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Effect of Several Quarternary Ammoniums on the Solvent Extraction of Europium(III) 2-Thenoyltrifluoroacetonate Anionic Complex into Chloroform

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, Kanagawa 237

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The solvent extraction of europium(III) in aqueous 0.1 mol dm^{-3} sodium chloride or sodium nitrate solutions with 2-thenoyltrifluoroacetone (Htta) into chloroform was measured in the absence and presence of tetraethylammonium, tetrapropylammonium, tetrapentylammonium, or tetradecyldimethylbenzylammonium (base$^+$). The addition of quarternary ammoniums enhanced the extraction, except for tetraethylammonium. This enhancement could be explained in terms of the extraction of the ternary complex, the Eu(tta)$_4^-$base$^+$, in addition to the Eu(tta)$_3$ complex. The difference in the enhancement of extraction with a different quarternary ammonium at a certain total concentration was much smaller than that expected from the difference in the size. This could be explained in terms that although the extraction of the anionic complex should be better when the size of the base$^+$ is larger, its concentration in the aqueous phase at equilibrium is lower because it is extracted with the other anions in the aqueous phase better than a smaller base$^+$. It was also found that the formation equilibrium of the ternary complex, the Eu(tta)$_4^-$base$^+$, by association of the neutral complex, Eu(tta)$_3$, with the ion-pair, tta$^-$base$^+$, in the organic phase is essentially not affected by the size of the base$^+$.

It was reported in previous papers[1—3] that the solvent extraction of europium(III) 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 an addition of a bulky cation, tetrabutylammonium (tba$^+$); this could be explained in terms of the extraction of an anionic complex, EuA$_4^-$tba$^+$, in addition to a neutral complex, EuA$_3$ (where A$^-$ is the β-diketonate ion). The present paper describes the solvent extraction of the anionic complex of europium(III) with Htta with several quarternary ammoniums (base$^+$). This was studied because the solvent extraction of the ion-pair of a certain given anion is usually better when the counter cation is larger; it is thus expected that the extraction of the anionic complex should also be better if the counter cation is larger. The quarternary ammoniums employed were tetraethylammonium (tea$^+$), tetrapropylammonium (tppa$^+$), tetrapentylammonium (tpta$^+$), and tetradecyldimethylbenzylammonium (Zephir Amine, tddmba$^+$). Based on the results from the present study as well as those obtained when the base$^+$ was tetrabutylammonium (tba$^+$) in a previous study,[3] the effect of the size of the counter cation on the solvent extraction equilibrium of the anionic complex is considered.

In the present study chloroform was used as the diluent. This was because when the quarternary ammonium is larger, and the solubility of the ion-pairs of reagents, tta$^-$base$^+$, and those with anions of the background salt (X$^-$), X$^-$base$^+$, is lower in the organic phase. Although this often causes the formation of precipitates when the diluent is carbon tetrachloride during the experiments, when the diluent is chloroform, such troubles are encountered much less.

It was found that the anions of the background salt in the aqueous phase were extracted as ion-pairs with the quarternary ammonium; this affected the extraction equilibria of the anionic metal complex. Thus, both aqueous 0.1 mol dm^{-3} sodium chloride and sodium nitrate solutions were employed as the aqueous phase in order to compare this effect of the background salt.

Statistical

In the present paper, all chemical species in the organic phase are denoted by the subscript "org"; those in the aqueous phase are given without any subscript. The volumes of the two liquid phases were assumed to be the same. Since most statistical treatments are similar to those described in previous papers,[1—3] only the main equations as well as those not given in the previous papers are given here.

