450 © 1993 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 66, 450—454(1993) [Vol. 66, No. 2

Effect of a Solvent on the Extraction of the Europium(III) 2-Thenoyltrifluoroacetonate Anionic Complex as Ion-Pairs with Tetrabutylammonium Ions

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(Received August 28, 1992)

The solvent extraction of europium(III) in aqueous 0.1 mol dm^{-3} sodium nitrate or sodium chloride solutions with 2-thenoyltrifluoroacetone (Htta) into chloroform, toluene, and 4-methyl-2-pentanone (MIBK) was studied in both the absence and presence of tetrabutylammonium ions (tba$^+$); the results were compared with those into carbon tetrachloride. When the diluent was chloroform or toluene, the extraction was greatly enhanced by the addition of tba$^+$, just as with carbon tetrachloride. This could be explained in terms of the extraction of the Eu(tta)$_4{}^-$tba$^+$ species, in addition to the Eu(tta)$_3$ species. However, this did not occur in the MIBK system, and was explained in terms of stable solvates with MIBK, which interfere with the addition of tta$^-$tba$^+$ ion-pairs on the Eu(tta)$_3$ species. The enhancement due to the extraction of Eu(tta)$_4{}^-$tba$^+$ was not very much different from that in the other solvent systems. This could be explained by assuming that although the amount of tta$^-$tba$^+$ in the organic phase was smaller in the order chloroform>toluene>carbon tetrachloride, the degree of association of this ion-pair with the Eu(tta)$_3$ in the organic phase was larger in the inverse order, and that these two opposite tendencies canceled each other out. The results were compared with the synergistic enhancement of the extraction of europium(III) with Htta by organophilic neutral ligands, such as tributylphosphate.

In previous papers[1,2] it was reported that the solvent extraction of europium(III) into carbon tetrachloride with benzoyltrifluoroacetone (Hbfa, 1-phenyl-4,4,4-trifluoro-1,3-butanedione) and 2-thenoyltrifluoroacetone (Htta, 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione) was greatly enhanced by the addition of tetrabutylammonium ions (tba$^+$). This was explained in terms of extraction of the anionic chelate complex as the ion-pair, EuA$_4^-$tba$^+$, which was extracted much better than the neutral chelate, EuA$_3$, (where A$^-$ is the β-diketonate ion). Furthermore, a similarity was found in the extraction equilibrium of EuA$_4{}^-$tba$^+$ with that of the adduct chelate, EuA$_3$L$_2$, (where L is an organophilic neutral ligand, such as tributylphosphate), in extraction systems where the "synergistic effect" was found.

It is known that the synergistic enhancement which is caused by the adduct formation of the neutral chelate with the neutral ligand is very much different for different diluents.[3,4] It is thus assumed that such a diluent effect should also be found regarding the association of the neutral chelate with the anion of a chelating ligand in ion-pairs with a bulky cation in the organic phase. In the present paper, the effect of a diluent on the extraction of the ternary europium(III) complex with Htta and tba$^+$ was studied when the solvent was chloroform, toluene, and 4-methyl-2-pentanone (MIBK). The results were compared with those obtained when the diluent was carbon tetrachloride, as described in a previous paper.[2] Furthermore, the effect of background salt in the aqueous phase on the extraction of the ternary complex was also studied with 0.1 mol dm^{-3} sodium nitrate and sodium chloride.

Statistical

In the present paper, any chemical species in the organic phase is denoted by the subscript "org" and that in the aqueous phase is shown without any subscript. The volumes of the two liquid phases were assumed to be the same. Since most of the statistical treatments were described in previous papers,[1,2] the main equations as well as those which were not given previously are presented in the present paper.

