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Solvent Extraction of Chromium(III) Perchlorate, Thiocyanate, Nitrate, Bromide, and Iodide with Trioctylphosphine Oxide in Hexane

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Chromium(III) ion was extracted from aqueous 1 mol dm^{-3} NaX (X^- = ClO_4^-, SCN^-, NO_3^-, Br^-, and I^-) solutions with trioctylphosphine oxide (TOPO) in hexane at 298 K. The extraction was rapidly equilibrated, except from a $NaNO_3$ solution. The number of TOPO molecules solvating to the extracted chromium(III) perchlorate and thiocyanate was 6. That to the bromide and iodide was 5. That to the nitrate was 5 at the beginning of extraction, and changed to 3 within a few hours of two-phase agitation. The hydration number of extracted $Cr(ClO_4)_3 \cdot 6TOPO$ was 17.2±0.5. The different solvation number of TOPO among these salts is supposed to be an unstable second hydration sphere of the extracted chromium(III) ion, which may be easily removed by the counter anions.

Although metal salts are scarcely soluble in non-polar solvents, they are extracted with neutral donor reagents. The present author studied the equilibrium in the extraction of metal perchlorates with trioctylphosphine oxide (TOPO) in hexane, since perchlorate ion is less coordinating to the metal ions, and is consequently convenient to examine the donation of TOPO.[1,2] Since this reagent is dissolved to an inert diluent upon use, the donation of TOPO is customarily expressed as "solvation". It is concluded from studies up to now that there are two chemical forms in the extracted metal perchlorates: one is solvated with three or four molecules of TOPO; the other is solvated with more than six molecules.[3] Thus, although the former species are mainly extracted to an organic solution of low TOPO concentration, the latter are extracted to the organic phase of higher TOPO concentrations. From the standpoint of hydration and the solvation behavior of the extracted species, although TOPO molecules are suggested to have direct solvation to the metal ion in the former species, the TOPO may combine with the hydration water of the metal ions in the latter species. In a previous paper the present author and his co-workers reported that the chromium(III) ion can be extracted with six TOPO molecules irrespective of the TOPO concentration.[4] Since the chromium(III) ion is inert, and is extracted in the form of hydrating ion, this is a reasonable result. For this reason, chromium(III) ion may be regarded as being a stable probe for trivalent ion-pair extraction. Thus, the extraction of chromium(III) halides, nitrate, and thiocyanate with TOPO was examined in the present study. If the hydrating chromium(III) ion is stable, even when it is solvated with TOPO molecules, the extraction behavior of these salts should be similar to that of typical ionic compounds, such as tetraalkyl ammonium salts, into less polar solvents.

Experimental

Reagents and Extraction Procedures. Ten grams of TOPO from Dojindo Laboratories were dissolved to 500 cm^3 cyclohexane and washed with 0.1 mol dm^{-3} aqueous sodium hydroxide and water. After the organic phase was passed through filter paper in order to remove the water, the solvent was evaporated, and the residue was recrystallized from hexane. The crystals were collected on a glass filter, washed with a small amount of cold acetone, and then dried under vacuum on P_2O_5. A weighed amount of TOPO was dissolved to a reagent-grade hexane. Chromium(III) perchlorate hexahydrate of Soekawa Chemicals Co. was used without further purification. It was dissolved to an aqueous 1 mol dm^{-3} NaX (X^- = ClO_4^-, SCN^-, NO_3^-, Br^-, and I^-) solution containing 0.01 mol dm^{-3} sulfuric acid. A certain volume of one of the chromium(III) solutions and the same volume of a hexane solution containing various amounts of TOPO were placed in a stoppered glass tube of 20 cm^3 volume. They were mechanically agitated for a quarter of an hour in a thermostatted room at 298 K and then separated by centrifugation. The extracted metal ion was stripped with an aqueous 0.1 mol dm^{-3} solution of the corresponding sodium salt containing 0.01 mol dm^{-3} sulfuric acid. The metal-ion concentration in the stock solutions and in the stripping solutions was determined by the atomic absorption spectrometry.

Measurements of the Hydration Number of the Extracts from an Aqueous Perchlorate Solution. An aqueous 0.1 mol dm^{-3} chromium(III) perchlorate solution was prepared by dissolving the crystals into 2.00 mol dm^{-3} perchloric acid and the concentrations of H^+ and Na^+ were adjusted to 0.01 and 0.39 mol dm^{-3}, respectively, (namely, the ionic strength was 1.0 mol dm^{-3}) by using aqueous 1.00 mol dm^{-3} sodium perchlorate and sodium hydroxide solutions and water. A certain volume of this aqueous chromium(III) perchlorate solution and a hexane solution of TOPO were agitated for 20 min and centrifuged. A portion of the organic phase was used to determine the water concentration in it by a Hiranuma Aq-6 type aquacounter (a coulometric Karl Fischer titrater) in a similar manner as that reported in a previous paper.[5] Another portion of the organic phase was taken for the determination of the metal-ion concentration in it. The hydration number was calculated from the total TOPO concentration, measured amounts of water, and metal-ion concentration in the organic phase while taking into account the adduct formation of TOPO with water.

