# Studies on the Hydrolysis of Metal Ions

26. Application of a Liquid Distribution Method to the Study of the Hydrolysis of Ag⁺

P. J. ANTIKAINEN* and D. DYRSSEN

Department of Inorganic Chemistry, Royal Institute of Technology, Stockholm 70, Sweden

The distribution of silver at 25°C between solutions of quinoline (Q) in benzene and 3 M Na(ClO$_4$,OH) has been studied as a function of [Q]$_{org}$, [OH⁻] and the silver concentration. In these experiments the reaction

$$Ag^+ \text{ (aq)} + 2 \text{ Q (org)} + ClO_4^- \text{ (aq)} \rightleftharpoons AgQ_2ClO_4 \text{ (org)}$$
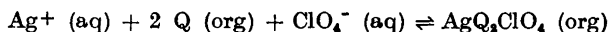
(eq. const. log K = 3.23 ± 0.02) was used for the study of the hydrolysis of Ag⁺ in 3 M NaClO$_4$ at low concentrations of silver. The data provide no evidence for the presence of significant amounts of polynuclear complexes. Furthermore, the data indicate that AgOH is not formed to any large extent in 3 M Na(ClO$_4$, OH). The value of log K_1K_2 = log[Ag(OH)$_2^-$][Ag⁺]$^{-1}$[OH⁻]$^{-2}$ was calculated to be 3.50 ± 0.10 in 3 M Na(ClO$_4$, OH). No evidence was found for Ag(OH)$_3^{2-}$ in solutions less alkaline than 0.5 M.

These conclusions are supported by measurements of the solubility of Ag$_2$O in 3 M Na(ClO$_4$,OH). The value of log K_{s2} = log [Ag(OH)$_2^-$] [OH⁻]$^{-1}$ was determined to be −3.82 ± 0.06. Together with the solubility product, K_{s0} = $10^{-7.42 \pm 0.02}$, determined by Hietanen [7] we obtained log K_1K_2 = 3.60 ± 0.08. The pH of the solubility minimum of Ag$_2$O is determined by this constant.

In connection with the distribution experiments the distribution constant, K_d, of quinoline between various organic solvents and 3 M NaClO$_4$ has been determined (Table 1).

T he hydrolysis of silver ions, Ag⁺, has been studied by several people. The data hitherto obtained have been collected together with values of K_{s0}, the solubility product, in Part II of the compilation of stability constants by Bjerrum, Schwarzenbach, and Sillén [1]. Rather different values of the equilibrium constants for the formation of AgOH and Ag(OH)$_2^-$ have been given. Moreover some authors have in addition suggested the hydroxo complexes

---

* Present address: Institute of Chemistry, University of Helsinki, Helsinki, Finland.

Ag_2OH^+ and $Ag(OH)_3{}^{2-}$. There seems to be some uncertainty about the existence of AgOH in solution. In a recent paper by Pleskov and Kabanov [2] a trinuclear complex, $Ag_3O(OH)_2{}^-$, has been claimed from emf data in alkaline solutions of Ag_2O. A critical discussion of available data will be presented in a subsequent paper by Biedermann and Sillén [9].

The purpose of this work was to apply the liquid distribution method to the study of the hydrolysis of Ag^+ in 3 M $Na(ClO_4,OH)$. The method allows the use of very low concentrations of silver in the aqueous phase; this would favor the mononuclear reactions. Also one usually does not obtain slow equilibria as with systems where a solid phase is present. In addition, a few measurements have been made of the solubility of silver oxide in 3 M $Na(ClO_4,OH)$. These solubility data are compared with data obtained from the distribution measurements.

EXPERIMENTAL

Determination of $[Ag]_{tot}$ *and* $[OH^-]$. The experiments were carried out in a room thermostated at 25°C. The Na^+ concentration in the aqueous phase was kept constant at 3 M using $NaClO_4$ and $NaOH$. The distribution between the organic phase, quinoline in benzene, and the aqueous phase, was measured by liquid counting using [110m]Ag as a tracer. 20th Century Electronic M6 liquid counter tubes (volume 10 ml, wall thickness approx. 30 mg/cm²) and Tracerlab Scalers were used for the radiometric determinations. In the solubility measurements the silver concentration of the aqueous phase was likewise determined radiometrically. Equilibration was attained by slow tilting (20—25 revolutions per min) of the solutions in glass-stoppered Pyrex centrifuge tubes; 1 h in the liquid distribution experiments, at least 2 days in the solubility measurements. The volume of the two phases in the liquid distribution measurements was 15 ml each. For the determination of the solubility of silver oxide, 15—40 ml 3 M $Na(ClO_4,OH)$ was used. After shaking, the phases were separated by centrifugation. Samples for liquid counting were withdrawn with 10 ml pipettes; in the solubility measurements the contamination by solid particles was avoided by sucking the solution through a capillary tube. The correction factor for the effect of the solvent composition on the counting rate was found to be 0.964 for the solvent pair quinoline-benzene/3 M $Na(ClO_4,OH)$; 2.96×10^{-4} M silver from sample 1 gave 19 604 cpm in the quinoline-benzene phase, but only 18 895 cpm in the aqueous phase. The determination of $-\log [OH^-]$ was carried out analytically in most cases; lower concentrations were measured potentiometrically with a Beckman glass electrode (Type 1190-72) using a solution of 0.01 M NaOH + 2.99 M $NaClO_4$ as reference ($-\log [OH^-] = 2.00$).

