ACTA CHEMICA SCANDINAVICA 18 (1964) 307–312

Solvent Extraction Studies of the Composition of Thallic Chloride Solutions

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The constants for the equilibria:

$$TlCl_2^+ + Cl^- \rightleftharpoons TlCl_3 \ (K_3)$$

and

$$TlCl_3 + Cl^- \rightleftharpoons TlCl_4^- \ (K_4)$$

have been determined in solutions produced by equilibrating water or heavy water solutions of sodium chloride (up to 0.1 M) containing thallic chloride labelled with ^{204}Tl, and dilute acid, with isopropyl ether.

For H_2O, $\mu \rightarrow 0$; $K_4 = 29.5 \pm 1.5$ (25°C), 20.8 ± 1 (35°C), 64 ± 2 (0°C), $K_3 = 1060 \pm 150$ (25°C):

for D_2O (96.2 %), $\mu \rightarrow 0$; $K_4 = 20.5 \pm 1.5$ (25°C):
for H_2O, $\mu = 0.5$ with sodium perchlorate; $K_4 = 23.8 \pm 0.5$ (25°C).

The heat of formation, and entropy change on formation, of $TlCl_4^-$ from $TlCl_3$ are calculated to be $\Delta H = -5.1 \pm 0.6$ kcal mole^{-1} and $\Delta S^\circ = -10 \pm 2$ cal.mole^{-1} degree.$^{-1}$

The maximum number of coordinated chloride ions necessary to explain the partition data is four: the experimental accuracy is such that not more than 3 % of the total thallium could have been present as undetected higher species even in the most concentrated chloride solutions studied. The results are compared with those of other workers.

It was early suggested[1] that, by analogy with known solids, aqueous solutions of thallic chloride may contain $TlCl_4^-$ and $TlCl_6^{-3}$. During recent years many potentiometric studies, published,[2-4] briefly reported,[5] and unpublished have been made of the thallic chloride system in concentrated perchlorate solutions. The potentiometric results fall into two groups, the first of which [3,4] appears to show that a solution in which the 'free'' chloride concentration is 0.1 M contains principally $TlCl_6^{3-}$ with some $TlCl_5^{2-}$, while the second group[2,5,6] find that only $TlCl_3$ and $TlCl_4^-$ are present in appreciable concentrations. The latter conclusion is confirmed by the work reported here.

The solvent extraction method employed is that used by Dodson[7] who found, not only that the extraction curve for $TlCl_3$ into isopropyl ether goes through a maximum with increasing chloride concentration, but also that, after this maximum, the decrease is compatible with the formation of only $TlCl_4^-$. It is this decreasing portion of the extraction curve which we have chosen to study, in order to obtain accurate values of K_4 for the equilibrium

$$TlCl_3 + Cl^- \rightleftharpoons TlCl_4^-$$

Under the conditions of our experiments, the results are independent of thallic concentration, of acid, of ionic strength, and allow an accurate determination of K_4.

We have also, in some cases, analysed the ascending part of the extraction curve and obtained good, but less accurate, values of K_3 for the equilibrium

$$TlCl_2^+ + Cl^- \rightleftharpoons TlCl_3$$

The results are also given of measurements made over a range of temperature and in heavy water, and it is planned to apply these to some current work on the rates of reaction of thallic complexes.

EXPERIMENTAL

^{204}Tl was obtained from the Kjeller Institutt for Atomenergi, Norway, as solid thallous nitrate labelled with ^{204}Tl. This was dissolved in water, precipitated with hydrochloric acid, oxidised with chlorine, evaporated and diluted to give the "stock" solution. The stock solution was standardised by iodine thiosulphate titration, and the thallous concentration (found to be 2.3 % of the total thallium) determined by counting, after extracting the thallic chloride from a concentrated hydrochloric acid solution into diethyl ether. No further reduction occurred in the time taken for the experiments (about one year).

