

## EXTRACTION OF HEXABROMOTHALLIC(III) ACID AND ITS CESIUM SALT IN NITROBENZENE

Marie STUDNIČKOVÁ and Luboš POLOLÁNIK

*Physical Chemistry Department,  
University J. E. Purkyně, 611 37 Brno and  
Research Institute of Macromolecular Chemistry, 656 49 Brno*

*Dedicated to Professor A. Okáč on occasion of his 75th birthday.*

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Extraction of bromothallic(III) acid and its cesium salt in nitrobenzene has been studied. Distribution ratios of thallium,  $D(\text{Tl})$ , and cesium,  $D(\text{Cs})$ , have been measured radiometrically with  $^{137}\text{Cs}$  and  $^{204}\text{Tl}$  emitters using a gamma spectrometer. Composition of the extracted acid,  $\text{H}_3\text{TlBr}_6$ , has been determined at constant concentration  $0.11\text{M}(\text{HClO}_4 + \text{HBr})$ . Solvation number of the cesium salt  $\text{CsH}_2\text{TlBr}_6$  is 8.5 at nitrobenzene concentrations above  $2\text{M}$  (in benzene). According to the values of equilibrium constant of the exchange of  $\text{Cs}^+$  by  $\text{H}^+$ , the anions of the title acid being the counter-ions,  $\text{H}_3\text{TlBr}_6$  can be considered to be a polybasic acid.

The complex acid  $\text{H}_{(n-3)}\text{TlX}_n$  ( $\text{X} = \text{halogen}$ ) in aqueous  $\text{HX}$  solutions, the concentration of  $\text{HX}$  being several mol/l, has its  $n$  equal to 4 or 6 according to different authors. The coordination number four is more frequent. The anion  $\text{TlX}_4^-$  was found potentiometrically<sup>1</sup> in  $10^{-2}\text{M}$ - $\text{Tl}(\text{III})$  solutions. A similar thallium to halogenide ratio was found in the particles  $\text{Tl}_2\text{X}_9^{3-}$  detected<sup>2</sup> by  $^{205}\text{Tl}$ -NMR in  $10^{-1}\text{M}$ - $\text{Tl}(\text{III})$  solutions. The particles  $\text{TlX}_4^-$  were detected<sup>3</sup> by Raman and IR spectroscopy in ether and tributyl phosphate extracts of aqueous  $\text{Tl}(\text{III})$  and  $\text{HX}$  solutions of similar concentrations ( $\approx 0.1\text{M}$ - $\text{Tl}(\text{III})$ ,  $10\text{M}$ - $\text{HX}$ ). From dilute  $\text{Tl}(\text{III})$  solutions ( $10^{-5}$  to  $10^{-3}\text{M}$ ) the anion  $\text{TlX}_4^-$  was extracted in the form of ion-pairs with bulky dyestuff cations in non-polar solvents (various types of extraction-photometric determination of  $\text{Tl}(\text{III})$ , e.g. ref.<sup>4</sup>). The same composition of the anion is obtained in extractions of  $10^{-3}\text{M}$  and more dilute solutions of the complex acid<sup>5</sup> or its salt<sup>6</sup> using strong donor-type solvents (tributyl phosphate<sup>5</sup>; 4-methyl-2-pentanone<sup>6</sup>).

The coordination number six was found potentiometrically in  $10^{-3}\text{M}$ - $\text{Tl}(\text{III})$  solutions<sup>7</sup>. Under similar conditions the particle  $\text{TlCl}_6^{3-}$  was found<sup>8</sup> by  $^{35}\text{Cl}$ -NMR method. It was also found<sup>3</sup> in more concentrated aqueous  $\text{Tl}(\text{III})$  solutions by Raman and IR spectroscopy.

Thus from available data it follows that the composition of the complex anions  $\text{TlX}_n^{(n-3)-}$  is affected by the components concentration ratio and solvation by a donor solvent. The particle  $\text{HTlCl}_4$  is suggested<sup>9</sup> for extraction with weak donor-type strongly polar solvents (nitrobenzene). According to ref.<sup>10</sup> solvation of electrolytes with nitrobenzene is of a rather physical nature, so that a competitive replacement of halogenide ligands by solvent in the complex  $\text{TCX}_6^{3-}$  cannot be considered. We de-

cided to study the extraction of bromothallic acids from solutions of similar composition to those mentioned in ref.<sup>7</sup> (where the acids HTIX<sub>4</sub>, H<sub>2</sub>TIX<sub>5</sub> and H<sub>3</sub>TIX<sub>6</sub> were found) in nitrobenzene. Composition of the extracted particle was verified by means of exchange extraction of cesium<sup>11</sup> with anion of the extracted acid as a counter-ion, which has not yet been studied.

