multiplied by $[tba^{+}]$; it can be given in terms of the extraction constants of each species. However, the enhancement of extraction, D_f/D_0, can be given more clearly on the basis of the association of the extracted neutral chelate, MA_3, with one ion-pair of the reagents, $A^{-}tba^{+}$, in the organic phase, as can be seen from Eq. 22. By using this statistical treatment the enhancement of metal extraction by the extraction of the $MA_4^{-}tba^{+}$ species can be given by the formation constant of the $MA_4^{-}tba^{+}$ species in Eq. 8, and the extraction constant of the ion-pairs of the ligand anion and the bulky cation, $A^{-}tba^{+}$, in Eq. 9.

The synergistic extraction of M^{3+} with the chelating extractant and a neutral ligand, L, can be written as

$$M^{3+}+3HA_{(org)}+nL_{(org)} \rightleftarrows MA_3L_{n(org)}+3H^{+}$$

and

$$K_{ex3,n}^{*}=[MA_3L_n]_{org}[H^{+}]^3[M^{3+}]^{-1}[HA]_{org}^{-3}[L]_{org}^{-n}. \quad (23)$$

This can also be written as

$$M^{3+}+3A^{-} \rightleftarrows MA_{3(org)},$$

$$D_0=[MA_3]_{org}/([M^{3+}]+[MA^{2+}]+[MA_2^{+}]+\cdots), \quad (24)$$

$$MA_{3(org)}+nL_{(org)} \rightleftarrows MA_3L_{n(org)},$$

$$\beta_{(org)n}=[MA_3L_n]_{org}[MA_3]_{org}^{-1}[L]_{org}^{-n}, \quad (25)$$

and

$$D=([MA_3]_{org}+[MA_3L]_{org}+[MA_3L_2]_{org}+\cdots)/([M^{3+}]+[MA^{2+}]+[MA_2^{+}]+\cdots). \quad (26)$$

However, under the conditions where only the MA_3L_2 species is the main extracted species and the MA_3 and MA_3L species are negligible, the following equations may be written if $[A^{-}]$ is identical:

$$D_a=[MA_3L_2]_{org}/([M^{3+}]+[MA^{2+}]+[MA_2^{+}]+\cdots) \quad (27)$$

and

$$D_a/D_0=\beta_{(org)2}[L]_{org}^2. \quad (28)$$

Experimental

All of the reagents were of reagent grade. The 2-thenoyltrifluoroacetone and tetrabutylammonium chloride were obtained from Tokyo Kasei Co. Aqueous solutions of lanthanum(III), europium(III), lutetium(III), scandium(III), and indium(III) were supplied by Wako Pure Chemical Industries, Ltd. Solvent extraction was carried out in a thermostated room at 298 K. Stoppered glass tubes (capacity 50 cm^3) were used to agitate the two liquid phases. The aqueous phase was a 0.1 mol dm^{-3} sodium nitrate solution buffered by acetate. The organic phase was carbon tetrachloride containing Htta.

The extraction of metal ions was measured as follows. A 10 cm^3 portion of the aqueous phase containing 1×10^{-4} mol dm^{-3} of one of the metal ions was placed in the tube. When the effect of the tta$^-$ concentration on the distribution ratio was measured, the pH of the aqueous phase was adjusted at various values while keeping the Htta concentration in the organic phase constant. When the effect of the tba$^+$ concentration on the distribution ratio was determined, various amounts of tba$^+$ were added into the aqueous phase while keeping the pH and the initial Htta concentration in the organic phase constant. A 10 cm^3 portion of carbon tetrachloride solution of Htta was then added. The two liquid phases in the tube were agitated with a mechanical shaker for 1 h and centrifuged off. A 4 cm^3 portion of the organic phase was transferred into another tube and the metal ion extracted into this organic phase was washed by 0.1 mol dm^{-3} nitric acid. The contents of the metal in this solution and in the equilibrated aqueous phase were determined by an ICP-AES (Seiko Instruments Inc. SPS-1200AR). The pH of the equilibrated aqueous phase was measured using a pH meter (Tokyo TOA Electronics Ltd. HM-30S).