The isopropyl ether was obtained from Riedel-de-Haën or British Drug Houses Ltd., stored after addition of hydroquinone, and redistilled immediately before use. No reduction of thallic species by traces of peroxides was found during the experiments.

Ion exchanged water was redistilled in an all quartz apparatus. Heavy water (99.8 %) was obtained from Norsk Hydro, Rjukan, and the deuterium oxide content of the solutions calculated from this to be 96.2 %.

Perchloric acid and sodium chloride were "Analar" grade, and sodium perchlorate solutions were prepared from "Analar" perchloric acid and sodium hydroxide.

A Philips universal counting apparatus (consisting of the units PW 4052, 4032, and 4022) was used together with a pour in liquid counter (18524 Philips) and a sectional lead castle.

Equal volumes of an aqueous solution containing labelled thallic chloride (1.042×10^{-4} M), perchloric acid (1.101×10^{-3} M) and sodium chloride (6×10^{-4} to 0.1 M), and of water saturated isopropyl ether, were isolated in a thermostat containing water at 25 ± 0.05°C or 35 ± 05°C or crushed ice and water. In one set of experiments the ionic strength of the aqueous solution was adjusted to 0.5 with sodium perchlorate solution and the isopropyl ether equilibrated with 0.5 M sodium perchlorate solution before use. Altering the thallic concentration to 3.126×10^{-4} M left the extraction ratio E = (counts/min/ml organic phase) /(counts/min/ml aqueous phase) = [counts/min] ml aqueous solution − [counts/min] ml aqueous phase]/[Counts/min) ml aqueous phase] unchanged. Increasing the hydrogen ion concentration to 2.000×10^{-3} M did not affect the results; lowering the acid concentration to 6×10^{-4} M did not alter the data after the maximum in the extraction curve, but hydrolysis occurred at low chloride concentrations. No detectable change in volume of the two phases occurred during equilibration.

A known volume of the aqueous thallic chloride solution (5 or 3 ml) was poured into the counting tube and counted (about 30 000 counts at a rate of 1000−2000 per minute) before, and after, equilibration with isopropyl ether. Corrections for background were always applied.

A possible error in this method is reduction of thallic thallium during equilibration. Repeated extractions into diethyl ether of the aqueous phases after addition of hydrochloric acid, showed that no increase in reduction occurred at the higher chloride concentrations used to determine K_4. At lower chloride concentrations up to 15 % reduction of the total thallium was found and was corrected for.

RESULTS AND METHOD OF TREATMENT OF RESULTS

The experimentally determined values of E (defined above) were in all cases plotted as ordinate *vs.* $\log_{10} C_{Cl^-}$, the logarithm of the total chloride concentration, and gave smooth curves with one pronounced maximum. The shape is reflected in the α_3 *vs.* $\log_{10} [Cl^-]$, the logarithm of the free chloride concentration, curve of Fig. 2 where the points shown are related to the E values by the equation

$$E = K_{D3}\alpha_3 \qquad (1)$$

K_{D3} is the distribution coefficient of $TlCl_3$ between the two phases and α_3 the fraction of total Tl(III) present as $TlCl_3$. The values at the lower chloride concentrations are given in Table 1.

Table 1. Data for solutions with total chloride concentration less than 6 mM, H_2O, 25°C.

$C_{Cl^-} \times 10^3$	$[Cl^-] \times 10^3$	E	α_2	α_3	α_4	K_3^C	$\mu \times 10^3$	K_3
0.659	0.433	0.0613	0.675	0.321	0.004	1144	1.171	1240
1.000	0.763	0.0825	0.558	0.432	0.010	1040	1.500	1140
1.161	0.915	0.0958	0.485	0.501	0.014	1154	1.654	1270
1.662	1.412	0.1025	0.441	0.537	0.022	870	2.147	970
2.164	1.905	0.1156	0.361	0.605	0.034	888	2.644	1000
2.665	2.388	0.1237	0.307	0.648	0.045	897	3.138	1020
3.668	3.446	0.1292	0.254	0.677	0.069	784	4.137	910
5.674	5.388	0.1374	0.166	0.720	0.114	809	5.133	960

