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The Extraction of the Chromium(III) Ion from Trichloroacetate Solutions to Inert Solvents Containing Trioctylphosphine Oxide

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Chromium(III) has been extracted with 0.1 mol dm^{-3} trioctylphosphine oxide(TOPO) in various inert solvents from a 0.1 mol dm^{-3} trichloroacetate(TCA$^-$) buffer solution of pH 3.5 to 6.0. As diluents of TOPO, hexane and cyclohexane are most effective, while chloroform is quite ineffective. The extraction mechanism has been clarified by analyzing separately the distribution of water, trichloroacetic acid(HTCA), and the Cr(III) ion between the aqueous and organic phases. Water and HTCA are present in the cyclohexane phase as $H_2O \cdot TOPO$ and HTCA·TOPO respectively. Chromium(III) is extracted with TOPO into cyclohexane as an ion-association complex like $Cr(H_2O)_6{}^{3+}(TCA^-)_3 \cdot 3TOPO$, and the extraction constant is $10^{7.68}$. It is concluded that the hexahydrated Cr(III) ion is solvated by three molecules of TOPO, forming an ion pair with three trichloroacetate anions. The extractability of Cr(III) in the present system depends most effectively on the concentration of HTCA-free TOPO in the organic phase.

In a previous report,[1] the present authors found that many metal ions, such as Th(IV), Bi(III), Tm(III), Fe(III), Cr(III), Al(III), Hg(II), Co(II), Mn(II), Ba(II), Ca(II), and Cs(I), could be extracted from trichloroacetate(TCA$^-$) buffer solutions into polar solvents involving a donor oxygen atom, but not into inert solvents. Additionally, chromiun(III) could be quantitatively extracted with not only polar organic solvents such as isopentyl alcohol, but also with benzene containing trioctylphosphine oxide(TOPO). From the similarity of the visible absorption spectra and the paper electrophoretic behavior of the extracted metals to those of the corresponding metal ions in the aqueous solution, an extraction mechanism of metal ions involving the formation of ion pairs of hydrated metal ions with trichloroacetate anions and solvation by polar solvents has previously been proposed.[1] On the other hand, recently several authors have reported that trichloroacetic acid(HTCA) forms extractable mixed-ligand complexes[2,3] or ion-pair complexes with positively charged chelates.[4]

The extraction of Cr(III) from trichloroacetate buffer solutions with inert solvents containing TOPO is very interesting as a means of clarifying the extraction mechanism in the ion-association system. In the present system, water, trichloroacetate, and TOPO all participate in the extraction process of Cr(III); their effects have been analyzed separately.

Experimental

Reagents. The trichloroacetic acid was purchased from the Kishida Chemical Co. and was dissolved in re-distilled water. A series of buffer solutions (pH 0—10) was prepared by mixing a HTCA solution (10^{-3}—0.2 mol dm^{-3}) and a sodium hydroxide solution of the same concentration as the HTCA solution used. Hereafter, a series of buffer solutions, for instance, prepared by mixing 0.2 mol dm^{-3} HTCA and 0.2 mol dm^{-3} NaOH, will be noted as the 0.1 mol dm^{-3} trichloroacetate buffer solution.

The trioctylphosphine oxide was obtained from the Dojindo Co.

The chromium(III) solution was prepared by dissolving its high-purity metal in 2 mol dm^{-3} hydrochloric acid. The radioisotope, ^{51}Cr, used as a tracer was purchased from the New England Nuclear Co. (U.S.A.).

The organic solvents, such as cyclohexane, benzene, carbon tetrachloride, and chloroform, were purified by the usual methods. The other reagents were of a guaranteed reagent grade and were used without further purification.

Apparatus. The electronic absorption spectra were measured with a Hitachi Model 323 recording spectrophotometer.

The pH value of an aqueous phase was measured with Hitachi-Horiba pH meters, M-5 and M-7.

A Kobe Kogyo Co., Model STL-200(NaI(Tl) crystal), well-type scintillation counter was used for the γ-counting.