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

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

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

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

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

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

$$\mathrm{Eu}^{3+} + 4\mathrm{A}^- + \mathrm{base}^+ \rightleftharpoons \mathrm{EuA}_4{}^-\mathrm{base}^+{}_{(\mathrm{org})};$$

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

For a statistical treatment of the extraction of ion-pairs, EuA$_4^-$base$^+$, the following equations can be written:

$$\mathrm{EuA_{3(org)} + A^-base^+{}_{(org)} \rightleftharpoons EuA_4{}^-base^+{}_{(org)}};$$
$$K_{\mathrm{org}} = [\mathrm{EuA_4{}^-base^+}]_{\mathrm{org}}[\mathrm{EuA_3}]_{\mathrm{org}}{}^{-1}[\mathrm{A^-base^+}]_{\mathrm{org}}{}^{-1} \quad (6)$$

For the extraction of A^- and the anion of background salt, X^-, as ion-pair with $\mathrm{base^+}$, the following equations can be written:

$$\mathrm{A^- + base^+ \rightleftharpoons A^-base^+{}_{(org)}}$$
$$K_{\mathrm{exAB}} = [\mathrm{A^-base^+}]_{\mathrm{org}}[\mathrm{A^-}]^{-1}[\mathrm{base^+}]^{-1} \quad (7)$$
$$\mathrm{X^- + base^+ \rightleftharpoons X^-base^+{}_{(org)}};$$
$$K_{\mathrm{exXB}} = [\mathrm{X^-base^+}]_{\mathrm{org}}[\mathrm{X^-}]^{-1}[\mathrm{base^+}]^{-1}. \quad (8)$$

In the absence of the metal ions, the distribution ratio of $\mathrm{base^+}$, D_{base}, may be introduced from Eqs. 7 and 8 as follows:

$$\begin{aligned} D_{\mathrm{base}} &= [\mathrm{base^+}]_{\mathrm{org,total}}/[\mathrm{base^+}] \\ &= \left([\mathrm{A^-base^+}]_{\mathrm{org}} + [\mathrm{X^-base^+}]_{\mathrm{org}}\right)/[\mathrm{base^+}] \\ &= K_{\mathrm{exAB}}[\mathrm{A^-}] + K_{\mathrm{exXB}}[\mathrm{X^-}]. \end{aligned} \quad (9)$$

$$D_{\mathrm{base}}[\mathrm{X^-}]^{-1} = K_{\mathrm{exAB}}[\mathrm{A^-}][\mathrm{X^-}]^{-1} + K_{\mathrm{exXB}}. \quad (10)$$

The distribution ratio of europium(III) extracted with A^- in the absence (D_0) and presence (D) of $\mathrm{base^+}$ can be written as follows:

$$D_0 = [\mathrm{EuA_3}]_{\mathrm{org}}/\left([\mathrm{Eu^{3+}}] + [\mathrm{EuA^{2+}}] + [\mathrm{EuA_2{}^+}] + \cdots\right) \quad (11)$$
$$D_0 = K_{\mathrm{ex3,0}}[\mathrm{A^-}]^3/\left(1 + \beta_1[\mathrm{A^-}] + \beta_2[\mathrm{A^-}]^2 + \cdots\right) \quad (12)$$

$$D = \left([\mathrm{EuA_3}]_{\mathrm{org}} + [\mathrm{EuA_4{}^-base^+}]_{\mathrm{org}}\right) / \left([\mathrm{Eu^{3+}}] + [\mathrm{EuA^{2+}}] + [\mathrm{EuA_2{}^+}]\cdots\right) \quad (13)$$

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

where β_n is the stability constant,

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

When the concentration of A^- in the aqueous phase is identical, the following equations can be introduced from Eqs. 4, 5, 6, 7, 12, and 14:

$$D/D_0 = 1 + K_{\mathrm{ex4,1}}K_{\mathrm{ex3,0}}{}^{-1}[\mathrm{A^-}][\mathrm{base^+}] \quad (15)$$
$$D/D_0 = 1 + K_{\mathrm{org}}K_{\mathrm{exAB}}[\mathrm{A^-}][\mathrm{base^+}]. \quad (16)$$

In the presence of $\mathrm{base^+}$, its free concentration can be written as

$$[\mathrm{base^+}]_{\mathrm{total}} = [\mathrm{base^+}] + [\mathrm{EuA_4{}^-base^+}]_{\mathrm{org}} + [\mathrm{A^-base^+}]_{\mathrm{org}} + [\mathrm{X^-base^+}]_{\mathrm{org}} \quad (17)$$

$$[\mathrm{base^+}] = \left([\mathrm{base^+}]_{\mathrm{total}} - [\mathrm{EuA_4{}^-base^+}]_{\mathrm{org}}\right) / \left(1 + K_{\mathrm{exAB}}[\mathrm{A^-}] + K_{\mathrm{exXB}}[\mathrm{X^-}]\right). \quad (18)$$

Experimental

All of the reagents and the experimental procedures were similar to those used in previous studies,[1—3] except that tetraethylammonium, tetrapropylammonium, tetrapentylammonium, or tetradecyldimethylbenzylammonium was used as the quarternary ammonium.