With the chelating extractant, the following equations can be written:

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

$$\mathrm{HA} \leftrightarrows \mathrm{H}^+ + \mathrm{A}^-\ ;\ K_\mathrm{a} = [\mathrm{H}^+][\mathrm{A}^-][\mathrm{HA}]^{-1}; \tag{2}$$

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

The equilibrium for the extraction of europium(III) with HA in both the absence and presence of tba$^+$ can be written as

$$\mathrm{Eu}^{3+} + 3\mathrm{A}^- \leftrightarrows \mathrm{EuA}_{3(\mathrm{org})};$$
$$K_{\mathrm{ex}3,0} = [\mathrm{EuA}_3]_\mathrm{org}[\mathrm{Eu}^{3+}]^{-1}[\mathrm{A}^-]^{-3} \tag{4}$$

$$\mathrm{Eu}^{3+} + 4\mathrm{A}^- + \mathrm{tba}^+ \leftrightarrows \mathrm{EuA}_4^-\mathrm{tba}^+_{(\mathrm{org})};$$
$$K_{\mathrm{ex}4,1} = [\mathrm{EuA}_4^-\mathrm{tba}^+]_\mathrm{org}[\mathrm{Eu}^{3+}]^{-1}[\mathrm{A}^-]^{-4}[\mathrm{tba}^+]^{-1}. \tag{5}$$

For the extraction of the ion-pairs, EuA$_4{}^-$tba$^+$, the following equations can be written as follows:

$$\mathrm{EuA}_{3(\mathrm{org})} + \mathrm{A}^-\mathrm{tba}^+_{(\mathrm{org})} \leftrightarrows \mathrm{EuA}_4^-\mathrm{tba}^+_{(\mathrm{org})};$$
$$K_\mathrm{org} = [\mathrm{EuA}_4^-\mathrm{tba}^+]_\mathrm{org}[\mathrm{EuA}_3]_\mathrm{org}^{-1}[\mathrm{A}^-\mathrm{tba}^+]_\mathrm{org}^{-1}. \tag{6}$$

For the extraction of A^- and the anion of the background salt, X^-, as ion-pair with tba^+, the following equations can be written:

$$A^- + tba^+ \leftrightarrows A^-tba^+_{(org)};$$
$$K_{exAB} = [A^-tba^+]_{org}[A^-]^{-1}[tba^+]^{-1} \quad (7)$$

$$X^- + tba^+ \leftrightarrows X^-tba^+_{(org)};$$
$$K_{exXB} = [X^-tba^+]_{org}[X^-]^{-1}[tba^+]^{-1}. \quad (8)$$

The distribution ratio of europium(III) with A^- in the absence (D_0) and presence (D) of tba^+ can be written as follows:

$$D_0 = [EuA_3]_{org}/([Eu^{3+}] + [EuA^{2+}] + [EuA_2^+] + \cdots) \quad (9)$$

$$= K_{ex3,0}[A^-]^3/(1 + \beta_1[A^-] + \beta_2[A^-]^2 + \cdots) \quad (10)$$

$$D = ([EuA_3]_{org} + [EuA_4^-tba^+]_{org})$$
$$/([Eu^{3+}] + [EuA^{2+}] + [EuA_2^+] + \cdots) \quad (11)$$

$$= (K_{ex3,0}[A^-]^3 + K_{ex4,1}[A^-]^4[tba^+])$$
$$/(1 + \beta_1[A^-] + \beta_2[A^-]^2 + \cdots), \quad (12)$$

where β_n is the stability constant and,

$$\beta_n = [EuA_n^{3-n}][Eu^{3+}]^{-1}[A^-]^{-n}.$$

When the concentration of A^- in the aqueous phase is identical, the following equations can be introduced from Eqs. 4, 5, 6, 7, 10, and 12:

$$D/D_0 = 1 + K_{ex4,1}K_{ex3,0}^{-1}[A^-][tba^+] \quad (13)$$

$$= 1 + K_{org}K_{exAB}[A^-][tba^+]. \quad (14)$$

In the presence of tba^+, the concentration of free tba^+ in the aqueous phase can be written as follows:

$$[tba^+]_{initial} = [tba^+] + [EuA_4^-tba^+]_{org}$$
$$+[A^-tba^+]_{org} + [X^-tba^+]_{org} \quad (15)$$

$$[tba^+] = ([tba^+]_{initial} - [EuA_4^-tba^+]_{org})$$
$$/(1 + K_{exAB}[A^-] + K_{exXB}[X^-]). \quad (16)$$

