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Solvent Extraction of Scandium(III) with Hexafluoroacetylacetone into Chloroform in the Absence and Presence of Tetrabutylammonium Ions or Trioctylphosphine Oxide

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Synopsis. The anionic chelate of scandium(III) with hexafluoroacetylacetone (Hhfa) was extracted into chloroform in the presence of the tetrabutylammonium ion (tba$^+$), though such an anionic chelate was not extracted when the chelating extractant was 2-thenoyltrifluoroacetone (Htta). The extraction was also studied in the same systems in the presence of trioctylphosphine oxide (TOPO); the extraction of the anionic complex, $\mathrm{Sc(hfa)_4^-tba^+}$, was compared with that of the adducts with TOPO, $\mathrm{Sc(hfa)_3(TOPO)}_n$.

In the course of a series studies concerning the solvent extraction of trivalent rare earth elements by β-diketones in conjunction with quarternary ammonium ions,[1—3] it was found that the extraction of scandium(III) with 2-thenoyltrifluoroacetone (Htta, 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione) was not enhanced by the addition of tetrabutylammonium ions (tba$^+$); this was different from the extractions of lanthanum(III), europium(III), and lutetium(III), which were extracted as the "ternary complex", $\mathrm{M(tta)_4^-tba^+}$ (M is the metal ions), under such conditions.[1] It was also found that only the first adduct of this chelate was extracted with tributylphosphate (TBP), $\mathrm{Sc(tta)_3TBP}$.[4,5] From these facts it was assumed that this metal ion could not form these complexes of higher coordination number because of the smaller ionic radius than that of the trivalent lanthanoid ions.

In the present work, the solvent extraction of scandium(III) with hexafluoroacetylacetone (Hhfa, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione) into chloroform in the absence and presence of tba$^+$ or trioctylphosphine oxide (TOPO) was studied. The extractant, Hhfa, was employed because its metal chelates usually show the highest ability to form adducts in the organic phase among the complexes of the several metal ions with other β-diketones.[6,7] The results were compared with the extractions of europium(III) under similar conditions.

Experimental

All of the reagents and the experimental procedures were similar to those in previous studies.[1—3] The organic phase was chloroform initially containing 2×10^{-3} to 0.1 mol dm^{-3} hexafluoroacetylacetone, and the aqueous phase was a 0.1 mol dm^{-3} sodium nitrate solution initially containing 1×10^{-5} mol dm^{-3} scandium(III).

Results and Discussion

In the present paper, the metal ion, $\mathrm{Sc^{3+}}$ or $\mathrm{Eu^{3+}}$, is represented by $\mathrm{M^{3+}}$; the β-diketones and TOPO are denoted by HA and L, respectively. All of the chemical species in the organic phase are denoted by the subscript "org", and those in the aqueous phase are shown without a subscript. The volumes of the two liquid phases are assumed to be the same. The data were treated in the same manner as described previously.[1—3]

The concentration of the extractant anion ($\mathrm{A^-}$) can be written as

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

where $K_\mathrm{d}=[\mathrm{HA}]_\mathrm{org}[\mathrm{HA}]^{-1}=10^{-1.75}$ (Hhfa) or $10^{1.85}$ (Htta) and $K_\mathrm{a}=[\mathrm{H^+}][\mathrm{A^-}][\mathrm{HA}]^{-1}=10^{-4.46}$ (Hhfa) or $10^{-6.33}$ (Htta).[8]

The above equations could approximately be used even when the metal ions, tba$^+$, and TOPO were present, since $[\mathrm{HA}]_{\mathrm{org,initial}}$ is always much higher than $[\mathrm{M(III)}]_{\mathrm{initial}}$, $[\mathrm{tba^+}]_{\mathrm{initial}}$, and $[\mathrm{L}]_{\mathrm{org,initial}}$.