Tetraethylammonium chloride, tetrapropylammonium chloride, and tetrapentylammonium chloride were obtained from Wako Pure Chemical Industries, Ltd. Tetradecyldimethylbenzylammonium chloride was obtained from Tokyo Kasei Co. The water content in the quarternary ammonium chlorides was determined using Karl Fischer's titration method.

The extraction of $\mathrm{tea^+}$, $\mathrm{tppa^+}$, and $\mathrm{tpta^+}$ as ion-pairs with chloride or nitrate ions in the aqueous phase and that with $\mathrm{tta^-}$ were measured in a manner similar to that described in previous papers.[1—3]

Results

The extraction of $\mathrm{Cl^-}$ or $\mathrm{NO_3{}^-}$ with $\mathrm{tea^+}$ and $\mathrm{tppa^+}$ into chloroform was negligible within the accuracy of the experiments; the K_{exXB} in Eq. 8 with these $\mathrm{base^+}$ were concluded to be lower than 10^{-1}. The extraction of $\mathrm{tta^-}$ with $\mathrm{tea^+}$ was also negligible; K_{exAB} in Eq. 7 with this $\mathrm{base^+}$ should also be lower than 10^{-1}. However, a measurable amount of the ion-pairs of $\mathrm{tta^-}$ with $\mathrm{tppa^+}$ was extracted. Figure 1 gives the extraction data, from which it can be seen that the log $D_{\mathrm{base}}[\mathrm{X^-}]^{-1}$ vs. log $[\mathrm{tta^-}][\mathrm{X^-}]^{-1}$ plot is a straight line with a slope of +1 with $\mathrm{tppa^+}$. On the basis of Eq. 10, it can be seen that although the extraction of $\mathrm{tta^-tppa^+}$ occurs, that of $\mathrm{X^-tppa^+}$ is negligible when X^- is $\mathrm{Cl^-}$ or $\mathrm{NO_3{}^-}$.

The extraction of $\mathrm{Cl^-tpta^+}$, $\mathrm{NO_3{}^-tpta^+}$, and $\mathrm{tta^-tpta^+}$ was very good and only a small part of $\mathrm{tpta^+}$ remained in the aqueous phase at equilibrium. Thus, an accurate determination of the concentration of $\mathrm{tpta^+}$ in the aqueous phase, which is necessary to calculate K_{exAB} in Eq. 7 and K_{exXB} in Eq. 8, was difficult. For this reason, the experiments used to determine K_{exAB} and K_{exXB} were carried out by adjusting the concentration of the background salt to be lower than 0.1 mol dm^{-3}. The concentration of sodium chloride or sodium nitrate solution was 1×10^{-2}, 2×10^{-2}, or 3×10^{-2} mol dm^{-3} for these experiments and the organic phase was chloroform containing either no or 1×10^{-2} mol dm^{-3} Htta. It was found that the values of K_{exAB} and K_{exXB} were not affected by the concentration of background salt under these conditions. As can be seen from Fig. 1, the log $D_{\mathrm{base}}[\mathrm{X^-}]^{-1}$ vs. log $[\mathrm{tta^-}][\mathrm{X^-}]^{-1}$ plot when $\mathrm{base^+}$ was $\mathrm{tpta^+}$ (it was also so when it was $\mathrm{tba^+}$ in Ref. 3) has two asymptotes; the slope of one is 0, and that of the other is +1. As can be seen from Eq. 10, this indicates that the extraction of both $\mathrm{X^-tpta^+}$ and $\mathrm{tta^-tpta^+}$ occurs. Since the extrac-