Choice of extracting system. It has been shown by Dyrssen, Krasovec, and Sillén [4] that Ag^+ can be extracted with chloroform from acid or neutral perchlorate solutions as $Ag(quinoline)_2ClO_4$. As quinoline does not react with alkali, it was thought that a two-phase system with quinoline and perchlorate would be very suitable for the determination of $[Ag^+]$ in an aqueous alkaline solution. However, chloroform is known to react with alkali forming, among other products, chloride ions. (It was found that a 0.1 M NaOH + 2.9 M $NaClO_4$ solution became 0.03 M in Cl^- after contact with chloroform for 24 h). A separate investigation by Mrs. Solweig Ekberg (*cf*. Table 1) showed that benzene could be a good choice as a diluent for quinoline and extracting solvent for $Ag(quinoline)_2ClO_4$. Benzene is a sufficiently stable organic solvent also. A few preliminary experiments with acridine showed that the solubility of its silver perchlorate complex was too low.

Reagents. Some insoluble matter was precipitated when the quinoline-benzene solutions, prepared from pure analytical grade products, were shaken with aqueous solutions containing silver. The quinoline solutions in benzene (0.5—0.8 M) had to be purified therefore by shaking them with a dilute solution of $AgClO_4$ (3×10^{-4} M) in distilled, chloride-free water. Traces of silver in the benzene phase were then removed by shaking with water repeatedly (at least six times). Still we obtained some losses of silver in the distribution experiments in the alkaline range, which were due probably to the collection

Table 1. Distribution constant, K_d, of quinoline between equal volumes of various organic solvents and 3 M $NaClO_4$ (0.001 M in NaOH). The concentration of quinoline in the aqueous phase after equilibration was determined spectrophotometrically at 273 — 283 mμ (except for hexone) and at the peak value around 312 mμ. 3 M $NaClO_4$ (with 0.001 M NaOH) saturated with the organic solvent were used as blanks. K_d was calculated as $[Q]'_{org}[Q]^{-1}_{aq} - 1$.

Solvent	Initial conc. of quinoline in the organic phase, $[Q]'_{org}$ M	log K_d
Chloroform	0.1	2.784 ± 0.020
Benzene	0.01	2.146 ± 0.002
Tri-n-butyl phosphate	0.02	2.123 ± 0.023
Methyl isobutyl carbinol	0.02	2.104 ± 0.023
Methyl isobutyl ketone	0.02	1.951 ± 0.001
Carbon tetrachloride	0.01	1.887 ± 0.056
*Iso*propylether	0.02	1.537 ± 0.018
n-Hexane	0.01 — 0.002	1.159 ± 0.018

of insoluble silver in the interphase. Although this seemed not to have any influence on the distribution ratio, it might have been worthwhile to have treated the organic phase with a solution of Ag_2O in, *e. g.*, 0.1 M NaOH in order to remove impurities that might react with silver in alkaline solutions only. The quinoline concentration in the benzene phase was determined spectrophotometrically at 312.5 mμ by Mrs. Ekberg.

The $NaClO_4$ was made from doubly recrystallized Na_2CO_3 p. a. and conc. $HClO_4$ p. a. The $NaClO_4$ was crystallized twice from distilled, chloride-free water according to a technique used by our colleagues at this laboratory [5]. The molarity of the $NaClO_4$ solution was determined from the specific gravity of the solution and the weight of $NaClO_4$ (dried at 110°C) per gram of the solution. The NaOH was of finest Merck quality and contained negligible amounts of chloride.