Results and Discussion

In the present paper the chemical equilibria are described using only stoichiometric units. This is because the aqueous solutions are maintained at a constant ionic strength of 1 mol dm^{-3} and the chemical species in the organic phase scarcely dissociate to ions. The activity of water in the organic phase should be constant as long as it is equilibrated with aqueous solutions of constant ionic strength. A change in the activity of water in the aqueous solution should influence the solubility of water into pure hexane. This change among different sodium salt solutions was, however, neglected because the water activity of aqueous 1 mol kg^{-1} sodium chloride solution is 0.967.[6] In the other sodium salt solutions it may be closer to unity than this value.

The extraction equilibrium of a chromium(III) salt with TOPO in hexane can be expressed by

$$\mathrm{Cr^{3+}} + 3\mathrm{X^-} + n\mathrm{TOPO_{(org)}} \rightleftarrows \mathrm{CrX_3}\cdot n\mathrm{TOPO_{(org)}},$$
$$K^*_{\mathrm{ex},n} = [\mathrm{CrX_3}\cdot n\mathrm{TOPO}]_{\mathrm{org}}/[\mathrm{Cr^{3+}}][\mathrm{X^-}]^3x^n. \tag{1}$$

Subscript 'org' denotes the chemical species in the organic phase; n is the solvation number of TOPO and x is the effective concentration of TOPO, which is discussed later in relation to the meaning of the asterisk attached to the constant.

The distribution ratio of metal ion is written as

$$D = [\mathrm{Cr^{3+}}]_{\mathrm{org,total}}/[\mathrm{Cr^{3+}}] = [\mathrm{CrX_3}\cdot n\mathrm{TOPO}]_{\mathrm{org}}/[\mathrm{Cr^{3+}}] = K^*_{\mathrm{ex},n}[\mathrm{X^-}]^3x^n. \tag{2}$$

The distribution ratios under different total concentrations of TOPO were treated by a personal computer. The value of x and the assumed constants were refined by a successive approximation. The hydrogen ion, chromium(III) ion, and $\mathrm{X^-}$ ion concentration at equilibrium were also computed in the process of calculating x and the extraction constant by a successive approximation.

Calculation of the Equilibrated TOPO Concentration. The initial TOPO concentration was usually less than 0.1 mol dm^{-3}, where the equilibrium of adduct formation with water was well expressed with stoichiometric units.[7] The solubility of TOPO into the aqueous phase is negligible. Since the co-extraction of HX and NaX is not always negligible, this was taken into the account in previous studies concerning the calculation of the free TOPO concentration. The material balance of TOPO is represented by

$$[\mathrm{TOPO}]_{\mathrm{org,total}} = [\mathrm{TOPO}]_{\mathrm{org}} + l[\mathrm{HX}\cdot l\mathrm{TOPO}]_{\mathrm{org}} + 3[\mathrm{NaX}\cdot 3\mathrm{TOPO}]_{\mathrm{org}} + n[\mathrm{CrX_3}\cdot n\mathrm{TOPO}]_{\mathrm{org}}. \tag{3}$$

The extraction constants for the acids[8] and sodium salts[9] were obtained on the basis of the TOPO concentration derived from Eq. 3. It was later found that TOPO in hexane forms two types of adducts with water: $\mathrm{TOPO}\cdot\mathrm{H_2O}$ and $2\mathrm{TOPO}\cdot3\mathrm{H_2O}$. Their formation constant is generally defined by $K_{pq} = [p\mathrm{TOPO}\cdot q\mathrm{H_2O}]_{\mathrm{org}}/[\mathrm{TOPO}]_{\mathrm{org}}{}^p$. The values were $K_{11} = 0.8$ and $K_{23} = 10$.[7] Then, Eq. 3 is changed to

$$[\mathrm{TOPO}]_{\mathrm{org,total}} = [\mathrm{TOPO}]_{\mathrm{org}} + l[\mathrm{HX}\cdot l\mathrm{TOPO}]_{\mathrm{org}} + 3[\mathrm{NaX}\cdot3\mathrm{TOPO}]_{\mathrm{org}} + [\mathrm{TOPO}\cdot\mathrm{H_2O}]_{\mathrm{org}} + 2[2\mathrm{TOPO}\cdot3\mathrm{H_2O}]_{\mathrm{org}} + n[\mathrm{CrX_3}\cdot n\mathrm{TOPO}]_{\mathrm{org}}. \tag{4}$$

