Bull. Chem. Soc. Jpn., **72**, 2703—2711 (1999)

Solvent Extraction Equilibria and Kinetics of Gallium(III) with 2-Thenoyltrifluoroacetone in the Absence and Presence of Trioctylphosphine Oxide in Toluene

Meri Yamada, Shinya Suganuma, Ichiro Tanaka, Tatsuya Sekine*,†

Department of Chemistry, Science University of Tokyo, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601

†Department of Applied Chemistry, Kanagawa Institute of Technology, 1030 Shimo-ogino, Atsugi, Kanagawa 243-0292

(Received July 8, 1999)

The rate and equilibrium of solvent extraction of gallium(III) from aqueous perchlorate solutions into toluene with 2-thenoyltrifluoroacetone (Htta) was measured in the absence and presence of trioctylphosphine oxide (TOPO). A synergistic enhancement of the extraction was found when TOPO was added. When a correction was made for the association of Htta and TOPO in the organic phase which decreased their concentrations available for the extraction, the extracted adducts was found to be in the form of $Ga(tta)_3(TOPO)_2$. The rate of extraction was not high and it was dependent on the second order with respect to Htta and the inverse second order with respect to H^+ in both the absence and the presence of TOPO. The rate was accelerated by addition of TOPO; the enhancement of the rate was proportional to the TOPO concentration.

Trivalent metal ions of group 13 elements are known to have six coordination sites; when they accept three anionic bidentate chelating ligands, association of further ligands should be difficult. Thus when these metal ions are extracted with a chelating extractant, it is considered that the extracted complex does not accept any more solvating type ligand and no ordinary synergistic enhancement of the extraction is expected. It was reported that the extraction of indium(III) with 2-thenoyltrifluoroacetone(1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione) into carbon tetrachloride was not enhanced by an addition of tributylphosphate (TBP) but rather an antagonistic effect was found when the TBP concentration was 0.1 mol dm^{-3}.[1] However, it was also reported later on that the solvent extraction of indium(III) and aluminum(III) by mixtures of a chelating extractant and a solvating extractant showed a synergistic effect.[2,3] In the present study, the solvent extraction of gallium(III) with Htta in toluene was measured from the standpoint of extraction equilibrium and of rate of extraction. It was found that an addition of trioctylphosphine oxide caused a marked enhancement of extraction; furthermore, the rate of solvent extraction of gallium(III) with Htta, which is rather low, was accelerated by the addition of TOPO.

Experimental

Reagents. All the reagents were analytical grade. 2-Thenoyltrifluoroacetone (Htta) and trioctylphosphine oxide (TOPO) were obtained from Dojindo Laboratories. The Htta was purified by recrystallization from petroleum ether. The TOPO was purified by recrystallization from cyclohexane three times. Toluene was washed several times with water before the use. A standard nitric acid solution of gallium(III) for the atomic absorption spectrometry was obtained from Kanto Chemicals Co.

Procedures. All the experiments were carried out in a thermostated room at 298 K. The nitric acid solution of gallium(III) was diluted by a sodium perchlorate solution. The aqueous phase contained 0.01 mol dm^{-3} perchloric acid and 0.09 mol dm^{-3} sodium perchlorate, but when the dependence of extraction of gallium(III) on the hydrogen-ion concentration was measured, 0.1 mol dm^{-3} sodium perchlorate solutions containing various amounts of 0.1 mol dm^{-3} perchloric acid were used; when the acid concentration was low, sulfanilate buffer was added. The effect of perchlorate on the extraction of gallium(III) was examined by using mixed solutions of 0.1 mol dm^{-3} sodium perchlorate and 0.1 mol dm^{-3} sodium nitrate containing 1×10^{-2} mol dm^{-3} perchloric acid. Crystals of Htta were dissolved in water-saturated toluene and the solution was left standing for at least 48 h in order to equilibrate the keto and enol form of Htta in this solution. When both Htta and TOPO were used as the extractant, the mixed solution was left standing for at least 48 h after the preparation in order to equilibrate the formation of associates of the two reagents.[4] The aqueous and organic solutions were placed in stoppered glass tubes (capacity 20 cm^3) and agitated in order to equilibrate the components. Then an amount of gallium(III) stock solution was added. The initial volume of the two phases was 5 cm^3 and the initial gallium(III) concentration in the aqueous phase was 1.5×10^{-4} mol dm^{-3}. The two phases were agitated for a certain given time by a mechanical shaker or by setting the tubes on a frame which rotated mechanically. Then the two phases were centrifuged off and the organic phase was transferred into another tube. To the separated organic phase was added the same volume of 4-methyl-2-pentanone (MIBK) containing 0.2 mol dm^{-3} TOPO and the mixture was agitated with 1 mol dm^{-3} perchloric acid in order to strip the extracted gallium(III). It was found that the addition of the MIBK solution of TOPO was effective in order to increase the rate of stripping of gallium(III) from the organic solution into the acid aqueous solution, as was reported with the stripping of beryllium(II) chelate from carbon tetrachloride.[5] This should be because the TOPO extracted the acid and destroyed the gallium complex in the organic phase and enhanced the rate of stripping.

In order to confirm whether the extraction equilibrium of gallium(III) was reached in the above experiments, the extraction equilibrium was also measured by a back-extraction method. The toluene solution which extracted gallium(III) was transferred into another tube and the same volume of an aqueous perchlorate solution was added. Then the two phases were agitated for a specified time. The organic phase was treated in the same manner as written with the forward extraction experiments and the distribution ratio of gallium(III) was obtained. The values obtained by the forward and backward extraction were confirmed to be similar.

The gallium(III) concentration in the equilibrated aqueous phase and in the stripped solution was determined by atomic absorption spectrophotometry. The hydrogen-ion concentration in the aqueous phase was measured by potentiometry using a standard solution, 1.00×10^{-2} mol dm^{-3} perchloric acid and 9.0×10^{-2} mol dm^{-3} sodium perchlorate as $-\log[\mathrm{H}^+] = 2.00$.

The extraction rate of gallium(III) was studied in an essentially similar manner as the measurements of extraction equilibrium, except that the two-phase agitation was stopped after it was continued for a specified time. In all the kinetic experiments, the two-phase agitation was continued for six different time intervals at a certain Htta and hydrogen-ion concentration.

The association equilibrium of Htta and TOPO in toluene was measured by a UV spectrophotometric method in the literature[4] as follows. An aqueous solution containing 0.09 mol dm^{-3} sodium perchlorate and 0.01 mol dm^{-3} perchloric acid was agitated with the same volume of toluene containing Htta and TOPO for 2 h, then the amount of Htta in the aqueous phase was measured from the absorption at 293 nm. The association was calculated from the decrease in the Htta concentration in the aqueous phase occurred by the addition of TOPO to the organic Htta solution.

Results

In the present paper, any chemical species in the organic phase is denoted by the subscript "org" and one in the aqueous phase is denoted by no subscript. The initial concentration is denoted by the subscript "init".