For the data treatment, the following equilibrium constants are defined:

$$K_{\mathrm{ex3,0}} = [\mathrm{MA_3}]_\mathrm{org}[\mathrm{M^{3+}}]^{-1}[\mathrm{A^-}]^{-3}, \qquad (2)$$

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

$$K_{\mathrm{org}} = [\mathrm{MA_4^-tba^+}]_\mathrm{org}[\mathrm{MA_3}]_\mathrm{org}^{-1}[\mathrm{A^-tba^+}]_\mathrm{org}^{-1}, \qquad (4)$$

$$K_{\mathrm{exAB}} = [\mathrm{A^-tba^+}]_\mathrm{org}[\mathrm{A^-}]^{-1}[\mathrm{tba^+}]^{-1}, \qquad (5)$$

$$\beta_n = [\mathrm{MA}_n^{3-n}][\mathrm{M^{3+}}]^{-1}[\mathrm{A^-}]^{-n}, \qquad (6)$$

and

$$\beta_{(\mathrm{org})n} = [\mathrm{MA_3L}_n]_\mathrm{org}[\mathrm{MA_3}]_\mathrm{org}^{-1}[\mathrm{L}]_\mathrm{org}^{-n}. \qquad (7)$$

The values of $[\mathrm{tba^+}]$ and $[\mathrm{L}]_\mathrm{org}$ were calculated in the same manner as in Refs. 3 and 9. The equations employed for the calculations are as follows:

$$[\mathrm{tba^+}] = [\mathrm{tba^+}]_{\mathrm{initial}}/(1+K_{\mathrm{exAB}}[\mathrm{A^-}]+K_{\mathrm{exXB}}[\mathrm{X^-}]), \qquad (8)$$

where $\mathrm{X^-}$ is the anion of the background salt in the aqueous phase ($\mathrm{NO_3^-}$) and $K_{\mathrm{exXB}}=[\mathrm{X^-tba^+}]_\mathrm{org}[\mathrm{X^-}]^{-1}[\mathrm{tba^+}]^{-1}=10^{1.3}$,[2]

$$[\mathrm{L}]_\mathrm{org} = \{-1-K_{\mathrm{LHA(org)1}}[\mathrm{HA}]_\mathrm{org} + \sqrt{(1+K_{\mathrm{LHA(org)1}}[\mathrm{HA}]_\mathrm{org})^2+8K_{\mathrm{LHA(org)2}}[\mathrm{HA}]_\mathrm{org}[\mathrm{L}]_{\mathrm{org,initial}}}\} /4K_{\mathrm{LHA(org)2}}[\mathrm{HA}]_\mathrm{org}, \qquad (9)$$

where $K_{\mathrm{LHA(org)}n}=[\mathrm{HAL}_n]_{\mathrm{org}}[\mathrm{HA}]_{\mathrm{org}}^{-1}[\mathrm{L}]_{\mathrm{org}}^{-n}$. The value of $K_{\mathrm{LHA(org)1}}$ and $K_{\mathrm{LHA(org)2}}$ of Hhfa are $10^{2.09}$ and $10^{2.80}$,[9] respectively; however, the association of Htta with TOPO in chloroform is negligible.[9]

The distribution ratio of metal ions, $[\mathrm{M(III)}]_{\mathrm{org,total}}/[\mathrm{M(III)}]_{\mathrm{aq,total}}$, in the absence ($D_0$) and presence of tba^+ (D_t) or TOPO (D_l) can be written as

$$D_0 = K_{\mathrm{ex3,0}}[\mathrm{A}^-]^3/(1+\beta_1[\mathrm{A}^-]+\beta_2[\mathrm{A}^-]^2+\cdots), \qquad (10)$$

$$D_\mathrm{t} = K_{\mathrm{ex3,0}}[\mathrm{A}^-]^3(1+K_{\mathrm{org}}K_{\mathrm{exAB}}[\mathrm{A}^-][\mathrm{tba}^+]) \\ /(1+\beta_1[\mathrm{A}^-]+\beta_2[\mathrm{A}^-]^2+\cdots), \qquad (11)$$

and

$$D_\mathrm{l} = K_{\mathrm{ex3,0}}[\mathrm{A}^-]^3(1+\Sigma\beta_{(\mathrm{org})n}[\mathrm{L}]_{\mathrm{org}}^n) \\ /(1+\beta_1[\mathrm{A}^-]+\beta_2[\mathrm{A}^-]^2+\cdots). \qquad (12)$$

