Solvent Extraction of the Hexaaquarhodium(III) Ion from Halogenated Carboxylate Solutions with Trioctylphosphine Oxide

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The extraction equilibrium of the inert hexaaquarhodium(III) ion has been studied. Rhodium(III) was quantitatively and rapidly extracted from 0.10 mol dm^{-3} trichloroacetate (TCA) or 0.010 mol dm^{-3} pentadecafluorooctanoate solutions to heptane containing 0.10 mol dm^{-3} trioctylphosphine oxide (TOPO) at pH 3—5. The extraction equilibria were achieved within 1 min at 298 K. From the equilibrium study in the TCA–TOPO system, the rhodium(III) species extracted into heptane was found to be Rh·3TCA·4TOPO, and the extraction constant was $10^{12.29}$. The rhodium(III) species in the organic phase was suggested to be the hexaaquarhodium(III) complex associated with TCA and TOPO.

Recently, much attention has been focused on the separation of metals of the platinum group. Solvent extraction is one of the powerful separation methods and is widely used in fundamental analytical chemistry and applied fields, such as hydrometallurgy. The various extraction systems which have been reported for the separation of the platinum metals were summarized in both a monograph[1)] and a review.[2)] The poor extractability of rhodium has often been pointed out. This is primarily ascribed to the very inert tendency of rhodium(III) toward the ligand substitution reactions with extracting agents. Thus, a thorough investigation of the extraction chemistry of rhodium(III) is inevitable.

In the extraction of such inert metals as rhodium(III), the chemical form of the metal in an aqueous solution seems to be of great importance. In this work a hexaaquarhodium(III) ion was prepared and used. Only a few papers have appeared concerning the extraction of hexaaquarhodium(III), in which it has been extracted into the inverted micelles of the organic solution formed by dinonylnaphthalenesulfonic acid.[3,4)]

In the present study the extraction of the hexaaquarhodium(III) ion was studied with such halogenated carboxylic acids as trichloroacetic acid (HTCA) and pentadecafluorooctanoic acid (HPDFO) in the presence of a hydrophobic base, trioctylphosphine oxide (TOPO), in nonpolar solvents at 298 K. The trichloroacetic acid–TOPO system has been used by one of the authors in the extraction of inert chromium(III) ions.[5)] The extraction equilibrium of hexaaquarhodium(III) ions in this system was studied in detail, and the composition of the extracted species as well as the extraction constant were determined.

Experimental

Reagents. Radioisotopes, ^{101m}Rh and ^{102m}Rh, were produced by 50 MeV bremsstrahlung irradiation of high-purity rhodium (99.99%) with the linear electron accelerator of Tohoku University. The rhodium target was dissolved in concentrated sulfuric acid with heating, neutralized with a sodium hydroxide solution to precipitate rhodium(III) hydroxide, and aged at 328—333 K for 24 h. To prepare a hexaaquarhodium(III) solution, the precipitate of rhodium(III) hydroxide was dissolved in concentrated perchloric acid, heated at 433—443 K for ca. 40 h, and diluted to be 0.2 mol dm^{-3} perchloric acid solution. The rhodium(III) species in the aqueous solution was ascertained to be the hexaaquarhodium(III) ion by the electronic absorption spectrum.[6,7)]

Trioctylphosphine oxide was obtained from Dojindo laboratories and purified as follows: a hexane solution (ca. 0.2 mol dm^{-3} TOPO) was washed with 0.5 mol dm^{-3} sodium hydroxide in 50% (v/v) methanol/water and then with water several times. After evaporation of hexane, the residue (purified TOPO) was dried over diphosphorus pentaoxide under vacuum.

Trichloroacetic acid was of guaranteed reagent grade and used as obtained. Sodium trichloroacetate solutions were prepared by mixing a trichloroacetic acid solution standardized by the acid–base titration and sodium hydroxide solutions. Pentadecafluorooctanoic acid (98% purity) was used without further purification.

Benzene and heptane were purified by ordinary methods. Water was doubly distilled and deionized. All other reagents used were of analytical reagent grade.

