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Solvent Extraction of Lanthanum(III), Europium(III), and Lutetium(III) with 5,7-Dichloro-8-quinolinol into Chloroform in the Absence and Presence of Tetrabutylammonium Ions or Trioctylphosphine Oxide

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(Received March 15, 1993)

The solvent extractions of lanthanum(III), europium(III), and lutetium(III) (M^{3+}) in 0.1 mol dm^{-3} sodium nitrate solutions with 5,7-dichloro-8-quinolinol(HA) into chloroform were studied in both the absence and presence of tetrabutylammonium ions (tba$^+$) or trioctylphosphine oxide (TOPO). In the absence of tba$^+$ or TOPO, the extracted species were the MA_3 and MA_3HA (self-adduct), though $MA_4^-tba^+$ was found when tba$^+$ was added; MA_3TOPO and $MA_3(TOPO)_2$ were found when TOPO was added in addition to the above mentioned two species. The anionic complex or TOPO adducts greatly enhanced the extraction. The data were statistically analyzed and the equilibrium constants for the extraction of these species, as well as the constants for the association of the HA, the A^-tba^+, or the TOPO on the MA_3 in the organic phase, were determined. The extraction of the MA_3 is better in the order $LaA_3 < EuA_3 < LuA_3$. Although the values of the association constant of the HA or the TOPO on the MA_3 are rather similar for the three metal chelates, the constants for A^-tba^+ are larger in the same order as mentioned above. Thus, the separation of these three metal ions by solvent extraction with this chelating extractant is not much affected by the addition of TOPO, but is greatly improved by the addition of tba$^+$.

In previous papers[1—5] it was reported that the solvent extraction of europium(III) with β-diketones containing the CF_3-group was very much enhanced by the addition of bulky cations, such as tetrabutylammonium ions (tba$^+$). These enhancements could in all cases be explained in terms of the extraction of the "ternary complex", $EuE_4^-tba^+$ (where E^- is the β-diketonate anion). The extraction equilibria were treated as the overall equilibria of (i) the extraction of the noncharged chelate, EuE_3, and the ion-pair of the reagent, E^-tba^+, and of (ii) the association of EuE_3 with E^-tba^+ in the organic phase. It was pointed out in these papers that the enhancement of metal chelate extraction due to the formation of a ternary complex was to some extent similar to the enhancement of the metal chelate extraction by the addition of neutral ligands, such as tributylphosphate (TBP) or trioctylphosphine oxide (TOPO), due to adduct formation in the organic phase (synergistic extraction). An additional study was thus made with the extraction of a ternary complex of europium(III), and with the synergistic extraction of this metal ion with TOPO when the extractant was 1-naphthoic acid.[6] This reagent was chosen in the previous study because a synergistic enhancement of the extraction of europium(III) with it was found by the addition of TBP, though it was much smaller than that observed when the extractant was 2-thenoyltrifluoroacetone (Htta, 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione).[7] In the present study, solvent extraction with 5,7-dichloro-8-quinolinol (dichlorooxine) in chloroform was observed in the both absence and presence of tba$^+$ or TOPO. This chelating extractant was chosen because its extraction of europium(III) also showed a synergistic effect with TBP, like that of 1-naphthoic acid.[7] The metal ions studied were lanthanum(III), europium(III), and lutetium(III), as in the previous studies.[2,8] The results were compared with those obtained when the extractant was Htta.

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 given without any subscript. The volumes of the two liquid phases were assumed to be the same. Since most of the statistical treatments were similar to those described in previous papers,[1—6] only the main equations, as well as those which were not previously given, are presented in this paper.

Under the conditions employed, since the H_2A^+ species is negligible, the concentration of the extractant anion(A^-) can be written as

$$[A^-] = [HA]_{org,initial}/\{1 + (K_d + 1)[H^+]K_a^{-1}\}, \qquad (1)$$

where $K_d = [HA]_{org}[HA]^{-1} = 10^{3.80}$[9] and $K_a = [H^+][A^-][HA]^{-1} = 10^{7.47}$.[9]

In the solvent-extraction systems of the metal ions (M^{3+}) with 5,7-dichloro-8-quinolinol, the extraction of a "self-adduct" (written as MA_3HA) occurs. However, the formation of an aqueous complex, such as MA^{2+}, was not experimentally found. The distribution ratio (D_0) of the metal ion can therefore be written as

$$\begin{aligned} D_0 &= ([MA_3]_{org} + [MA_3HA]_{org})[M^{3+}]^{-1} \\ &= K_{ex3,0}[A^-]^3(1 + \beta_{(org)self}[HA]_{org}), \qquad (2) \end{aligned}$$

where $K_{ex3,0} = [MA_3]_{org}[M^{3+}]^{-1}[A^-]^{-3}$ and $\beta_{(org)self} = [MA_3HA]_{org}[MA_3]_{org}^{-1}[HA]_{org}^{-1}$.