The word "free or effective TOPO concentration" thus came to have duplicate meanings: with and without considering the adduct formation of TOPO with water. In the present paper they are distinguished by x and y; namely, x is the free TOPO concentration considered the adducts formation with water and y is without consideration of it; y is represented by x as

$$y = [\mathrm{TOPO}]_{\mathrm{org}} + [\mathrm{TOPO}\cdot\mathrm{H_2O}]_{\mathrm{org}} + 2[2\mathrm{TOPO}\cdot3\mathrm{H_2O}]_{\mathrm{org}} = x + K_{11}x + 2K_{23}x^2. \tag{5}$$

Equation 4 can be rewritten as

$$[\mathrm{TOPO}]_{\mathrm{org,total}} = y + l\mathrm{K}_{\mathrm{ex\ H}(l)}[\mathrm{H^+}][\mathrm{X^-}]\mathrm{y}^l + 3\mathrm{K}_{\mathrm{ex,Na(3)}}[\mathrm{Na^+}][\mathrm{X^-}]\mathrm{y}^3 + nK^*_{\mathrm{ex},n}[\mathrm{Cr^{3+}}][\mathrm{X^-}]^3x^n. \tag{6}$$

Since the extraction constants for the acid and sodium salts have been defined by using y in previous studies, the extraction constant defined by x is distinguished by the asterisk mark on it. On the basis of Eq. 6, the value of x was calculated by a successive-approximation method in the process of calculating the extraction constant. The values of the known constants are: $K_{\mathrm{ex,H}(l)} = 1600$ ($\mathrm{HClO_4}$, $l = 2$), 320 (HSCN, $l = 1$), 60 (HI, $l = 2$), 7.2 ($\mathrm{HNO_3}$, $l = 1$), 2.2 (HBr, $l = 2$), and $K_{\mathrm{ex,Na(3)}} = 10.3$ ($\mathrm{NaClO_4}$), 2.4 (NaSCN), and 0.35 (NaI), respectively. Co-extraction of sodium nitrate and sodium bromide was negligible.[9]

Extraction of Chromium(III) Salts with TOPO. The distribution ratios of the chromium(III) ion extracted from aqueous 1 mol dm^{-3} sodium salt solutions are shown in Fig. 1 against the total and calculated (x) TOPO concentration. A series of calculations was carried out assuming solvation numbers of 3 to 8. A part of the results are filed in Table 1. The constants which gave the least value of the standard deviation (S.D., defined as follows,) were taken:

$$\mathrm{S.D.} = \left\{\sum(D_{\mathrm{calc}} - D_{\mathrm{exp}})^2/N\right\}^{1/2}. \tag{7}$$

Here, D_{calc} and D_{exp} is the calculated and experimentally obtained distribution ratio of the chromium(III) ion, respectively; N is number of experimental data employed for the calculation.

The slope of the solid lines in the figure is given by integers: 6 for $\mathrm{X^-} = \mathrm{ClO_4^-}$ and $\mathrm{SCN^-}$, 5 for $\mathrm{I^-}$ and $\mathrm{Br^-}$, and 4 for $\mathrm{NO_3^-}$. The extraction behavior of the nitrate is discussed in the next paragraph. For thiocyanate, only the upper 8 points in Fig. 1 were used for the calculation. When all of the points were used, the calculations even using two constants in combination of $n = 3$ and 6, 4 and 6, or 5 and 6 did not give any effective improvement.