The synergistic extraction of europium(III) with the chelating extractant and a neutral ligand, L, can be written as follows when the concentration of A^- in the aqueous phase is identical:

$$D = ([EuA_3]_{org} + [EuA_3L]_{org} + [EuA_3L_2]_{org} + \cdots)$$
$$/([Eu^{3+}] + [EuA^{2+}] + [EuA_2^+] + \cdots), \quad (17)$$

$$EuA_{3(org)} + nL_{(org)} \leftrightarrows EuA_3L_{n(org)};$$
$$\beta_{(org)n} = [EuA_3L_n]_{org}[EuA_3]_{org}^{-1}[L]_{org}^{-n}, \quad (18)$$

and

$$D/D_0 = 1 + \beta_{(org)1}[L]_{org} + \beta_{(org)2}[L]_{org}^2 + \cdots. \quad (19)$$

Experimental

All of the reagents and the experimental procedures were similar to those used in previous studies,[1,2] except that chloroform, toluene, and MIBK were used as the diluent and sodium chloride was also used as the background salt. Thus, only the experiments which were not described previously are given in this section.

The two-phase distribution constant for the extraction of Htta between toluene and a 0.1 mol dm^{-3} sodium nitrate solution was determined by the method described in a previous paper.[5]

The extraction equilibrium of tba^+ as ion-pairs with nitrate or chloride ions in the aqueous phase and that with tta^- was measured in a manner similar to that described in previous papers,[1,2] except for the following points. After the aqueous phase containing tba^+ and the organic phase containing tta^- were agitated and centrifuged off, the diluent was evaporated by passing a nitrogen stream. The residue, a mixture of Htta, tta^-tba^+, and $NO_3^-tba^+$ or Cl^-tba^+, was dissolved in 5 cm^3 of 0.1 mol dm^{-3} nitric acid or hydrochloric acid; the solution was then agitated with 5 cm^3 of carbon tetrachloride. By this procedure, although the Htta was nearly quantitatively extracted into the organic phase, the extraction of tba^+ as tta^-tba^+ and $NO_3^-tba^+$, or as Cl^-tba^+ was negligible; it remained quantitatively in the aqueous phase under these conditions. The tba^+ in this aqueous solution was then determined by the method described in previous papers.[1,2]

Results and Discussion

When the diluent was carbon tetrachloride or toluene, the extraction of ion-pairs of the background anion as $NO_3^-tba^+$ or Cl^-tba^+ was found to be negligible; the extraction of tba^+ should be less than 1% of that in the initial aqueous phase. However, a measurable amount of these ion-pairs was extracted into chloroform and MIBK. The extraction constant, K_{exXB}, in Eq. 8, was calculated based on the experimental data obtained in the absence of tta^-. This value is listed in Table 1. When both tta^- and tba^+ are present in aqueous sodium nitrate or sodium chloride solution, the distribution ratio of tba^+, D_{tba}, can be written as

$$D_{tba} = [tba^+]_{org,total}[tba^+]_{aq,total}^{-1}$$

Table 1. Extraction Constant of tba^+ as Ion-Pairs with Background Anions (cf. Eq. 8)
Org. phase: the solvent initially containing 0.1 mol dm^{-3} Htta.
Aq phase: 0.1 mol dm^{-3} sodium nitrate or sodium chloride solution.

	Log K_{exXB}	
	X^-:NO_3^-	X^-:Cl^-
CCl_4	—[a]	—[a]
$CHCl_3$	1.3	0.1
$C_6H_5CH_3$	—[a]	—[a]
MIBK	1.3	0.04

a) The extraction was negligible.

$$= ([\mathrm{A}^-\mathrm{tba}^+]_{\mathrm{org}} + [\mathrm{X}^-\mathrm{tba}^+]_{\mathrm{org}})[\mathrm{tba}^+]^{-1}_{\mathrm{aq,total}}$$
$$= K_{\mathrm{exAB}}[\mathrm{A}^-] + K_{\mathrm{exXB}}[\mathrm{X}^-], \qquad (20)$$

where X^- represents NO_3^- or Cl^-. The experimental results are given in Fig. 1. From these data, the extraction constant of the ion-pair, tta^-tba^+, K_{exAB}, in Eq. 7 was calculated on the basis of Eq. 20. The obtained values are listed in Table 2. The solid curves in Fig. 1 were calculated by introducing the values of K_{exXB} and K_{exAB} in Tables 1 and 2 into Eq. 20. As can be seen from Fig. 1, the slope of each plot is +1 and, thus, the tba^+ in the chloroform phase is mainly in the form of tta^-tba^+ if $[tta^-]$ is higher than 10^{-3} or 10^{-5} mol dm^{-3}, respectively, when the background salt is sodium nitrate or sodium chloride. However, when $[tta^-]$ is lower than these, the effect of the co-extraction of X^-tba^+ should be taken into account. When the diluent was toluene or carbon tetrachloride, the effect of the extraction of $NO_3^-tba^+$ and Cl^-tba^+ was negligible under the conditions of the present study.

