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Solvent Extraction Equilibria of Thallium(III) from Weakly Acidic Chloride Solutions into 4-Methyl-2-pentanone

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Synopsis. From the distribution data of thallium (III) between 4-methyl-2-pentanone and 4 mol dm^{-3} sodium perchlorate solutions containing chloride ions at pH 2, the $Na^+TlCl_4^-$ species in the organic phase and the $TlCl_2^+$, $TlCl_3$, and $TlCl_4^-$ species in the aqueous phase were recognized. The equilibrium constants for the formation and extraction of these complexes were determined.

The solvent extraction of thallium(III) chloride complexes for various analytical purposes has been carried out in most cases from hydrochloric acid solutions, and the chemical form of the extracted species is known to be $HTlCl_4$.[1] When the acidity of the aqueous phase is not high and/or the solvent is nonpolar, however, the extraction of thallium(III) chloride species containing no hydrogen ions can be expected. Walters and Dodson[2] demonstrated that, with 0.0365 mol dm^{-3} tributylphosphate (TPB) in hexane, thallium(III) was extracted as the $TlCl_3(TBP)_2$ species from aqueous solutions containing perchloric and hydrochloric acid at an ionic strength of 0.5 mol dm^{-3}, but Widmer and Dodson[3] showed that, with 0.730 mol dm^{-3} TBP in octane, the $HTlCl_4$ species was also extracted from the same solutions.

Since the thallium(III) tetrachloride complex anion can be well extracted, along with the hydrogen ion, from acid chloride solutions, the present authors considered that this complex anion might also be extracted with cations other than the hydrogen ion from weakly acid chloride solutions into solvating-type polar organic solvents. Therefore, they measured the extraction of thallium(III) from 4 mol dm^{-3} $Na(Cl, ClO_4)$ solutions at pH 2 with 4-methyl-2-pentanone and with hexane containing 0.03 mol dm^{-3} TBP at 298 K and compared the results of these two series of experiments.

Experimental

All of the reagents were of an analytical grade. The sodium perchlorate was recrystallized three times from water. Both the 4-methyl-2-pentanone and TBP were washed with 0.1 mol dm^{-3} perchloric acid, water, and a 0.1 mol dm^{-3} sodium hydroxide solution successively, and then several times with water. Thallium(III) nitrate was dissolved in 4 mol dm^{-3} of a sodium perchlorate solution containing 0.1 mol dm^{-3} perchloric acid and a small amount of sodium chloride; a stock solution containing 1.0×10^{-2} mol dm^{-3} of thallium(III) was thus prepared. The metal concentration was checked by a colorimetric method using 8-quinolinol.[4] All of the procedures were carried out at 298 K. A portion of an aqueous 4 mol dm^{-3} $Na(Cl,ClO_4)$ solution containing 1×10^{-6} to 1×10^{-3} mol dm^{-3} of thallium (III) and the same volume of 4-methyl-2-pentanone or hexane containing TBP was placed in a stoppered glass tube. The two phases were agitated vigorously for 30 s. After they had then been centrifuged, a portion of the aqueous phase was transferred into another glass tube and hydrochloric acid and a solution of Malachite Green were added. The concentrations of hydrochloric acid and Malachite Green in the resulting solution were 3×10^{-1} and 1×10^{-4} mol dm^{-3} respectively. This solution was shaken with benzene. The organic phase was then transferred into another tube and shaken with a solution containing hydrochloric acid and Malachite Green at the same concentrations as above in order to wash off the perchlorate ions coextracted with the metal complex. The thallium(III) in the sample was determined from the absorption of this organic solution at 635 nm. The molar extinction coefficient was 5.5×10^4. The distribution ratio of thallium(III) was defined as:

$$D = [Tl(III)]_{org,total}/[Tl(III)]_{total}$$

where 'org' denotes the chemical species in the organic phase and where a lack of a subscript denotes those in the aqueous phase. The total thallium(III) concentration in the organic phase was determined from the difference between its initial and equilibrium concentrations in the aqueous phase. When the metal concentration in the initial aqueous phase was high, a correction was made for the decrease in the free-chloride concentration due to the extraction of the chloride complex.

Results

The distribution ratio may generally be expressed by the following equation;

$$D = ([TlCl_3]_{org}+[Na^+TlCl_4^-]_{org})/\sum[TlCl_n^{3-n}] \quad (1)$$

Extraction with 4-Methyl-2-pentanone. The distribution ratio was found to be independent of the hydrogen-ion concentration, at least between pH 1 and 2.5. The open circles in Fig. 1 give the extraction data with 4-methyl-2-pentanone at pH 2. It was found that these extraction data could be analyzed by using the following equation, derived from Eq. (1):

$$D = K\mathrm{ex}_4[Na^+][Cl^-](K_3^{-1}[Cl^-]^{-1}+1+K_4[Cl^-])^{-1} \quad (2)$$

where

$$K_n = [TlCl_n^{3-n}][TlCl_{n-1}^{4-n}]^{-1}[Cl^-]^{-1} \quad (3)$$

$$K\mathrm{ex}_4 = [Na^+TlCl_4^-]_{org}[TlCl_3]^{-1}[Cl^-]^{-1}[Na^+]^{-1} \quad (4)$$

The values for the constants in Eq. (2) were determined by a curve-fitting method.[5] The solid curve for the open circles in Fig. 1 was calculated by introducing these values into Eq. (2). It is possible that a part of the $Na^+TlCl_4^-$ ion-pair undergoes dissociation in this polar organic solvent, but, for the reasons already presented in a previous paper,[6] this effect should be negligible under the conditions employed in the present study.

