Studies on the Hydrolysis of Metal ions

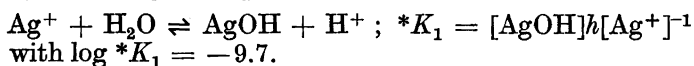## Part 29. The Hydrolysis of the Silver Ion, Ag+, in Acid Self-medium *

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The hydrolysis of the Ag+ ion has been investigated at 25°C by measuring the hydrogen ion concentration in the self-medium [3] 1 M Ag+(NO$_3$-) with a glass electrode. The data, which indicate an extremely slight hydrolysis at log [H+] $\geq$ −6.3, can be explained by the equilibrium Ag+ + H$_2$O $\rightleftharpoons$ AgOH + H+ with log *K_1 $\leq$ −11.1; the effect may also be due to polynuclear complexes. No evidence was found for the presence of appreciable amounts of polynuclear hydrolysis products proposed previously [1].

L ittle data can be found in the literature which throw light on the hydrolysis equilibria of the Ag+ ion. In 1933 Johnston, Čuta and Garrett [1] concluded that about 40 % of the dissolved silver in a saturated solution of Ag$_2$O is present as positively charged polynuclear ions such as Ag$_2$OH+. Their argument is based on a comparison of the analytically determined total silver concentration with the conductometrically measured ionic concentration. Evidence was found by these authors that the concentration of the uncharged species AgOH cannot exceed 0.01 [Ag(I)]$_{total}$.

In 1954 Faucherre [2] studied the hydrogen ion concentration of AgNO$_3$ solutions in the ionic medium 0.2 M NO$_3^-$ with a glass electrode. He explained the increase of log [H+] from −6 to −5, as log [Ag(I)] varied from −2 to −1, by assuming the equilibrium

Ag+ + H$_2$O $\rightleftharpoons$ AgOH + H+ ; *K_1 = [AgOH]h[Ag+]$^{-1}$
with log *K_1 = −9.7.

The hydrolysis equilibrium of Ag+ is not easy to investigate because the Ag+ ion is a very weak acid and the solubility product of Ag$_2$O is low (pK_s is about 7.7). As a result the acidity range where appreciable hydrolysis occurs but no precipitate is formed is narrow. If solutions dilute in [Ag+] are investigated, the useful acidity range can be made wider. This was attempted several years ago in this laboratory, but due to the low buffer capacity of dilute silver

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solution and to the premature precipitation of Ag_2O no conclusive results could be obtained. In any case the study of dilute solutions can only yield information on mononuclear products.

METHOD OF INVESTIGATION

Recently a method has been proposed by Hietanen and Sillén [3] — the self-medium method — which is particularly suitable for studying the hydrolysis equilibria of such a weak acid as the Ag^+ ion. In the self-medium method the equilibrium concentration of hydrogen ions is measured in solutions containing, at a high and constant concentration, one of the reacting ions and a counter ion which does not take part in the reaction to be studied. The solutions may also contain a small amount of an inert (*i.e.* non protolyzing) cation or anion in order to keep the counter ion concentration constant when the acidity is varied.

In a series of measurements, which may be carried out conveniently as a potentiometric titration, the acidity is changed by replacing the inert ion with H^+ or OH^- ions. If the acidity changes are small and therefore only a small part of the reacting ions is transformed to the hydrolysis products, the composition of the solution is altered only slightly, so that the activity factors may be considered as constants. The advantage of the self-medium method is that the presence of hydrolysis products $Me_q(OH)_p$ (Me = metal ion) with high q/p can easily be detected under conditions when the solutions have an appreciable buffer capacity.

This paper summarizes our hydrogen ion concentration measurements using a glass electrode in a series of 1 M $AgNO_3$ solutions of varying acidity. $AgNO_3$ was chosen because it can be easily purified by recrystallization, in contrast to $AgClO_4$. It is essential to use as pure reagents as possible when the hydrolysis of weak acids is to be studied.

The solutions were prepared by mixing one (''S_o'') of low acidity with another one (''T'') containing about 0.02 M HNO_3. The results obtained in this work, as well as those found in solutions of 3 M ClO_4^-, show that the hydrolysis of Ag^+ is negligible for log $[H^+] > -4$, consequently in the 0.02 M HNO_3 + 1.00 M $AgNO_3$ solution, ''T'', the hydrogen ion concentration h is equal to the analytical excess of hydrogen ions $H = [NO_3^-] - [Ag^+]$.