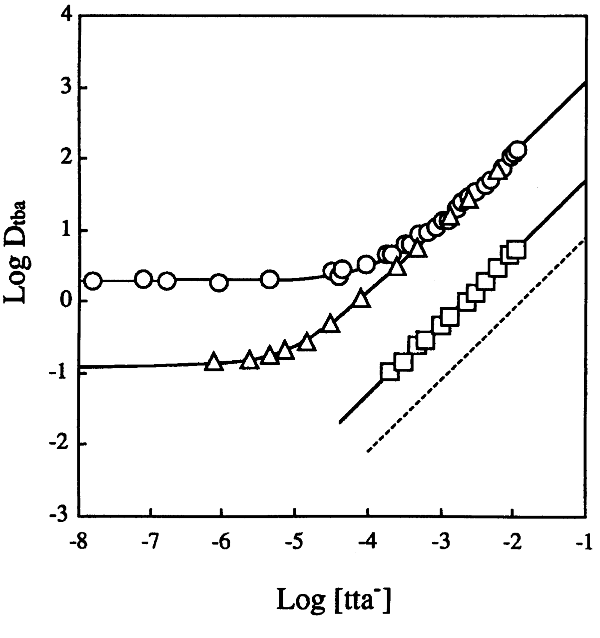

Fig. 1. Distribution ratio of tetrabutylammonium ions as a function of the concentration of 2-thenoyltrifluoroacetonate anion. The diluent is chloroform and the background salt is sodium nitrate (○) or sodium chloride (△); the diluent is toluene and the background salt is sodium nitrate (□). The dotted line gives the results when the diluent is carbon tetrachloride and the background salt is sodium nitrate (Ref. 2). The solid lines are calculated by Eq. 20, using the values given in Tables 1 and 2.

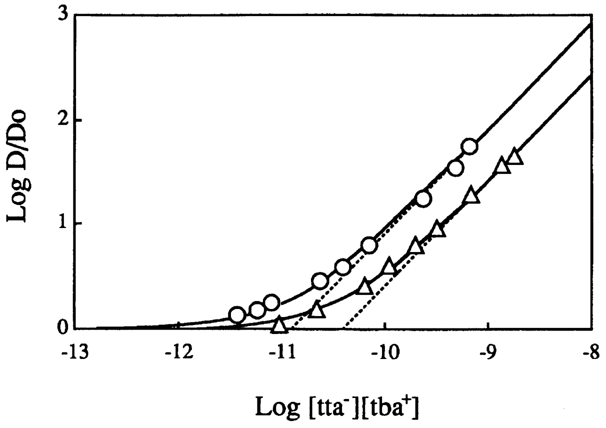

Fig. 3. Increase in the distribution ratio as a function of the quantity, $[tta^-]$ multiplied by $[tba^+]$ in the aqueous phase. Org. phase: Chloroform (○) and toluene (△) initially containing 0.1 mol dm^{-3} of Htta. Aq phase: 0.1 mol dm^{-3} sodium nitrate solution at pH 3.6 for chloroform and pH 3.5 for toluene.