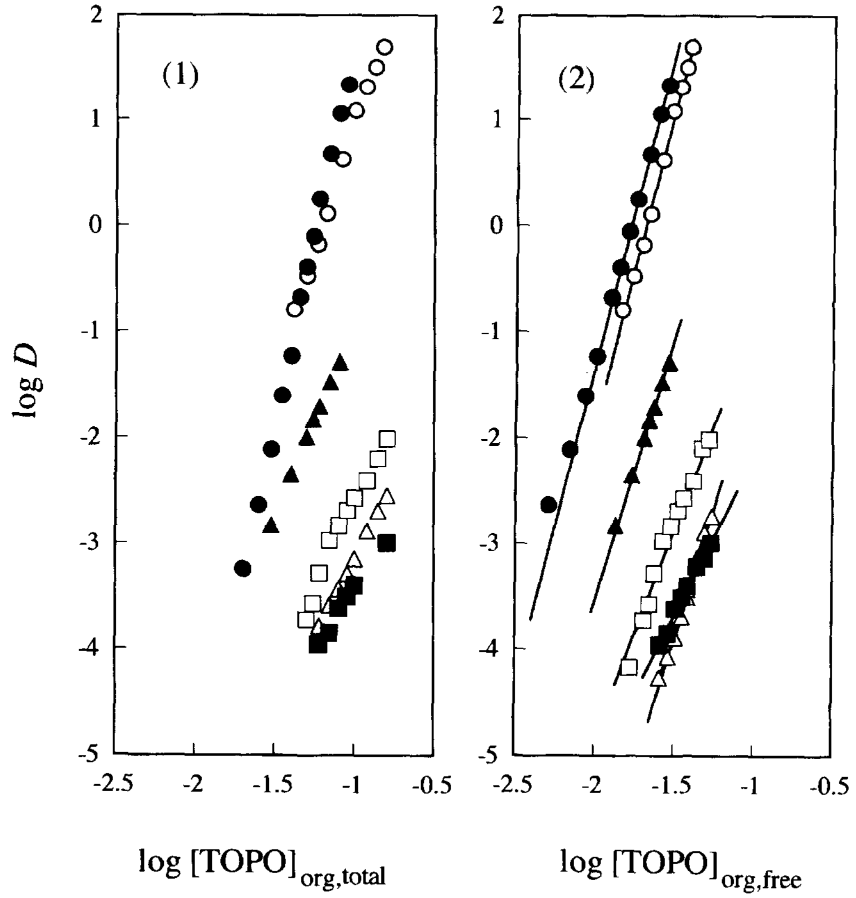

Fig. 1. Extraction of the chromium(III) salts with TOPO in hexane from aqueous 1 mol dm^{-3} NaX solutions containing 0.01 mol dm^{-3} sulfuric acid. X^- is SCN^- (●), ClO_4^- (○), I^- (▲), NO_3^- (□), and Br^- (△). Closed squares indicate the "background" extraction where the aqueous solution does not contain any sodium salts.

Table 1. Results of the Calculation for the Extraction Constant of the Chromium(III) Salts Assuming the Solvation of *n* TOPO Molecules

n	ClO_4^-		SCN^-		I^-		Br^-	
	$\log K^*_{ex,n}$	S.D.	$\log K^*_{ex,n}$	S.D.	$\log K^*_{ex,n}$	S.D.	$\log K^*_{ex,n}$	S.D.
4	6.94 ± 0.82	0.3141	7.18 ± 0.75	0.2554	4.77 ± 0.20	0.0749	2.13 ± 0.30	0.1134
5	8.53 ± 0.46	0.1676	8.93 ± 0.33	0.1126	$\underline{6.41 \pm 0.09}$	0.0325	$\underline{3.56 \pm 0.13}$	0.0484
6	$\underline{10.13 \pm 0.14}$	0.0543	$\underline{10.67 \pm 0.09}$	0.0290	8.14 ± 0.38	0.1391	4.97 ± 0.31	0.1188
7	11.73 ± 0.41	0.1514	12.42 ± 0.46	0.1591	9.83 ± 0.65	0.2385	6.41 ± 0.59	0.2190

The limit of errors is the value to give 3σ. The underlined values are taken as the best fit constant.

Since all of these aqueous phases contained a small amount of perchlorate ion originating from the crystals of this metal salt, the extraction of the chromium(III) ion from the aqueous solution in which any sodium salts were added was measured as the "background extraction". The results are shown in Fig. 1 by the filled squares. The slope of this plot was three, which means that this will be other extraction than the perchlorate since the chromium(III) perchlorate is extracted as $n = 6$. The co-existing anions were 0.019 mol dm^{-3} perchlorate ion, 0.01 mol dm^{-3} of the sulfate or hydrogen sulfate ion, and very small amount of hydroxide ion (pH may be approximately 1.8). The hydrolysis of chromium(III) ion in aqueous solution should be negligible because the equilibrium constant as $\log [CrOH^{2+}][H^+]/[Cr^{3+}]$ is around 1×10^{-4}.[10] Although the chemical form of this background extraction is not yet known, it is necessary to take it into account to calculate the net distribution ratio of the bromide, because the extraction of chromium(III) bromide from a 1 mol dm^{-3} sodium bromide solution was of a similar magnitude to that of the "background extraction". For all practical purposes, the "background extraction" was represented as some species with an extraction constant of $K^*_{ex,3} = 6.5$ supposing $[X^-] = 1$ mol dm^{-3} although the concentration of anions is not unity. A calculation for bromide was carried out by applying this "background extraction".