In the presence of tba$^+$, the distribution ratio can be written as

$$\begin{aligned} D &= ([\mathrm{MA_3}]_\mathrm{org} + [\mathrm{MA_3HA}]_\mathrm{org} + [\mathrm{MA_4^-tba^+}]_\mathrm{org})[\mathrm{M^{3+}}]^{-1} \\ &= K_\mathrm{ex3,0}[\mathrm{A^-}]^3(1 + \beta_\mathrm{(org)self}[\mathrm{HA}]_\mathrm{org}) \\ &\quad + K_\mathrm{ex4,1}[\mathrm{A^-}]^4[\mathrm{tba^+}], \end{aligned} \tag{3}$$

where $K_\mathrm{ex4,1} = [\mathrm{MA_4^-tba^+}]_\mathrm{org}[\mathrm{M^{3+}}]^{-1}[\mathrm{A^-}]^{-4}[\mathrm{tba^+}]^{-1}$. The extraction of the ternary complex can be treated by assuming the following equilibrium:

$$\begin{aligned} &\mathrm{MA_{3(org)}} + \mathrm{A^-tba^+_{(org)}} \rightleftharpoons \mathrm{MA_4^-tba^+_{(org)}}; \\ &K_\mathrm{org} = [\mathrm{MA_4^-tba^+}]_\mathrm{org}[\mathrm{MA_3}]_\mathrm{org}^{-1}[\mathrm{A^-tba^+}]_\mathrm{org}^{-1}. \end{aligned} \tag{4}$$

The distribution ratio can thus be written as

$$\begin{aligned} D = K_\mathrm{ex3,0}[\mathrm{A^-}]^3(1 &+ \beta_\mathrm{(org)self}[\mathrm{HA}]_\mathrm{org} \\ &+ K_\mathrm{org}K_\mathrm{exAB}[\mathrm{A^-}][\mathrm{tba^+}]), \end{aligned} \tag{5}$$

where $K_\mathrm{exAB} = [\mathrm{A^-tba^+}]_\mathrm{org}[\mathrm{A^-}]^{-1}[\mathrm{tba^+}]^{-1}$. In the absence of metal ions, the distribution ratio of tba$^+$, D_tba, can be written as

$$\begin{aligned} D_\mathrm{tba} &= [\mathrm{tba^+}]_\mathrm{org,total}/[\mathrm{tba^+}] \\ &= ([\mathrm{A^-tba^+}]_\mathrm{org} + [\mathrm{X^-tba^+}]_\mathrm{org})/[\mathrm{tba^+}] \\ &= K_\mathrm{exAB}[\mathrm{A^-}] + K_\mathrm{exXB}[\mathrm{X^-}], \end{aligned} \tag{6}$$

where X$^-$ is the anion of the background salt in the aqueous phase, and $K_\mathrm{exXB} = [\mathrm{X^-tba^+}]_\mathrm{org}[\mathrm{X^-}]^{-1}[\mathrm{tba^+}]^{-1}$. When the concentration of A$^-$ in the aqueous phase is identical, the following equations can be introduced from Eqs. 2, 3, and 5:

$$\begin{aligned} D/D_0 &= 1 + K_\mathrm{ex4,1}K_\mathrm{ex3,0}^{-1}[\mathrm{A^-}][\mathrm{tba^+}] \\ &\quad /(1 + \beta_\mathrm{(org)self}[\mathrm{HA}]_\mathrm{org}) \end{aligned} \tag{7}$$

$$\begin{aligned} &= 1 + K_\mathrm{org}K_\mathrm{exAB}[\mathrm{A^-}][\mathrm{tba^+}] \\ &\quad /(1 + \beta_\mathrm{(org)self}[\mathrm{HA}]_\mathrm{org}). \end{aligned} \tag{8}$$

The free concentration of tba$^+$ in the aqueous phase can be written as

$$\begin{aligned} [\mathrm{tba^+}]_\mathrm{initial} &= [\mathrm{tba^+}] + [\mathrm{MA_4^-tba^+}]_\mathrm{org} \\ &\quad + [\mathrm{A^-tba^+}]_\mathrm{org} + [\mathrm{X^-tba^+}]_\mathrm{org}, \end{aligned} \tag{9}$$

$$\begin{aligned} [\mathrm{tba^+}] &= ([\mathrm{tba^+}]_\mathrm{initial} - [\mathrm{MA_4^-tba^+}]_\mathrm{org}) \\ &\quad /(1 + K_\mathrm{exAB}[A^-] + K_\mathrm{exXB}[\mathrm{X^-}]). \end{aligned} \tag{10}$$