Extraction and Back Extraction of Rhodium(III). An aqueous solution (5 cm^3) of 4×10^{-3}—1×10^{-1} mol dm^{-3} halogenated carboxylate containing 8×10^{-5} mol dm^{-3} hexaaquarhodium(III) labeled with ^{101m,102m}Rh was shaken for 1 min to 3 h with an organic solution (5 cm^3) containing 5×10^{-3}—1×10^{-1} mol dm^{-3} TOPO at 298 K. After centrifugation, an aliquot of each phase was taken. The γ-activity was measured with a well-type NaI(Tl) scintillation counter and the distribution ratio (D_M) calculated. The pH value of the aqueous phase was measured immediately after shaking. The ionic strength was adjusted to 0.1 mol dm^{-3} with sodium nitrate.

For back extraction, the organic phase (5 cm^3) containing rhodium(III), prepared by the forward extraction described above, was shaken with the aqueous phase (5 cm^3) pre-equilibrated with an organic solution of TOPO. The distribution ratio and the equilibrium pH value were measured in the same manner as that described above.

Extraction of Trichloroacetic Acid. An aqueous solution

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of 0.1 mol dm^{-3} trichloroacetate was shaken with a heptane solution of 2×10^{-3}—1×10^{-1} mol dm^{-3} TOPO for 5 min at 298 K. After centrifugation, an aliquot of the organic phase was taken, added to a small volume of water, and titrated with the standardized sodium hydroxide solution with vigorous agitation. The distribution ratio of trichloroacetic acid was calculated from the concentration of trichloroacetic acid extracted into the organic phase and the initial concentration of trichloroacetate in the aqueous phase.

Results and Discussion

Extraction Behavior of Rhodium(III). The extraction of hexaaquarhodium(III) from trichloroacetate or pentadecafluorooctanoate solutions into various organic solvents containing TOPO was tried at 298 K. The agitation of both phases was carried out for only 5 min. The results for the 0.10 mol dm^{-3} trichloroacetate–0.10 mol dm^{-3} TOPO system are shown in Fig. 1. A quantitative extraction of rhodium(III) can be accomplished using heptane as a diluent of TOPO; rhodium(III) of more than 99% is readily extracted at pH 3—5. However, rhodium(III) is scarcely extracted into chloroform. The extraction increases in the following order: chloroform<1,2-dichloroethane<nitrobenzene≈benzene<heptane. This order agrees with that observed in the extraction of chromium(III) with trichloroacetate and TOPO,[5] as well as in the synergic extraction of europium(III) with 4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione and TOPO.[8] Such a large observed solvent effect reveals the importance of the reaction between the extracted metal species and TOPO in the organic phase, e.g., solvation or adduct formation. The lowering of extraction in the low- and high-pH region is ascribed to the extraction of trichloroacetic acid with TOPO in the organic phase and the hydrolysis of rhodium(III) ion in the aqueous phase, respectively (vide infra).

Figure 2 shows the extraction curves of rhodium(III) in the 0.010 mol dm^{-3} pentadecafluorooctanoate–0.10 mol dm^{-3} TOPO system. The distribution ratio was independent of the shaking time from 1 to 180 min. The extraction increases in the following order: chloroform<nitrobenzene≈benzene≈1,2-dichloroethane< heptane. Though the extraction behavior is quite similar to that in the trichloroacetate–TOPO system, rhodium(III) could be quantitatively extracted into most of the solvents studied. Since pentadecafluorooctanoic acid has a larger molecular size and a higher hydrophobic character than does trichloroacetic acid, the extraction ability of the former is much higher.

A further study concerning the extraction equilibrium of the hexaaquarhodium(III) ion was made (see below) in the trichloroacetate–TOPO–heptane system in order to elucidate the composition of the extractable rhodium(III) species.

Extraction Equilibrium of Trichloroacetic Acid with TOPO. The extractability of rhodium(III) seems to be significantly affected by the extraction of