In the calculation for iodide, the combination of two extraction constants, $n = 4$ and 5, gave a remarkable decrease in the S.D. value to 0.0086. The values of the constants were $\log K^*_{ex,4} = 4.21 \pm 0.09$ and $\log K^*_{ex,5} = 6.30 \pm 0.03$. Nevertheless, the present author preferred to use the simpler result given in Table 1, because the extraction of bromide could be explained with a single constant.

Rate of Extraction of the Chromium(III) Nitrate. The extraction equilibrium of chromium(III) perchlorate with TOPO in hexane can be attained within several minutes.[4] Similar experiments were also carried out in the present study. The distribution ratios at different agitation times are shown in Fig. 2 for other chromium(III) salts. Only extraction from a nitrate solution depended on the agitation time. A first-order reaction was supposed concerning the increase in the extracted nitrate. Equation 8 can be written by using the value of infinite concentration of chromium(III) ion in the organic phase, $[\mathrm{Cr}^{3+}]_{\mathrm{org},\infty}$. This value was obtained by a successive-approximation fitting of the rate data to

$$\log\{([\mathrm{Cr}^{3+}]_{\mathrm{org},\infty} - [\mathrm{Cr}^{3+}]_{\mathrm{org}})/([\mathrm{Cr}^{3+}]_{\mathrm{org},\infty} - [\mathrm{Cr}^{3+}]_{\mathrm{org,blank}})\} = -kt/2.3. \qquad (8)$$

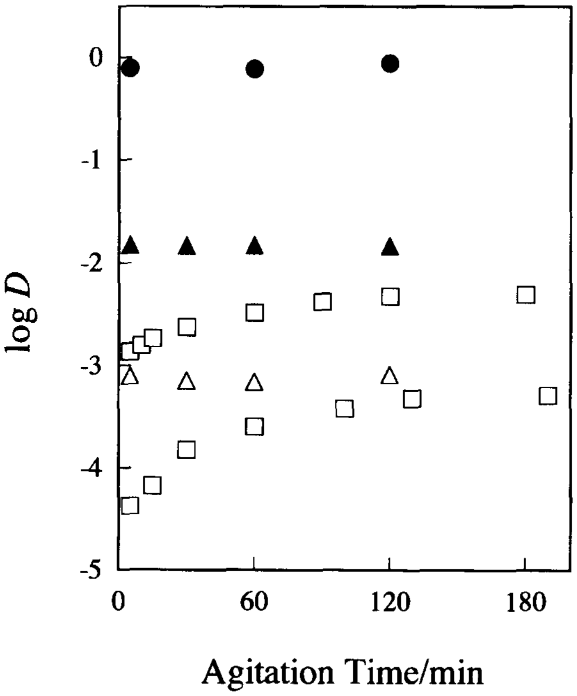

Fig. 2. Extraction of the chromium(III) salts in relation to the agitation time. The initial TOPO concentrations are : 0.055 mol dm^{-3} (● SCN$^-$ and ▲ I$^-$), 0.10 mol dm^{-3} (△ Br$^-$ and upper □ $\mathrm{NO_3}^-$), and 0.04 mol dm^{-3} (lower □ $\mathrm{NO_3}^-$).

The free TOPO concentration in each run was calculated in the manner mentioned above, and is listed in Table 2. The values of x should be constant during agitation, because the extracted amount of chromium(III) is negligible compared to the total TOPO concentrations. The chromium(III)-ion concentration in the organic phase attributed to "background extraction" was estimated by $[\mathrm{Cr}^{3+}]_{\mathrm{org,blank}} = 6.5[\mathrm{Cr}^{3+}]x^3$. The rate constant was independent of the concentration of TOPO. The extraction constant at infinite agitation was estimated from the infinite distribution ratio as $K^*_{\mathrm{ex},n\infty} = D_\infty/x^n[\mathrm{NO_3}^-]^3$. As given in Table 2, the number n was estimated to be 3 and the extraction constant to be 155. Thus, the solvation number of TOPO for nitrate seems to be 5 (more exactly larger than 4) at the beginning of extraction, as can be seen in Fig. 1, but reduces to 3 during two-phase agitation.