When the concentration of A^- in the aqueous phase is determined in an experiment in the presence of tba^+ or TOPO, the value of D_0 can be calculated by using Eq. 10 while introducing the experimentally obtained equilibrium constants. By using the experimentally obtained D_t or D_l and the thus-calculated D_0, the enhancement of the extraction can be treated by the following equations introduced from Eq. 10 to Eq. 12:

$$D_\mathrm{t}/D_0 = 1+K_{\mathrm{org}}K_{\mathrm{exAB}}[\mathrm{A}^-][\mathrm{tba}^+] \qquad (13)$$

and

$$D_\mathrm{l}/D_0 = 1+\beta_{(\mathrm{org})1}[\mathrm{L}]_{\mathrm{org}}+\beta_{(\mathrm{org})2}[\mathrm{L}]_{\mathrm{org}}^2+\cdots. \qquad (14)$$

Figure 1 gives the extraction curves of scandium(III) and europium(III) with Hhfa in the absence and presence of tba^+ or TOPO. Figure 2 gives the enhancement of the extraction of these metal ions with Hhfa or Htta as a function of the concentration of $\mathrm{TOPO}_{(\mathrm{org})}$. Separate experiments were also carried out with the extraction of scandium(III) with Htta into chloroform, instead of carbon tetrachloride in Ref. 1 in the absence and presence of tba^+. The results showed that the extraction into chloroform was not enhanced by the addition of tba^+, like as into carbon tetrachloride. The experimental data were treated by a successive-approximation method using a least-squares computer program on the basis of Eq. 10 to Eq. 14. The values of K_{exAB} used in these calculations were taken from Refs. 2 and 3. The values of the stability and extraction constants used in Eq. 2 to Eq. 7, thus obtained, are listed in Table 1. The calculated plots given by the solid lines fit well with the experimental data. Thus, the constants given in Table 1 should be reasonable.

As can be seen from the above results, $\mathrm{Sc(hfa)_3}$ forms higher complexes more readily than does $\mathrm{Sc(tta)_3}$ in the organic phase: although scandium(III) is extracted as $\mathrm{Sc(hfa)_4^-tba^+}$, it is not extracted as $\mathrm{Sc(tta)_4^-tba^+}$. The stability of $\mathrm{Sc(hfa)_3TOPO}$ and $\mathrm{Sc(hfa)_3(TOPO)_2}$ is higher than that of $\mathrm{Sc(tta)_3TOPO}$ and $\mathrm{Sc(tta)_3(TOPO)_2}$. The extraction of the second adduct of the scandium(III) tta^- chelate occurs with TOPO, but it is not found when the neutral ligand is TBP, which is a weaker electron donor than TOPO.[10] Only $\mathrm{Sc(tta)_3TBP}$ was found to be extracted in a previous study.[4,5] Furthermore, $\mathrm{Eu(hfa)_3}$ formed a third adduct with TOPO, $\mathrm{Eu(hfa)_3(TOPO)_3}$, though the highest adduct of $\mathrm{Eu(tta)_3}$ was the second one, $\mathrm{Eu(tta)_3(TOPO)_2}$.[10] Katsuta et al. reported[11] that the solvent extraction of scandium(III) with acetylacetone (2,4-pentanedione, Hacac) into heptane was enhanced by the addition of 3,5-dichlorophenol (DCP)[12,13] and the extracted species were the association complex $\mathrm{Sc(acac)_3(DCP)}_n$, where n was one to three. They were not similar type adducts as those with electron donors, such as $\mathrm{Sc(tta)_3TBP}$.