Calculation of K_4. The extraction data from the chloride concentration range > 10 and up to 100 mM were used to calculate K_4: in this range $TlCl_3$ and $TlCl_4^-$ were assumed to be the only thallic species present. $1/E$ was then plotted against C_{Cl^-} and, as the chloride concentration is much greater than the total thallium concentration, the intercept of such a plot is $1/K_{D3}$ and the slope K_4/K_{D3}. Fig. 1 illustrates this for solutions with added perchlorate ($\mu = 0.5$). The points given are each the average of the three values (with $[H^+]$, 2.000×10^{-3}, 1.101×10^{-3} and 6.00×10^{-4} M) and in some cases with $C_{Tl(III)}$ equal to 1.042×10^{-4}, in others 3.126×10^{-4}. The three values did not differ from each other by more than ±3 %; the scatter was random. The procedure was checked by including the extraction data around the maximum of the extraction curve ($C_{Cl^-} \leq 10$ mM) after calculation of K_3 as below, and plotting α_4/α_3, where $\alpha_4 = [TlCl_4^-]/C_{Tl(III)}$, against the concentration of free chloride. In all cases a good straight line, passing through the origin, and of slope K_4 was obtained.

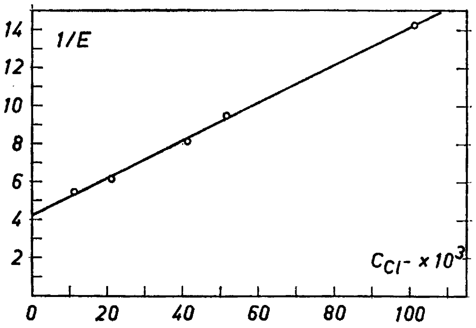

Fig. 1. Plot of reciprocal of extraction ratio, *E*, *vs.* total chloride concentration, $\mu = 0.5$, 25°C.

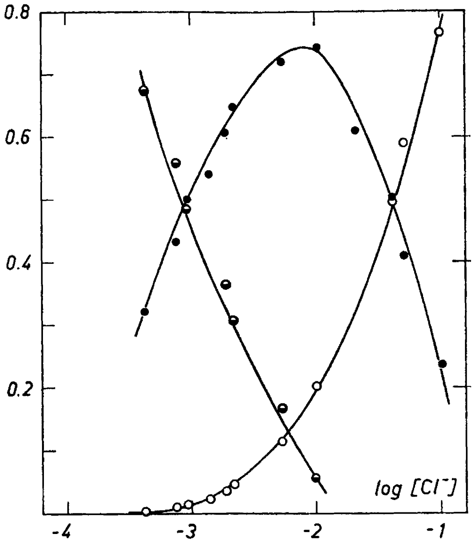

Fig. 2. Plot of α_2 (◓), α_3 (●), α_4 (○) *vs.* logarithm of free chloride concentration, $\mu \rightarrow 0$, H_2O, 25°C.

Calculation of K_3. Except for water at 25°C, only a few measurements were made in the range of chloride concentration below 10 mM where all three species $TlCl_2^+$, $TlCl_3$ and $TlCl_4^-$ were found to be present in appreciable concentrations. α_3, for all solutions, was calculated using eqn. 1; α_4 using K_4, α_3, and the concentration of free chloride; $\alpha_2 = [TlCl_2^+]/C_{Tl(III)}$ by difference. The concentration of free chloride could no longer be taken as the total chloride concentration and was calculated from the equation

$$[Cl^-] = C_{Cl^-} - 2[TlCl_2^+] - 3[TlCl_3] - 4[TlCl_4^-] \qquad (2)$$

The concentration ratios K_3^C for the equilibrium

$$TlCl_2^+ + Cl^- \rightleftharpoons TlCl_3$$

were obtained by successive approximation, and were converted to thermodynamic constants K_3 using the simple Debye expression. The ionic strength

Table 2. Table of association and distribution constants.