An Iwaki KM-Shaker was used for the agitation of an aqueous and an organic phase at 340 strokes per min.

The water content of an organic phase was determined by using a Karl Fisher-Titrator E 452 Metrom.

Extraction and Back-extraction Procedure. In a 50-cm^3 centrifuge tube with a ground-glass stopper, 10 cm^3 of an inert organic solvent containing from 10^{-3} to 10^{-1} mol dm^{-3} TOPO was placed, then 10 cm^3 of a trichloroacetate buffer solution, adjusted to the desired pH value, containing from 10^{-4} to 10^{-1} mol dm^{-3} of the Cr(III) ion, and its radioactive tracer were added. Then the contents were vigorously shaken by using a shaker for 1 to 20 min at room temperature (20—25 °C). After centrifugation, a 3-cm^3 portion was pipeted out from each phase, then the radioactivity was counted by the use of a scintillation counter, and the percentage of extraction(%E) of Cr(III) was calculated from the ratio of the counting rate of the two phases: $\%E = D/(1+D) \times 100$, where D is the distribution ratio of Cr(III). The pH value of the aqueous phase was measured after the extraction equilibrium had been established in all cases.

In the back-extraction procedure, 5 cm^3 of the organic phase, prepared by the extraction procedure described above, was shaken with 5 cm^3 of a trichloroacetate buffer solution adjusted to the desired pH value for from 1 to 20 min. The percentage of back-extraction(%E_b) was determined in the same manner as in the extraction procedure.

Determination of Trichloroacetic Acid. The method described in the literature[5] was somewhat modified for the determination of the trichloroacetate ion in the present investigation: the concentration of the trichloroacetate buffer solution used in this investigation was too high to be determined by Fujiwara's pyridine-alkali reaction; therefore, after

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the extraction, 5 $\mathrm{cm^3}$ of the aqueous phase was taken out and diluted with water to form about a 10^{-4} mol $\mathrm{dm^{-3}}$ trichloroacetate solution. Thus, a test solution was prepared. In a 20-$\mathrm{cm^3}$ centrifuge tube, a 1-$\mathrm{cm^3}$ portion of the test solution was placed together with 5 $\mathrm{cm^3}$ of pyridine. Ten $\mathrm{cm^3}$ of a 10 mol $\mathrm{dm^{-3}}$ sodium hydroxide solution was then added, and the content were vigorously shaken for 1 to 2 min. The tube was kept at 92±2 °C for just 3 min in a thermostat. After dipping the tube in water to cool it for 3 min, it was allowed to stand at room temperature for 30 to 60 min. Immediately after centrifugation, the absorbance of the pyridine layer was measured at 520 nm against the reagent blank.

Determination of Water Content of Organic Phase. In order to determine the water content of the cyclohexane phase after the extraction, an aliquot of the organic phase was submitted to Karl Fisher titration by the amperometric method. The potencies of the Karl Fisher reagent used were 1.9 to 2.6 mg $\mathrm{H_2O/cm^3}$.

Results and Discussion

We tried to use various solvents as diluents of TOPO for the extraction of Cr(III) from a 0.1 mol $\mathrm{dm^{-3}}$ trichloroacetate buffer solution. The results are shown in Fig. 1, where the extraction decreases in this order: hexane, cyclohexane>toluene>benzene>nitrobenzene, carbon tetrachloride>chloroform. This order agrees with that observed in the extraction of europium nitrate with tributylphosphate in various diluents.[6] In the present extraction system, the effect of diluents may be ascribable to the differences in the interaction between TOPO and each diluent molecule, *e.g.*, dispersion forces, dipole-dipole interactions, or hydrogen bonds. In Fig. 1 the lowering of the distribution ratio of Cr(III) in the range of pH values higher than 5 is ascribed to the precipitation of the hydrated Cr(III) oxide in this pH range.