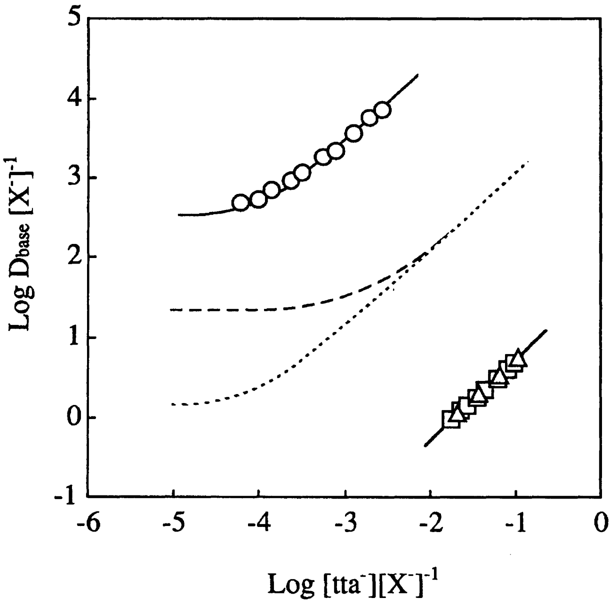

Fig. 1. Distribution ratio of tppa$^+$ and tpta$^+$ as a function of the concentration of 2-thenoyltrifluoroacetonate anion.
Org. phase: chloroform initially containing 1×10^{-2} or 0.1 mol dm^{-3} 2-thenoyltrifluoroacetone. Aq phase: (□) 0.1 mol dm^{-3} sodium chloride and 1×10^{-3} mol dm^{-3} tppa$^+$, (△) 0.1 mol dm^{-3} sodium nitrate and 1×10^{-3} mol dm^{-3} tppa$^+$, (○) 1×10^{-2}, 2×10^{-2}, or 3×10^{-2} mol dm^{-3} sodium chloride and 1×10^{-3} mol dm^{-3} tpta$^+$ at initial. The dotted and broken lines are the results with 1×10^{-3} mol dm^{-3} tba$^+$ in 0.1 mol dm^{-3} sodium chloride and sodium nitrate solution in Ref. 3. The lines were calculated on the basis of Eq. 10, which provided the values of K_{exAB} and K_{exXB} given in Table 1.

tion of NO$_3$$^-$tpta$^+$ was very good, a determination of the K_{exAB} value of tta$^-$tpta$^+$ was possible only when the aqueous phase was a sodium chloride solution. The values of K_{exXB} were determined by experiments in the absence of tta$^-$. The obtained values of K_{exAB} and K_{exXB} are given in Table 1.

Since the extraction constants of the ion-pairs of NO$_3$$^-$ and Cl$^-$ with tddmba$^+$ could not be determined accurately by the method employed in the present study, the literature values[5] listed in Table 1 were used for the calculations. The extraction of the ion-pair of tta$^-$ was also very good, and this extraction constant with tddmba$^+$ was calculated from the extraction data concerning europium(III), as will be described.

The extraction constant of europium(III) in aqueous 0.1 mol dm^{-3} sodium chloride or sodium nitrate solutions with tta$^-$, $K_{\mathrm{ex3,0}}$ in Eq. 4, and the stability constant, β_1, were determined from data obtained in the absence of any quaternary ammonium; they are $K_{\mathrm{ex3,0}}=10^{16.1}$ and $\beta_1=10^{4.5}$, and agree well with the values given in a previous paper.[3)]

Table 1. Extraction Constants of Quaternary Ammoniums as Ion-Pairs with 2-Thenoyltrifluoroacetonate Anion or with the Background Anion (cf. Eqs. 7 and 8)
Org. phase: chloroform containing none or 0.1 mol dm^{-3} Htta. Aq phase: 0.1 mol dm^{-3} sodium chloride or sodium nitrate solution. (When base$^+$ is tpta$^+$ the organic phase is none or 1×10^{-2} mol dm^{-3} Htta and aqueous phase is 1×10^{-2}, 2×10^{-2}, or 3×10^{-2} mol dm^{-3} sodium chloride or sodium nitrate solution.)

	log K_{exXB}		log K_{exAB}
	NaCl	NaNO$_3$	
tea$^+$	—	—	—
tppa$^+$	—	—	1.7
tba$^+$	0.1$^{a)}$	1.3$^{a)}$	4.1$^{a)}$
tpta$^+$	2.5	3.6	6.4
tddmba$^+$	4.7$^{b)}$	5.7$^{b)}$	8.8

log K_a in Eq. 1 and log K_d in Eq. 2 of Htta employed for the calculation were −6.33 and 1.85 respectively. These were taken from Ref. 4 but the aqueous phase in this previous study was 0.1 mol dm^{-3} NaClO$_4$. a) Taken from Ref. 3. b) Taken from Ref. 5.