Temp. °C	Solvent	Ionic strength	K_{D3}	K_4	K_3
25	H_2O	0.5	0.244 ± 0.005	23.8 ± 0.5	(900 ± 300)
25	H_2O	→ 0	0.191 ± 0.002	29.5 ± 1.5	1060 ± 150
25	D_2O(96.2 %)	→ 0	0.187 ± 0.002	20.5 ± 1.5	
0	H_2O	→ 0	0.941 ± 0.005	64 ± 2	(205 ± 50)
0	D_2O(96.2 %)	→ 0	(0.941)	(60 ± 10)	(280 ± 10)
35	H_2O	→ 0	0.168 ± 0.005	20.8 ± 1	

of these solutions varied from 1 × 10^{-3} to 7 × 10^{-3} and was largely due to the added acid.

The calculated values of K_4, K_3 and K_{D3} are given in Table 2. When only four or five extraction measurements were made, the values, together with the biggest observed differences from the mean value, are given in parentheses.

No attempt was made to obtain and analyse results at very low chloride concentrations, where $TlCl^{2+}$ would be expected to be present in appreciable concentrations, as the E values would be very small. The smooth change with $\log_{10}[Cl^-]$ of the values for α_2, α_3 and α_4 at 25°C and water ($\mu \rightarrow 0$) as illustrated in Fig. 2, together with the excellent agreement over the whole concentration range, shows that the K_3, K_{D3}, and K_4 values accurately represent the whole measured extraction curve.

From K_4 at 0°C and 25°C for dilute solutions in water, ΔH for the formation of $TlCl_4^-$ from $TlCl_3$ is calculated to be -5.1 ± 0.6 kcal $mole^{-1}$ and the standard entropy change of formation $\Delta S^\circ = -10 \pm 2$ cal $mole^{-1}$ $degree^{-1}$.

DISCUSSION

The results show clearly that in aqueous solutions containing up to 0.1 M "free" chloride there is no evidence that the coordination number of the thallic ion for the chloride ion is greater than four. The experimental accuracy is such, that if a concentration of a five-coordinated chloro ion equal to, or greater than, 3 % of the total thallic concentration had been present, then there would have been a detectable curvature in the $1/E$ vs. C_{Cl^-} plots; this was not found. Our results therefore support those of the workers [2,5,6], who have found only complexes up to $TlCl_4^-$ in such solutions. A closer comparison is possible between the results at an ionic strength of 0.5 and those of King.[5] These latter were determined by potentiometric titration, which gives the product of the K values, in this case K_3K_4 being found to be 1.98×10^4. The product of K_4 and the less accurate K_3, given in Table 2, is 2.15×10^4. In view of the approximate value given by us for K_3, we consider that the product value given by King may be the better one: the method we have used, however, gives K_4 alone, so that, for this, we prefer our value (23.8) to that of King, which is larger.

The difference in K_4 (25°C) found for H_2O and D_2O is real. There seems to be no obvious reason why K_{D3} should differ in the two solvents, the values given in Table 2 being those which best "fit" the experimental results; however if the average value ($K_{D3} = 0.189$) is used the difference in K_4 still remains appreciable (K_4 in H_2O becomes 28.8 ± 1 and in D_2O 21.2 ± 1).

We have no similar data to compare with these, but the known small solvation of negatively charged ions suggests that the difference reflects the increased bonding of D_2O over H_2O to the uncharged thallic chloride molecule. This is in accordance with the suggestion previously made by the senior author [8] when discussing acid dissociation of the uncomplexed thallic ion in the two solvents. During recent years many papers[9-13] on the solubility of salts in heavy water have appeared; the fact that in all cases the solubility is less than in H_2O suggests that for the two cases discussed above it is inner coordinated water which should be considered; this presupposes that $TlCl_3$ also has inner coordinated water.

Acknowledgements. The authors wish to thank Professor R. W. Dodson, Professor E. L. King, and Dr. S. Ahrland, for access to unpublished work.

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Received October 23, 1963.