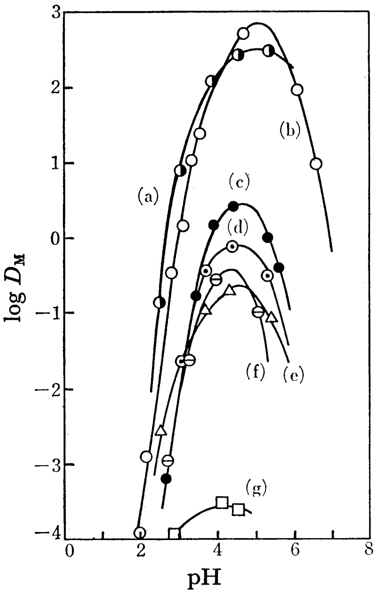

Fig. 1. Extraction of Cr(III) from 0.1 mol $\mathrm{dm^{-3}}$ TCA$^-$ buffer solution into various organic solvents containing TOPO in 0.1 mol $\mathrm{dm^{-3}}$. Hexane(a), cyclohexane(b), toluene(c), benzene(d), nitrobenzene(e), carbon tetrachloride(f), chloroform(g).

Chromium(III) could also be extracted from perchlorate solutions into cyclohexane containing 0.1 mol $\mathrm{dm^{-3}}$ TOPO, but the percentages of extraction from 0.1 mol $\mathrm{dm^{-3}}$ and 0.5 mol $\mathrm{dm^{-3}}$ perchlorate solutions at a pH value of 4.0 were only 22% and 85% respectively. In view of this fact, in place of perchlorate sodium chloride was used in order to keep the ionic strength of the aqueous phase constant (0.1). The concentrations of TOPO in cyclohexane and of trichloroacetate in the aqueous phase were kept as low as below 0.1 mol $\mathrm{dm^{-3}}$ in order to minimize the difference between the molar concentration and the thermodynamic activity.

Extraction of Water with TOPO. The extraction equilibrium of water by TOPO in cyclohexane can be given as follows:

$$\mathrm{H_2O} + q\mathrm{TOPO_{(org)}} \rightleftharpoons \mathrm{H_2O}\cdot q\mathrm{TOPO_{(org)}}, \tag{1}$$

where (org) designates the organic phase. Since the concentration of water in dilute solutions is considered constant, the extraction constant of water is written as

$$K_{\mathrm{H_2O}} = \frac{[\mathrm{H_2O}\cdot q\mathrm{TOPO}]_{\mathrm{org}}}{[\mathrm{TOPO}]^{q}_{\mathrm{org}}}. \tag{2}$$

Taking logarithms,

$$\log\,[\mathrm{H_2O}\cdot q\mathrm{TOPO}]_{\mathrm{org}} = q\log\,[\mathrm{TOPO}]_{\mathrm{org}} + \log K_{\mathrm{H_2O}}, \tag{3}$$

where $[\mathrm{TOPO}]_{\mathrm{org}}$ means the equilibrium concentration of the free TOPO. The amount of free TOPO remaining in the organic phase was calculated by deducting the amount of TOPO combined with water in the organic phase from that of the TOPO initially taken.

The plot of $\log[\mathrm{H_2O}]_{\mathrm{org}}$ *vs.* $\log[\mathrm{TOPO}]_{\mathrm{org}}$ gave a straight line with a slope of unity. From this slope, the species in cyclohexane was determined to be $\mathrm{H_2O\cdot TOPO}$, which was just compatible with the $\mathrm{H_2O\cdot TOPO}$ in carbon tetrachloride reported by Conocchioli *et al.*[7]

Extraction of Trichloroacetic Acid with TOPO. The extraction equilibrium may be written as

$$\mathrm{HTCA} + i\mathrm{TOPO_{(org)}} \rightleftharpoons \mathrm{HTCA}\cdot i\mathrm{TOPO_{(org)}}. \tag{4}$$

Therefore, the extraction constant of trichloroacetic acid is

$$K_{\mathrm{HTCA}} = \frac{[\mathrm{HTCA}\cdot i\mathrm{TOPO}]_{\mathrm{org}}}{[\mathrm{HTCA}][\mathrm{TOPO}]^{i}_{\mathrm{org}}}. \tag{5}$$