The apparent first-order rate constant for the extraction of the nitrate was estimated to be $k = 6\times10^{-5}$ s^{-1}. This is much larger than the pseudo first-order rate constant of the exchange reaction of hydration water in an aqueous solution, 5.8×10^{-7} (at 300 K)[11] or 4.3×10^{-7} s^{-1} (at 298 K),[12] regarding the activity of water as unity. A similar order of the rate of extraction to the present results was found in the extraction of this cation with acetylacetone into carbon tetrachloride (the rate-determining reaction was guessed to be the formation of the first complex, $\mathrm{Cr(OH)^{2+}}$+Hacac).[13] It is hard to think that either the TOPO molecule or nitrate ion forms the inner complex of the chromium(III) ion. Although the residence time of water molecules in the outer hydration sphere is reported to be short in aqueous solution ($< 5\times10^{-9}$ s),[14] complete destruction and reconstruction of the second hydration shell would be not so fast. Consequently, the specific rate found in the extraction of the chromium(III) nitrate is suggested to be caused by some rearrangement of the $\mathrm{NO_3}^-$ ion in the second hydration sphere of the chromium(III) ion in the organic phase, associated with the release of hydration waters and TOPO molecules hydrogen-bonding on them. In any case, extraction at infinite agitation was taken as the result for the nitrate, even though the extraction mechanism is not yet obvious.

Hydration of Ions Extracted with TOPO. Hydration of the extracted chromium(III) perchlorate was examined by extraction from an aqueous chromium(III) perchlorate solution of very high concentration. The experimental data (the initial concentrations of Cr^{3+}, Na^+, H^+, $\mathrm{ClO_4}^-$, and TOPO and

Table 2. Extraction of the Chromium(III) Nitrate with TOPO in Hexane

$[\mathrm{TOPO}]_{\mathrm{total}}$	$[\mathrm{Cr}^{3+}]_{\mathrm{initial}}$	$\log x$[a)]	$[\mathrm{Cr}^{3+}]_{\mathrm{org,\,blank}}$[b)]	$[\mathrm{Cr}^{3+}]_{\mathrm{org},\,\infty}$	$\log(k/\mathrm{s}^{-1})$	$\log D_\infty$	$\log K^*_{\mathrm{ex},3,\infty}$
mol dm^{-3}	10^{-3} mol dm^{-3}		10^{-7} mol dm^{-3}	10^{-5} mol dm^{-3}			
0.040	4.99	−1.776	2.0	0.38	−4.31	−3.118	2.21
0.055	4.99	−1.655	4.5	1.00	−4.02	−2.698	2.27
0.070	4.93	−1.567	7.9	1.17	−4.34	−2.625	2.08
0.100	4.93	−1.440	18.6	3.62	−4.31	−2.134	2.19
Average					−4.25		2.19

a) The x is free TOPO concentration corrected for the co-extraction of $\mathrm{H_2O}$ and $\mathrm{HNO_3}$. b) The chromium(III)-ion concentration in hexane attributed to the "background extraction" calculated by $[\mathrm{Cr}^{3+}]_{\mathrm{org,blank}} = 6.5[\mathrm{Cr}^{3+}]x^3$.

the equilibrated concentration of the Cr^{3+} ion in the organic phase) were treated by the same program to calculate the extraction constant of chromium(III) perchlorate. In this extraction system the co-extraction of $HClO_4$ and $NaClO_4$ and, consequently, the extraction of water accompanied by these species, was negligible, since the greatest amount of TOPO was consumed by solvation to chromium(III) ion. From this calculation the extraction constant was obtained to be $\log K^{*}_{ex,6} = 10.12 \pm 0.41$ (S.D. = 0.1014), which is almost the same value as that given in Table 1. This coincidence should be the proof of the assumption that the aggregation of the extracted metal salt is negligible. The hydration number (h_n) was calculated by

$$h_n = ([H_2O]_{org,total} - [H_2O]_{org,blank} - [TOPO\cdot H_2O]_{org} - 3[2TOPO\cdot 3H_2O]_{org})/[Cr(III)]_{org,total} = ([H_2O]_{org,total} - 3\times 10^{-3} - K_{11}x - 3K_{23}x^2)/[Cr(III)]_{org}. \qquad (9)$$

The value of x for each experiment was calculated in the process of calculating the extraction constant. Thus, the hydration number of chromium(III) salt in the organic phase was obtained from the measured total concentration of water and chromium(III) ion in the organic phase. The obtained hydration number is shown in Fig. 3 against the extracted amount of the metal ion. The averaged value was 17.2±0.5 for the hexasolvate of TOPO.