Extraction with TBP in Hexane. The distribution

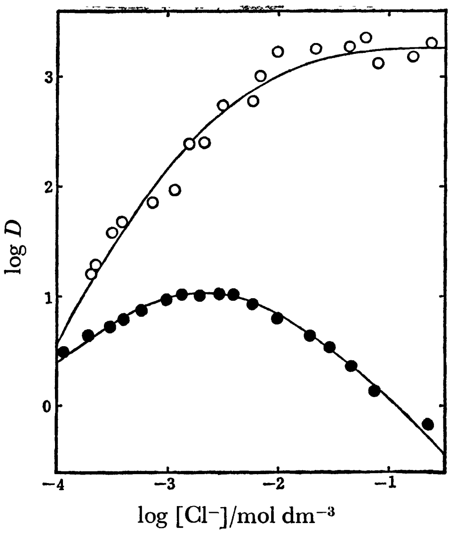

Fig. 1. Distribution ratio of thallium(III) as a function of chloride concentration. Org. phase: closed circles hexane containing 3.0×10^{-2} mol dm^{-3} of TBP and open circles 4-methyl-2-pentanone. Aq. phase: 4 mol dm^{-3} Na(Cl, ClO$_4$) at pH 2. Temperature 298 K.

Table 1. Equilibrium constants for the complexes

Org. phase: 4-methyl-2-pentanon for $K\mathrm{ex}_4$ and hexane containing TBP for $K\mathrm{ex}_3$.
Aq. phase: 4 mol dm^{-4} Na(Cl, ClO$_4$) at pH 2.
Temperature: 298 K.

log K_3	log K_4	log $K\mathrm{ex}_3$	log $K\mathrm{ex}_4$
3.22	2.12	4.26	4.79

ratio was found to be second-order dependent on the TBP concentration in its concentration range between 5×10^{-3} to 5×10^{-2} mol dm^{-3} and independent of the hydrogen ion concentration, at least between pH 0.6 and 2.5. The closed circles in Fig. 1 give the extraction data when the TBP concentration was 3×10^{-2} mol dm^{-3} at pH 2. It was found that the extraction data could be analyzed by using the following equation:

$$D = K\mathrm{ex}_3[\mathrm{TBP}]_{\mathrm{org}}^2(K_3^{-1}[\mathrm{Cl}^-]^{-1}+1+K_4[\mathrm{Cl}^-])^{-1} \qquad (5)$$

where:

$$K\mathrm{ex}_3 = [\mathrm{TlCl_3(TBP)_2}]_{\mathrm{org}}[\mathrm{TlCl_3}]^{-1}[\mathrm{TBP}]_{\mathrm{org}}^{-2} \qquad (6)$$

The data were also analyzed by the curve-fitting method. The stability constants of the aqueous complexes were found to be identical with those obtained by the 4-methyl-2-pentanone extraction. The values for the constants in Eq. (5) are listed in Table 1. The solid curve for the closed circles in Fig. 1 was calculated by introducing these values into Eq. (5).

Discussion

Since the data at the chloride concentrations lower than 1×10^{-4} mol dm^{-3} could not be obtained by the method employed in this study, the formation constants, K_1 and K_2, could not be determined. However, the Tl^{3+} and TlCl^{2+} species should be negligible in the chloride-concentration range of the present study. The reported stability constants for the thallium(III) chloride complexes[2,7–9] are, for all practical purposes, in agreement with the present values; the values reported for log k_3 are 2.75 (0.4), 2.68 and 2.74 (0.5), 3.10 (1.2), 3.08, 3.15, and 3.55 (3), and 3.41 (4) and for log K_4 are 2.25 (0.4), 1.60 and 1.81 (0.5), 2.5 (1.2), 2.17, 2.22, and 2.36 (3), and 2.79 (4) respectively, when the ionic concentration in the solution is at the value in the parentheses. No evidence for the higher complexes was observed in the chloride-concentration range of the present study.

The extraction curve with TBP reported by Walters and Dodson[2] is quite similar to that in Fig. 1. However, the $K\mathrm{ex}_3$ value given by the previous authors is 9.7×10^2 when the diluent was octane;[3] this is probably due to the difference in the salting-out effect. Such a large difference in the partition coefficient of metal complexes in TBP extraction when the electrolyte concentration in the aqueous phase was different was also found in a previous work on the extraction of the In(SCN)$_3$ species.[10]

It is marked that only the neutral complex, TlCl$_3$, was extracted into hexane containing a small amount of TBP, even from the aqueous phase of the high sodium-ion concentration, while only the anionic complex as an ion-pair was extracted into the polar solvent, 4-methyl-2-pentanone.

It is obvious that the chloride complexes of thallium(III) are much more stable than the corresponding complexes of indium(III) because, for the latter metal ion, only the first and second chloride complexes were found in the chloride concentration range from 10^{-4} to 10^{-1} mol dm^{-3}, and the extractability of the thallium(III) as chloride complex is much higher than that of indium(III), because the latter was not extracted into those solvents under conditions identical with those of the present study.[6,11]

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