In the above equation, water is put aside out of consideration. As will be described later, the water molecule present as $\mathrm{H_2O\cdot TOPO}$ in the organic phase may be readily exchanged with trichloroacetic acid. Therefore, it can be assumed that the formation of the water complex of TOPO has no influence on the extraction of trichloroacetic acid. Then, the dissociation equilibrium of trichloroacetic acid in the aqueous phase is also given:

$$\mathrm{HTCA} \rightleftharpoons \mathrm{TCA^-} + \mathrm{H^+}. \tag{6}$$

The acid dissociation constant of HTCA is

$$K_{\mathrm{a}} = \frac{[\mathrm{TCA^-}][\mathrm{H^+}]}{[\mathrm{HTCA}]}. \tag{7}$$

Equation 5 is rewritten by putting Eq. 7 in it,

$$K_{\mathrm{HTCA}} = \frac{K_a[\mathrm{HTCA}\cdot i\mathrm{TOPO}]_{\mathrm{org}}}{[\mathrm{TCA}^-][\mathrm{H}^+][\mathrm{TOPO}]^i_{\mathrm{org}}} = \frac{D_{\mathrm{HTCA}}K_a}{[\mathrm{H}^+][\mathrm{TOPO}]^i_{\mathrm{org}}}, \qquad (8)$$

where D_{HTCA} is the distribution ratio of trichloroacetic acid. Taking logarithms of Eq. 8,

$$\log D_{\mathrm{HTCA}} = i\log[\mathrm{TOPO}]_{\mathrm{org}} - \mathrm{pH} - \log K_a + \log K_{\mathrm{HTCA}}. \qquad (9)$$

D_{HTCA} was determined at varying pH values of the aqueous phase for the equilibrium with various concentrations of TOPO as has been described above. Some of the results obtained are shown in Fig. 2, which indicates that the concentration of trichloroacetic acid in the organic phase decreases with the increase in the pH. This suggests that the concentration of TOPO free from trichloroacetic acid increases with the increase in the pH and that almost all of the TOPO becomes free from acid above pH 5.0.

On the other hand, the equilibrium concentration of water in the organic phase after the extraction of trichloroacetic acid is shown against the pH value of the aqueous phase in Fig. 3(a). Water is found to be released from cyclohexane with a lowering of the pH value until pH 2, and then the water concentration nearly reaches solubility in pure cyclohexane. Superposing this Fig. 3(a) on Fig. 2, it can be seen that TOPO tends to combine more strongly with trichloroacetic acid than with water, because the concentration of trichloroacetic acid in the organic phase shows a reverse trend to that of water.

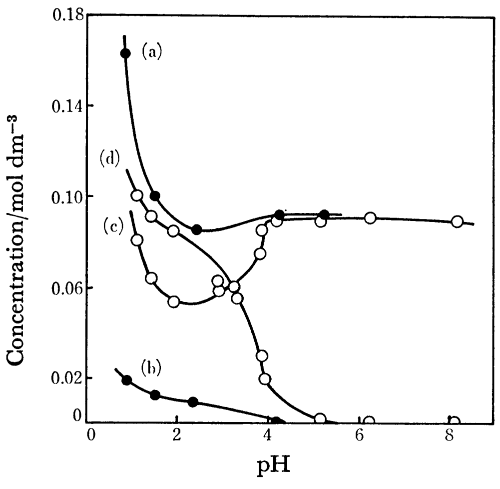

Fig. 2. Concentration of trichloroacetic acid in the organic and the aqueous phase after the extraction from 0.1 mol dm^{-3} TCA$^-$ buffer solution of various pH values. (a) and (c): HTCA in the aqueous phase, (b) and (d): HTCA in the organic phase, (a) and (b): the concentration of TOPO in cyclohexane is 0.01 mol dm^{-3}. (c) and (d): The concentration of TOPO in cyclohexane is 0.1 mol dm^{-3}.