The starting solution S_o of low acidity had to be prepared in a special way because addition of dilute NaOH to 1 M $AgNO_3$ always caused a precipitation of Ag_2O, which redissolved very slowly, whatever precautions were taken to avoid a local excess of OH^-. The CO_2-free 1 M $AgNO_3$ solution to be used as the starting solution was passed through a tube containing about 20 g Ag_2O to remove the minute amounts of excess hydrogen ions. This procedure ensures that the solution comes into intimate contact with the Ag_2O particles so that excess hydrogen ions are removed without the introduction of foreign ions. The solubility of Ag_2O is so low that the total silver concentration remains practically unchanged.

In all experiments we have found the analytical excess of hydrogen ions in the starting solution, H_o, to be negative, which indicates that the method used to prepare partially hydrolyzed solutions is an effective one. It is common

experience in this laboratory that equilibrium is established much more rapidly between a solid and a liquid by passing the liquid through a column of the solid than by shaking.
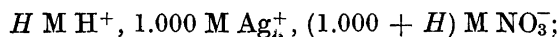
The hydrogen ion concentration at equilibrium was measured by using the cell
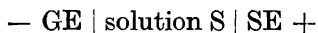
$$- \text{GE} \mid \text{solution S} \mid \text{SE} +$$

where GE denotes the glass electrode, SE is the reference half-cell

$$\mid 1.000 \text{ M KNO}_3 \mid 0.990 \text{ M KNO}_3, 0.0100 \text{ M AgNO}_3 \mid \text{AgCl, Ag.}$$
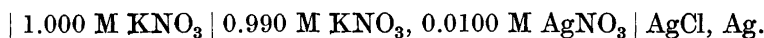
Solution S had the general composition (neglecting the very small correction for H_o, see below)

$$H \text{ M H}^+, 1.000 \text{ M Ag}_4^+, (1.000 + H) \text{ M NO}_3^-;$$

In all experiments H was kept below 0.01 M.

The emf of this cell can be written at 25°C

$$E = E_o - 59.15 \log h + E_j \tag{1}$$

where E_o is a constant and E_j is the liquid junction potential between solution S and 1 M KNO$_3$. E_j was determined by measuring E in the h range 0.01 to 0.1 M where the hydrolysis is quite negligible. The equation $E_j = 52 h$ mV was found to describe the data to a good approximation.

The liquid junction potential of the junction h M H$^+$, $(1.000-h)$ M Na$^+$, 1.000 M ClO$_4^-$ $\mid$ 1 M NaClO$_4$ has been previously measured in this laboratory (G. Biedermann unpublished work); up to $h = 0.1$ M the data could be represented by the equation $E_j = 64 h$ mV, which is reasonably close to the E_j values found for the junction studied in this work.

A series of measurements ("titration") was started with a known volume, V_o ml, of a partially hydrolysed solution with an initially unknown deficit of H$^+$ $(- H_o)$. To this solution an increasing amount V_T ml of an acid solution T (1 M AgNO$_3$, H_T M HNO$_3$) was added.

For each point H is given by the equation

$$H = \frac{V_T H_T + V_o H_o}{V_T + V_o} \tag{2}$$

In a first approximation we neglected H_o, obtaining the approximate value

$$H_1 = \frac{V_T H_T}{V_o + V_T} = H - \frac{H_o V_o}{V_o + V_T} \tag{3}$$

As H_1 increases, $(H_1 - H)/H_1$ decreases and

$$E + 59.15 \log H_1 - E_j(H_1) \tag{4}$$

tends to E_o.

For each point of a series of measurements (4) was calculated and for $H_1 > 0.005$ M was found to be constant within $\pm$ 0.1 mV; this constant value for (4) was accepted as the correct E_o. We could then calculate h from (1) for each point.

The difference between the free and analytical hydrogen ion concentration is

$$h - H = BZ \tag{5}$$

where B is the total silver concentration and Z is the average number of OH bound per silver ion.

From (2), (3), and (5) we find

$$\left(\frac{V_o + V_T}{V_o} \right) (h - H_1) = BZ \left(\frac{V_o + V_T}{V_o} \right) + H_o \tag{6}$$

The left hand side can now be calculated from known quantities; it tends to H_o as the hydrolysis is suppressed. Indeed, a constant value was obtained within the limits of experimental uncertainty in our experiments in the log h range -5 to -3.5 indicating that hydrolysis is negligible for log $h > -5$. This value was taken to be equal to H_o. For a log h higher than about -3.5 $(h - H_1)$ could not be obtained with sufficient accuracy because the absolute uncertainty increases both for h and H_1. On the other hand, the relative uncertainty is constant, we have estimated a maximal error $\Delta h/h = 0.01$ and $\Delta H_1/H_1 = 0.001$.