Extraction Equilibrium of Gallium(III). The forward extraction of gallium(III) with Htta proceeded rather slowly. Under certain conditions, extraction equilibrium was reached by the two-phase agitation by setting the tubes on the rotating flame for 1 week. Under some conditions, the backward extraction of gallium(III) from the organic to the aqueous phase was examined. The distribution ratio obtained by the forward extraction and the backward extraction agreed with each other when the concentration of each component in the two phases was identical and the two phases were agitated for a time long enough to achieve the equilibrium. Figure 1 gives the distribution ratio as a function of $-\log[\mathrm{H}^+]$ at equilibrium with 0.01 mol dm^{-3} Htta at initial.

In order to examine if the extracted species contained any perchlorate ions which were added as sodium perchlorate in the aqueous phase, the solvent extraction of gallium(III) was also measured when the aqueous phase was a mixture of 0.1 mol dm^{-3} sodium perchlorate and 0.1 mol dm^{-3} sodium nitrate at $-\log[\mathrm{H}^+]$ was 2. The organic phase for these experiments initially contained 0.028 mol dm^{-3} Htta and 0.012 mol dm^{-3} TOPO. It was found even when the perchlorate concentration changed from 0.02 to 0.1 mol dm^{-3} (and thus nitrate concentration was 0.08 to 0 mol dm^{-3}), the distribution ratios were similar. From these, it was concluded that the extracted gallium(III) species did not contain any perchlorate ions even when the gallium(III) was extracted with the both extractants, tta$^-$ and TOPO.

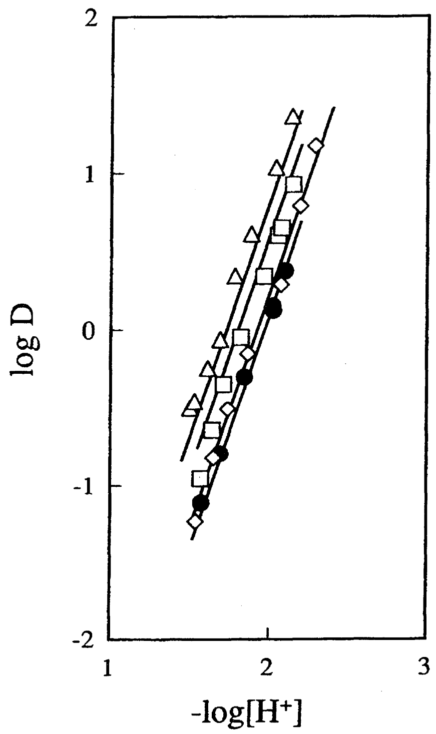

Fig. 1. Distribution ratio of gallium(III) when it is extracted with Htta and TOPO in toluene from aqueous perchlorate solutions as a function of hydrogen-ion concentration. The solid line is calculated by Eqs. 4 and 18. The values of K_{ex30}, and $\beta_{(\mathrm{org})2}$ are listed in Table 1. Aq phase: 0.1 mol dm^{-3} (Na,H)ClO$_4$ containing 0.01 mol dm^{-3} sulfanilate buffer. pH is 1.5 to 2.3, $[\mathrm{Ga}^{3+}]_{\mathrm{init}}$ is 1.5×10^{-4} mol dm^{-3}. Org. phase: toluene, $[\mathrm{Htta}]_{\mathrm{org,init}}$ is 0.01 mol dm^{-3}, $[\mathrm{TOPO}]_{\mathrm{org,init}}$ is 0 (●), 0.01 (◇), 0.03 (□), and 0.1 (△) mol dm^{-3}.

The distribution ratio as a function of the Htta concentration at equilibrium was measured when the $-\log[\mathrm{H}^+]$ was 2.0. The results are given in Fig. 2, in which the Htta concentration in the organic phase at equilibrium is given on the abscissa. From the results in the absence of TOPO in Figs. 1 and 2, the following equations can be obtained.

The slope of the plot in the absence of TOPO is +3 and the extraction equilibrium can be given by the following equation;

$$\mathrm{Ga}^{3+} + 3\mathrm{Htta}_{(\mathrm{org})} \rightleftarrows \mathrm{Ga(tta)}_{3(\mathrm{org})} + 3\mathrm{H}^+. \tag{1}$$

The equilibrium constant for this extraction can be written as:

$$K_{\mathrm{ex30}} = [\mathrm{Ga(tta)_3}]_{\mathrm{org}}[\mathrm{H}^+]^3[\mathrm{Ga}^{3+}]^{-1}[\mathrm{Htta}]_{\mathrm{org},0}^{-3}. \tag{2}$$

Here $[\mathrm{Htta}]_{\mathrm{org},0}$ denotes the concentration when no TOPO is added. The distribution ratio of gallium(III) can be written as:

$$D_0 = [\mathrm{Ga(tta)_3}]_{\mathrm{org}}[\mathrm{Ga}^{3+}]^{-1}. \tag{3}$$

Here, the chelate complexes in the aqueous phase were assumed to be negligible. From Eqs. 2 and 3, the following

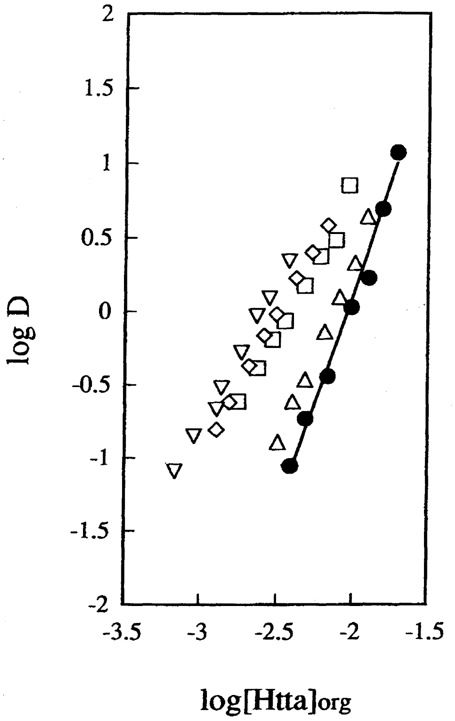

Fig. 2. Distribution ratio of gallium(III) when it is extracted with Htta and TOPO in toluene from aqueous perchlorate solutions as a function of Htta concentration. The solid line is calculated by Eq. 4 and the value of K_{ex30} is listed in Table 1. Aq. phase: 0.1 mol dm^{-3} (Na,H)ClO$_4$ containing 0.01 mol dm^{-3} sulfanilate buffer at pH 2, $[Ga^{3+}]_{init}$ is 1.5×10^{-4} mol dm^{-3}. Org. phase: toluene. $[Htta]_{org,init}$ is 0.0015—0.02 mol dm^{-3}, $[TOPO]_{org,init}$ is 0 (●), 0.01 (△), 0.03 (□), 0.04 (◇), and 0.05 (▽) mol dm^{-3}.

equation can be written:

$$D_0 = K_{ex30}[Htta]^3_{org,0}[H^+]^{-3}. \tag{4}$$

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

$$K_d = [Htta]_{org}[Htta]^{-1}, \tag{5}$$

$$K_a = [H^+][tta^-][Htta]^{-1}. \tag{6}$$

When the initial concentration of Htta in toluene was 5.71×10^{-3} mol dm^{-3} or 3.81×10^{-3} mol dm^{-3} and when no TOPO was added, the concentration of Htta in the aqueous phase after two-phase agitation was measured to be 1.28×10^{-4} mol dm^{-3} or 8.50×10^{-5} mol dm^{-3} when pH was 2; consequently the acid dissociation was negligible and thus K_d was obtained to be $10^{1.64}$ under the both conditions.