Although the addition of 1×10^{-3} mol dm^{-3} (at initial) of tea$^+$ did not change the extraction, that of the other quaternary ammoniums enhanced the extraction. The results of extraction from sodium chloride solutions are given in Fig. 2a, and that from sodium nitrate solutions are given in Fig. 2b. The results, except for those with tddmba$^+$, were statistically analyzed on the basis of Eqs. 12 and 14. The equilibrium constant, $K_{\mathrm{ex4,1}}$, as well as K_{org}, which can be calculated from $K_{\mathrm{ex4,1}}$, $K_{\mathrm{ex3,0}}$, and K_{exAB}, were obtained, as listed in Table 2.

The extraction data with tta$^-$ and tddmba$^+$ were statistically analyzed as follows. By introducing Eq. 18 into Eq. 14, the following equation is obtained:

$$D=\frac{K_{\mathrm{ex3,0}}[\mathrm{A}^-]^3+K_{\mathrm{ex4,1}}[\mathrm{A}^-]^4E/\left(F+K_{\mathrm{exAB}}[\mathrm{A}^-]\right)}{1+\beta_1[\mathrm{A}^-]+\beta_2[\mathrm{A}^-]^2+\cdots}, \tag{19}$$

where

$$E=[\mathrm{base}^+]_{\mathrm{total}}-[\mathrm{Eu(tta)}_4{}^-\mathrm{base}^+]_{\mathrm{org}}$$

and

$$F=1+K_{\mathrm{exXB}}[\mathrm{X}^-].$$

Under conditions in which $[\mathrm{Eu(tta)_4}^-\mathrm{base}^+]_{\mathrm{org}}\gg[\mathrm{Eu(tta)_3}]_{\mathrm{org}}$, the value of $[\mathrm{Eu(tta)_4}^-\mathrm{base}^+]_{\mathrm{org}}$ is estimated to be the same as that of $[\mathrm{Eu(III)}]_{\mathrm{org,total}}$, which can be determined experimentally. When the background salt is in large excess to the total amount of base$^+$, the value of [X$^-$] can be regarded as being the same as $[\mathrm{X}^-]_{\mathrm{initial}}$. The values of $K_{\mathrm{ex3,0}}$, β_1, and K_{exXB} have already been determined (K_{exXB} of tddmba$^+$ was obtained from the literature). Thus, only $K_{\mathrm{ex4,1}}$ and K_{exAB} are unknown in Eq. 19. The following two parameters, Y and Z, can be obtained from the already known values:

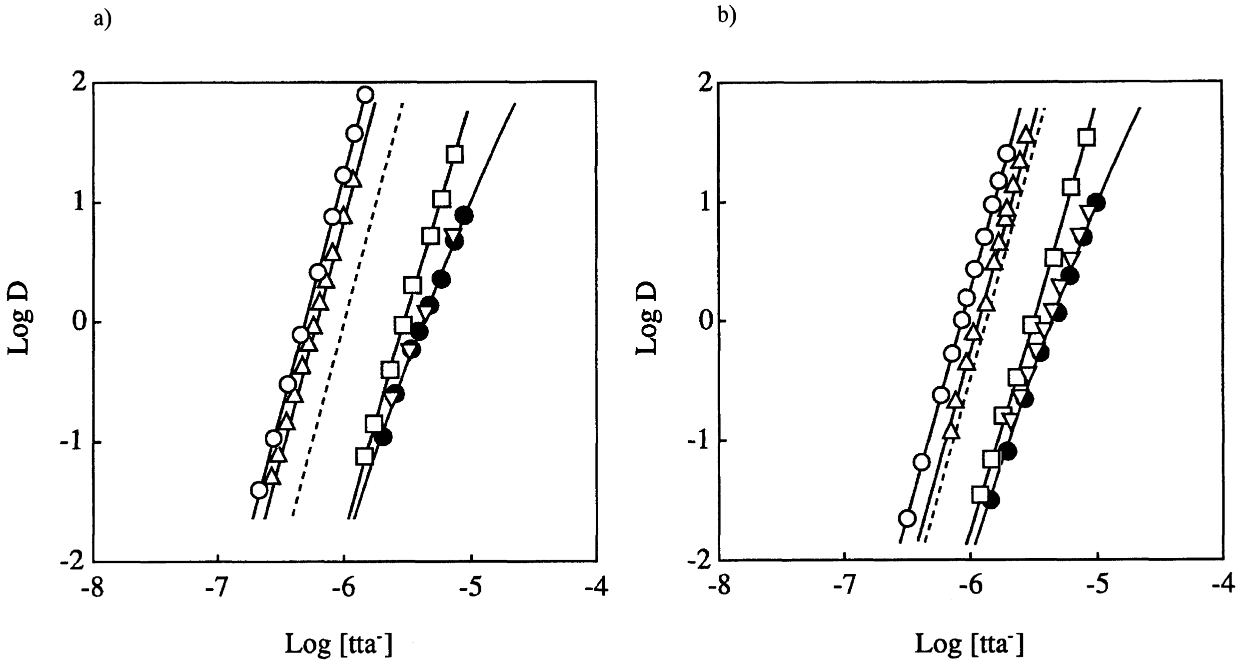

Fig. 2. Extraction curves of europium(III) with 2-thenoyltrifluoroacetone and quarternary ammoniums. Org. phase: Chloroform initially containing 0.1 mol dm^{-3} 2-thenoyltrifluoroacetone. Aq phase: a) 0.1 mol dm^{-3} sodium chloride, b) 0.1 mol dm^{-3} sodium nitrate. The aqueous phase initially contains no quarternary ammonium (●), 1×10^{-3} mol dm^{-3} tea$^+$ (▽), 1×10^{-3} mol dm^{-3} tppa$^+$ (□), and 1×10^{-3} mol dm^{-3} tpta$^+$ (△). The organic phase initially contains 1×10^{-3} mol dm^{-3} tddmba$^+$Cl$^-$ (○). The dotted line gives the plot when 1×10^{-3} mol dm^{-3} tba$^+$ (at initial) is added into the aqueous phase in Ref. 3. The solid lines were calculated by Eq. 14 using the values in Tables 1 and 2.

Table 2. Extraction Constant of 2-Thenoyltrifluoroacetonate Complex as Ion-Pairs with Quarternary Ammoniums and Formation Constant of Anionic Complexes of Present Work (cf. Eqs. 5 and 6)

	log $K_{ex4,1}$		log K_{org}	
	NaCl	NaNO$_3$	NaCl	NaNO$_3$
tppa$^+$	25.0	24.9	7.2	7.1
tba$^+$	27.1[a)]	27.1[a)]	6.9[a)]	6.9[a)]
tpta$^+$	29.5	29.4	7.0	6.9
tddmba$^+$	32.0	32.1	7.1	7.2

The extraction constant of the Eu(tta)$_3$ complexes, $K_{ex3,0}$ in Eq. 4, and the stability constant of the Eu(tta)$^{2+}$ complex in the aqueous phase both in the 0.1 mol dm^{-3} sodium chloride and sodium nitrate solutions was log $K_{ex3,0}=16.1$ and log $\beta_1=4.5$. a) Taken from Ref. 3.

$$Y=[A^-]^3E \Big/ \left\{D\left(1+\beta_1[A^-]+\beta_2[A^-]^2+\cdots\right)-K_{ex3,0}[A^-]^3\right\} \qquad (20)$$

and

$$Z=F[A^-]^{-1}. \qquad (21)$$

From Eqs. 19, 20, and 21, the following equation can be introduced:

$$Z=K_{ex4,1}Y-K_{exAB}. \qquad (22)$$

The values of K_{exAB} and $K_{ex4,1}$ were determined on the basis of Eq. 22 using sets of values for Y and Z obtained from the experimental data. The calculation was made by a successive-approximation method using a least-squares computer program. The obtained values are listed in Tables 1 and 2. Figure 3 is a log Y vs. log Z plot for tppa$^+$, tba$^+$ (the data were taken from Ref. 3), tpta$^+$, and tddmba$^+$. The solid lines in Fig. 3 were calculated on the basis of Eq. 22 using the values given in Tables 1 and 2. These lines agree well with the data calculated on the basis of Eqs. 20 and 21, as described above. This should indicate that the data analysis for the determination of K_{exAB} and $K_{ex4,1}$ of extraction with tddmba$^+$ in the present study should be reasonable.