The hydration number of the chromium(III) ion in an aqueous perchlorate solution has been reported to be 19 from trace diffusion,[15] 18—20 from solution X-ray diffraction,[16] and 21—24 from neutron diffraction.[17] Broadbent et al.[17] have stated that anions intruding into the outer-hydration sphere is the reason for the uncertain hydration number. Thus, most of the hydration waters of the chromium(III) ion in aqueous solution are transferred to the organic phase when it is extracted as the perchlorate in the present system. The hydration number of the calcium(II) ion in nitrobenzene (where the ions are dissociated) has been reported to be 14,[18] which is also similar in aqueous solution. However, the calcium(II) perchlorate is extracted with TOPO in hexane together with only 2—3 molecules of water.[7] This drastic reduction of the hydration number of chromium(III) ion does not occur in the extraction of chromium(III) perchlorate. Although the hydration numbers of the other chromium salts were not measured, they may be similar or smaller than this; the cation should hold at least the first hydration sphere of six H_2O molecules. Imura et al. extracted chromium(III) trichloroacetate with TOPO into cyclohexane, and reported the solvation number of TOPO to be three and the hydration number of the extract to be 6.2.[19] Since the TOPO molecules are believed to be hydrogen-bonded with the hydration water of the chromium(III) ion, this small solvation number of TOPO would correspond to the loss of outer hydration shell.

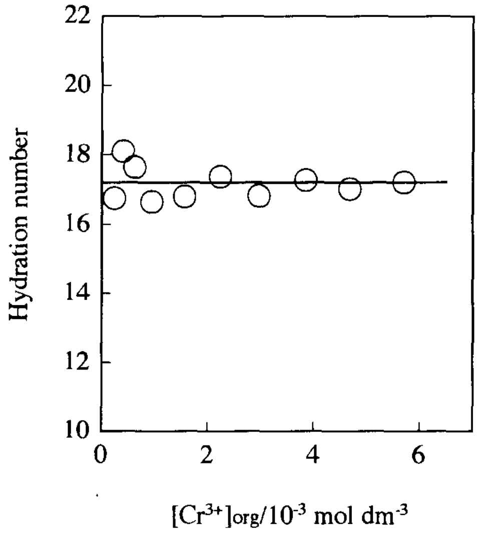

Fig. 3. The hydration number of the chromium(III) perchlorate extracted with TOPO in hexane. Concentration of TOPO is calculated by supposing the hexasolvate. Solid line gives $h_n = 17.2$.

On the basis of the OH and OD stretching band, Bergström[16] pointed out that the second-sphere water molecules of trivalent cations form hydrogen bonds with the outer water with comparable strength to those formed by the first sphere water molecules of divalent cations, e.g., Ni^{2+} and Mg^{2+}. In extraction with TOPO these divalent metal perchlorates are extracted as tetrasolvate and hexa- or heptasolvate.[3] The hydration number of the tetrasolvate is 0 (Ni^{2+}) and 4—6 (Mg^{2+}), but that of both hexa- and pentasolvate is 13. Thus, the hydration behavior of the chromium(III) perchlorate seems to be similar to that of the hexasolvate of these divalent metal ions, but that of the trichloroacetate resembles the tetrasolvate of these divalent metal ions. Therefore, the chromium(III) ion would lose the water molecules of the second hydration sphere as easily as the tetrasolvates of these divalent metal perchlorates lose the first hydration sphere. In the other words, the second hydration sphere of the chromium(III) ion would be easily removed, and the hydration number is supposed to be different when chromium(III) ion is extracted with different counter ions or with a different solvation number of TOPO.

This difference may be caused by the affinity of the anions to the hydration water. Some anions also hydrate in organic solvents. For example, when these anion are extracted into nitrobenzene, the hydration number in it is: 4.0 (Cl^-), 2.1 (Br^-), 1.7 (NO_3^-), 1.1 (SCN^-), 0.9 (I^-), and 0.2 (ClO_4^-).[18] Also, the hydration number of these ions extracted as an ion pair with a tetrabutylammonium ion into 1,2-dichloroethane is: 2.7 (Cl^-), 2.0 (Br^-), 1.3 (NO_3^-), 1.0 (SCN^-), 0.8 (I^-), and 0.3 (ClO_4^-).[5] This hydration on anions can be explained as follows. The basicity of an anion is evaluated based on an experimental parameter of donicity, donor number (DN) of Gutmann, from the adduct formation equilibrium of bis(acetylacetonato)oxovanadium(IV) in nitromethane as: I^- 15.8, Br^- 20.7, Cl^- 26.2, SCN^- 35.7.[20] The enthalpy of electron donor-electron acceptor association has been proposed in combination with the acceptor number (AN) of the electron accepting substance as $\Delta H = DN \times AN/100$ in kcal mol^{-1}.[21] Since the acceptor number for H_2O is 56, this estimation gives 40—80 kJ mol^{-1} for ΔH on the association of water and these anions. This means that they have a rather strong affinity to water in aprotic solvents. Since the anions are separated from cations in nitrobenzene, hydration of anions should be independent of the kind of counter cation. Suppose that the anions of chromium(III) salts in the organic phase stay in the second hydration sphere. Under such circumstances an anion would compete with the water molecule of the second hydration sphere of the chromium(III) ion for the hydrogen-bonding site of the first hydration sphere. If the ability to form a hydrogen bond corresponds to the donor number, it may be in the order $I^- < H_2O < Br^- < SCN^-$, since the donor number for water is 18.0. Thus, some anions might replace the second hydration water with them, whereas others do not.