The Htta concentration can be written by the following equations and the values can be calculated by using the constants, K_d and K_a (in Ref. 6), which are listed in Table 1.

$$[Htta]_{org,init} = [Htta]_{org,0} + [Htta] + [tta^-], \tag{7}$$

$$[Htta]_{org,0} = [Htta]_{org,init}/\{1+(1+K_a[H^+]^{-1})K_d^{-1}\}. \tag{8}$$

The extraction of gallium(III) from this 0.1 mol dm^{-3} perchlorate solution only with TOPO was found to be negligible ($\log D < -2$ with 0.1 mol dm^{-3} TOPO).

Table 1. Summary of the Equilibrium Constants

$\log K_a$	$\log K_d$	$\log K_{as}$	$\log K_{ex30}$	$\log \beta_{(org)2}$
−6.33	1.64	1.37	0.12	4.32

When TOPO was added to the solvent extraction system with Htta, the extraction of gallium(III) was enhanced. In other words, a synergistic effect was observed. The results of the extraction with Htta in the presence of TOPO are also given in Figs. 1 and 2 by open symbols. As is seen from Fig. 1, the distribution ratio of gallium(III) is higher when TOPO was added. When both Htta and TOPO are present in the organic phase, the association of the reagents should occur. This should decrease the concentration of Htta and TOPO and it should make the extraction poorer than when the association would not occur.

The association equilibrium of Htta and TOPO in the organic phase was examined. The distribution data obtained were treated as follows. The distribution ratio of Htta should be written for these experiments as:

$$D_{Htta} = ([Htta]_{org} + [Htta{\cdot}TOPO]_{org})[Htta]^{-1}_{org}, \tag{9}$$

The association equilibrium can be written as:

$$Htta_{(org)} + TOPO_{(org)} \rightleftarrows Htta{\cdot}TOPO_{(org)}, \tag{10}$$

$$K_{as} = [Htta{\cdot}TOPO]_{org}[Htta]^{-1}_{org}[TOPO]^{-1}_{org}. \tag{11}$$

When the association of Htta and TOPO occurs, the following equation can be written:

$$\begin{aligned}[Htta]_{org,init} &= [tta^-] + [Htta] + [Htta]_{org} + [Htta{\cdot}TOPO]_{org}\\ &= [Htta]_{org}(K_aK_d^{-1}[H^+]^{-1} + K_d^{-1} + 1 + K_{as}[TOPO]_{org}).\end{aligned} \tag{12}$$

The extraction of perchloric acid with TOPO can be written as:[7]

$$H^+ + ClO_4^- + 2TOPO_{(org)} \rightleftarrows H^+ClO_4^-(TOPO)_{2(org)}, \tag{13}$$

$$K_{exacid} = [H^+ClO_4^-(TOPO)_2]_{org}[H^+]^{-1}[ClO_4^-]^{-1}[TOPO]^{-2}_{org}. \tag{14}$$

Since the two-phase distribution constant of TOPO should be very large, its concentration in the aqueous phase should be negligible and the following equation can be obtained:

$$\begin{aligned}[TOPO]_{org,init} &= [TOPO]_{org} + [Htta{\cdot}TOPO]_{org}\\ &\quad +2[H^+ClO_4^-(TOPO)_2]_{org}\\ &= [TOPO]_{org} + K_{as}[Htta]_{org}[TOPO]_{org}\\ &\quad +2K_{exacid}[H^+][ClO_4^-][TOPO]^2_{org}.\end{aligned} \tag{15}$$

By combining Eqs. 12 and 15 one can calculate the "free" Htta and TOPO concentration at equilibrium from the value of $[Htta]_{org,init}$ and $[TOPO]_{org,init}$ by using the values of constants in Table 1 on the basis of the description in Ref. 7. By a successive approximation method using 16 data points when $[TOPO]_{org,init}$ was 7.59×10^{-4} to 1.14×10^{-1} mol dm^{-3} and when $[\mathrm{Htta}]_{\mathrm{org,init}}$ was 5.71×10^{-3} mol dm^{-3}, the value of association constant in Eq. 11 was obtained to be $K_{\mathrm{as}} = 10^{1.37}$, as is listed in Table 1. In the present study, the total gallium(III) concentration was 1.5×10^{-4} mol dm^{-3}. Since the experiments were made by using a large excess of Htta and TOPO, the "free" Htta and TOPO concentration can be calculated on the bases of Eqs. 12 and 15 by neglecting the amounts of the reagents combined with gallium(III). The extraction data of gallium(III), when the initial Htta concentration was 1.0×10^{-2} mol dm^{-3} and the initial TOPO concentration was 1.0×10^{-2}, 3.0×10^{-2}, and 1.0×10^{-1} mol dm^{-3}, are also given in Fig. 1 by open symbols. As is seen from Eqs. 12 and 15, the free concentration of Htta and TOPO was lowered by the association of the reagents and thus the enhancement of the extraction by the addition of TOPO, which is recognized from Fig. 1, is an apparent one. The distribution ratio experimentally obtained was affected both by the enhancement due to the adduct formation (synergistic effect) and by the impairment by the decrease in the "free" Htta concentration and the "free" TOPO concentration (antagonistic effect).

The extraction of gallium(III) when the initial value of $-\log[\mathrm{H}^+]$ was 2.0 in the aqueous phase and when the initial value of TOPO concentration was 0.01 to 0.05 mol dm^{-3} in the organic phase was determined as a function of the Htta concentration. The results are given in Fig. 2 by open symbols. Because of the association of Htta and TOPO, the Htta concentration at equilibrium was lower than the initial value and, even when the initial TOPO concentration was identical, the TOPO concentration at equilibrium was different when the initial Htta concentration was different. The slope of the plot for the open symbols in Fig. 2 is clearly lower than +3. This is due to the decrease in the concentrations of both Htta and TOPO at equilibrium from the initial values.