## EXPERIMENTAL

### Reagents and Methods

Nitrobenzene was distilled, the other chemicals used (Lachema, Brno) were of *p.a.* purity grade. Solution of <sup>204</sup>Tl was prepared by dissolution of metallic thallium in nitric acid. Solution of TlBr<sub>3</sub> was prepared according to ref.<sup>4</sup> by oxidation of TlNO<sub>3</sub> solution with bromine water in the presence of NaBr. Excess bromine was removed by boiling. The aqueous phase contained HBr, HClO<sub>4</sub>, 2 · 10<sup>-3</sup>M-TlBr<sub>3</sub> (either <sup>204</sup>Tl-labelled or inactive) and traces of <sup>137</sup>Cs. Constant ionic strength (0.11M) was maintained in all the experiments. Nitrobenzene formed the organic phase except for the experiments given in Fig. 3 where nitrobenzene-benzene mixture was used.

The same volumes of aqueous and organic phases (5 ml) were shaken in a rotation shaker for 30 min. According to preliminary measurements equilibrium was reached before the extraction end. The distribution ratios of metals, D(Me), were measured radiometrically using a VAM-15 D apparatus (Vakutronik, Dresden). The gamma spectra were measured with a VAM-120 apparatus (Vakutronik, Dresden) with a NaI(Tl) crystal. Error in the area of the photo-peak record was within 2 to 7%, log D(Me) being within ±1.6. The areas were measured with a polar planimeter K 800 (MOM, Budapest) according to ref.<sup>12</sup>. The distribution ratios of the metals found from the peak areas were compared with the values obtained from activity measurements.

## RESULTS AND DISCUSSION

### Composition of the Extracted Particle

We followed the extraction of trivalent thallium from aqueous solutions having similar composition to those in potentiometric experiments<sup>7</sup> (*i.e.* the overall concentration  $c(\text{Tl}) = 2 \cdot 10^{-3}\text{M}$ , the overall bromide concentration  $\log c(\text{Br})$  within  $-2.4$  to  $-1$ ). However, we used a lower ionic strength (0.11M), which was limited by the overall acidity to allow the determination of the exchange extraction constant  $K_{\text{H}}^{\text{Cs}}$ .

Composition of the extracted particle can be determined from the experimental data in Fig. 1. The bilogarithmical dependence of the distribution ratio  $D(\text{Tl})$  of thallium *vs* the overall bromide concentration  $c(\text{Br})$  has a slope equal to 4.1. The  $c(\text{Tl})$  concentration is sufficiently high, so that the value  $\bar{n}$  in Eq. (1) cannot be neglected (for  $c(\text{Br}) \rightarrow 0$ ).

$$d \log D(\text{Tl})/d \log c(\text{Br}) = n - \bar{n}, \quad (1)$$

$n$  and  $\bar{n}$  stand for number of ligands in the extracted particle and the Bjerrum's

formation function, respectively. As very stable complexes are formed in aqueous phase (according to ref.<sup>7</sup>  $\log \beta_4 = 26.1$ ;  $\log \beta_5 = 29.2$ ;  $\log \beta_6 = 31.6$  at ionic strength 1.2 at room temperature;  $\beta_i = [\text{TIBr}_i]/[\text{TI}][\text{Br}]^i$ , equilibrium concentrations without charges), the Bjerrum formation function  $\bar{n}$  is given by Eq. (2).

$$\bar{n} = (c(\text{Br}) - [\text{Br}])/c(\text{TI}) \approx c(\text{Br})/c(\text{TI}). \quad (2)$$