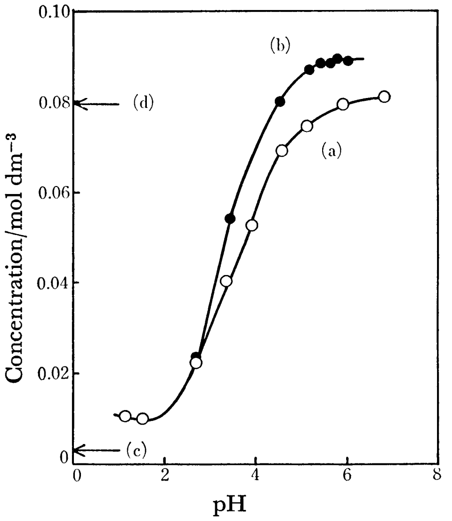

Fig. 3. Water content in the organic phase after the extraction at various pH values. (a): 0.1 mol dm^{-3} TOPO in cyclohexane—0.1 mol dm^{-3} TCA$^-$ buffer solution system, (b): in the presence of 1.9×10^{-3} mol dm^{-3} Cr(III), (c): water content in pure cyclohexane, (d): water content in cyclohexane containing TOPO in 0.1 mol dm^{-3}.

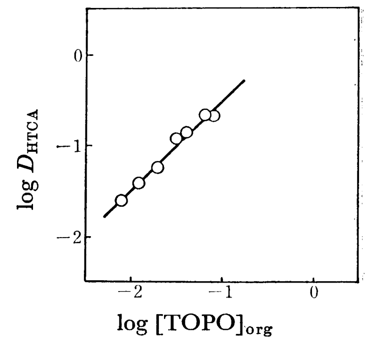

Fig. 4. Plot of log D_{HTCA} vs. log[TOPO]$_{\mathrm{org}}$ at pH 4.0. Aqueous phase: 0.1 mol dm^{-3} TCA$^-$ buffer solution.

Since TOPO molecules combined with water are readily available for the extraction of trichloroacetic acid, the complex formation of TOPO with water may be negligible in this acid-extraction equilibrium. Therefore, in Eq.9 the equilibrium concentration of TOPO was calculated by deducting the amount of TOPO combined with trichloroacetic acid in the organic phase from that of TOPO initially taken, that is, $[\mathrm{TOPO}]_{\mathrm{org}}$ (acid extraction) = [TOPO](initial) $-i[\mathrm{HTCA}\cdot i\mathrm{TOPO}]$. From Fig. 2, the concentration of TOPO combined with trichloroacetic acid was obtained directly from the concentration of trichloroacetic acid in the organic phase. The log-log plot of D_{HTCA} *vs.* the equilibrium concentration of TOPO obtained by calculating as $i=1$ is shown in Fig. 4, in which the log-log plot has a slope of unity. When the D_{HTCA} was plotted against the equilibrium concentration of TOPO obtained by assuming $i=2$ or $i=3$, no slope consistent with the assumed value of i was obtained. Consequently, the species of trichloroacetic acid extracted in cyclohexane was identified as HTCA·TOPO, and the extraction constant of trichloroacetic acid, $K_{\mathrm{HTCA}}=10^{3.8}$ was obtained by putting known numerical values in Eq. 9. Compared with the extraction of other acids with TOPO,[8] the extraction constant of trichloroacetic acid is larger than those of such other acid as perchloric and thiocyanic acid. This may be attributed to the larger molar volume of trichloroacetic acid.