The extraction of gallium(III) in aqueous 0.1 mol dm^{-3} perchlorate solutions initially containing 1.0×10^{-2} mol dm^{-3} hydrogen ions with 1.0×10^{-2} mol dm^{-3} Htta at initial was enhanced when TOPO was added to the organic phase. In order to estimate the enhancement of extraction by the addition of TOPO statistically, the association of Htta and TOPO and the extraction of perchloric acid with TOPO were taken into account. The enhancement of gallium extraction with Htta by the addition of TOPO, the synergic effect, can be explained by the formation of adducts of $\mathrm{Ga(tta)_3}$ chelate with TOPO. The equilibrium can be written as:

$$\mathrm{Ga(tta)_{3(org)}} + n\mathrm{TOPO_{(org)}} \rightleftarrows \mathrm{Ga(tta)_3(TOPO)}_{n\mathrm{(org)}}, \tag{16}$$

$$\beta_{(\mathrm{org})n} = [\mathrm{Ga(tta)_3(TOPO)}_n]_{\mathrm{org}}[\mathrm{Ga(tta)_3}]_{\mathrm{org}}^{-1}[\mathrm{TOPO}]_{\mathrm{org}}^{-n}. \tag{17}$$

When the formation of chelate complexes in the aqueous phase is negligible and when the extracted $\mathrm{Ga(tta)_3}$ associates with TOPO, the distribution ratio can be written as:

$$\begin{aligned} D = &([\mathrm{Ga(tta)_3}]_{\mathrm{org}} + [\mathrm{Ga(tta)]_3(TOPO)}]_{\mathrm{org}} \\ &+[\mathrm{Ga(tta)_3(TOPO)_2}]_{\mathrm{org}} + \cdots)[\mathrm{Ga}^{3+}]^{-1} \\ &= K_{\mathrm{ex30}}[\mathrm{Htta}]_{\mathrm{org}}^3[\mathrm{H}^+]^{-3}\left(1+\sum(\beta_{(\mathrm{org})n}[\mathrm{TOPO}]_{\mathrm{org}}^n)\right). \end{aligned} \tag{18}$$

$$D^*/D_0^* = 1 + \beta_{(\mathrm{org})1}[\mathrm{TOPO}]_{\mathrm{org}} + \beta_{(\mathrm{org})2}[\mathrm{TOPO}]_{\mathrm{org}}^2 + \cdots. \tag{19}$$

Here $D_0^* = D_0[\mathrm{Htta}]_{\mathrm{org},0}^{-3}[\mathrm{H}^+]_0^3$ and $D^* = D[\mathrm{Htta}]_{\mathrm{org}}^{-3}[\mathrm{H}^+]^3$. The values of $[\mathrm{H}^+]$ at equilibrium can experimentally be measured and the change in the Htta and TOPO concentration can be calculated on the basis of Eq. 19 by a successive approximation method using a least squares computer program. After trials, the data were found to be explained by considering the terms $[\mathrm{Ga(tta)_3}]_{\mathrm{org}}$ and $[\mathrm{Ga(tta)_3(TOPO)_2}]_{\mathrm{org}}$; the formation of the first adduct, $\mathrm{Ga(tta)_3(TOPO)}$, was assumed to be negligible. The distribution ratio corrected on the basis of Eq. 19 as a function of the corrected TOPO concentration on the basis of Eq. 15 is given in Fig. 3. The solid curve in Fig. 3 gives the calculated curve on the basis of Eq. 19 by introducing $\beta_{(\mathrm{org})1} = 0$, and $\beta_{(\mathrm{org})2} = 10^{4.32}$.

The data given in Fig. 1 by open symbols are also affected by the decrease in the concentration of Htta, TOPO and hydrogen ions. The $-\log[\mathrm{H}^+]$ in Fig. 1 is an experimentally measured value at equilibrium. The initial Htta concentration, 1.0×10^{-2} mol dm^{-3}, decreases by the partition into the aqueous phase, and in the presence of TOPO, it also decreases by the association of Htta and TOPO. When the initial TOPO concentration was 1.0×10^{-2}, 3.0×10^{-2}, and 1.0×10^{-1} mol dm^{-3}, and the Htta initial concentration was 1.0×10^{-2} mol dm^{-3}, the Htta concentrations at equilibrium came to be 8.4×10^{-3}, 6.2×10^{-3}, and 3.1×10^{-3} mol dm^{-3}, and the TOPO concentrations at equilibrium were calculated to be 8.4×10^{-3}, 2.6×10^{-2}, and 9.3×10^{-2} mol dm^{-3}. However, it was calculated from the values in Ref. 7, in which the solvent employed was hexane, that the extraction of perchloric acid with TOPO was slight when the hydrogen-ion concentration was 0.01 mol dm^{-3}. However, when

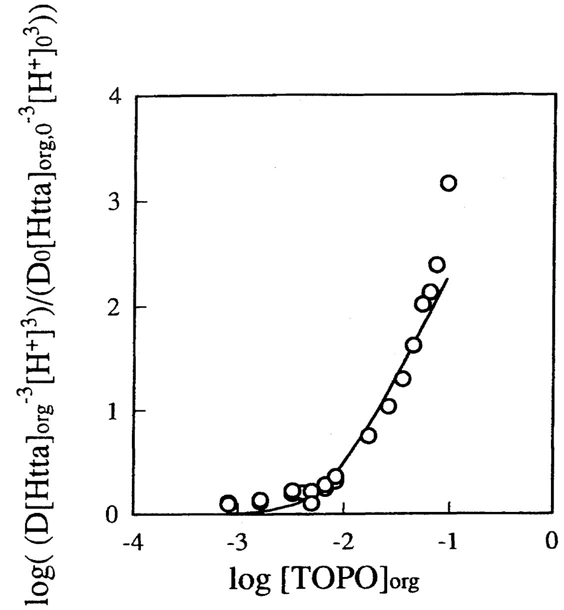

Fig. 3. Increase of distribution ratio as a function of TOPO after the change in the concentration of Htta and H$^+$ is normalized. Aq. phase: 0.1 mol dm^{-3} (Na,H)ClO$_4$ containing 0.01 mol dm^{-3} sulfanilate buffer at pH 2, $[\mathrm{Ga}^{3+}]_{\mathrm{init}}$ is 1.5×10^{-4} mol dm^{-3}. Org. phase: toluene. $[\mathrm{Htta}]_{\mathrm{org,init}}$ is 0.01 mol dm^{-3}, $[\mathrm{TOPO}]_{\mathrm{org,init}}$ is 0 to 0.1 mol dm^{-3}. The solid line was calculated by Eq. 18.

the hydrogen-ion concentration was higher than these, the decrease of Htta and TOPO concentration due to the association became smaller because the TOPO concentration also decreased by extraction of perchloric acid and this was collected on the basis of the hydrogen-ion concentration. The solid lines in Fig. 1 were calculated by taking account of all of these changes in the concentrations.