The extraction equilibrium of tba$^+$ as ion-pairs with tta$^-$ was measured as described in Ref. 1. A portion of a 0.1 mol dm^{-3} sodium nitrate solution containing some amount of tba$^+$ and buffered at a certain pH was placed in a tube, and a carbon tetrachloride solution of Htta was added. The two phases were agitated for 30 min and then centrifuged. The organic phase was transferred into another tube and washed by 0.05 mol dm^{-3} nitric acid. The thus-obtained aqueous phase was then transferred into another tube; after the pH was measured the solution was neutralized by a sodium hydroxide solution. After an excess amount of sodium picrate (at initial 2×10^{-3} mol dm^{-3}) was added to this neutralized aqueous phase it was agitated with the same volume of chloroform in order to extract the tba$^+$ quantitatively as ion-pairs of picrate ions. The tba$^+$, thus extracted, was determined from the absorption of the picrate ion at 359 nm.

Results and Discussion

The extraction of reagents, tta$^-$ and tba$^+$, as ion-pairs into the organic phases was obtained as given in Table 1, and the extraction constant in Eq. 9 was determined to be $10^{1.9}$, though the value is somewhat erroneous.

Figure 1 gives the extraction curve of the metal ions with 0.1 mol dm^{-3} Htta (at initial) in the organic phase in the absence (closed symbols) and presence (open symbols) of 1×10^{-3} mol dm^{-3} of tba$^+$ (at initial). The plots of scandium(III) and indium(III) are nearly straight lines with a slope of +3 and, thus, the chelate complexes in the aqueous phase of these two metal ions are negligible under these conditions, as can be seen from Eq. 11. However, some deviation from a straight line with a slope of +3 was found with the extraction of the three lanthanoid ions. These data were statistically

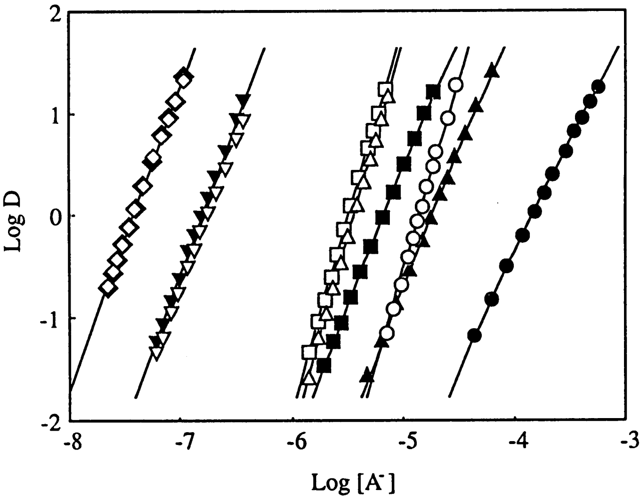

Fig. 1. Distribution ratio of metal ions as a function of the concentration of 2-thenoyltrifluoroacetonate anion. Org. phase: carbon tetrachloride initially containing 0.1 mol dm^{-3} of 2-thenoyltrifluoroacetone. Aq phase: 0.1 mol dm^{-3} sodium nitrate solution containing no tba$^+$ or 1.0×10^{-3} mol dm^{-3} tba$^+$ at initial. The symbols are La(III) (●, ○), Eu(III) (▲, △), Lu(III) (■, □), In(III) (▼, ▽), and Sc(III) (◆, ◇). The closed symbols indicate the data obtained in the absence of tba$^+$ and the open symbols indicate the data in the presence of tba$^+$. The solid lines were calculated based on Eq. 14, which is introduced the values given in Table 2a.

