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On the Hydrolysis of the Tetrachloroaurate(III) Ion

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As part of a series of investigations of gold(III) complexes in aqueous solutions, the equilibria between $AuCl_4^-$ and OH^- in sodium perchlorate medium have been studied. The experiments were carried out as emf titrations at a constant ionic strength of 3 M, and for each titration the total concentrations of gold and chloride ions were kept constant. They varied from 5×10^{-3} to 100×10^{-3} M for gold, and from 21×10^{-3} to 410×10^{-3} M for chloride ions. The emf values were measured with a Radiometer PHM 4 potentiometer, using a glass electrode, calibrated regularly against a hydrogen gas electrode. The measurements were performed in the pH range $1.0 \leq pH \leq 6.5$. The points obtained from a titration and from a back titration for identical total concentrations of gold and chloride both fell on the same curve.

The experimental points all fell on very smooth curves, when plotted as $Z = f(\log h)$, where Z is the average number of OH^- bound to each Au in the solutions.

A preliminary analysis of the experimental data using a "curve-fitting" method, very similar to those published by Sillén,[1] showed that the equilibria in the solutions could be explained by the formation of $AuCl_4^-$, $AuCl_3(H_2O)$, $AuCl_3(OH)^-$, and $AuCl_2(OH)_2^-$. At higher Z values, the species $AuCl(OH)_3^-$ and $Au(OH)_4^-$ are probably also present. This is in good agreement with previous results obtained by Bjerrum [2] who showed the existence of the ions $AuCl_n(OH)_{4-n}^-$ where $n = 0, 1, 2, 3, 4$.

The preliminary constants obtained for the following two reactions

$$AuCl_4^- + H_2O \rightleftharpoons Au(OH)Cl_3^- + H^+ + Cl^- \quad (1)$$

$$AuCl_4^- + 2H_2O \rightleftharpoons Au(OH)_2Cl_2^- + 2H^+ + 2Cl^- \quad (2)$$

are $\beta_1 = 10^{-6.22}$ M^2 and $\beta_2 = 10^{-13.26}$ M^4, which are very close to those obtained by Bjerrum.[2]

In addition, the equilibrium constant for the reaction $Au(OH)Cl_3^- + H^+ \rightleftharpoons Au(H_2O)Cl_3$ has been found to be $10^{2.72}$ M^{-1}. This complex was not considered by Bjerrum,[2] but Fry *et al.*[3] recently assumed the existence of a species $Au(H_2O)Cl_3$ to explain their kinetic experiments on the aqueous hydrolysis of $AuCl_4^-$. They were not able, however, to determine any equilibrium constant from their measurements.

Refinement of the experimental data by computer methods is now in progress, and the results will soon be published in this journal.

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