The data given in Fig. 2 are also affected by these decreases of the concentrations. As is seen from Fig. 2, even when the Htta concentrations on the abscissa are the calculated values at equilibrium, the slope of the plot when the initial TOPO concentration was the same was apparently smaller than +3. This was not expected when the $Ga(tta)_3$ species is extracted and the gallium(III) chelates with tta^- in the aqueous phase were negligible. This was due to the fact that the TOPO concentration became lower when the Htta concentration was higher, even when the initial TOPO concentration was constant, and thus the extraction was impaired by any decrease in both the Htta and TOPO concentrations and the synergistic enhancement due to the addition of TOPO appeared smaller than was expected from the initial concentration. Then the decrease in the concentrations of both the reagents made the distribution ratio lower than the value estimated by using the initial concentrations of Htta and TOPO. Furthermore, the extraction of perchloric acid by TOPO should occur and this extraction is second order dependent on the TOPO concentration. This was reported in Ref. 7 and is given as Eq. 14 in the present study. The data were statistically analyzed by taking these into account. It was calculated that the effect due to the extraction of perchloric acid was only slight but the effect due to the association of Htta and TOPO was marked. Figure 4 gives the dependence of the corrected distribution ratio on the basis of Eq. 18 as a function of the corrected Htta concentration on the basis of Eq. 12. As is seen from Fig. 4, all of the data in Fig. 2 show the thirdorder dependence of the distribution ratio on the Htta concentration at equilibrium. This indicates that the extracted gallium(III) complex contained three tta- ions and two TOPO molecules, that is, the chemical form was $Ga(tta)_3(TOPO)_2$. The association constant, $\beta_{(org)2}$, in Eq. 17 was calculated from all of the data in Figs. 1, 2, and 3 as is listed in Table 1.

Rate of Extraction. As was reported, the association of Htta and TOPO in an organic solvent is not a fast reaction; but in an organic solvent-aqueous solution system, it proceeds much more rapidly than in a single organic solution system and the distribution equilibrium of Htta is reached much more quickly.[4] In the present study, this equilibrium of association of Htta and TOPO in the solvent extraction systems was usually reached within 5 min. When the system contained Htta but no TOPO, the extraction of gallium(III) proceeded slowly, as was described. The rate of extraction can be given by the following equation:

$$v = -\mathrm{d}[\mathrm{Ga^{III}}]/\mathrm{d}t = k_0[\mathrm{Ga^{III}}][\mathrm{Htta}]^a_{\mathrm{org}}[\mathrm{H^+}]^b \cdots, \tag{20}$$

where k_0 is the rate constant. This equation can be rewritten as:

$$\log([\mathrm{Ga^{III}}]/[\mathrm{Ga^{III}}]_{\mathrm{init}}) = -(k_{\mathrm{obsd}}/2.303)t. \tag{21}$$

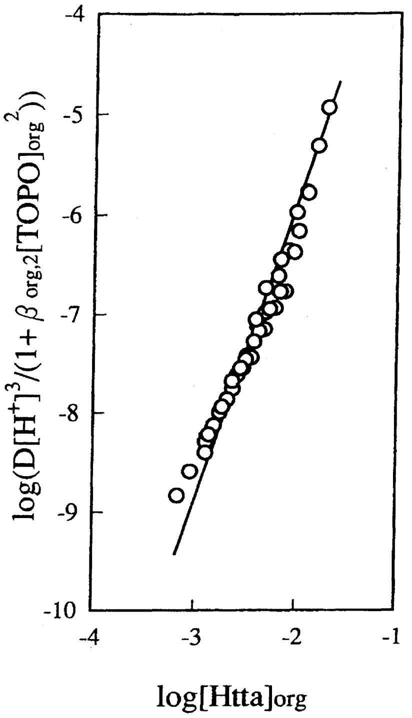

Fig. 4. Distribution ratio of gallium(III) when it is extracted with Htta and TOPO. The change in TOPO concentration is normalized in toluene-aqueous perchlorate system as a function of Htta concentration. The solid line was calculated by Eqs. 4 and 18. The values of K_{ex30}, and $\beta_{(\mathrm{org})2}$ are listed in Table 1. Aq. phase: 0.1 mol dm^{-3} (Na,H)-ClO_4 containing 0.01 mol dm^{-3} sulfanilate buffer at pH 2, $[\mathrm{Ga^{3+}}]_{\mathrm{init}}$ is 1.5×10^{-4} mol dm^{-3}. Org. phase: toluene. $[\mathrm{Htta}]_{\mathrm{org,init}}$ is 0.0015 to 0.02 mol dm^{-3}, $[\mathrm{TOPO}]_{\mathrm{org,init}}$ is 0 to 0.05 mol dm^{-3}.

The observed rate constant for this extraction may be defined as:

$$k_{\mathrm{obsd}} = k_0[\mathrm{Htta}]^a_{\mathrm{org}}[\mathrm{H^+}]^b \cdots. \tag{22}$$

When the two phase agitation was made from 5 to 60 min, the mode of two-phase agitation, whether the two-phase in the tubes were agitated by a rapidly moving shaker or by a rotating frame work at 20 rotations per minute, was found not to affect the rate.

From the experimental data, the $\log([\mathrm{Ga^{III}}]/[\mathrm{Ga^{III}}]_{\mathrm{init}})$ vs. t plot was made and the slope of plot in the early stage after the start of experiments was determined. The observed rate constant can be calculated from the value of slope thus obtained on the basis of Eqs. 21 and 22. Such plots were made by using the data of a series of experiments when the $[\mathrm{H^+}]$ was kept constant but $[\mathrm{Htta}]_{\mathrm{org}}$ was different. Figure 5 gives the results both in the absence and presence of TOPO. Similar plots were also made by using the data of another series of experiments when $[\mathrm{Htta}]_{\mathrm{org}}$ was kept constant but $[\mathrm{H^+}]$ was different. Figure 6 gives the $\log k_{\mathrm{obsd}}$ vs. $-\log[\mathrm{H^+}]$ plot when the initial Htta concentration was kept at 2.5×10^{-2} mol dm^{-3}. As is seen from Figs. 5 and 6, the values of k_{obsd} are proportional to $[\mathrm{H^+}]^{-2}$ and to $[\mathrm{Htta}]^2_{\mathrm{org}}$, respectively, in