The radioactive isotope of silver was obtained by thermal neutron irradiation of a weighed piece of pure silver at A.E.R.E., Harwell, England. The silver was dissolved in nitric acid and the silver concentration was checked gravimetrically as AgCl. The initial specific activities of the two silver samples used were 1.2 and 12 mC per gram Ag, respectively. Stock solutions of the radioactive silver were prepared in 3 M $NaClO_4$.

APPLICATION OF THE LAW OF MASS ACTION TO THE DATA

Symbols. The following symbols and definitions are used:

[ ]   concentrations in the aqueous phase
[ ]$_{org}$ concentrations in the benzene phase
Q   quinoline
K_1 $= [AgOH][Ag^+]^{-1}[OH^-]^{-1}$
K_2 $= [Ag(OH)_2^-][AgOH]^{-1}[OH^-]^{-1}$
With two liquid phases:
K $= [AgQ_2ClO_4]_{org}[Ag^+]^{-1}[Q]^{-2}_{org}[ClO_4^-]^{-1}$ (equil. constant)
q $= [Ag]_{total, org}[Ag]^{-1}_{total, aq}$ (net distribution ratio)
φ $= q[Q]^{-2}_{org}[ClO_4^-]^{-1}$ and $y = -\log \varphi$ [OH$^-$] (auxiliary functions)
In equilibrium with Ag_2O:
K_{s0} $= [Ag^+][OH^-]$
K_{s1} $= [AgOH] = K_{s0}K_1$
K_{s2} $= [Ag(OH)_2^-][OH^-]^{-1} = K_{s0}K_1K_2 = K_{s1}K_2$

Distribution measurements. The quantity measured in the distribution experiments is the net distribution ratio

$$q = [Ag]_{total,org}[Ag]^{-1}_{total,aq}$$

It may be seen from Table 2 ($[OH^-] \approx 10^{-7}$ M, $[ClO_4^-] = 3$ M) that $q[Q]^{-2}_{org}$ is constant for a range of values of $[Q]_{org}$ and silver concentration in both phases. This is a strong indication that silver is extracted as monomeric AgQ_2ClO_4. As the concentration of quinoline in the aqueous phase was low due to a high value of the distribution constant (*cf.* Table 1), silver complexes with quinoline were not likely to be formed in the aqueous phase in any appreciable amount. Furthermore, it was shown by Dyrssen, Kraševec, and Sillén [4] that the distribution of silver between quinoline in chloroform and perchlorate solutions in the range pH 3—10 was function of $[Q]^2_{org}[ClO_4^-]$ only. Thus we may assume that the extraction of silver takes place by the following reaction (eq. const. *K*):

$$Ag^+ \text{ (aq)} + 2 \text{ Q (org)} + ClO_4^- \text{ (aq)} \rightleftharpoons AgQ_2ClO_4 \text{ (org)}$$
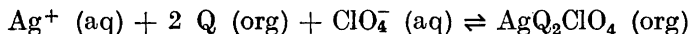
In the presence of a complexing ion like OH^- the expression for q will be

$$q = \frac{[AgQ_2ClO_4]_{org}}{[Ag^+] + [AgOH] + [Ag(OH)_2^-] + [\text{other hydroxo complexes}]} \quad (1a)$$

or

$$\log q = \log K [Q]^2_{org} [ClO_4^-] - \log (1 + K_1[OH^-] + K_1K_2[OH^-]^2 + \ldots) \quad (1b)$$

Other hydroxo complexes would appear in eqn. (1b) as terms with higher powers of $[OH^-]$ (*e.g.* $Ag(OH)_3^{2-}$) or of $[Ag^+]$ (*e.g.* $Ag_2(OH)_2$). Further the equation presupposes that silver is not extracted as AgQ_2OH. In fact, at the silver concentrations used practically no silver was found to be extracted by a solution of quinoline in benzene from a solution of Ag(I) in 0.5 M NaOH as long as no ClO_4^- was present.

Eqn. (1b) may be written as

$$y = \log (q^{-1}[Q]^2_{org}[ClO_4^-] [OH^-]^{-1}) = -\log \varphi [OH^-] = \log K^{-1}K_1 +$$
$$+ \log (K_1^{-1}[OH^-]^{-1} + 1 + K_2[OH^-]) \quad (1c)$$