The extraction curves of europium(III) with 0.1 mol dm^{-3} Htta (at initial) in the organic phase in the absence (open symbols) and presence (closed symbols) of 1×10^{-3} mol dm^{-3} of tba^+ (at initial) for chloroform as diluent are given in Fig. 2a; those for toluene and MIBK are given in Fig. 2b (for MIBK, the initial concentration of tba^+ was 1×10^{-4} mol dm^{-3}). Plots for carbon tetrachloride in Ref. 2 are also given in Fig. 2a. A statistical analysis of the data in both the absence and presence of tba^+ was carried out on the basis of Eqs. 10 and 12. It was concluded from the analysis that the first complex, $Eu(tta)^{2+}$, should be taken into account. The value of the stability constant, β_1, and the extraction constants, $K_{ex3,0}$ in Eq. 4 and $K_{ex4,1}$ in Eq. 5, obtained by using a least-squares computer program are listed in Table 2. Each solid line in Figs. 2a and 2b is the calculated extraction curve on the basis of Eq. 10 or Eq. 12 by using the values of the constants given in Tables 1 and 2. The value of β_1 agrees with that reported in a previous paper.[2)]

The enhancement of extraction by the addition of tba^+ was determined as a function of the tba^+ concentration by using Eq. 16 when the concentration of tta^- was approximately kept constant. The data are given in Fig. 3. The solid lines shown in Fig. 3 were calculated on the basis of Eq. 13 by using the values of the equilibrium constants given in Table 2. The value of log $K_{ex4,1}K_{ex3,0}{}^{-1}$ or log $K_{org}K_{exAB}$ can also be obtained from the intercept of the asymptote of the plot of log D/D_0 vs. log $[tta^-][tba^+]$ with the X-axis, as can be seen from Eq. 13 or 14.[1)] The experimental data agreed well with the lines calculated by using the extraction constants given in Table 2.

It can be concluded that the extraction of the ion-pairs is better into chloroform than into carbon tetrachloride, as is clearly seen from the values of K_{exXB} and K_{exAB} given in Tables 1 and 2.

The following constants could not be determined from the data of the present study:

$$\mathrm{Eu}^{3+} + 4\mathrm{A}^- \leftrightarrows \mathrm{EuA}_4^-;$$
$$\beta_4 = [\mathrm{EuA}_4^-][\mathrm{Eu}^{3+}]^{-1}[\mathrm{A}^-]^{-4}. \qquad (21)$$

Table 2. Summary of Equilibrium Constants in Eqs. 1, 4, 5, 6, 7, and β_1
Org. phase: the solvent initially containing 0.1 mol dm^{-3} Htta.
Aq phas: 0.1 mol dm^{-3} sodium nitrate solution.

	Log $K_{\mathrm{ex3,0}}$	Log $K_{\mathrm{ex4,1}}$	Log K_{org}	Log β_1	Log K_{exAB}	Log K_{d}
CCl_4	14.4$^{a)}$	24.8$^{a)}$	8.5$^{a)}$	4.4$^{a)}$	1.9$^{a)}$	1.32$^{b)}$
$CHCl_3$	16.1	27.1	6.9	4.5	4.1	1.85$^{b)}$
$C_6H_5CH_3$	16.2	26.6	7.6	4.5	2.7	1.73$^{c)}$
MIBK	21.1	—	—	—	4.5	2.22$^{b)}$

a) Taken from Ref. 2. b) Taken from Ref. 6 (CCl_4, $CHCl_3$) and Ref. 3 (MIBK) but the aqueous phase in these previous studies was 0.1 mol dm^{-3} $NaClO_4$. The pK_a of Htta employed for the calculation, 6.33, was also taken from Ref. 6. c) Determined in the present study by the method in Ref. 5.