EXPERIMENTAL DETAILS

$AgNO_3$ solutions were prepared from AgNO$_3$ p.a., Merck, which was purified by recrystallization and then dried at 140°C. Care was taken to avoid contamination with dust. Ag_2O was made by adding 0.1 M Ba(OH)$_2$ dropwise to 0.1 M AgNO$_3$ at 60—70°C; both solutions were prepared by dissolving the purified substances in CO$_2$-free water. The precipitated Ag$_2$O was washed with hot CO$_2$-free water until the washings gave no reaction for Ba^{2+}. The precipitation, washing and the transfer of Ag$_2$O to the column were made in a specially constructed apparatus in a purified nitrogen atmosphere.

HNO_3 solutions were made from 65 % HNO$_3$ p.a. Merck. They were standardized to an accuracy of 0.1 % against KHCO$_3$, and via NaOH solution against hydrazinium sulfate. $Ba(OH)_2$ solutions were prepared from Ba(OH)$_2$(H$_2$O)$_8$ p.a. Merck, which was made carbonate- and chloride-free by double recrystallization. A 0.25 M Ba(OH)$_2$ solution had a scarcely perceptible turbidity, indicating that the carbonate content was very low. $Nitrogen$ from a cylinder was purified by passing through 1 M H$_2$SO$_4$ and 1 M NaOH. Doubly distilled water, made CO$_2$-free by passing N$_2$ through it for several hours, was used to prepare all the solutions, which were stored and transferred in a nitrogen atmosphere.

The measurements were carried out employing the technique usual in this laboratory [4]. E was determined with a valve potentiometer PHM 4, Copenhagen, which was calibrated against a Leeds & Northrup compensator of the type K3; the reading accuracy of the valve potentiometer was 0.1 mV. A Beckman glass electrode of type No. 1190—80 was employed, which attained a constant potential within about 10 min and which remained constant within ± 0.1 mV for several hours.

All measurements were made in a paraffin-oil thermostat at 25.0 ± 0.1 °C.

RESULTS

Three series of measurements were made, and each time a fresh Ag$_2$O preparation was used to react with the starting solution. A typical series is shown in Table 1; the additions below 3 ml were made with a weight burette. It may be inferred from the table that the experimental conditions were chosen adequately to obtain the constants E_o and H_o with a satisfactory accuracy.

Table 1. Starting solution So: 49.98 ml AgNO$_3$ 1.000 M passed through a column filled with Ag$_2$O. Acid solution T: V_T ml AgNO$_3$ 1.000 M, HNO$_3$ 0.01983 M.

	V_T ml	E mV	H_1 M	E_j mV	$E + 59.15 \times \log H_1 - E_j(H_1)$ mV	h M	$Z\left(\dfrac{V_T}{V_0} + 1\right) + H_0$ M	Z
1	—	334.2	.—	—	—	5.06×10^{-7}	5.06×10^{-7}	1.6×10^{-5}
2	0.0764	245.1	$3.02_6\times10^{-5}$	—	155.2	1.62×10^{-5}	$(-1.41\pm0.02)\times10^{-5}$	2×10^{-6}
3	0.1395	221.9	5.52	—	147.5	4.00	(-1.52 ± 0.04)	
4	0.2285	206.0	9.02	—	144.2	7.43	(-1.6 ± 0.1)	
5	0.3190	195.9	$1.25_8\times10^{-4}$	—	142.6	1.10×10^{-4}	(-1.6 ± 0.1)	
6	0.4122	188.7	1.62_2	—	141.9	1.46	(-1.6 ± 0.1)	
7	0.5013	183.1	1.96_9	—	141.3	1.81	(-1.6 ± 0.2)	
8	0.7256	173.0	2.83_7	—	140.6	2.68	(-1.6 ± 0.3)	
9	1.1818	159.9	4.58	—	139.8	4.47	(-1.1 ± 0.5)	
10	3.19	135.2	$1.19_0\times10^{-3}$	0.1	139.6	1.17×10^{-3}	(-2 ± 1)	
11	5.19	123.4	1.86_5	0.1	139.3	1.86		
12	7.19	116.0	2.49_4	0.1	139.4	2.48		
13	11.20	106.3	3.63_0	0.2	139.2			
14	21.21	93.8	5.90_8	0.3	139.1			
15	31.23	87.4	7.62_6	0.4	139.2			
16	41.25	83.2	8.96_6	0.5	139.1			

$E_0 = 139.2 \pm 0.1$ mV $H_0 = (-1.6 \pm 0.1) \times 10^{-5}$ M

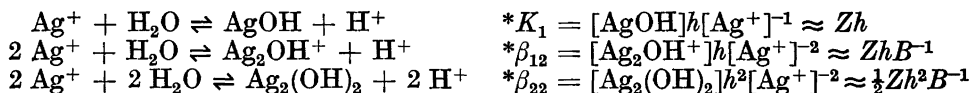Table 2 summarizes the results of our measurements.