In the presence of TOPO (denoted by L), the distribution ratio can be written as

$$\begin{aligned} D &= ([\mathrm{MA_3}]_\mathrm{org} + [\mathrm{MA_3HA}]_\mathrm{org} + [\mathrm{MA_3L}]_\mathrm{org} \\ &\quad + [\mathrm{MA_3L_2}]_\mathrm{org} + \cdots)[\mathrm{M^{3+}}]^{-1} \\ &= K_\mathrm{ex3,0}[\mathrm{A^-}]^3(1 + \beta_\mathrm{(org)self}[\mathrm{HA}]_\mathrm{org} \\ &\quad + \beta_\mathrm{(org)1}[\mathrm{L}]_\mathrm{org} + \beta_\mathrm{(org)2}[\mathrm{L}]_\mathrm{org}^2 + \cdots), \end{aligned} \tag{11}$$

where $\beta_{(\mathrm{org})n} = [\mathrm{MA_3L}_n]_\mathrm{org}[\mathrm{MA_3}]_\mathrm{org}^{-1}[\mathrm{L}]_\mathrm{org}^{-n}$. When the concentration of A$^-$ in the aqueous phase is identical, the following equations can be introduced from Eqs. 2 and 11:

$$\begin{aligned} D/D_0 = 1 &+ (\beta_\mathrm{(org)1}[\mathrm{L}]_\mathrm{org} + \beta_\mathrm{(org)2}[\mathrm{L}]_\mathrm{org}^2 + \cdots) \\ &/(1 + \beta_\mathrm{(org)self}[\mathrm{HA}]_\mathrm{org}). \end{aligned} \tag{12}$$

Since the association of 5,7-dichloro-8-quinolinol and TOPO in the organic phase was observed to be negligible under the conditions of the present study, it is not mentioned here.

Experimental

All of the reagents and the experimental procedures were similar to those discussed in the previous papers,[1—6] except that 5,7-dichloro-8-quinolinol, which was obtained from Tokyo Kasei Co., was used as the cheating extractant.

When the distribution ratio was measured as a function of the A$^-$ concentration, the pH of the aqueous phase was adjusted at various values, though the initial 5,7-dichloro-8-quinolinol concentration in the organic phase was always kept at 4×10^{-2} mol dm^{-3}. These experiments were carried out in the absence and presence of 1×10^{-4} mol dm^{-3} to 1×10^{-2} mol dm^{-3} tba$^+$ or 1×10^{-3} mol dm^{-3} to 3×10^{-2} mol dm^{-3} TOPO. When the effect of the concentration of 5,7-dichloro-8-quinolinol in the organic phase on the distribution ratio was determined, experiments were carried out in which the initial concentration of this chelating extractant in the organic phase was 8×10^{-3} to 4×10^{-2} mol dm^{-3}.

The distribution of 5,7-dichloro-8-quinolinol between chloroform containing TOPO and a 0.1 mol dm^{-3} sodium nitrate solution was determined in a similar manner as that described in Ref. 6.

Results

The extraction of tba$^+$ with 5,7-dichloro-8-quinolinolate ion (A$^-$) from aqueous 0.1 mol dm^{-3} sodium chloride solutions into chloroform is given in Fig. 1. This aqueous solution was employed for these experiments instead of a sodium nitrate solution in order to make the determination of the constant more accurate. This is because (as previously discussed[3]) although more than half of the tba$^+$ in the aqueous phase is extracted from 0.1 mol dm^{-3} sodium nitrate solutions as the $\mathrm{NO_3^-tba^+}$ into chloroform, since the extraction from 0.1 mol dm^{-3} sodium chloride solutions is much less, the effect of background salt on the accuracy of this extraction constant should be much smaller. The difference in K_exAB when the aqueous phase was 0.1 mol dm^{-3} sodium nitrate and sodium chloride was negligible with Htta.[3,4] The data given in Fig. 1 were treated on the basis of Eq. 6. The value of extraction constant, K_exAB, was determined to be $10^{3.06}$.

Figure 2 gives the distribution ratio of the metal ions as a function of the concentration of A$^-$ in the aqueous phase by keeping $[\mathrm{HA}]_\mathrm{org,initial}$ at 4×10^{-2} mol dm^{-3}. It also gives the distribution ratio when 1×10^{-2} mol dm^{-3} tba$^+$ (at initial) was added into the aqueous phase of these systems. Figure 3 gives the distribution ratio when 1×10^{-2} mol dm^{-3} TOPO (at initial) was added

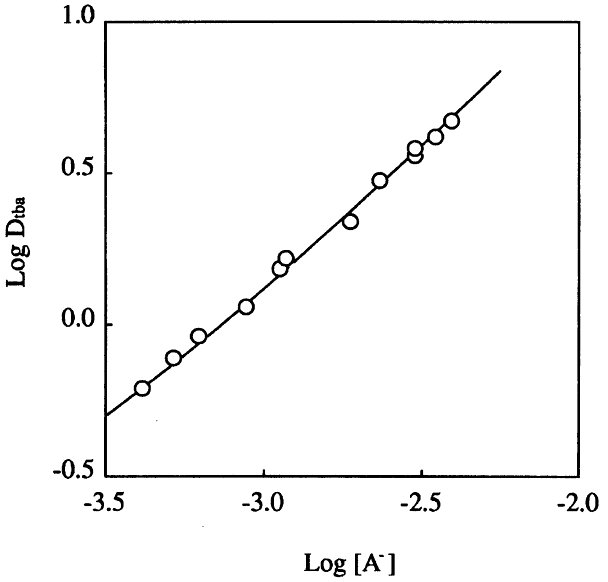

Fig. 1. Distribution ratio of tetrabutylammonium ions as a function of the 5,7-dichloro-8-quinolinolate anion concentration. Org. phase: chloroform initially containing 4×10^{-2} mol dm^{-3} 5,7-dichloro-8-quinolinol Aq phase: 0.1 mol dm^{-3} sodium chloride containing 1×10^{-3} mol dm^{-3} tetrabutylammonium ions. The solid line is calculated on the basis of Eq. 6 using the values $K_{\mathrm{exAB}}=10^{3.06}$ and $K_{\mathrm{exXB}}=10^{0.1}$.