Validity range of this relation was determined by comparison of the  $\bar{n}$  values calculated according to Eq. (2) with those published in ref.<sup>7</sup> (Fig. 2). If experimental values  $\bar{n}$  from Eq. (2) are added to those of the left side of Eq. (1), the average value 6.3 is obtained for the number of ligands. The number of bromide ligands in the extracted particle can be verified also by the so called molar ratio method<sup>1,3</sup>. This method is applicable for very little dissociated complexes, which is fulfilled in our case. The dependence  $D(\text{TI})$  distribution ratio vs  $c(\text{Br})/c(\text{TI})$  ratio shows a break at the value  $c(\text{Br})/c(\text{TI}) = 6$  (Fig. 2). The same composition of the extracted particle is indicated by curve 2 in Fig. 1. Let us presume that this curve corresponds to extraction of cesium in the form of the salt  $\text{CsH}_{(n-4)}\text{TIBr}_n$  (denoted as CsA). Slope of the bilogarithmical dependence  $D(\text{Cs})$  vs  $c(\text{Br})$  is, for low  $c(\text{Br})$  values, given by a relation formally identical with Eq. (1). The formation function of the cesium salt at the right side of this relation would be  $\bar{n}(\text{Cs}) = (c(\text{A}) - [\text{A}])/c(\text{Cs}) \approx 0$ , because cesium is present in traces ( $\approx 10^{-6}\text{M}$ ). Curve 2 in Fig. 1 has a slope equal to 6.2, which corresponds to extraction of cesium salt of the complex acid  $\text{H}_3\text{TIBr}_6$ .

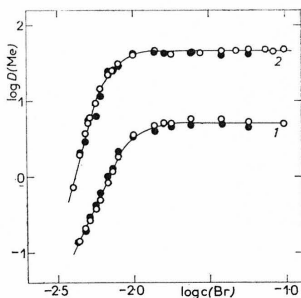


FIG. 1

Dependence of Distribution Ratios of Bromothallic(III) Acid,  $D(\text{TI})$ , and its Cesium Salt,  $D(\text{Cs})$ , on Overall Concentration of HBr in System  $c(\text{Br})$

Medium of  $\text{HClO}_4$ , overall acid concentration 0.11M. The full and empty circles correspond to gamma spectrometer and activity measurements, respectively. Curve 1  $D(\text{TI})$ , 2  $D(\text{Cs})$ .

### Solvation of Ion-Pairs in Organic Phase

Solvation number of the ion-pair ( $\text{Cs}^+$ ,  $\text{A}^-$ ) in the organic phase can be determined<sup>10</sup> from the slope of bilogarithmical dependence of the extraction constant  $K_{\text{ex}}$  on nitrobenzene concentration  $c(\text{NB})$  in the organic phase ( $\text{mol l}^{-1}$ ). Nitrobenzene was diluted with benzene. The extraction constant is given by relation  $K_{\text{ex}} = [\text{Cs}^+]_{\text{org}} \cdot [\text{A}^-]_{\text{org}} / [\text{Cs}^+][\text{A}^-]$ , where the square brackets mean the equilibrium concentrations, and org means organic phase. Having a constant  $c(\text{TI})$  concentration and  $c(\text{Br}) < 6 c(\text{TI})$  (see Fig. 1), we can put

$$K_{\text{ex}} \approx D(\text{Cs}) D(\text{TI}) . \quad (3)$$

From the straight line 3 in Fig. 3 we found the value 8.5 for the solvation number of the ion-pair ( $\text{Cs}^+$ ,  $\text{H}_2\text{TI}(\text{Br})_6^-$ ) ( $c(\text{NB})$  being above 2M).

Solvation numbers of acids  $\text{HMeX}_4$  are determined<sup>14</sup> from the slope of dependence  $\log D(\text{Me})$  vs  $\log c(\text{NB})$  according to a simple relation which, however, need not be fulfilled in the case of the acid  $\text{H}_3\text{TI}(\text{Br})_6$ . Slope of this dependence for this acid has the values 1.8 and 4.9 at  $c(\text{NB})$  below and above 4M, respectively (Fig. 3, curve 2). For the acids  $\text{HInBr}_4$  and  $\text{HFeCl}_4$  ref.<sup>14</sup> gives the values 3 and 6 for  $c(\text{NB})$  below and above 2M, respectively.

### Exchange Extraction of Cesium

Equilibrium constant of exchange of ions  $\text{Cs}^+$  by  $\text{H}^+$  during extraction of electrolytes by polar solvents is given<sup>11</sup> by relation  $K_{\text{H}}^{\text{Cs}} = [\text{Cs}^+]_{\text{org}}[\text{H}^+] / [\text{Cs}^+][\text{H}^+]_{\text{org}}$ . The exchange extraction constants defined as quotient of extraction constants of the electrolytes  $\text{CsA}$  and  $\text{HA}$  in nitrobenzene–water system are only determined by equi-