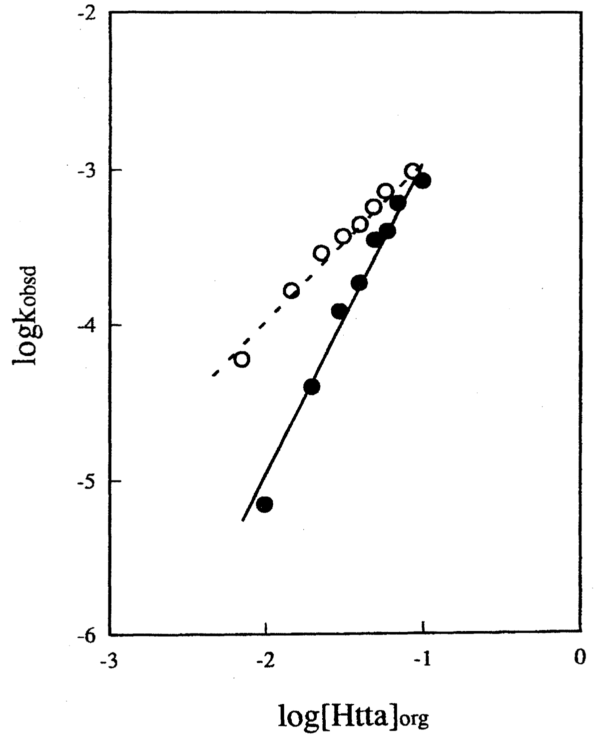

Fig. 5. Dependence of the rate of solvent extraciton of gallium(III) with Htta and TOPO in toluene–aqueous perchlorate system as a function of Htta concentration. The solid line was calculated by Eq. 20. k_0 is taken from Table 2. Aq. phase: 0.1 mol dm^{-3} (Na,H)ClO$_4$. pH = 2, $[Ga^{3+}]_{init}$ is 1.5×10^{-4} mol dm^{-3}. Org. phase: toluene. $[Htta]_{org,init}$ is 0.01 to 0.1 mol dm^{-3}. $[TOPO]_{org,init}$ is 0 (●) and 0.02 (○) mol dm^{-3}.

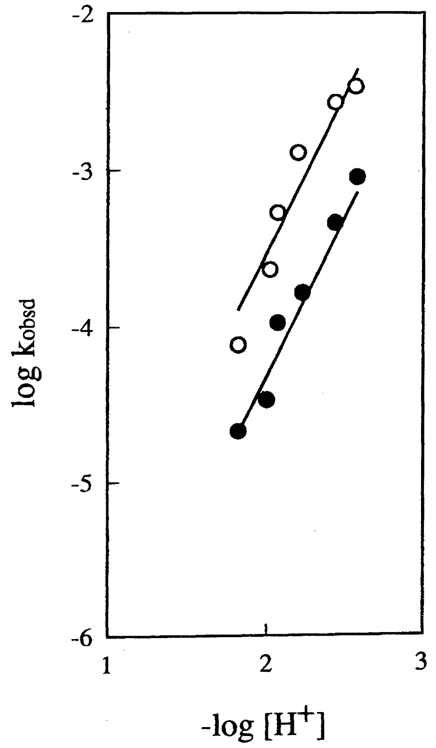

Fig. 6. Dependence of the rate of solvent extraciton of gallium(III) with Htta and TOPO in toluene–aqueous perchlorate system as a function of hydrogen-ion concentration. The solid line was calculated by Eqs. 20 and 23. The values of k_0 and k_1 are listed in Table 2. Aq. phase: 0.1 mol dm^{-3} (Na,H)ClO$_4$ buffered by acetate buffer, $[Ga^{3+}]_{init} = 1.5 \times 10^{-4}$ mol dm^{-3}. Org. phase: toluene. $[Htta]_{org,init}$ is 0.025 mol dm^{-3}. $[TOPO]_{org,init}$ is 0 (●) and 0.02 (○) mol dm^{-3}.

the absence of TOPO. From these, it can be concluded that the value of "a" in Eq. 16 is +2, and "b" is −2, respectively.

It was found that the rate of extraction was much higher when TOPO was added than when no TOPO was present, when the Htta concentration was the same. The open circles in Fig. 5 give the dependence of the observed rate constant. The open circles of Fig. 5 give the observed rate constant for the extraction when the initial concentration of TOPO was 2.0×10^{-2} mol dm^{-3} and $[H^+]$ was 1.0×10^{-2} mol dm^{-3} as a function of the Htta concentration at equilibrium. As is seen from Fig. 5, the slope of the plot for the open circles is smaller than +2. The open circles in Fig. 6 give the observed rate constant when the initial concentration of Htta and TOPO was 2.5×10^{-2} mol dm^{-3} and 2.0×10^{-2} mol dm^{-3}, respectively. The slope of the plot for the open circles is +2 in Fig. 6. It is seen from both Figs. 5 and 6 that the rate of extraction of gallium(III) with Htta is higher in the presence of TOPO. However, as the concentration of both Htta and TOPO decreases by their association in the organic phase, the increases in the rate of Htta extraction in the presence of TOPO should apparently be smaller when it is calculated by using the initial concentration of the reagents. As was already described, when TOPO was added into the organic phase containing Htta, an association occurred and both Htta and TOPO concentrations decreased. This was corrected by calculations on the basis of Eqs. 12 and 15 for each series of experimental data, as was done with the statistical treatment of the equilibrium data. Although a more general expression should be possible, the rate of extraction can be written by a simpler equations as is given below because the dependence of the rate on $[H^+]$ and $[Htta]_{org}$ was found to be the same in both the absence and the presence of TOPO. These suggest that in the absence of TOPO, the controlling reaction is the formation of the second complex of gallium(III) with Htta as given in the following equations. The rate in the presence of TOPO should be written as:

$$
\begin{aligned}
v &= -d[Ga^{III}]/dt \\
&= k_0[Ga^{III}][Htta]_{org}^{a}[H^+]^{b} + k_1[Ga^{III}][Htta]_{org}^{a'}[H^+]^{b'}[TOPO]_{org}^{c'} \cdots .
\end{aligned} \tag{23}
$$

In order to examine the dependence of the rate on the Htta concentration, a series of experiments were made under the same $[H^+]_{init}$ and $[TOPO]_{org}$. The open circles in Fig. 5 give the data. Since the association of Htta and TOPO decreases the free Htta concentration, the Htta concentrations on the abscissa in Fig. 5 are the free Htta concentrations calculated on the basis of Eq. 12. As is seen from Fig. 5, the plot of $\log k_{obsd}$ vs. $\log [Htta]_{org}$ in the presence of initial 2.0×10^{-2}

mol dm^{-3} TOPO is a straight line with a slope of +1, which is shown by the dotted line. However, the TOPO concentration is not constant, even though the initial values are identical, when the Htta concentration is different. The dependence of the rate on TOPO when the initial Htta and H^+ concentration was kept constant was measured. The results are given in Fig. 7a. Due to the association of Htta and TOPO, the TOPO concentration is lower than the initial value. The TOPO concentration in Fig. 7a is the value for this decrease corrected on the basis of Eq. 15. As is seen from Fig. 7a, the addition of TOPO does not seem to increase the rate of extraction of Ga^{3+} with Htta very much, especially when the calculated TOPO concentration is lower than 3.0×10^{-2} mol dm^{-3}. However, this is again an apparent effect. Although the effect of the change in [H^+] due to the extraction of perchloric acid with TOPO was calculated to be negligible, the Htta concentration decreased markedly by the association with TOPO and this should lower the rate of extraction. Thus the effect due to the decrease in the Htta concentration was corrected by assuming that the rate should also be second order dependent on Htta, which will be confirmed later as will be given in Fig. 8. Figure 7b gives the corrected observed rate constant for the Htta concentration as a function of the calculated TOPO concentration. As is seen from Fig. 7b, the rate is first order dependent on the TOPO concentration and thus the much smaller dependence of the rate on the TOPO concentration in Fig. 7a than in Fig. 7b can be concluded to be due to the decrease of the Htta concentration on which the rate is second order dependent. This second order dependence of the rate on the Htta concentration and first order dependence on the TOPO concentration was further confirmed with the data in Fig. 5. Figure 8 gives the data in Fig. 5 by using the corrected observed rate constant. It is seen from Fig. 7b that the rate is assumed to be first order dependent on the TOPO