into the organic phase, as well as plots of the distribution ratio in the absence of TOPO (taken from Fig. 2). The latter are given by the dotted line. The plot of lutetium(III) in the absence of TOPO is quite similar to that of europium(III) in the presence of TOPO at this concentration. As can be seen from Figs. 2 and 3, the extraction was enhanced by the addition of tba$^+$ or TOPO. The slope of the plot became larger when tba$^+$ was added, but did not change when TOPO was added. The enhancement of extraction in Fig. 2 can be explained by the extraction of ternary complexes, $\mathrm{MA_4^-tba^+}$ and that in Fig. 3 by the formation of adducts with TOPO, $\mathrm{MA_3(TOPO)}_n$, such as the extractions with β-diketones and 1-naphthoic acid.[1—6)].

In these solvent-extraction systems, the extraction of a self-adduct occurs. In order to calculated the formation constant of the self-adduct, $\beta_{\mathrm{(org)self}}$, the distribution ratio was determined as a function of $[\mathrm{HA}]_{\mathrm{org}}$. For this calculation, the following equation can be introduced from Eq. 2.

$$D_0[\mathrm{A}^-]^{-3} = K_{\mathrm{ex3,0}}(1+\beta_{\mathrm{(org)self}}[\mathrm{HA}]_{\mathrm{org}}). \qquad (13)$$

Figure 4 gives the values of $D_0[\mathrm{A}^-]^{-3}$ when $[\mathrm{HA}]_{\mathrm{org,initial}}$ was 8×10^{-3} to 4×10^{-2} mol dm^{-3}. Under conditions in which $[\mathrm{HA}]_{\mathrm{org,initial}}$ was always much higher than $[\mathrm{A}^-]$, $[\mathrm{HA}]$, and $[\mathrm{M(III)}]_{\mathrm{initial}}$, the value of $[\mathrm{HA}]_{\mathrm{org}}$ was estimated to be similar to that of $[\mathrm{HA}]_{\mathrm{org,initial}}$.

The data given in Figs. 2 and 4 were calculated on the basis of Eqs. 2 and 13 by a successive-approximation method using a least-squares computer program. The obtained extraction constant, $K_{\mathrm{ex3,0}}$, and formation constants of the self-adduct, $\beta_{\mathrm{(org)self}}$, are listed in Table 1. The solid lines in Figs. 2 and 4, and the dotted lines in Fig. 3 were calculated on the basis of Eq. 2 or Eq. 13 by using the values given in Table 1.

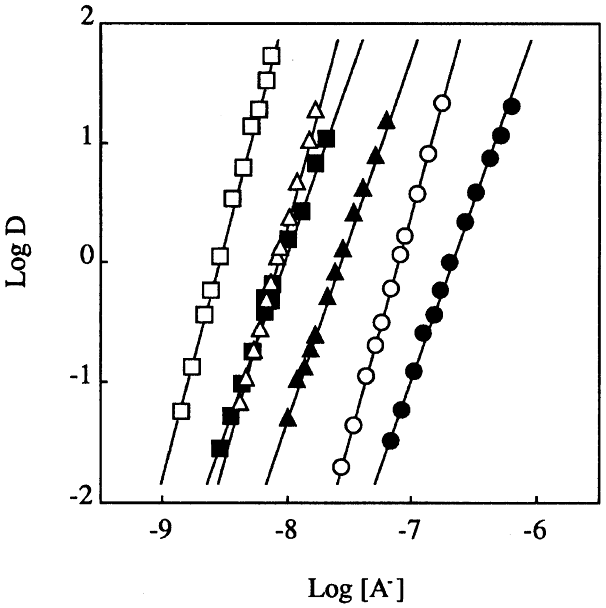

Fig. 2. Distribution ratio of the metal ions as a function of the 5,7-dichloro-8-quinolinolate anion concentration in the absence and presence of tetrabutylammonium ions. Org. phase: chloroform initially containing 4×10^{-2} mol dm^{-3} 5,7-dichloro-8-quinolinol. Aq phase: 0.1 mol dm^{-3} sodium nitrate containing no tba$^+$ (closed symbols) and initially containing 1×10^{-2} mol dm^{-3} tba$^+$ (open symbols). The metal ions are La(III) (●,○), Eu(III) (▲, △), and Lu(III) (■, □). The solid lines are calculated by Eqs. 2 and 5 using the values in Table 1.