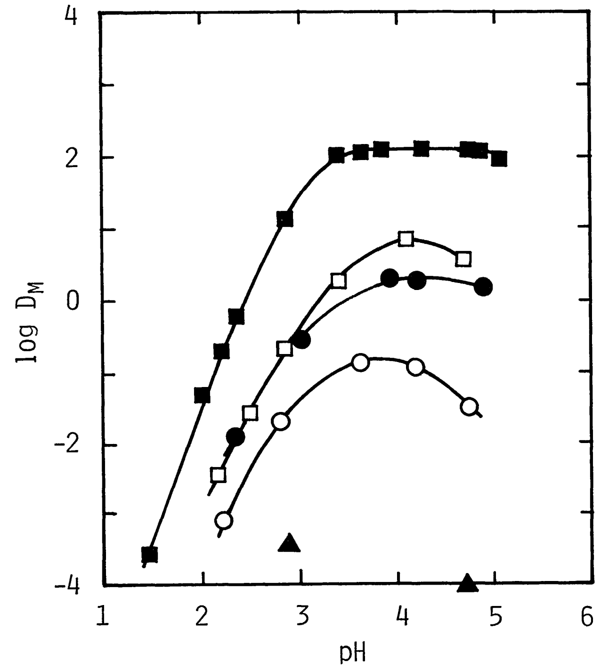

Fig. 1. Extraction of rhodium(III) from 0.10 mol dm^{-3} trichloroacetate solutions into various organic solvents containing 0.10 mol dm^{-3} TOPO. Shaking time: 5 min. ■, Heptane; □, benzene; ●, nitrobenzene; ○, 1,2-dichloroethane; ▲, chloroform.

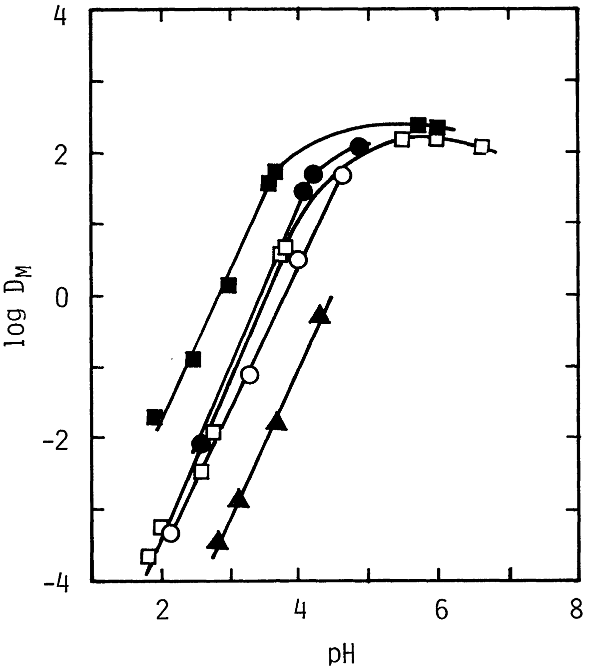

Fig. 2. Extraction of rhodium(III) from 0.010 mol dm^{-3} pentadecafluorooctanoate solutions into various organic solvents containing 0.10 mol dm^{-3} TOPO. Shaking time: 5 min. ■, Heptane; □, benzene; ●, nitrobenzene; ○, 1,2-dichloroethane; ▲, chloroform.

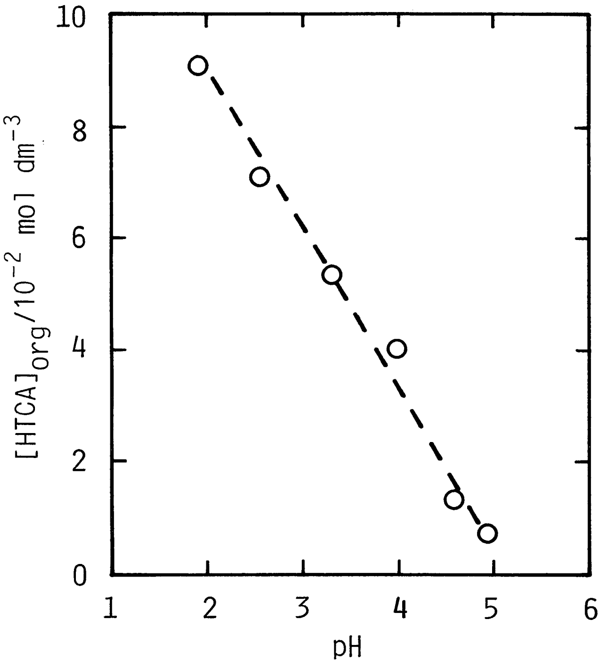

Fig. 3. Variation of the trichloroacetic acid concentration in the heptane phase with pH in the 0.10 mol dm^{-3} trichloroacetate-0.10 mol dm^{-3} TOPO system.