Table 2.

No. of series	$H_0 \times 10^5$	$\log h$	$Z \times 10^5$	$\log {}^*K_1$	$\log {}^*\beta_{12}$	$\log {}^*\beta_{22}$
(1)	(-1.0 ± 0.1)	(-5.82)	(1.15 ± 0.1)	(-10.8)	(-10.8)	(-16.9)
(2)	-1.7 ± 0.1	-6.33	1.7 ± 0.1	-11.10	-11.10	-17.73
(3)	-1.6 ± 0.1	-6.30	1.6 ± 0.1	-11.10	-11.10	-17.70

The H_0 and Z values obtained in series (1) — which are set in brackets — are somewhat less accurate than those determined in the two others because at first no weight burette was used for the small additions.

In each series only the first point could be utilized to calculate Z because Z values less than 10^{-5} could not be obtained with satisfactory accuracy.

To explain the $Z(\log h)$ data we shall try what seems to be the three simplest assumptions on the main reaction

$$Ag^+ + H_2O \rightleftharpoons AgOH + H^+ \qquad {}^*K_1 = [AgOH]h[Ag^+]^{-1} \approx Zh$$
$$2\,Ag^+ + H_2O \rightleftharpoons Ag_2OH^+ + H^+ \qquad {}^*\beta_{12} = [Ag_2OH^+]h[Ag^+]^{-2} \approx ZhB^{-1}$$
$$2\,Ag^+ + 2\,H_2O \rightleftharpoons Ag_2(OH)_2 + 2\,H^+ \qquad {}^*\beta_{22} = [Ag_2(OH)_2]h^2[Ag^+]^{-2} \approx \tfrac{1}{2}Zh^2B^{-1}$$

Although great pains were taken to avoid contamination of the solutions we do not feel justified to claim that the extremely small Z values are not partly due to the presence of some impurity. We can therefore only conclude

$$\log {}^*K_1 \leqq -11.1; \log {}^*\beta_{12} \leqq -11.1; \log {}^*\beta_{22} \leqq -17.7$$

In the light of the present results it does not seem likely as suggested by Johnston, Čuta and Garrett [1] that the difference claimed between the analytically and conductometrically determined silver concentrations in a saturated solution of Ag_2O is due to the presence of Ag_2OH^+. If the saturated solution of Johnston *et al.* had contained 5.8×10^{-5} M Ag^+, 1.39×10^{-4} M OH^- and 8.1×10^{-5} M Ag_2OH^+, as they seem to suggest, one would calculate $\log {}^*\beta_{12} = -5.76$ and for the equilibrium

$$\tfrac{1}{2}Ag_2O(s) + \tfrac{1}{2}H_2O + Ag^+ \rightleftharpoons Ag_2OH^+$$
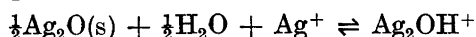
$\log K = 0.15^*$. If these values were correct in our solution with $[Ag(I)]_{tot} = 1$ M, $\log h = -6.3$ we would calculate $Z \sim 0.35$ whereas we find 1.7×10^{-5}. It would moreover have been possible to dissolve Ag_2O in 1 M $AgNO_3$ to a value $Z \sim 0.37$.

In a following paper [6] a critical survey of the data on the solubility equilibria of Ag_2O will be given. On the basis of this survey we believe that the inconsistency between the analytical and conductance data of Johnston, Čuta and Garrett [1] is to be ascribed to the presence of minute amounts of impurities, *e.g.* CO_2, which may seriously influence the composition of a solution of such a low buffer capacity as a saturated solution of Ag_2O.

The $\log {}^*K_1$ value obtained in this work is considerably lower than that found by Faucherre [2]. This author assumed the analytical excess of hydrogen ions to be negligible in a CO_2-free solution of $AgNO_3$. However, according to our experience a minute amount of HNO_3 is inevitably occluded in the crystal; the HNO_3 impurity cannot be removed below the melting point of $AgNO_3$.

REFERENCES

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2. Faucherre, J. *Bull. soc. chim. France* **1954** 253.
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4. see *e.g.* Biedermann, G. *Arkiv Kemi* **9** (1956) 277.
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* On different assumptions Näsänen [5] has calculated $\log \beta_{12}^* = -6.61$. Näsänen has assumed that the mobility of Ag_2OH^+ is negligible, whereas we set it equal to the mobility of Ag^+.

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