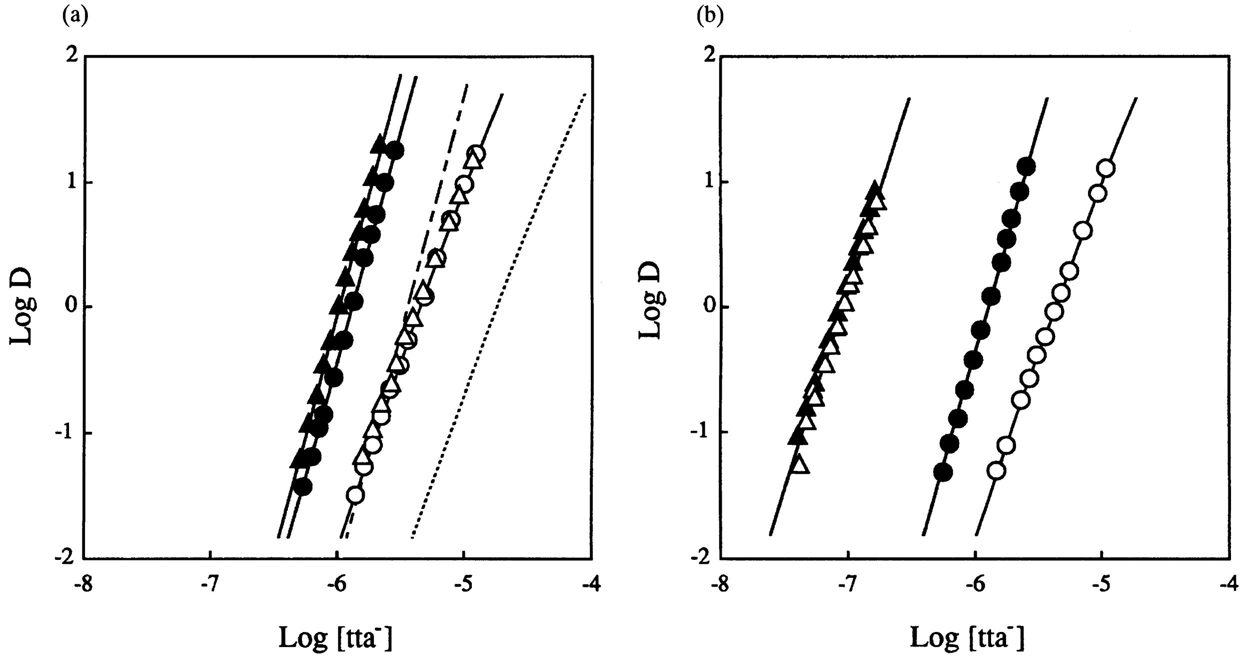

Fig. 2. Distribution ratio of europium(III) as a function of the concentration of 2-thenoyltrifluoroacetonate anion. The initial Htta concentration in the organic phase is 0.1 mol dm^{-3}. The open symbols indicate the absence of tetrabutylammonium ions and the closed symbols indicate the data in the presence of 1.0×10^{-3} mol dm^{-3} tetrabutylammonium ions at initial (for MIBK, 1.0×10^{-4} mol dm^{-3} at initial). The lines are calculated by Eq. 10 or Eq. 12, using the values given in Table 2. a. The diluent is chloroform and the background salt is sodium nitrate (○, ●) or sodium chloride (△, ▲). The dotted and broken lines are plots, respectively, in the absence and presence of 1.0×10^{-3} mol dm^{-3} tba$^+$, when the diluent is carbon tetrachloride and the background salt is sodium nitrate taken from Ref. 2. b. The diluent is toluene and the background salt is sodium nitrate (○, ●) and the diluent is MIBK and the background salt is sodium nitrate (△, ▲).

$$\mathrm{EuA_4^-} + \mathrm{tba^+} \leftrightarrows \mathrm{EuA_4^-tba^+_{(org)}};$$
$$K_{\mathrm{exCB}} = [\mathrm{EuA_4^-tba^+}]_{\mathrm{org}}[\mathrm{EuA_4^-}]^{-1}[\mathrm{tba^+}]^{-1}. \quad (22)$$

However, the following relation could be obtained from Eqs. 5, 21, and 22:

$$K_{\mathrm{ex4,1}} = \beta_4 K_{\mathrm{exCB}}. \quad (23)$$

Since the value of β_4 should be independent of the solvent, the ratio of $K_{\mathrm{ex4,1}}$ in the solvent extraction systems should be equal to the ratio of K_{exCB} in Eq. 22. In other words, $K_{\mathrm{ex4,1}}$ is proportional to the extractability of the anionic complex, Eu(tta)$_4{}^-$tba$^+$, in Eq. 22. It can be seen that the magnitude of $K_{\mathrm{ex4,1}}$ is larger according to the following order: carbon tetrachloride<toluene<chloroform.