Extraction of Cr(III) with TOPO. Compared with the two simple cases above, the equilibria of the whole extraction process of Cr(III) from trichloroacetate buffer solutions into cyclohexane containing TOPO may be more complicated. The present authors tried first the extraction and the back-extraction of Cr(III). In Fig. 5 the results are shown, together with the extraction conditions. The extraction and the back-extraction curves are symmetrical with each other; therefore, the whole extraction process may be reversible under the given conditions, and the attainment of the equilibria may be as quick as 1 min. In addition, the extraction of Cr(III) in varying amounts was carried out under the same conditions as in the foregoing experiment; the results are shown in Fig.6. When the initial concentration of Cr(III) was less than 2×10^{-3} mol dm^{-3}, the distribution ratio of Cr(III) was constant at a pH value of 3.5. The polymerized or dissociated species of Cr(III) in the organic phase can be left out of consideration. From these results, the present authors obtain the following equation:

$$\mathrm{Cr(H_2O)_6^{3+}} + m\mathrm{TCA^-} + n\mathrm{TOPO_{(org)}} \rightleftharpoons$$
$$\mathrm{Cr(H_2O)}_p{}^{3+}(\mathrm{TCA^-})_m\cdot n\mathrm{TOPO_{(org)}} + (6-p)\mathrm{H_2O} \quad (10)$$

$$K_\mathrm{M} = \frac{[\mathrm{Cr(H_2O)}_p^{3+}(\mathrm{TCA^-})_m\cdot n\mathrm{TOPO}]_\mathrm{org}}{[\mathrm{Cr(H_2O)_6^{3+}}][\mathrm{TCA^-}]^m[\mathrm{TOPO}]^n_\mathrm{org}}$$
$$= \frac{D_\mathrm{M}}{[\mathrm{TCA^-}]^m[\mathrm{TOPO}]^n_\mathrm{org}}, \quad (11)$$

where K_M is the extraction constant of Cr(III), and D_M, the distribution ratio. Taking logarithms of Eq. 11,

$$\log D_\mathrm{M} = m\log[\mathrm{TCA^-}] + n\log[\mathrm{TOPO}]_\mathrm{org} + \log K_\mathrm{M}. \quad (12)$$

Equation 12 is rewritten by putting Eq. 9 in it:

$$\log D_\mathrm{M} = m\log[\mathrm{TCA^-}] + n\,\mathrm{pH} + \log K_\mathrm{M}$$
$$-n\log K_\mathrm{HTCA} + n\log D_\mathrm{HTCA} + n\log K_\mathrm{a}. \quad (13)$$

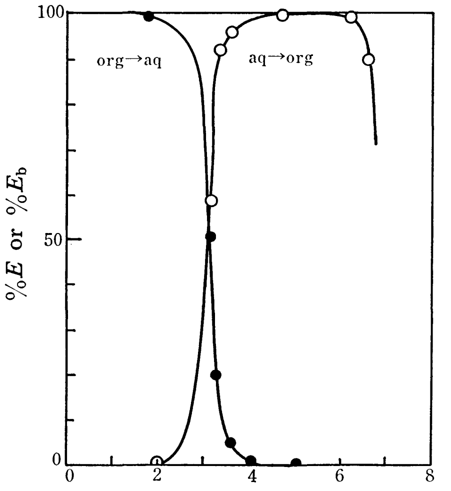

Fig. 5. Extraction and back-extraction of Cr(III) in 0.1 mol dm^{-3} TOPO - cyclohexane - 0.1 mol dm^{-3} TCA$^-$ buffer system. Concentration of Cr(III): 2×10^{-4} mol dm^{-3}, shaking time: 5 min.

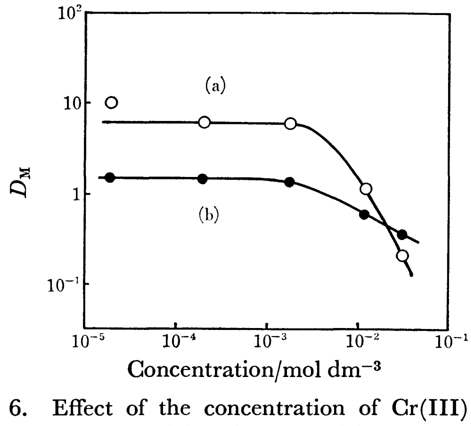

Fig. 6. Effect of the concentration of Cr(III) on the extraction from 0.1 mol dm^{-3} TCA$^-$ buffer solution of pH 3.5. (a): 0.1 mol dm^{-3} TOPO in cyclohexane, (b): 0.2 mol dm^{-3} TOPO in benzene.