Figure 5 gives the enhancement of the extraction due to the addition of tba$^+$ as a function of $[\mathrm{A}^-][\mathrm{tba}^+]$, by keeping $[\mathrm{HA}]_{\mathrm{org,initial}}$ at 4×10^{-2} mol dm^{-3}. As can be seen from Fig. 5, the limiting slope of the plot is +1. This agrees with the number of associating ion-pairs of the reagents, $\mathrm{A^-tba^+}$, with the neutral chelate, $\mathrm{MA_3}$. This can be assumed to be unity according to Eqs. 7 and 8. The values of $K_{\mathrm{ex4,1}}K_{\mathrm{ex3,0}}^{-1}/(1+\beta_{\mathrm{(org)self}}[\mathrm{HA}]_{\mathrm{org}})$ in Eq. 7, and $K_{\mathrm{org}}K_{\mathrm{exAB}}/(1+\beta_{\mathrm{(org)self}}[\mathrm{HA}]_{\mathrm{org}})$ in Eq. 8, where $[\mathrm{HA}]_{\mathrm{org}}$ was kept constant, were determined by a least-squares computer program. By using the values of K_{exAB}, $K_{\mathrm{ex3,0}}$, and $\beta_{\mathrm{(org)self}}$, in Table 1, and by assuming that $[\mathrm{HA}]_{\mathrm{org}}$ was the same as $[\mathrm{HA}]_{\mathrm{org,initial}}$, the values of $K_{\mathrm{ex4,1}}$ and K_{org} were calculated as are listed in Table 1. The solid lines in Figs. 2 and 5 were calculated on the basis of Eqs. 5 and 8 by using the values in Table 1.

The distribution of 5,7-dichloro-8-quinolinol between a 0.1 mol dm^{-3} sodium nitrate solution and chloroform

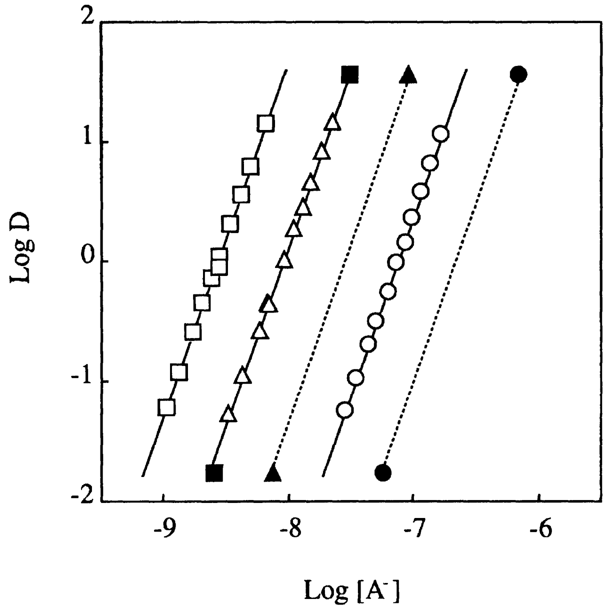

Fig. 3. Distribution ratio of the metal ions as a function of the 5,7-dichloro-8-quinolinolate anion concentration. Org. phase: chloroform initially containing 4×10^{-2} mol dm^{-3} of 5,7-dichloro-8-quinolinol and 1×10^{-2} mol dm^{-3} trioctylphosphine oxide. Aq phase: 0.1 mol dm^{-3} sodium nitrate. The metal ions are La(III) (○), Eu(III) (△), and Lu(III) (□). The solid lines are calculated by Eq. 11 using the values given in Table 1. The dotted lines are the plots when TOPO is absent taken form Fig. 2: The metal ions are indicated by the closed symbols. The plot of Lu(III) in the absence of TOPO overlaps with Eu(III) in the presence of 1×10^{-2} mol dm^{-3} TOPO.

containing TOPO was determined as a function of the concentration of TOPO. However, when the TOPO concentration was lower than 0.1 mol dm^{-3}, since the distribution of this chelating reagent was concluded to be not affected by TOPO, the association of 5,7-dichloro-8-quinolinol and TOPO in this solvent was negligible. This agrees with the tendency that the association of β-diketones with TOPO is much less in chloroform than, for example, in carbon tetrachloride.[10]

Figure 6 gives the extraction enhancement as a function of the TOPO concentration by keeping $[\mathrm{HA}]_{\mathrm{org,initial}}$ at 4×10^{-2} mol dm^{-3}. A statistical analysis of the data was carried out based on Eq. 12. It was concluded from the analysis that both $\mathrm{EuA_3TOPO}$ and $\mathrm{EuA_3(TOPO)_2}$ were formed; the values of $\beta_{(\mathrm{org})1}/(1+\beta_{(\mathrm{org})\mathrm{self}}[\mathrm{HA}]_{\mathrm{org}})$ and $\beta_{(\mathrm{org})2}/(1+\beta_{(\mathrm{org})\mathrm{self}}[\mathrm{HA}]_{\mathrm{org}})$ were determined by using a computer program. The formation constants, $\beta_{(\mathrm{org})1}$ and $\beta_{(\mathrm{org})2}$, were calculated from these values ($\beta_{(\mathrm{org})\mathrm{self}}$ in Table 1 and $[\mathrm{HA}]_{\mathrm{org}}$). The obtained values are also listed in Table 1. The solid lines in Figs. 3 and 6 were calculated based on Eqs. 11 and 12 by using the values given in Table 1.