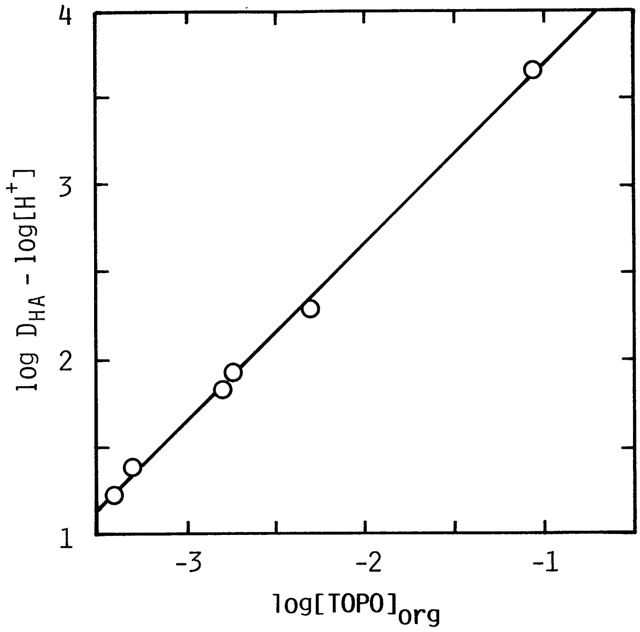

Fig. 4. Effect of the equilibrium concentration of TOPO in the organic phase on the distribution ratio of trichloroacetic acid. 0.10 mol dm^{-3} trichloroacetate, 0.0025—0.10 mol dm^{-3} TOPO. pH 2.80—4.58.

trichloroacetic acid with TOPO. Figure 3 shows the variation of the concentration of trichloroacetic acid extracted into the heptane phase at various pH. The acid concentration in the organic phase increases with a decrease in the pH, and reaches about 0.09 mol dm^{-3} at pH 2, i.e., 90% of the total concentration of trichloroacetate. Since trichloroacetic acid is a strong acid ($pK_a=-0.46$[9]), it should be completely dissociated in the aqueous phase within such a pH range. Hence, the extraction of trichloroacetic acid is not ascribed to the protonation of trichloroacetate following the distribution of the acid into heptane, but to the association among protons, trichloroacetate, and TOPO in the organic phase, as was previously discussed regarding the extraction of trichloroacetic acid with TOPO[5] and various acids with organophosphorus extractants.[10] The equilibrium concentrations of the trichloroacetate ion in the aqueous phase and of TOPO in the organic phase are lowered by association from the initial concentration of the respective agents. Thus, the extraction equilibrium of trichloroacetic acid with TOPO must be clarified in order to obtain the equilibrium concentration of the trichloroacetate ion and TOPO. The extraction equilibrium can be written as

$$\mathrm{H^+ + TCA^- + }i\,\mathrm{TOPO_{org}} \rightleftharpoons \mathrm{HTCA}\cdot i\,\mathrm{TOPO_{org}}, \quad (1)$$

$$K_{\mathrm{ex,HA}} = \frac{[\mathrm{HTCA}\cdot i\,\mathrm{TOPO}]_{\mathrm{org}}}{[\mathrm{H^+}][\mathrm{TCA^-}][\mathrm{TOPO}]_{\mathrm{org}}^{\,i}}, \quad (2)$$

where $K_{\mathrm{ex,HA}}$ stands for the extraction constant of trichloroacetic acid and the subscript org, the organic phase. The distribution ratio (D_{HA}) of trichloroacetic acid can be given as

$$D_{\mathrm{HA}} = \frac{[\mathrm{HTCA}\cdot i\,\mathrm{TOPO}]_{\mathrm{org}}}{[\mathrm{TCA^-}]}. \quad (3)$$

From Eqs. 2 and 3, the following equation is derived:

$$\log D_{\mathrm{HA}} = i \log[\mathrm{TOPO}]_{\mathrm{org}} + \log[\mathrm{H^+}] + \log K_{\mathrm{ex,HA}}. \quad (4)$$

Using this equation, the equilibrium concentration of TOPO in the organic phase was calculated by deducing the amount of TOPO associated with trichloroacetic acid in the organic phase from that of TOPO initially taken. Figure 4 shows a plot of $\log D_{\mathrm{HA}}-\log[\mathrm{H^+}]$ against $\log[\mathrm{TOPO}]_{\mathrm{org}}$, which was obtained by setting $i=1$. The plot is a straight line with a slope of 1.0, as was expected. When $i=2$ or $i=3$ was assumed, no slope corresponding to the each assumption was obtainable. Consequently, the extracted species was found to be HTCA·TOPO and the extraction constant, $\log K_{\mathrm{ex,HA}}=4.66\pm0.05$, was obtained. The equilibrium concentration of TOPO and trichloroacetate can be readily calculated using this value.