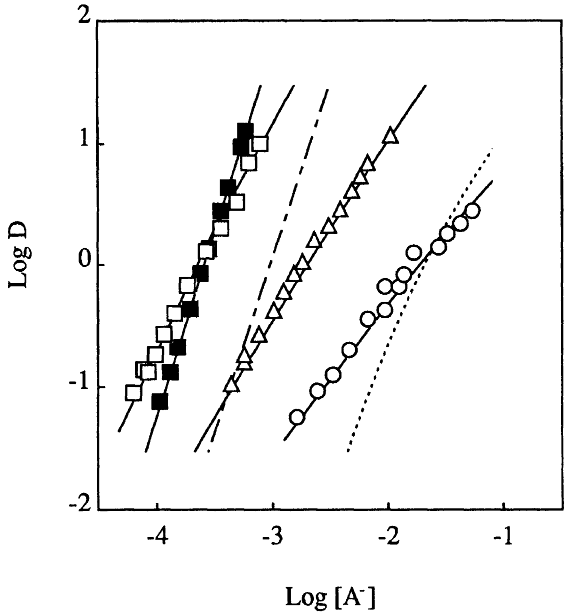

Fig. 1. Distribution ratio of scandium(III) and europium(III) as a function of the concentration of hexafluoroacetylacetonate anion. Scandium(III): in the absence (○) and presence of 1×10^{-3} mol dm^{-3} tba^+ (△) or 1×10^{-4} mol dm^{-3} TOPO (□) at initial. Europium(III): in the absence (dotted line taken from Ref. 3) and presence of 1×10^{-3} mol dm^{-3} tba^+ (broken line taken from Ref. 3) or 1×10^{-3} mol dm^{-3} TOPO (■) at initial. The solid lines are calculated by Eq. 10 to Eq. 12 using the values in Table 1 and K_{exAB} taken from Refs. 2 and 3.

In a previous paper,[3] it was pointed out that (i) the extractability of the ion-pair, $\mathrm{hfa^-tba^+}$, is nearly the same as the $\mathrm{tta^-tba^+}$; the K_{exAB} is $10^{4.0}$ and $10^{4.1}$, respectively, and (ii) the association constant of the $\mathrm{Eu(hfa)_3}$ with $\mathrm{hfa^-tba^+}$ is also nearly the same as that of the $\mathrm{Eu(tta)_3}$ with $\mathrm{tta^-tba^+}$; the K_{org} is $10^{6.8}$ and $10^{6.9}$, respectively. When the association constant of $\mathrm{Sc(tta)_3}$ with $\mathrm{tta^-tba^+}$ in the organic phase would be similar to that of $\mathrm{Sc(hfa)_3}$ with $\mathrm{hfa^-tba^+}$, the determination of the enhancement of Htta extraction sys-

Table 1. Summary of Equilibrium Constants
Org. phase: chloroform containing Htta or Hhfa. Aq phase: 0.1 mol dm^{-3} sodium nitrate solution.

		$\log K_{ex3,0}$	$\log \beta_1$	$\log \beta_2$	$\log K_{ex4,1}$	$\log K_{org}$	$\log \beta_{(org)1}$	$\log \beta_{(org)2}$	$\log \beta_{(org)3}$
Sc(III)	Htta	23.0	—	—	—	—	4.6	7.3	—
	Hhfa	9.4	4.7	7.7	17.7	4.3	6.8	10.5	—
Eu(III)	Htta	16.1$^{a)}$	4.5$^{a)}$	—	27.1$^{a)}$	6.9$^{a)}$	5.4$^{c)}$	7.6$^{c)}$	—
	Hhfa	5.4$^{b)}$	1.1$^{b)}$	3.4$^{b)}$	16.2$^{b)}$	6.8$^{b)}$	—$^{d)}$	10.8	14.1

a) Taken from Ref. 2. b) Taken from Ref. 3. c) Taken from Ref. 10. d) Error is too large to confirm this species. e) $\log K_{exAB}$ in Eq. 5 of Htta and Hhfa employed for the calculation are 4.1 and 4.0, respectively. These are taken from Refs. 2 and 3.

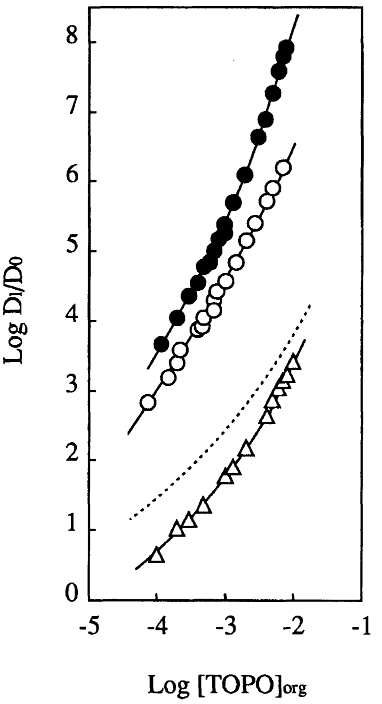

Fig. 2. Increase in the distribution ratio. The organic phase initially contained 2×10^{-3} to 0.1 mol dm^{-3} of Hhfa or Htta. The values of D_0 are calculated on the basis of Eq. 10 by using the value of [A$^-$] experimentally obtained. The symbols are as follows. (○): scandium(III) and (●): europium(III) with Hhfa and TOPO$_{(org)}$. (△): scandium(III) with Htta and TOPO$_{(org)}$. The solid lines are calculated by Eq. 14 using the values given in Table 1. The dotted line gives the data of europium(III) with Htta and TOPO$_{(org)}$ taken from Ref. 10.