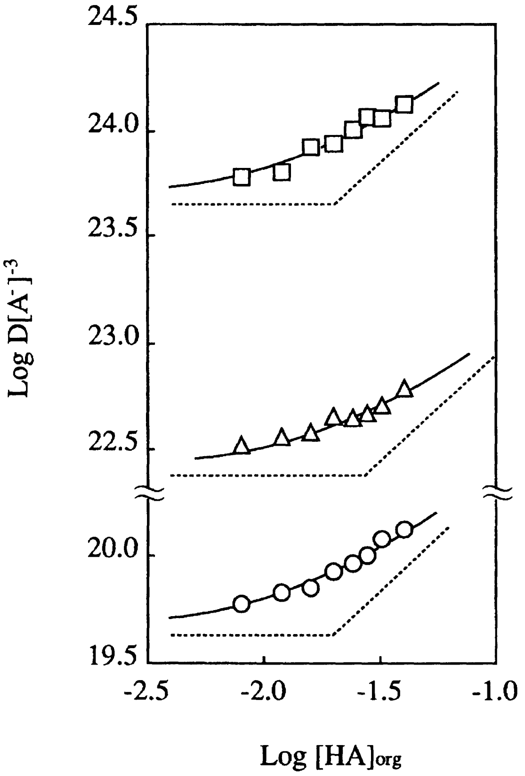

Fig. 4. The $\log D[\mathrm{A}^-]^{-3}$ vs. $\log\,[\mathrm{HA}]_{\mathrm{org}}$ plot in the absence of tba^+ and TOPO. Org. phase: chloroform initially containing 8×10^{-3} to 4×10^{-2} mol dm^{-3} of 5, 7- dichloro- 8- quinolinol. Aq phase: 0.1 mol dm^{-3} sodium nitrate at $[\mathrm{A}^-]$ is 1.6×10^{-7}—2.1×10^{-7} mol dm^{-3} for La(III), 2.0×10^{-8}—2.4×10^{-8} mol dm^{-3} for Eu(III), and 6.6×10^{-9}—7.1×10^{-9} mol dm^{-3} for Lu(III). The metal ions are La(III) (○), Eu(III) (△), and Lu(III) (□). The solid lines are calculated by Eq. 13 using the values given in Table 1. The dotted lines are the asymptotes for the solid lines.

Discussion

From the results in the absence of tba^+ and TOPO, it can be concluded that the extraction of polynuclear species, such as $\mathrm{M}_n\mathrm{A}_{3n}(\mathrm{HA})_m$ (where n is larger than unity), is negligible under the conditions of the present study. This is for the following reasons. As can be seen from Fig. 2, the determined $\log D$ was in the range -1.5 to $+1.5$. The initial concentration of the metal ions was always 1×10^{-4} mol dm^{-3}. From the distribution ratio, it can be seen that the metal concentration in the organic phase is 9.6×10^{-5} mol dm^{-3} when $\log D$ is $+1.5$ and is 2.9×10^{-6} mol dm^{-3} when $\log D$ is -1.5. The metal concentration in the highest extractant anion concentration is thus more than 30-times higher than that in the lowest extractant anion concentration. However, all of these data can be well explained within the limit of the experimental error by assuming only the extraction of mononuclear species on the basis of Eq. 2. Moreover, as was pointed out in Ref. 6

Table 1. Summary of the Equilibrium Constants
Org. Phase: Chloroform. Aq Phase: 0.1 mol dm^{-3} Sodium Nitrate.

	$\log K_{ex3,0}$	$\log \beta_{(org)self}$	$\log K_{ex4,1}$	$\log K_{org}$	$\log \beta_{(org)1}$	$\log \beta_{(org)2}$
La(III)	19.6	1.7	30.9	8.2	3.2	5.6
Eu(III)	22.4	1.6	34.8	9.3	3.0	5.6
Lu(III)	23.7	1.7	36.8	10.0	3.3	5.9

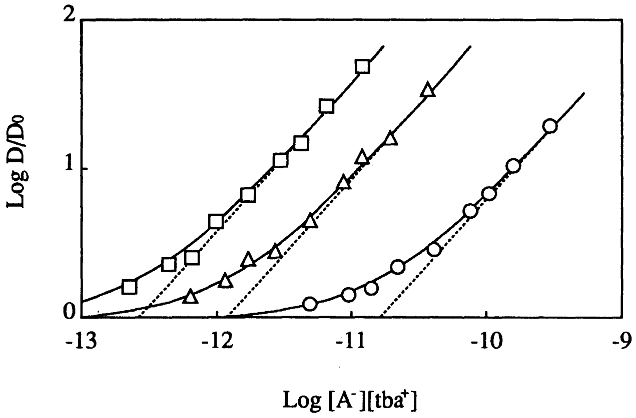

Fig. 5. Increase in the distribution ratio of the metal ions as a function of the quantity, [A$^-$] multiplied by [tba$^+$], in the aqueous phase. Org. phase: chloroform initially containing 4×10^{-2} mol dm^{-3} 5,7-dichloro-8-quinolinol. Aq phase: 0.1 mol dm^{-3} sodium nitrate initially containing 1×10^{-4} to 1×10^{-2} mol dm^{-3} tba$^+$ at [A$^-$] is 9.0×10^{-8}—1.6×10^{-7} mol dm^{-3} for La(III), 1.0×10^{-8}—2.4×10^{-8} mol dm^{-3} for Eu(III), and 3.6×10^{-9}—8.5×10^{-9} mol dm^{-3} for Lu(III). The metal ions are La(III) (○), Eu(III) (△), and Lu(III) (□). The solid lines are calculated by Eq. 8 using the values given in Table 1. The dotted lines are the asymptotes of the solid lines.