Extraction Equilibrium of Rhodium(III) with Trichloroacetate and TOPO. Figure 5 shows both the extraction and back extraction of hexaaquarhodium-

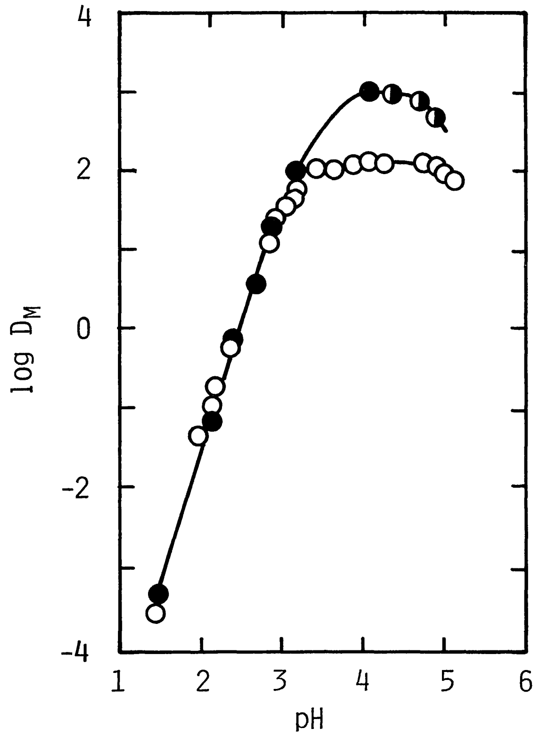

Fig. 5. Forward and backward extraction of rhodium(III) in the 0.10 mol dm^{-3} trichloroacetate–0.10 mol dm^{-3} TOPO–heptane system. ○, Forward extraction at the shaking time 5 min; ●, backward extraction at the shaking time 5 min; ◑, backward extraction at the shaking time 30 min.

(III). The distribution ratio of rhodium(III) was independent on the shaking time in a pH region lower than about 3; that is, the logarithmic values of the distribution ratio in forward extraction at pH 2.57 for three different shaking time (1, 5, and 30 min) were −2.44, −2.46, and −2.47, respectively; the same was true in backward extraction. In Fig. 5 the distribution ratio obtained from forward extraction is in good agreement with that obtained from backward extraction. These facts demonstrate that the extraction equilibrium in the present system was completely achieved within an agitation time of only 1 min. The extraction of the inert hexaaquarhodium(III) ion is surprisingly rapid in this trichloroacetate–TOPO system.

On the other hand, a disagreement between the distribution ratio in forward extraction and that in backward extraction at around pH 4 was observed. This difference in the distribution ratios was gradually reduced with the shaking time; the log D_M values in both forward and backward extraction at pH 3.9 were almost consistent at 2.7 after shaking for 27 h. This phenomenon can be ascribed to a slow extraction reaction, which may be caused by the hydrolysis and polymerization of hexaaquarhodium(III) ion in the aqueous phase within such a pH range.[11] Hence, equilibrium studies regarding the extraction of rhodium(III) were performed below pH 3 at which the rapid equilibrium could be always achieved.

The effect of the rhodium(III) concentration on the distribution ratio of rhodium(III) was examined in the 0.10 mol dm^{-3} trichloroacetate–0.10 mol dm^{-3} TOPO system at pH 2.90. The logarithmic values of the distribution ratio were 1.28, 1,28, and 1.26 at 8.1×10^{-6}, 8.1×10^{-5}, and 8.1×10^{-4} mol dm^{-3} of the rhodium(III) concentration, respectively. Since the distribution ratio is independent on the rhodium(III) concentration, no polymerization of the extracted species occurs in the organic and the aqueous phase.