Table 1. Solvent Extraction Data of 2-Thenoyltrifluoroacetonate and Tetrabutylammonium Ions as Ion-Pairs. Org. Phase: Carbon Tetrachloride Initially Containing 0.1 mol dm^{-3} Htta. Aq Phase: 0.1 mol dm^{-3} Sodium Nitrate Solution. $K_{\mathrm{exAB}}=[\mathrm{A^-tba^+}]_{\mathrm{org}}[\mathrm{A^-}]^{-1}[\mathrm{tba^+}]^{-1}$

$[\mathrm{tba^+}]_{\mathrm{initial}}$	pH	$[\mathrm{A^-}]$	$[\mathrm{tba^+}]$	$[\mathrm{A^-tba^+}]_{\mathrm{org}}$	K_{exAB}
1.0×10^{-3}	5.52	7.10×10^{-4}	9.81×10^{-4}	6.67×10^{-5}	$10^{1.98}$
2.0×10^{-3}	5.86	1.54×10^{-3}	1.83×10^{-3}	2.67×10^{-4}	$10^{1.98}$
2.5×10^{-3}	5.56	7.70×10^{-4}	2.65×10^{-3}	1.82×10^{-4}	$10^{1.95}$
3.0×10^{-3}	6.06	2.42×10^{-3}	2.58×10^{-3}	5.41×10^{-4}	$10^{1.94}$
4.0×10^{-3}	6.20	3.31×10^{-3}	3.26×10^{-3}	8.89×10^{-4}	$10^{1.92}$
5.0×10^{-3}	6.00	2.09×10^{-3}	4.65×10^{-3}	9.18×10^{-4}	$10^{1.97}$
7.5×10^{-3}	6.28	3.91×10^{-3}	6.14×10^{-3}	1.86×10^{-3}	$10^{1.89}$
1.0×10^{-2}	6.35	4.57×10^{-3}	8.23×10^{-3}	2.90×10^{-3}	$10^{1.89}$

K_{exAB} Av.$=10^{1.94}$

treated on the basis of Eq. 11; it was concluded that though the formation of the first complex, Mtta^{2+}, should be taken into account, the higher complexes are negligible. It was found in some solvent extraction systems that one molecule of undissociated form of the chelating extractant, HA, added to the neutral chelate in the organic phase and a "self-adduct", $\mathrm{MA_3HA}$, was formed. However, this should not occur in the systems of the present study under the conditions employed, as was reported previously.[2] The values of the stability constant of the aqueous tta^- complexes obtained by using a least-squares computer program are listed in Table 2a.

As can be seen from Fig. 1, although the extraction of three lanthanoid ions is greatly enhanced by the addition of tba^+, the extraction of scandium(III) and indium(III) are nearly the same, even when the same amount of tba^+ is added. Plots of the three lanthanoid ions in the presence of tba^+ are always nearly straight lines with a slope of +4. This should be due to the fact that extraction in the presence of tba^+ was carried out at a much lower pH and, thus, in the lower $[\mathrm{tta}^-]$ region in the aqueous phase than in its absence. For this reason, the formation of tta^- complexes in the aqueous phase was only slight, as can be seen from Eq. 14. From these data, the equilibrium constant for the extraction of $\mathrm{M(tta)_3}$ and $\mathrm{M(tta)_4^-tba^+}$ as well as the formation constant of the $\mathrm{M(tta)_4^-tba^+}$ species from the $\mathrm{M(tta)_3}$ species in the organic phase were also calculated in the same manner as in the previous paper.[1] The values are listed in Table 2a. The values with praseodymium(III) and neodymium(III) obtained in another study[4] are also given in Table 2a.

Table 2. Extraction and Formation Constants of Complexes

(a) Extraction constant of tta^- neutral complexes and anionic complexes as ion-pairs with tba^+, and formation constants of anionic complexes of present work (cf. Eqs. 5, 7, 8, and 12). K_a and K_d were taken from Ref. 3 but the aqueous phase in this previous study was 0.1 mol dm^{-3} $\mathrm{NaClO_4}$; the value is $K_a=10^{-6.33}$ and $K_d=10^{1.32}$.

	Log $K_{\mathrm{ex}3,0}$	Log $K_{\mathrm{ex}4,1}$	Log β_1	Log K_{org}	Remarks
La^{3+}	12.2	22.6	4.4	8.5	#
Pr^{3+}	13.2	23.8	4.3	8.5	##
Nd^{3+}	13.5	24.0	4.4	8.4	##
Eu^{3+}	14.4	24.8	4.4	8.5	#
Lu^{3+}	15.7	25.0	4.8	7.4	#
In^{3+}	20.4	—	—	—	#
Sc^{3+}	22.3	—	—	—	#

Present work. ## Ref. 4.