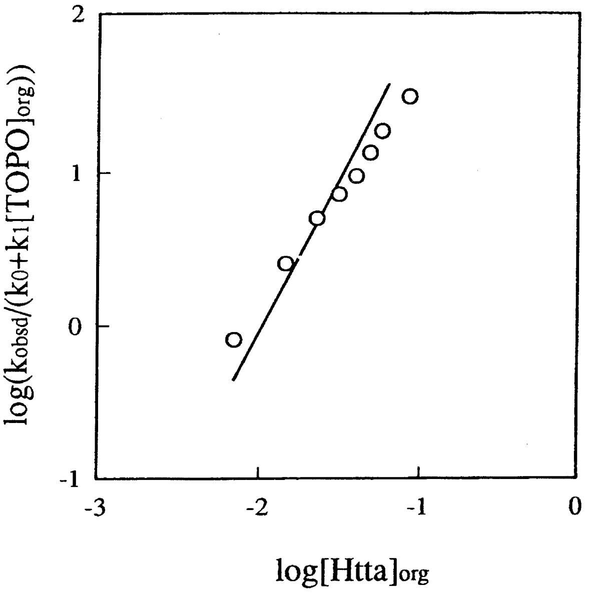

Fig. 8. Dependence of the rate of solvent extraciton of gallium(III) with Htta and TOPO in toluene–aqueous perchlorate system as a function of Htta concentration. The data are taken in the TOPO concentration is normalized. The solid line was calculated by Eqs. 20 and 23. The values of k_0 and k_1 are listed in Table 2. Aq. phase: 0.1 mol dm^{-3} (Na,H)ClO$_4$. pH 2, [Ga^{3+}]$_{init}$ is 1.5×10^{-4} mol dm^{-3}. Org. phase: toluene. [Htta]$_{org,init}$ is 0.01 to 0.1 mol dm^{-3}. [TOPO]$_{org,init}$ is 0 (●) and 0.02 (○) mol dm^{-3}.

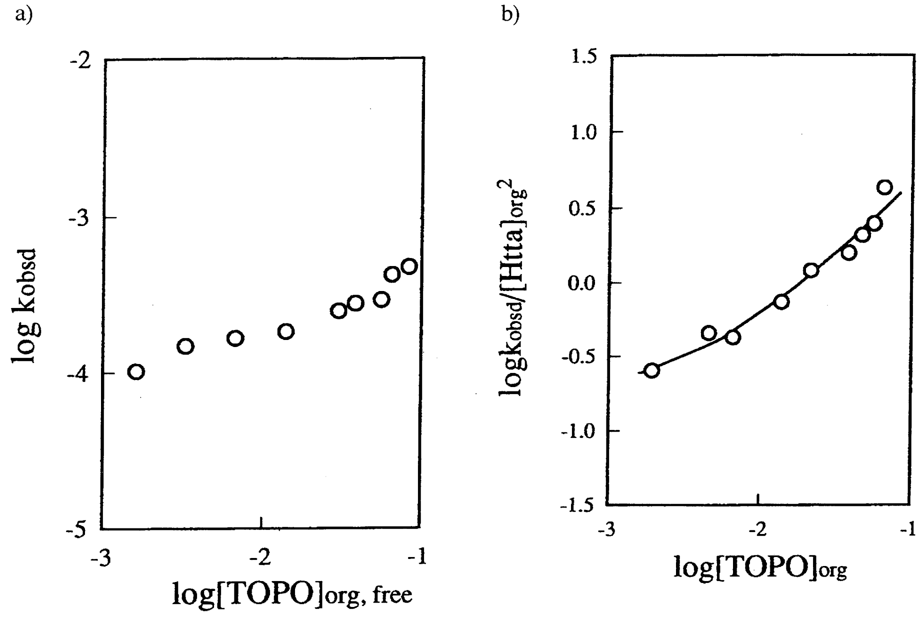

Fig. 7. Dependence of the rate of solvent extraciton of gallium(III) with Htta and TOPO in toluene–aqueous perchlorate system as a function of TOPO concentration. (a) gives the data when no correction was made. (b) gives the data obtained after the change in the concentration of Htta is normalized. The solid line was calculated by Eqs. 20 and 23. The values of k_0 and k_1 are listed in Table 2. Aq. phase: 0.1 mol dm^{-3} (Na,H)ClO$_4$. pH = 2, [Ga^{3+}]$_{init}$ is 1.5×10^{-4} mol dm^{-3}, Org. phase: toluene. [Htta]$_{org,init}$ is 0.025 mol dm^{-3}. [TOPO]$_{org,init}$ is 0.003 to 0.1 mol dm^{-3}.

concentration. Since the increase in the rate by the addition of TOPO is very large, in other words, $k_0 \ll k[\mathrm{TOPO}]_{\mathrm{org}}$ the plot can nearly be represented by the straight line of slope +2. From the data in Figs. 5, 6, 7, and 8, the values "a'", "b'", and "c'" in Eq. 23 were concluded to be 2, −2, and 1. Although the rate is very much enhanced by TOPO, still the dependence of the rate is second and inverse second order dependent on $[\mathrm{Htta}]_{\mathrm{org}}$ and $[\mathrm{H}^+]$ even in the presence of TOPO. The values of rate constants for the solvent extraction of gallium(III) with Htta both in the absence and presence of TOPO are listed in Table 2.

Table 2. Summary of the Rate Constants

$\log k_0$ (s^{-1})	$\log k_1$ (s^{-1})
−4.93	−2.35

Discussion

Gallium(III) complex is usually hexacoordinated. Thus, when three tta^- ions are combined with a Ga^{3+} ion, there should be left no sites to accept a further ligand if each of the tta^- ions still occupies two coordination sites. However, the results of extraction equilibrium obtained in the present study suggest that addition of TOPO to the gallium(III)–Htta extraction system causes enhancement of the extraction, which should be called a synergistic effect. Imura, Oshiro, and Ohashi[8] reported that the solvent extraction of gallium(III) in 0.1 $\mathrm{mol\,dm^{-3}}$ sodium perchlorate with 2,4-pentanedione (Hacac) in heptane or carbon tetrachloride was enhanced by an addition of 3,5-dichlorophenol. The results were explained by these authors in terms of formation of an outer-sphere complex of tris(acetylactonato)gallium(III) with 3,5-dichlorophenol. The outer-sphere complex was studied by IR and ^{1}H NMR spectrophotometry. Thus in this previous work the enhancement of extraction should be due to an addition of 3,5-dichlorophenol to the complex, but the associating ligand combined with the acetylacetonate ion; the central gallium(III) should still be hexacoordinated by acac^- even after the addition of 3,5-dichlorophenol. In this previous study, the association of Hacac and 3,5-dichlorophenol was not especially taken into account. There have been reports on the solvent extraction of gallium(III) with some extractants[9—11] but there have been no reports with any evidence that the extraction of gallium(III) with an acidic extractant is enhanced by a second neutral extractant such as TOPO.[10]