Then the number of trichloroacetate ions participating in the extraction equilibrium of Cr(III) was estimated. The equilibrium concentration of trichloroacetate in the aqueous phase was obtained directly from Fig.2 without any corrections for the trichloroacetate extracted together with Cr(III), since the concentration of Cr(III) was as low as 2×10^{-4} mol dm^{-3}. The plot of $\log D_\mathrm{M}$ *vs.* $\log[\mathrm{TCA^-}]$ at a constant pH value has a slope of $m=3$, as is shown in Fig. 7. This suggests that the electrically neutral species, $\mathrm{Cr(H_2O)}_p{}^{3+}(\mathrm{TCA^-})_3$, is formed in the aqueous phase and is extracted with TOPO into the organic phase.

The ratio of Cr(III) to TOPO in the extracted species was determined by plotting $\log D_\mathrm{M}$ against $\log[\mathrm{TOPO}]_\mathrm{org}$ at a constant TCA$^-$ concentration. The equilibrium concentration of TOPO was calculated in the same manner as in the acid extraction described above. As is shown in Fig. 8, the log-log plot has a slope of $n=3$, so the chromium(III) ion seemed to be solvated with three TOPO molecules.

The difference in the water concentration, as is shown in Fig. 3(a,b), shows that the additional water is extracted with Cr(III). The relationship between the concentration of Cr(III) extracted in the cyclohexane phase and the increment of water caused by

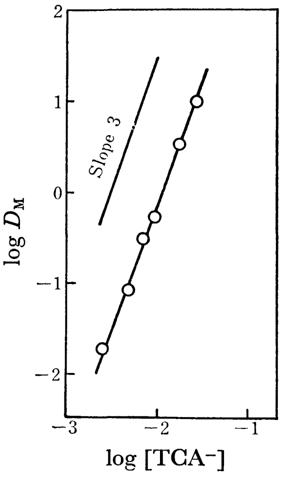

Fig. 7. Dependence of the distribution ratio of Cr(III) on the concentration of trichloroacetate in the aqueous phase at a constant pH value of 3.5.

TABLE 1. RELATIONSHIP BETWEEN THE CONCENTRATION OF Cr(III) AND THE INCREMENT OF WATER IN CYCLOHEXANE AFTER THE EXTRACTION OF Cr(III) WITH TOPO

pH of buffer solution	$[Cr]_{org}$ / 10^{-2} mol dm^{-3}	$[H_2O]_{org}$ / 10^{-2} mol dm^{-3}	$[H_2O]_{org}/[Cr]_{org}$
3.00[a]	0.067	0.45	6.7
3.20[a]	0.14	0.90	6.4
3.33[a]	0.17	1.1	6.5
4.50[a]	0.19	1.2	6.3
5.00[a]	0.19	1.2	6.3
5.50[a]	0.19	1.1	5.8
6.00[a]	0.19	1.0	5.3
3.51[b]	1.20	7.5	6.3
			mean value$=6.2\pm0.3$

Extraction conditions: organic phase: 10 cm^3 of 0.1 mol dm^{-3} TOPO in cyclohexane, aqueous phase: 10 cm^3 of a 0.1 mol dm^{-3} TCA$^-$ buffer solution. a) The initial concentration of Cr(III) in the aqueous phase was 0.19×10^{-2} mol dm^{-3}. b) The initial concentration of Cr(III) in the aqueous phase was 3.1×10^{-2} mol dm^{-3}.

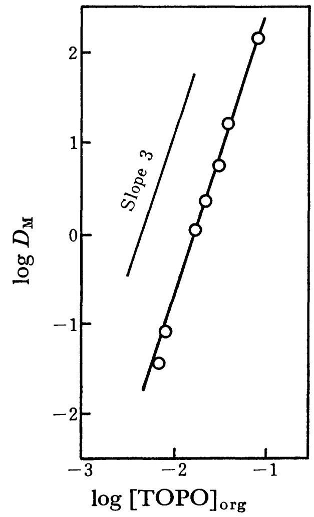

Fig. 8. Dependence of the distribution ratio of Cr(III) on the concentration of free TOPO in the organic phase at pH 4.0.