Discussion

As can be seen from Table 1, the extraction of anions with a certain quarternary ammonium is better in the order Cl$^-$<NO$_3{}^-$<tta$^-$; that of a certain anion with the quarternary ammoniums is better in the order tea$^+$<tppa$^+$<tba$^+$<tpta$^+$<tddmba$^+$. This order agrees with the general tendency regarding the extraction of various ion-pairs;[5,6] that is, extraction is better when the ions are larger.

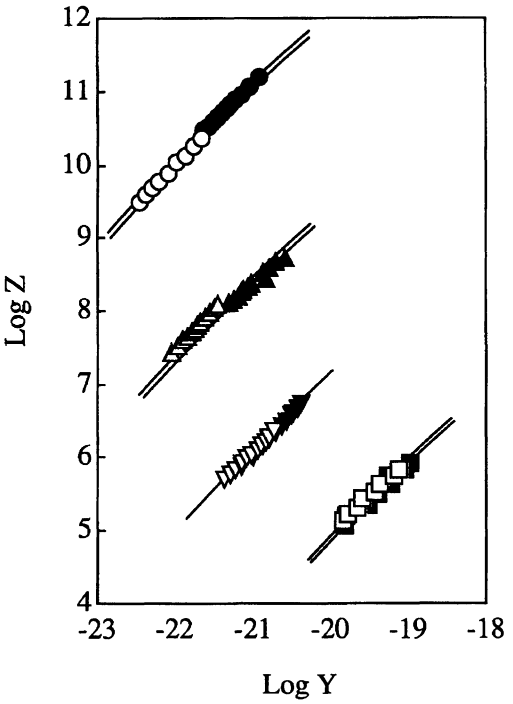

Fig. 3. Plot of log Y (in Eq. 20) vs. log Z (in Eq. 21) calculated from the data given in Figs. 2a and 2b. The data of tba$^+$ were taken from Ref. 3. Org. phase: Chloroform initially containing 0.1 mol dm^{-3} 2-thenoyltrifluoroacetone. Aq phase: 0.1 mol dm^{-3} sodium chloride (open symbols) and 0.1 mol dm^{-3} sodium nitrate (closed symbols). The aqueous phase initially contains 1×10^{-3} mol dm^{-3} tppa$^+$ (□, ■), 1×10^{-3} mol dm^{-3} tba$^+$ (▽, ▼), and 1×10^{-3} mol dm^{-3} tpta$^+$ (△, ▲). The organic phase initially contains 1×10^{-3} mol dm^{-3} tddmba$^+$Cl$^-$ (○, ●).

As was written, the extraction constant of Eu(tta)$_3$, $K_{\mathrm{ex3,0}}$ in Eq. 4, and the stability constant of the aqueous tta$^-$ complex, β_1, are similar in 0.1 mol dm^{-3} sodium chloride and sodium nitrate solutions. This is probably due to the fact that the complex formation of europium(III) with Cl$^-$ or NO$_3{}^-$ in the aqueous phase is only slight.[7] The equilibrium constant for the association in the organic phase, K_{org}, is not affected by the nature of the aqueous phase, as can be seen from Table 2. This is reasonable, since the chemical properties of the organic phase should not be seriously affected by the background salt in the aqueous phase. However, as can be seen from Figs. 2a and 2b the enhancement of the extraction by the quarternary ammoniums is to some extent larger when the background salt in the aqueous phase is sodium chloride than when it is sodium nitrate. This is an apparent effect, as it can be seen from the values of $K_{\mathrm{ex4,1}}$ and K_{org} given in Table 2. The value of $K_{\mathrm{ex4,1}}$ is similar for a certain given quarternary ammonium within the experimental accuracy, whether the background salt in the aqueous phase is sodium chloride or sodium nitrate. The same can also be concluded regarding the value of K_{org}. The reason for this greater effect of the addition of base$^+$ in the sodium chloride solution system should be that the free concentration of base$^+$ in Eq. 18 at a certain given concentration of tta$^-$ is higher in sodium chloride solutions than in sodium nitrate solutions when the total concentration of base$^+$ is the same. This higher free concentration of base$^+$ in the sodium chloride solution should cause a greater enhancement of the extraction, D/D_0, at a certain concentration of tta$^-$, as can be seen from Eqs. 15 and 16.