In the present study, the hexahcoordinated tris(thenoyltrifluoroacetonato)gallium(III) was concluded to combine with two molecules of unidentate ligand, TOPO. Only from the solvent extraction equilibrium study, it is not possible to conclude whether the associated TOPO combines with the central metal ion by forming a coordination bond or it combines with the tta^- ion of the $\mathrm{Ga(tta)_3}$ by forming an outer-sphere complex by a hydrogen bond. However, when the associating ligand, TOPO, would form an associate with the complex by forming a hydrogen bond, there is no such hydrogen atom to associate with an oxygen atom both in the complex and in the associating ligand. In the previous study, the 3,5-dichlorophenol is employed as the associating ligand with the tris(acetylacetonato)gallium(III) chelate and this has such a hydrogen atom to form the hydrogen bond in the enol group. This seems to suggest that the TOPO molecules should combine with the central gallium(III) ion in the chelate. Since the tris(thenoyltrifluoroacetonato)gallium(III) should have no vacant sites to make further coordination bonds, one possible explanation for this may be that in the adduct chelate, $\mathrm{Ga(tta)_3(TOPO)_2}$, two tta^- ions coordinate with the metal ion not as a bidentate ligand but as an unidentate ligand. Thus the TOPO molecules can occupy the coordination sites which have been occupied by the tta^- ions before the adduct formation. The reason why the $\mathrm{Ga(tta)_3}$ chelate forms only the adduct with two TOPO molecules but does not form an adduct with one TOPO molecule can not be explained up to now. It is seen from the results in Fig. 3, and from the value of adduct formation constant, $\beta_{(\mathrm{org})2}$, in Table 1, TOPO is not a very effective adduct forming ligand with the $\mathrm{Ga(tta)_3}$ chelate. In the organic phase, TOPO forms the associate with Htta and the association constant of these reagents is rather large. This association of Htta and TOPO lowers the free Htta concentration and this impairs the extraction of $\mathrm{Ga(tta)_3}$, in other words, an antagonistic effect is caused by TOPO. Thus the addition of TOPO causes both the synergistic effect and the antagonistic effect for the solvent extraction of gallium(III) with Htta. The results show that the former is larger than the latter and so the extraction was enhanced.

It was found that the forward extraction of gallium(III) with Htta into toluene was slow and also the backward extraction of gallium(III) extracted as the $\mathrm{Ga(tta)_3}$ chelate from the toluene to aqueous phase was a slow reaction. These made the acid stripping of the extracted the $\mathrm{Ga(tta)_3}$ chelates slow. As was described, when the toluene which extracted gallium(III) as the $\mathrm{Ga(tta)_3}$ chelate was mixed with MIBK containing TOPO and the mixture was agitated with 1 $\mathrm{mol\,dm^{-3}}$ perchloric acid, the quantitative stripping could be achieved within a much shorter time than when these were not added. A similar type of acceleration of acid stripping of a metal complex from the organic solvent was already reported with the stripping of beryllium(II) as benzoylacetonate complex in a previous paper.[5] The acceleration of acid stripping should be because the added TOPO and also MIBK extracted the acid from the aqueous phase; so the destruction of the chelate complex by the acid should also occur in the organic phase. Since the rate of extraction of gallium(III) was second order dependent on Htta and inverse second order on the hydrogen ions, it can be assumed that the controlling reaction was the formation of the second complex of gallium(III) with Htta in the aqueous phase in the absence of TOPO, as can be described by one of the following equations:

$$\mathrm{Ga(tta)^{2+} + tta^- \rightarrow Ga(tta)_2{}^+}, \tag{24}$$

$$\mathrm{Ga(tta)OH^+ + Htta \rightarrow Ga(tta)_2{}^+ + H_2O}. \tag{25}$$

In a previous paper,[12] the rate of extraction of gallium(III) in 0.1 mol dm^{-3} sodium perchlorate with Htta into chloroform was reported to be first order dependent on the Htta concentration in the organic phase and inverse second order dependent on the hydrogen ions. Thus the dependence of the rate of extraction on the Htta concentration in this previous study is different from that in the present study. The present authors cannot explain this difference in the dependence of the rate on Htta, although the diluent was different in these two studies.

Furthermore, the rate of extraction in the presence of TOPO when the dominant extracted species in the organic phase was $Ga(tta)_3(TOPO)_2$ was also dependent on the second and inverse second order on the concentration of Htta in the organic phase and hydrogen ions in the aqueous phase and also first order dependent on the TOPO concentration in the organic phase.

The rate of extraction in the presence of TOPO was higher than that in its absence. Since TOPO has three quite hydrophobic octyl groups, the distribution constant, $K_d = [TOPO]_{org}[TOPO]^{-1}$, should be very large; thus its concentration in the aqueous phase which is equilibrated with the organic phase should be very low. For this reason, it is assumed that even though TOPO accelerates the extraction, the controlling reaction may not occur in the aqueous phase where the TOPO concentration is extremely low. Since the TOPO concentration in the aqueous phase should be very low, TOPO may not react directly with the formation of the second complex in the aqueous phase. Thus the authors can not explain the reaction mechanism and the reason why the Htta extraction is accelerated by the TOPO. In order to make a clear explanation for the acceleration of the tta$^-$ extraction with TOPO, further kinetic experiments under different conditions should be necessary.

References

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

2 J. P. Brunette, M. Taheri, G. Goetz-Grandmont, and M. J. F. Leroy, *Solvent Extr. Ion Exch.*, **3**, 309 (1985).

3 H. Imura, A. Oshiro, and R. Shiga, *Solvent Extr. Ion Exch.*, **13**, 1009 (1995).

4 A. Hokura and T. Sekine, *Anal. Sci.*, **13**, 19 (1997).

5 T. Sekine and T. Kurihara, *Anal. Sci.*, **2**, 137 (1986).

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

7 M. Niitsu and T. Sekine, *J. Inorg. Nucl. Chem.*, **37**, 1054 (1975).

8 H. Imura, A. Oshiro, and K. Ohashi, *Anal. Sci.*, **14**, 1093 (1998).

9 V. S. Vartak and M. V. Shinde, *Talanta*, **45**, 925 (1998).

10 Y. Yang, M. Xue, X. Jiang, and S. Sun, *Shandong Daxue Xuebao, Ziran Kexueban*, **32**, 317 (1997).

11 J. Mukherjee and S. P. Bag, *Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem.*, **36**, 818 (1997).

12 T. Sekine, Y. Komatsu, and J. Yumikura, *J. Inorg. Nucl. Chem.*, **35**, 3891 (1973).