Extractability of Chromium(III) Salts with TOPO. The magnitude of extraction constants of metal salts can only be compared numerically with each other so long as the dimensions concerning to the TOPO concentration are the same in the definition of the extraction constant. Thus, it is compared by the free energy of extraction, given by

$$\Delta G^\circ_{\mathrm{ex}} = -RT\ln K^*_{\mathrm{ex},n}. \qquad (10)$$

The value $K^*_{\mathrm{ex},n}$ gives the distribution ratio of the metal ion between an aqueous solution containing the X^- ion by 1 mol dm^{-3} and an organic solution containing free TOPO by 1 mol dm^{-3}. This is only an ideal extraction system, because at least the solubility of TOPO into hexane is limited. In the present extraction system the extracted species may be regarded as an ion pair of a large trivalent cation solvating TOPO molecules. Thus, the results can be compared with another typical ion-pair extraction system. For such a typical system, the extraction of tetrabutylammonium salts (TBA^+X^-) into 1,2-dichloroethane[5] may be suitable. Although nitrobenzene or chloroform is widely utilized as a solvent for the extraction of ionic salts, extracted salts into nitrobenzene are almost completely dissociated into the component ions and chloroform is a solvent of hydrogen-bond donor in which hydrogen-bonding species may specifically behave. The extraction of tetraalkylammonium salts to xylene would be also desirable from this aspect; however, the results given in the literature[22] are not sufficient with respect to the kind of anion. The extraction constant of tetrabutylammonium salt is defined as $K_{\mathrm{ex}} = [TBA^+X^-]_{\mathrm{org}}/[TBA^+][X^-]$ and the free energy of extraction is defined in a similar manner to Eq. 10. In Fig. 4, the free energy of extraction for the chromium(III) salts is plotted against that of tetrabutylammonium salts. The broken lines are drawn with a slope of 3 so as to pass on the point for the perchlorate or thiocyanate. If most points fall on the line, the extraction behavior of both extraction systems resembles each other. The scattered points in Fig. 4 indicate that the results are not so. For example, the chromium(III) perchlorate and chromium(III) thiocyanate, which have identical solvation numbers of TOPO, give a similar magnitude of free energy of extraction. From the standpoint of ion-pair extraction, however, the point for the thiocyanate in Fig. 4 deviates by ca. 30 kJ mol^{-1} upward from the corresponding point on the line given to pass on the point for the perchlorate. This means that chromium(III) thiocyanate has an advantage by ca. 30 kJ mol^{-1} in the processes of extraction with TOPO. In the above paragraph, the enthalpy of the association of the anion and water is estimated to be 40—80 kJ mol^{-1}. Not all of this energy would contribute to the free energy of extraction, because this enthalpy is effective in both aqueous and organic solutions. In any case, the affinity of the anion to the hydration water of the chromium(III) ion may play an important role in the present extraction system.

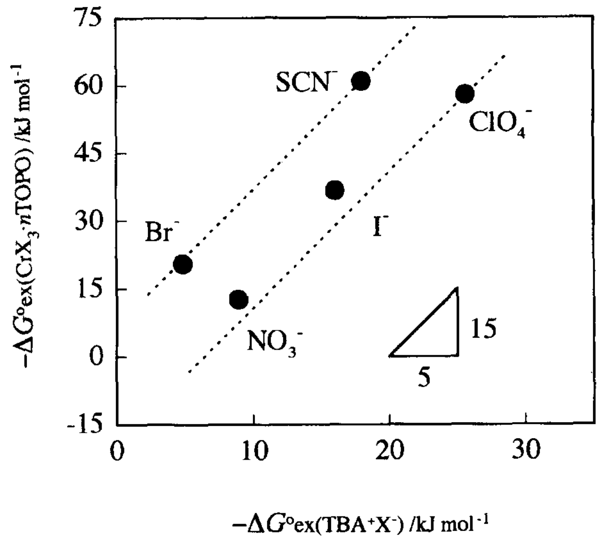

Fig. 4. Gibbs free energy of the extraction of chromium(III) salts with TOPO in hexane plotted against the Gibbs free energy of an ion-pair extraction of the tetrabutylammonium salts into 1,2-dichloroethane. The broken lines are drawn with the slope of 3 so as to pass on the point of perchlorate or thiocyanate.

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