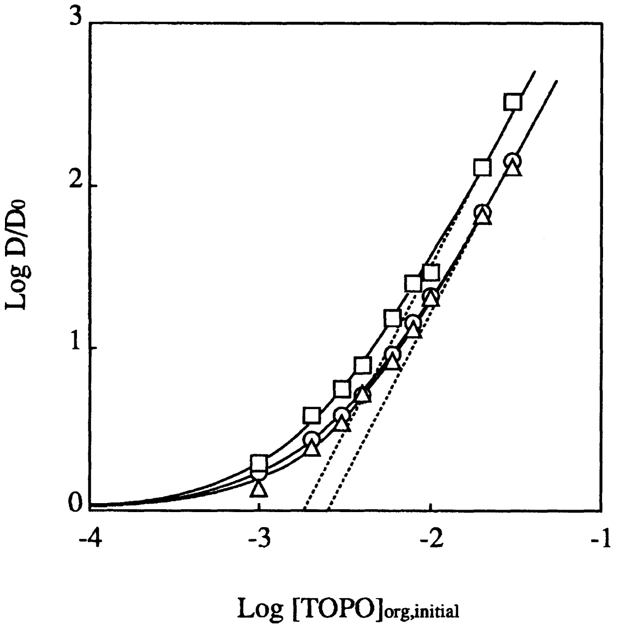

Fig. 6. Increase in the distribution ratio as a function of log [TOPO]$_{org}$. Org. phase: chloroform initially containing 4×10^{-2} mol dm^{-3} 5,7-dichloro-8-quinolinol and 1×10^{-3} to 3×10^{-2} mol dm^{-3} TOPO. Aq phase: 0.1 mol dm^{-3} sodium nitrate at [A$^-$] is 6.6×10^{-8} mol dm^{-3} for La(III), 1.0×10^{-8} mol dm^{-3} for Eu(III), and 3.8×10^{-9} mol dm^{-3} for Lu(III). The metal ions are La(III) (○), Eu(III) (△), and Lu(III) (□). The solid lines are calculated by Eq. 12 using the values given in Table 1. The dotted lines are the asymptotes of the solid lines.

(the data in Fig. 4 in this previous paper), although the slope of log [M(III)]$_{org,total}$ vs. log [M^{3+}][A$^-$]^3 should be +1 when only the mononuclear species is extracted, the slope should be larger than +1 if the extraction of a polynuclear species occurs. It has been confirmed that the slope of this plot calculated from the experimental data given in Fig. 2 is in all the cases +1.

In the absence of tba$^+$ and TOPO the extracted species were the MA_3 and MA_3HA, as can be seen from Eq. 2 and Fig. 4. The molar ratio of the two species in the organic phase is dependent on the HA concentration in the organic phase. It can be calculated from the value of $\beta_{(org)self}$ (which is $10^{1.6}$ for EuA_3 and $10^{1.7}$ for both LaA_3 and LuA_3) that even when [HA]$_{org}$ is as low as 1×10^{-3} mol dm^{-3}, about 5% of the metal species in the organic phase is in the MA_3HA form. Moreover, when [HA]$_{org}$ is 4×10^{-2} mol dm^{-3}, which is the highest concentration of [HA]$_{org}$ in the present study, 60 to 70% of the extracted species is in the MA_3HA form. Thus, for estimating the amount of metal ions extracted with the extractant, both concentrations, [A$^-$] and [HA]$_{org}$, should be taken into account. It can be seen from Table 1 that the value of $\beta_{(org)self}$ is nearly the same with the three metal ions. This means that the separation of these three in an aqueous solution by extraction with 5, 7-dichloro-8-quinolinol may not change, even when the [HA]$_{org}$ is different and/or when [A$^-$] is different.

When the effect of ternary complexes or adducts on extraction with 5,7-dichloro-8-quinolinol is estimated, the self-adduct in the organic phase should also be considered. As can be seen from Eqs. 8 and 12, the enhancement of extraction calculated based on the experimental data contains the effect of a self-adduct. The estimated enhancement partly contains the overall effect of the addition of A$^-$tba$^+$ or TOPO on the MA_3HA species. This is an exchange reaction of HA in the self-adduct with A$^-$tba$^+$ or TOPO. This can be seen from Eq. 8 or 12: the enhancement of the extraction due to the formation of the ternary complex or of the adducts,

D/D_0, is smaller by a factor of $(1+\beta_{(\mathrm{org})\mathrm{self}}[\mathrm{HA}]_{\mathrm{org}})^{-1}$ than when no self-adduct would be formed. For example, when the value of $\beta_{(\mathrm{org})\mathrm{self}}$ is $10^{1.7}$ and when $[\mathrm{HA}]_{\mathrm{org}}$ is 4×10^{-2} mol dm^{-3}, the factor is 0.33, or the enhancement is 33% of that achieved when all species are in the $\mathrm{MA_3}$ form.