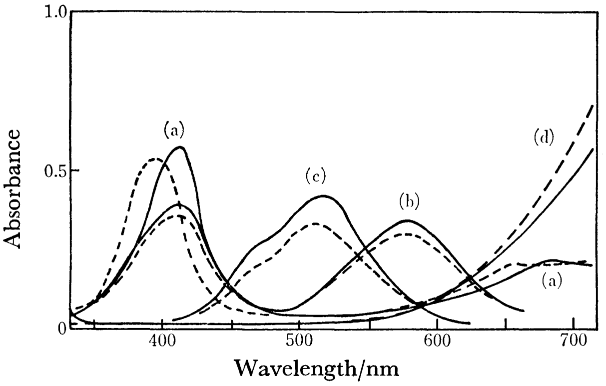

Fig. 9. Absorption spectra of the organic phase(——) after the extraction with 0.1 mol dm^{-3} TOPO and the aqueous phase(----) before the extraction. (a): Ni(II), (b): Cr(III), (c): Co(II), (d): Cu(II). Extraction conditions; organic phase: 0.1 mol dm^{-3} TOPO in cyclohexane, aqueous phase: 0.1—0.5 mol dm^{-3} TCA$^-$ buffer solution of pH 4—5.

the extraction of Cr(III) is summarized in Table 1. The amount of water co-extracted with the Cr(III)–TCA$^-$–TOPO complex is about 6.2 times that of the Cr(III) extracted. This suggests that a common species of Cr(III) in the aqueous solution, $Cr(H_2O)_6{}^{3+}$, may be extracted into the organic phase as it is.

This is confirmed by the fact that the absorption spectrum of the extracted Cr(III) species in the organic phase is similar to that of hexaaquachromium(III) in the aqueous solution(Fig. 9(b)). In Fig. 9 the spectra of Co(II), Ni(II), and Cu(II) before and after their extraction in the present system are compared with those of Cr(III). The absorption bands of Co(II), Ni(II), and Cu(II) extracted with TOPO were all shifted to longer wave lengths than those of aqua complexes in the aqueous phase. This suggests that the TOPO molecule acts on the inner solvation sphere of all the metals except Cr(III). On the other hand, a previous report[1)] has shown that the inner solvation sphere of any metal does not alter upon its extraction into isopentyl alcohol. These differences may be accounted for by the strong basicity of TOPO and the fast substitution rates of water molecules in the inner coordination sphere of metals other than Cr(III). The absorption bands of Cr(III) were gradually shifted to longer wave lengths when the extract was allowed to stand in the presence of an excess of TOPO. Moreover, the back-extraction curve shown in Fig. 5 was also shifted to a lower pH region; *i.e.*, the shift of $pH_{1/2}$, the pH at the half-extraction, was 0.5 when the extract was allowed to stand for about 48 h at room temperature. These facts suggest that the water molecules in the inner solvation sphere of the Cr(III) extracted are very slowly replaced by TOPO molecules in the organic phase.

On the basis of the above results, it may be stated that the predominant species of Cr(III) extracted from the trichloroacetate buffer solution into cyclohexane containing TOPO is the ion-association complex, $Cr(H_2O)_6{}^{3+}(TCA^-)_3\cdot3TOPO$, and that the extraction constant of this complex is $10^{7.68}$. In this complex, six molecules of water seem to be present in the inner solvation sphere of Cr(III), while three molecules of the trichloroacetate ion as well as three molecules of TOPO seem to be present in the outer solvation sphere. The extractability of the Cr(III) ion in the present extraction system depends most on the concentration of TOPO free from trichloroacetic acid in the organic phase and, consequently, on the pH value of the aqueous phase.

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