As has been described above, the extraction of the background anion is negligible when the diluent is carbon tetrachloride and toluene. Furthermore, only a small part of tba$^+$ is extracted as tta$^-$tba$^+$ under the experimental conditions employed. Thus, a statistical analysis of the data can be made by using the initial tba$^+$ concentration in the aqueous phase if the correction is made for a decrease due to the extraction of tta$^-$tba$^+$ and Eu(tta)$_4{}^-$tba$^+$. When the diluent is chloroform, on the other hand, the decrease in the concentration of tba$^+$ in the aqueous phase, due to the

Table 3. Formation Constant of Adducts of $Eu(tta)_3$ with TBP Taken from Ref. 3

	Log $\beta_{(org)1}$	Log $\beta_{(org)2}$
CCl_4	5.46	8.46
$CHCl_3$	3.62	5.44

extraction of the background anion, NO_3^- or Cl^-, is not negligible, even when the salt concentration is 0.1 mol dm^{-3}. This causes a decrease in the concentration of tba^+ in the aqueous phase, as well as that of tta^-tba^+ in the organic phase, as can be seen from Eq. 16. This should, thus reduce the enhancement due to the extraction of the ternary complex, as can be seen from Eq. 14. Although the difference is not very large, this effect of the background anion can be clearly seen in Fig. 2a; even though the initial concentration of tba^+ is the same, the enhancement of extraction is to some extent larger when the background salt is sodium chloride, than when it is sodium nitrate. The same tendency should generally be found if the metal ion does not form stable chloride complexes as dose europium(III).[7] Such an effect of the back ground salt should be larger if its concentration is higher, as can be seen from Eq. 8.

This type of extraction equilibrium for the $Eu(tta)_4^-tba^+$ complex is similar to that for the adduct chelate, $Eu(tta)_3L_2$, where L is an organophilic neutral ligand, such as tributylphosphate (TBP) or trioctylphosphine oxide (TOPO), in extraction systems where the "synergistic effect" was found.[3] Both the formation of the anionic complex and of the neutral adduct complex should change the coordination number of europium(III) from six (that in the $Eu(tta)_3$) to eight (that in the $Eu(tta)_4^-tba^+$ or $Eu(tta)_3L_2$) in the organic solvent. In this previous paper, the adduct formation of the $Eu(tta)_3$ chelate with TBP in carbon tetrachloride, chloroform, and MIBK was discussed, and it was pointed out that the adduct formation constants, $\beta_{(org),n}$ in Eq. 18 were larger in carbon tetrachloride than in chloroform. However, when the diluent was MIBK, no adduct with the other ligand was found for the $Eu(tta)_3$ chelate. The equilibrium constants for the adduct formation of the tta^- chelate of europium(III) with TBP in the previous paper are summarized in Table 3. A similar trend was found in the present study; the formation constant of the anionic complex, K_{org}, in Eq. 6 was larger in carbon tetrachloride than in chloroform. When the diluent was MIBK, the addition of tba^+ had no effect on the distribution ratio for all practical purposes, as can be seen in Fig. 2b. The reason for this should be due to the association or solvation of the chelate with MIBK, which is the major component of the organic phase, and it should interfere with the association with TBP or tta^-tba^+.

It is generally accepted that non-polar solvents, such as carbon tetrachloride, are less favorable as the solvent for the extraction of an ion-pair than polar ones. Furthermore, it is expected that the extraction of the ion-pair, tta^-tba^+, is worse in the following order: chloroform > toluene > carbon tetrachloride. On the other hand, the synergistic enhancement of metal chelates with neutral ligands is larger in the inverse order. The same should be expected for the association of the $Eu(tta)_3$ chelate with the tta^-tba^+ ion-pair in the organic solvents. This is clearly seen from Table 2, in which K_{org} is 40-times larger in carbon tetrachloride than in chloroform. The results of an enhancement of the extraction observed in the present study are the over-all effect of the extraction of tta^-tba^+ and the association of $Eu(tta)_3$ and tta^-tba^+. These two competing effects, which are larger in the inverse direction, cancel out each other and cause a smaller difference in the enhancement of extraction in different solvents than that expected only from the difference in K_{org}.

As can be seen from the results of the present study, the chemical equilibria of the extraction of ternary complexes are affected by several factors and, thus, it is more complicated than the extraction of adducts of metal chelate with a neutral ligand in synergistic extraction systems. The value of K_{org} in Eq. 6 may be helpful for understanding these complicated solvent extraction equilibria.

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