tem should be extremely difficult. This is because although the enhancement of extraction cannot be estimated from the value of [tba$^+$], it can be possibly estimated from the value of [A$^-$] [tba$^+$], as can be seen from Eq. 13. The value of $K_{ex3,0}$ of scandium(III) with tta$^-$ into chloroform is $10^{23.0}$, and that with hfa$^-$ is $10^{9.4}$. In order to make the D_0 of scandium(III) extraction with Htta into chloroform in the experimentally measurable range, $10^{-2} < D_0 < 10^2$, the value of [A$^-$] should be in the range $10^{-8.3}$ mol dm^{-3}<[A$^-$]<$10^{-7.0}$ mol dm^{-3}. When 1×10^{-3} mol dm^{-3} of tba$^+$ (at initial) is added into the aqueous phase, the value of [tta$^-$] [tba$^+$] should be in the range $10^{-10.5}$ to $10^{-11.8}$ and the enhancement, $\log D_t/D_0$, is calculated by Eq. 13 to be 2.9×10^{-3} to 1.3×10^{-4} if the K_{org} in the Htta extraction system would be similar to that in the extraction systems with Hhfa, $10^{4.3}$. These enhancements should be too small to be recognized experimentally. On the other hand, when the [tta$^-$] would be similar to the [hfa$^-$] in Fig. 1, that is, 10^{-4} to 10^{-2} mol dm^{-3}, (this is only a statistical assumption because then the pH should be 5.2 to 7.2 and the effect of hydrolysis of scandium(III) should not be negligible), the value of D_0 of the extraction with Htta should be so high as to be calculated in the range $10^{11.0}$ to $10^{17.0}$. Thus, even when such an enhancement would occur, the determination should be impossible by experiments.

The present work started from the estimation that scandium(III) chelates in the ScA_3 form cannot add one bidentate ligand or two unidentate ligands in the organic phase. However, it has been found that both the anionic complex and the second adduct with TOPO were extracted when the β-diketone was Hhfa. The reason why the Hhfa extraction is enhanced by the anionic complex but the Htta extraction is not enhanced by the same type complex, cannot be explained only on the basis of the solvent-extraction data. Further studies are necessary regarding this problem.

References

1) J. Noro and T. Sekine, *Bull. Chem. Soc. Jpn.*, **65**, 2729 (1992).

2) J. Noro and T. Sekine, *Bull. Chem. Soc. Jpn.*, **66**, 450 (1993).

3) J. Noro and T. Sekine, *Bull. Chem. Soc. Jpn.*, **66**, 1647 (1993).

4) T. Sekine and D. Dyrssen, *J. Inorg. Nucl. Chem.*, **29**, 1481 (1967).

5) K. Akiba, T. Ishikawa, and N. Suzuki, *J. Inorg. Nucl. Chem.*, **33**, 4161 (1971).

6) T. Sekine and N. Ihara, *Bull. Chem. Soc. Jpn.*, **44**, 2942 (1971).

7) S. Nakamura and N. Suzuki, *Polyhedron*, **5**, 1850 (1986).

8) T. Sekine, Y. Hasegawa, and N. Ihara, *J. Inorg. Nucl. Chem.*, **35**, 3968 (1973).

9) T. Sekine, T. Saito, and H. Iga, *Bull. Chem. Soc. Jpn.*, **56**, 700 (1983).

10) T. Sekine and D. Dyrssen, *J. Inorg. Nucl. Chem.*, **29**, 1475 (1967).

11) S. Katsuta, H. Imura, and N. Suzuki, *Anal. Sci.*, **7**, 661 (1991).

12) S. Katsuta, H. Imura, and N. Suzuki, *Bull. Chem. Soc. Jpn.*, **64**, 2470 (1991).

13) S. Katsuta, H. Imura, and N. Suzuki, *J. Radioanal. Nucl. Chem.*, **157**, 255, (1992).