The degree of enhancement due to the formation of adducts with TOPO of these three metal ions is also to some extent similar to that due to the formation of the self-adduct. As can be seen from Table 1, the values of $\beta_{(\mathrm{org})2}$, which are important when the TOPO concentration is not very low, are nearly similar to those of the chelates of these three metal ions. On the other hand, the acceptability of the $\mathrm{MA_3}$ complexes for $\mathrm{A^-tba^+}$ species is about one order different between the $\mathrm{LaA_3}$ and $\mathrm{EuA_3}$, and between the $\mathrm{EuA_3}$ and $\mathrm{LuA_3}$. As can be seen from Table 1, the value of K_{org} is larger in the order $\mathrm{LaA_3}<\mathrm{EuA_3}<\mathrm{LuA_3}$. This tendency is opposite to that found when $\mathrm{M(tta)_3}$ forms anionic complexes with the $\mathrm{tta^-tba^+}$ ion-pair in the organic phase:[2)] the acceptability of the $\mathrm{tta^-tba^+}$ ion-pair is higher in the order $\mathrm{La(tta)_3}\approx\mathrm{Eu(tta)_3}>\mathrm{Lu(tta)_3}$ in carbon tetrachloride[2)] as well as in chloroform. The values of K_{org} for these associations in carbon tetrachloride have already been reported in Ref. 2 and in chloroform; they were found to be $10^{6.9}$, $10^{6.9}$, and $10^{6.0}$, respectively, for $\mathrm{La(tta)_3}$, $\mathrm{Eu(tta)_3}$, and $\mathrm{Lu(tta)_3}$ in separate experiments. However, as can be seen from Fig. 2, the apparent enhancement of extraction due to the addition of $\mathrm{tba^+}$ is almost similar among these three lanthanoid ions, even though the values of K_{org} are very different from each other. This is due to the fact that the extractant anion concentration, $[\mathrm{A^-}]$, in Fig. 2 is higher in the order for extraction: La(III)>Eu(III)>Lu(III); the higher $[\mathrm{A^-}]$ is more favorable for the extraction of a ternary complex, as can be seen from Eqs. 7 and 8.[2,5)]

It was pointed out in previous papers[2,8)] that the addition of $\mathrm{tba^+}$ or TBP did not improve the separation of lanthanum(III), europium(III), and lutetium(III) very much by solvent extraction with 2-thenoyltrifluoroacetone in carbon tetrachloride; in some cases, the separation was even impaired. The separation of these three metal ions by extraction with 5,7-dichloro-8-quinolinol in the presence of TOPO was also not improved, as can be seen from Eq. 11 and the values of the adduct formation constants, $\beta_{(\mathrm{org})n}$, given in Table 1. However, the separation of these three by the extraction with 5,7-dichloro-8-quinolinol is greatly improved by the addition of $\mathrm{tba^+}$. The reason is as follows. When both $[\mathrm{A^-}]$ and $[\mathrm{HA}]_{\mathrm{org}}$ are identical, as in certain given solvent-extraction systems, the value, $(1+\beta_{(\mathrm{org})\mathrm{self}}[\mathrm{HA}]_{\mathrm{org}}+K_{\mathrm{org}}K_{\mathrm{exAB}}[\mathrm{A^-}][\mathrm{tba^+}])$ in Eq. 5, is larger in the order of K_{org}, since $\beta_{(\mathrm{org})\mathrm{self}}$ are rather similar to each other among the metal ions. The value in the parenthesis is thus dependent only on K_{org}. Since the value of $K_{\mathrm{ex3,0}}$ is larger in the order La(III)<Eu(III)<Lu(III), and the value of K_{org} is also larger in this order, the difference between the resulting D by the multiplication of the two terms, is much larger than the difference in the $K_{\mathrm{ex3,0}}$ of the metal ions.

As can be seen from the results given in the present work, as well as also from those in this series studies,[1—6)] the solvent extraction of the metal ion with a chelating extractant is affected by the addition of the anion of the extractant, which is extracted as ion-pairs with a large cation, $\mathrm{base^+}$, on the $\mathrm{MA_3}$ neutral chelate. This is also true regarding the strongly solvating neutral ligand, L. The effect of the formation complexes having a higher coordination number in the organic phase is rather similar in some cases, but it is very different in other cases; this is dependent on the combination of the two extractants. It should be caused by the overall effect of the ability of the $\mathrm{MA_3}$ as an acceptor as well as that of the $\mathrm{A^-base^+}$ or L as a donor in an organic solvent. However, since we do not understand these properties very well at present, further information is indispensable in order to reasonably elucidate these phenomena in organic solvents.

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