(b) Formation constants of the adducts with TBP taken from Ref. 2.

	Log $\beta_{(\mathrm{org})1}$	Log $\beta_{(\mathrm{org})2}$
La^{3+}	4.83	9.33
Eu^{3+}	5.15	8.89
Lu^{3+}	5.69	6.60
In^{3+}	—	—
Sc^{3+}	3.44	—

Since the slope of the plot is different in both the absence (it is about +3) and presence (it is about +4) of tba^+, the enhancement of extraction by the addition of a certain amount (in Fig. 1 it is 1×10^{-3} mol dm^{-3}) of tba^+ can not be compared when the concentration of tta^- is different. Figure 2 gives the enhancement of extraction as a function of the quantity $[\mathrm{tta}^-][\mathrm{tba}^+]$ in the aqueous phase at equilibrium. In this way the enhancement of the extraction of two metal ions can be compared, even when the tta^- ion concentration is different, as can be seen from Eqs. 16 and 22. The $\log K_{\mathrm{org}}$ obtained from the results given in Fig. 2 agreed well with the value obtained from the results given in Fig. 1, according to Table 2a.

In Fig. 1, enhancement of extraction due to the addition of 1×10^{-3} mol dm^{-3} of tba^+ (at initial) is larger in the order $\mathrm{La}^{3+}>\mathrm{Eu}^{3+}>\mathrm{Lu}^{3+}$. This is an apparent effect. As can be seen from Eqs. 15 and 16 or Eqs. 21 and 22, the value of D/D_0 or D_f/D_0 when $[\mathrm{tta}^-]$ is identical is dependent on the quantity $[\mathrm{tta}^-][\mathrm{tba}^+]$; when the concentration of tba^+ is the same, it is dependent on the concentration of the tta^- ion. Extraction in the absence of tba^+ is better in the order $\mathrm{La}^{3+}<\mathrm{Eu}^{3+}<\mathrm{Lu}^{3+}$; for example, in order to achieve the 50% extraction, or $\log D=0$, the concentration of tta^- is about one order lower for Eu^{3+} than that for La^{3+}.

In the present study enhancement of extraction when the ternary complex is extracted was considered from the stand point of anionic complex formation in the organic phase. By the formation of the anionic complex, coordination with the ligand should change from six (that of $\mathrm{M(tta)_3}$) to eight (that of $\mathrm{M(tta)_4^-tba^+}$) in the

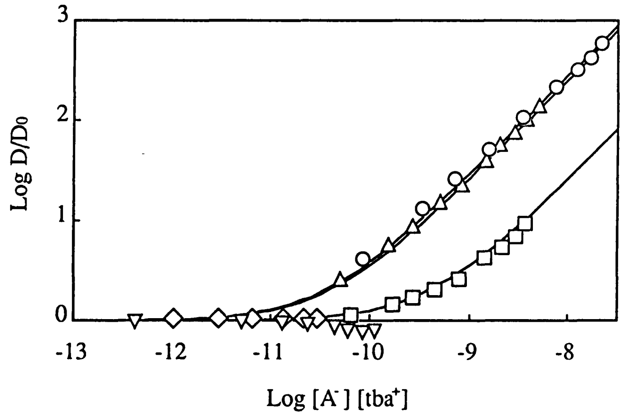

Fig. 2. Increase in the distribution ratio as a function of the quantity, $[\mathrm{tta}^-]$ multiplied by $[\mathrm{tba}^+]$ in the aqueous phase. Org. phase: carbon tetrachloride initially containing 0.1 mol dm^{-3} 2-thenoyltrifluoroacetone. Aq. phase: 0.1 mol dm^{-3} sodium nitrate solution at the same pH for a certain given metal ion but containing various amount of tba^+. La(III) at pH 4.1 (○), Eu(III) at pH 3.4 (△), Lu(III) at pH 3.3 (□), In(III) at pH 1.9 (▽), and Sc(III) at pH 1.3(◇).