The extraction equilibrium of rhodium(III) with the trichloroacetate ion (TCA$^-$) and TOPO can be expressed as

$$\mathrm{Rh}^{3+} + m\,\mathrm{TCA}^- + n\,\mathrm{TOPO}_{\mathrm{org}} \rightleftharpoons \mathrm{Rh}\cdot m\,\mathrm{TCA}\cdot n\,\mathrm{TOPO}_{\mathrm{org}}, \tag{5}$$

$$K_{\mathrm{ex,M}} = \frac{[\mathrm{Rh}\cdot m\,\mathrm{TCA}\cdot n\,\mathrm{TOPO}]_{\mathrm{org}}}{[\mathrm{Rh}^{3+}][\mathrm{TCA}^-]^m[\mathrm{TOPO}]_{\mathrm{org}}^n}, \tag{6}$$

where $K_{\mathrm{ex,M}}$ stands for the extraction constant of rhodium(III). The distribution ratio of rhodium(III) under the present experimental conditions can be written as

$$D_{\mathrm{M}} = \frac{[\mathrm{Rh}\cdot m\,\mathrm{TCA}\cdot n\,\mathrm{TOPO}]_{\mathrm{org}}}{[\mathrm{Rh}^{3+}]}. \tag{7}$$

Therefore,

$$\log D_{\mathrm{M}} = m \log[\mathrm{TCA}^-] + n \log[\mathrm{TOPO}]_{\mathrm{org}} + \log K_{\mathrm{ex,M}}. \tag{8}$$

Figure 6 shows a plot of log D_M−3log [TCA$^-$] against the logarithmic value of the equilibrium concentration of TOPO in the organic phase, where it was assumed that the number of TCA molecules associated with the rhodium(III) ion, m, is three, based on the electrical neutrality with respect to the extractable species. The plot gives a straight line with a slope of 3.8 in the low-concentration region of TOPO, where the extraction of trichloroacetic acid with TOPO is negligible and the ionic strength in the aqueous phase is almost constant. Therefore, the rhodium(III) ion is solvated with four molecules of TOPO in the organic phase.

To ascertain that the number of the trichloroacetate molecules associated with the rhodium(III) ion is three, a plot of log D_M−4log [TOPO]$_{\mathrm{org}}$ against log [TCA$^-$] was made using n=4. The result is shown in Fig. 7. A straight line with a slope of 2.7 was obtained; the result is compatible with that expected, m=3. Therefore, the rhodium(III) species extracted into

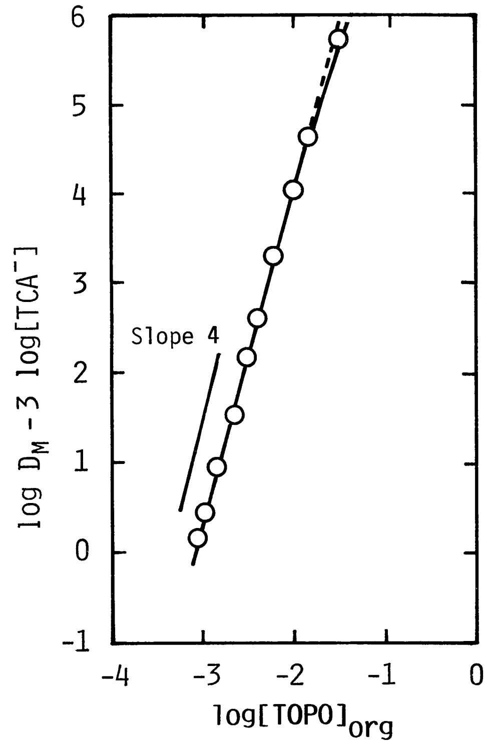

Fig. 6. Effect of the equilibrium concentration of TOPO in the organic phase on the distribution ratio of rhodium(III). 0.10 mol dm^{-3} trichloroacetate, pH 2.90, shaking time: 5 min.