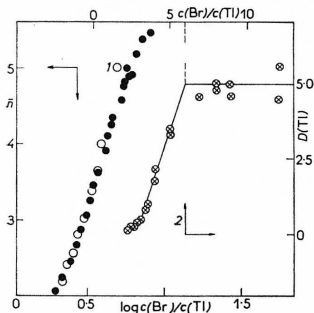


FIG. 2

Dependence of Bjerrum's Formation Function  $\bar{n}$  of Bromothallates and their Distribution Ratio  $D(\text{TI})$  on Ratio of Overall Concentrations of Ligand,  $c(\text{Br})$ , and Metal,  $c(\text{TI})$

Curve 1  $\bar{n}$  vs  $\log c(\text{Br})/c(\text{TI})$ ; full circles are taken from ref.<sup>7</sup>, the empty ones are our values according to Eq. (2). Curve 2  $D(\text{TI})$  vs  $c(\text{Br})/c(\text{TI})$  (method of molar ratios). Experimental data from curve 1 in Fig. 1.

librium concentrations of the cations in the both phases and do not depend on the nature of the counter-ion  $A^-$ . Constancy of the values  $K_H^{Cs}$  was verified for various kinds of the counter-ions; out of the anions of complex acids these were tetrachloroferrate(III) (ref.<sup>15</sup>), tetrachloroaurate(III) (ref.<sup>15</sup>) and tetraiodobismuthate(III) (ref.<sup>11</sup>). The same characteristic of the  $Cs^+/H^+$  ion exchange was found<sup>16</sup> with polybasic acid  $H_7P(Mo_2O_7) \cdot 20 \cdot 5 H_2O$ . The equilibrium concentration  $[H^+]_{org}$  is  $3 \cdot 6 H^+$  per one P atom in this case. The values  $\log K_H^{Cs}$  found<sup>16</sup> in  $10^{-3}M$  solutions of this acid at  $25^\circ C$  are:  $3 \cdot 06$  ( $1 \cdot 2M-HCl$  in aqueous phase),  $2 \cdot 98$  ( $0 \cdot 1M-HNO_3$ ) and  $2 \cdot 77$  ( $0 \cdot 1M-HClO_4$ ).

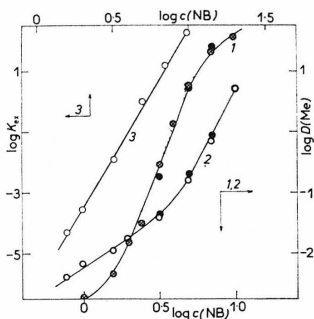
In the exchange extraction of cesium with the anion  $H_2TiBr_6^-$  as counter-ion we presume that the equilibrium concentration  $[H^+]_{org}$  is given by the concentration of  $H_3TiBr_6$  in the organic phase with respect to the basicity  $i$  of this acid. This presumption is equivalent with the statement that hydrobromic acid does not contribute to  $[H^+]_{org}$ , which was fulfilled<sup>14,15</sup>. The exchange constant is then given by relation (4).

$$K_H^{Cs} = D(Cs) \left\{ \frac{c(H)[D(Tl) + 1]}{D(Tl) i c(Tl)} - 1 \right\}, \quad (4)$$

where  $c(H)$  stands for the overall concentration of  $H^+$ . Introduction of experimental values into Eq. (4) gives the following values for various basicities  $i$  of the acid  $H_3TiBr_6$ :  $\log K_H^{Cs} = 3 \cdot 41$  ( $i = 1$ );  $3 \cdot 12$  ( $i = 2$ );  $2 \cdot 95$  ( $i = 3$ ) (for  $0 \cdot 11M-HBr$  and  $2 \cdot 10^{-3}M-Tl(III)$ , temperature about  $20^\circ C$ ). Comparison of the given values with those of ref.<sup>16</sup> for a polybasic heteropolyacid and with thermodynamic value of this constant ( $3 \cdot 00$ ; ref.<sup>17</sup>) shows that the investigated acid behaves as polybasic during the ion exchange. Thereby its composition was indirectly confirmed, too.

FIG. 3  
Dependence of  $D(Cs)$ ,  $D(Tl)$ , and  $K_{ex}$  on Nitrobenzene Concentration,  $c(NB)$ , in Organic Phase (benzene)

Medium of  $HClO_4$ ,  $0 \cdot 02M-HBr$ , overall acid concentration  $0 \cdot 11M$ . Curve 1  $D(Cs)$ , 2  $D(Tl)$ , 3  $K_{ex}$  according to Eq. (3). The full circles were obtained from measurements with gamma spectrometer, the other circles were obtained from activity measurements.



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