organic solvent. A similar type of increase in the coordination with the ligand also occurs in the adduct formation of metal chelates with the neutral ligand molecule in the organic phase in synergistic extraction systems discussed in previous papers.[2] In one of these papers, the adduct formation of tta$^-$ complexes, M(tta)$_3$, of these five metal ions with neutral ligands, such as tributylphosphate (TBP) in carbon tetrachloride, was discussed. It was found that the tta$^-$ complexes of these three lanthanoid ions in the organic phase formed stable adducts with one or two molecules of TBP. Although the tta$^-$ complex of scandium(III) formed an adduct with only one TBP molecule, no evidence was found regarding an adduct with two TBP molecules. Furthermore, no adduct was found with the tta$^-$ complex of indium(III) with TBP in carbon tetrachloride; even an impairment of the extraction was found in the higher concentration range of TBP. The equilibrium constants for the adduct formation of these metal tta$^-$ chelates with TBP in the previous paper are summarized in Table 2b.

It can be seen from Table 2a that the values of the formation constant of the M(tta)$_4^-$tba$^+$ complexes of lanthanoid ions in carbon tetrachloride, K_{org} in Eq. 8, are similar among the trivalent lanthanoids except for lutetium(III). The formation constant of the lutetium(III) tta$^-$ anionic complex is about one order lower than the other lanthanoid ions of lower atomic number. As can be seen from Table 2b, this trend is somewhat similar to that found among the over-all formation constant of M(tta)$_3$(TBP)$_2$, $\beta_{(\mathrm{org})2}$ in Eq. 25, in a previous study.[2] As can be seen from these facts, the formation of anionic chelates, M(tta)$_4^-$tba$^+$, and that of the adduct chelates, M(tta)$_3$(TBP)$_2$, in carbon tetrachloride seems to be a similar type of chemical phenomena by which the complex adds two oxygen atoms in the coordination sphere, though in the former the ligand is bidentate and the chemical species formed is negatively charged. It should thus be in the form of an ion-pair in this nonpolar solvent. However, in the latter adducts, the added ligand is unidentate and the formed species is non-charged. The situation regarding the formation of the anionic chelate is to some extent similar to that of a neutral adduct chelate with a bidentate neutral ligand, such as heterocyclic amines,[5–7] even though there is no problem regarding the concentration of the chelating ligand on the addition of a neutral ligand on the extracted chelate in the organic phase. It is reasonable that the ability of the metal chelates in carbon tetrachloride to accept a bidentate ligand is similar to the addition of two molecules of a unidentate ligand, such as TBP, among the three lanthanoid chelates. The Sc(tta)$_3$ chelate can accept one unidentate ligand, such as TBP, in its coordination sphere, but can not accept two unidentate ligands or one bidentate ligand, such as tta$^-$. There should be essentially no possibility to accept further ligands in the In(tta)$_3$ chelate.

The separation factor of two metal ions, M1 and M2, which can be represented by $D_{\mathrm{M1}}/D_{\mathrm{M2}}$ at a certain given chelating extractant and hydrogen-ion concentration, is nearly the same in both the absence and presence of the lanthanoids(III), except for lutetium(III). This is because the value of K_{org} in Eq. 8 is similar among these metal ions. However, since the formation constant of the M(tta)$_4^-$tba$^+$ complex of lutetium(III) is much lower than those of the other four lanthanoids, the separation factor of lutetium(III) from these other lanthanoid ions is greatly impaired. The separation factor of the lanthanoids(III) from scandium(III) and indium(III), which are extracted much better than the lanthanoids(III) but do not form the M(tta)$_4^-$tba$^+$ complex, is also impaired for the same reason.

This should be a clear approach to estimate the solvent extraction of ternary complexes to compare the extractability of the anionic complexes, as shown in a previous paper.[8] In the present study the formation of the MA$_4^-$ complex in the aqueous phase could not be measured and, consequently, the extractability of such anionic complexes as ion-pairs with a certain cation can not be discussed. However, the statistical treatment employed in the study, that is, enhancement of extraction is treated in terms of an increase in the concentration of the metal in the organic phase due to the formation of an anionic complex in the organic phase enables a systematic consideration of these complicated extraction systems. This approach also enables a comparison of the extraction data of ternary complexes with different extractants, as was pointed out in a previous paper.[1]

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