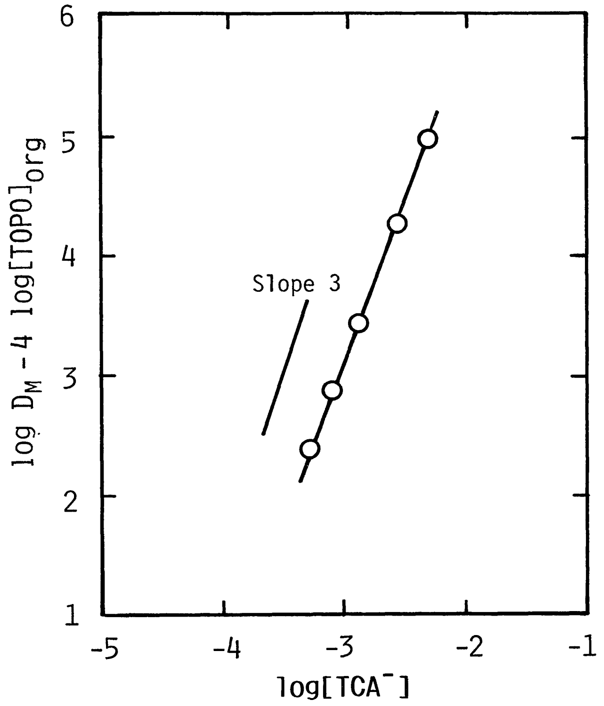

Fig. 7. Effect of the equilibrium concentration of trichloroacetate in the aqueous phase on the distribution ratio of rhodium(III). 0.10 mol dm^{-3} TOPO, pH 2.90, 0.10 mol dm^{-3} NaNO$_3$, shaking time: 5 min.

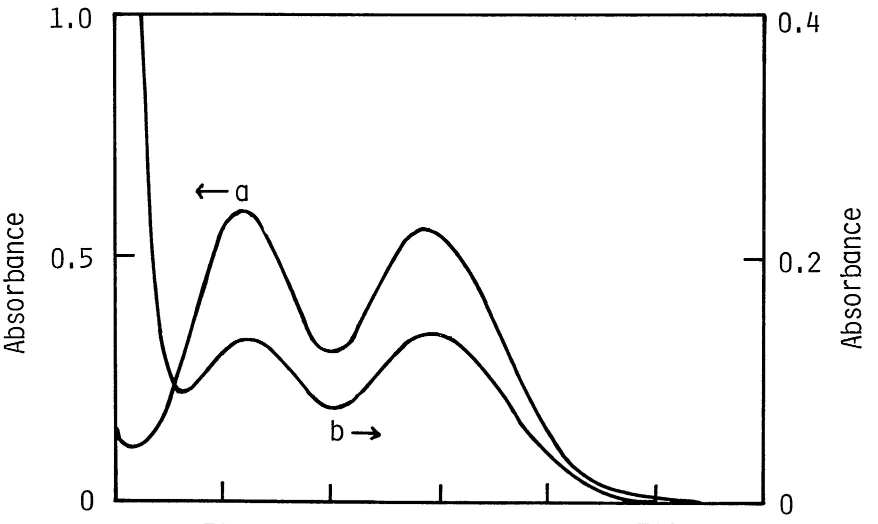

Fig. 8. Absorption spectra of the hexaaquarhodium(III) ion in perchloric acid solution and the rhodium(III) species extracted into the heptane phase containing 0.10 mol dm^{-3} TOPO from a 0.10 mol dm^{-3} trichloroacetate solution at pH 3.18. a, 1.1×10^{-2} mol dm^{-3} hexaaquarhodium(III) ion; b, 2.2×10^{-3} mol dm^{-3} rhodium(III) extracted.

heptane was found to be Rh·3TCA·4TOPO, and the extraction constant, $\log K_{\mathrm{ex,M}}=12.29\pm0.06$, was obtained. The composition of the extractable species was the same as that in the rhodium(III)–2,4,6-trinitrophenol–TOPO system.[12)]

The electronic absorption spectrum of the rhodium(III) species extracted into heptane was measured and compared with that of the hexaaquarhodium(III) ion in an aqueous perchlorate solution. The spectra of both rhodium(III) species shown in Fig. 8 are very similar to each other. Taking account of the very inert property of the hexaaquarhodium(III) ion, it is impossible to rapidly exchange the coordinated water molecules with TOPO or TCA^- molecules. Consequently, in the present extraction system rhodium(III) is extracted as a hexaaquarhodium(III) complex, which is associated with the four molecules of TOPO and the three molecules of trichloroacetate ions. This extractable species can be considered to be an outer-sphere complex and the following model may be speculated: four TOPO and three trichloroacetate molecules may be present on the octahedral faces of the hexaaquarhodium(III) ion to most effectively interact with the central metal, as well as the coordinated water by coulombic and charge-dipole interaction, hydrogen bonding, etc.

In conclusion, an inert rhodium(III) species, could be very rapidly and quantitatively extracted in an ion-association system comprising the halogenated carboxylates and TOPO at room temperature. This rapidity of the extraction could be explained in terms of the extraction of the hydrated rhodium(III) without any ligand substitution. The present system is very useful for the extraction of such inert metal ions.

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