It can be seen from Table 2 that the value of K_{org} is essentially not affected when the quarternary ammonium is different. In other words, even when the molar volume of the counter cation is greatly different, the association equilibrium of Eu(tta)$_3$ with tta$^-$base$^+$ in the organic phase is not different. This should be due to the fact that although the base$^+$ is indispensable for dissolving the tta$^-$ and Eu(tta)$_4{}^-$ complexes in the organic phase, the association of Eu(tta)$_3$ with the anion in the ion-pair of tta$^-$base$^+$ involves the coordination of the two oxygen atoms in the tta$^-$ ion. This should not be greatly affected by the nature of the counter cation which is combined with the tta$^-$ ion electrostatistically.

As can be seen from Figs. 2a and 2b, although the enhancement of extraction is markedly different between tppa$^+$ and tba$^+$, the difference is smaller than this between tba$^+$ and tpta$^+$ and between tpta$^+$ and tddmba$^+$. In other words, the effect of the molar volume is much smaller among the larger three quarternary ammoniums. It is assumed from the general tendency of the extraction of ion-pairs that the Cl$^-$, NO$_3{}^-$, tta$^-$, and Eu(tta)$_4{}^-$ anions should be extracted better when the molar volume of the counter cation is larger. This is clearly seen from the values of K_{exXB}, K_{exAB}, and $K_{\mathrm{ex4,1}}$ given in Tables 1 and 2. The value of each constant is larger by two, or two and a half orders larger from tppa$^+$ to tba$^+$, from tba$^+$ to tpta$^+$, and from tpta$^+$ to tddmba$^+$. Thus, each value of K_{exAB} and $K_{\mathrm{ex4,1}}$ with tddmba$^+$ is seven orders larger than that with tppa$^+$. However, the enhancement of the extraction of europium(III) by the addition of the quarternary ammonium at the same total concentration is not very much different, even though the molar volume is greatly different. This is also an apparent effect. Although the value of $K_{\mathrm{ex4,1}}$ is larger when the counter cation is larger, the free concentration of the base$^+$ in the aqueous phase at equilibrium is lower due to the much better extraction of the larger base$^+$ with tta$^-$ and with X$^-$. Thus, even when the total concentration of the quarternary ammonium is the same, the concentration at equilibrium should be lower in the order tea$^+$>tppa$^+$>tba$^+$>tpta$^+$>tddmba$^+$. Thus, although the Eu(tta)$_4{}^-$ species is extracted better by a larger counter cation than is a smaller one, the concentration of the larger cation in the aqueous phase at equilibrium is much lower than that of the smaller one when the total concentration is the same, as can be seen from

Eq. 18. This causes a relatively small difference in the enhancement of extraction at the same total concentration of base$^+$ at a certain concentration of tta$^-$, as can be seen from Figs. 2a and 2b. This can also be explained as follows. Since most of base$^+$ initially added is present in the organic phase as the tta$^-$base$^+$ ion-pairs, the difference in the concentration of this ion-pair is rather small, even though the concentration of base$^+$ in the aqueous phase at equilibrium is very much different when the size of the base$^+$ is greatly different.

The extraction equilibrium of the anionic metal complex is affected by several factors in the liquid–liquid system. As can be seen from the above, this causes several apparent effects concerning an enhancement of the extraction of the ternary complex. It is thus difficult to estimate the enhancement of solvent extraction of a metal complex by the addition of a certain bulky cation quantitatively when the values of the equilibrium constants are not known.

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