The curve $y = -\log \varphi [OH^-]$ against $\log [OH^-]$ will have two asymptotes, namely

$$[OH^-] \to 0; \quad y = -\log [OH^-] -\log K; \quad i.e. \quad \varphi = K \quad (2a)$$

$$[OH^-] \to \infty; \quad y = \log [OH^-] + \log K_1K_2 -\log K \quad (2b)$$

The intersection of the asymptotes at

$$[OH^-] = [OH^-]_0 \text{ and } y = y_0$$

gives

$$- 2 \log [OH^-]_0 = \log K_1K_2 \quad (3a)$$

and

$$y_0 = \log (K^{-1}K_1^{1/2}K_2^{1/2}) \quad (3b)$$

The point at $[OH^-] = [OH^-]_0$ on the distribution curve is

$$y'_0 = \log \, K^{-1}K_1(K_1^{-\frac{1}{2}}K_2^{\frac{1}{2}} + 1 + K_1^{-\frac{1}{2}}K_2^{\frac{1}{2}}) \qquad (4)$$

The difference between this point and the point of intersection of the asymptotes is

$$y'_0 - y_0 = \log \, (1 + \log \, K_1^{\frac{1}{2}}K_2^{-\frac{1}{2}} + 1) \qquad (5)$$

i.e., this quantity is determined by $K_1K_2^{-1}$, the ratio between the two consecutive constants. The smallest value of $y'_0 - y_0$ is log 2, which corresponds to the case when AgOH may be neglected ($K_1 = 0$, see Fig. 1).

Solubility measurements. It is not possible to determine from solubility measurements whether silver oxide dissolves in water as polynuclear fractions of the solid phase, *e.g.* $Ag_2(OH)_2$, as the concentrations of such species will not vary with the composition of the solvent. Assuming the same species to exist in the aqueous phase as previously in the distribution experiments, we obtain
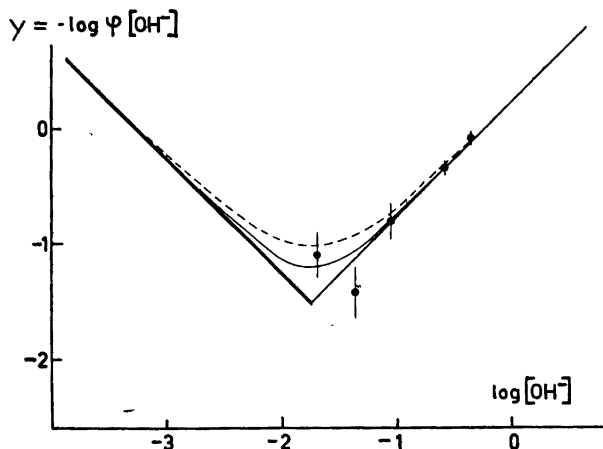
$$[Ag]_{total} = [Ag^+] + [AgOH] + [Ag(OH)_2^-] \qquad (6a)$$

or

$$[Ag]_{total} = [AgOH](K_1^{-1}[OH^-]^{-1} + 1 + K_2[OH^-]) \qquad (6b)$$

[AgOH] is constant ($= K_{s1}$) in the presence of solid Ag_2O.
The curve log $[Ag]_{total}$ against log $[OH^-]$ will have the same form as the curve $y = -\log \varphi \, [OH^-]$ against log $[OH^-]$ for the distribution data (eqn. 1c). Eqns. 2—5 will be the same except that K_{s1} must be substituted for $K^{-1}K_1$, and

Fig. 1. The distribution of Ag — ¹¹⁰ᵐAg between solutions of quinoline in benzene and 3 M Na(ClO₄,OH) plotted as $y = -\log \varphi \, [OH^-]$ against log $[OH^-]$. The data are taken from Table 2. The equations for the curves with their two asymptotes are given in the text. The full-drawn curve has been calculated for $K_1 = 0$ and the dashed curve for $K_1 = K_2$. The position of the asymptote will slope -1 is calculated from values of φ in Table 2, where the hydrolysis of Ag^+ has no influence on the distribution ($[OH^-] \approx 10^{-7}$ M).
    The point of intersection of the two asymptotes gives log $K_1K_2 = 3.50 \pm 0.10$.

Table 2. Distribution of Ag-^{110m}Ag between quinoline in benzene and 3 M Na(ClO$_4$,OH) solutions as a function of the concentrations of quinoline, silver, NaOH, and NaClO$_4$.

$-\log$ [Q]$_{org}$	$-\log$ [Ag]$_{tot, org}$	$-\log$ [Ag]$_{tot, aq}$	$\log q$	$\log \varphi$
[OH$^-$] $\approx 10^{-7}$ M, [ClO$_4^-$] = 3 M				
1.227	5.000	6.235	1.235	3.212
1.403	5.022	5.939	0.917	3.246
1.558	5.094	5.702	0.608	3.247
1.704	5.184	5.473	0.289	3.220
2.102	5.620	5.151	-0.489	3.238
		mean value: $\log \varphi = 3.23 \pm 0.02$ ($= \log K$)		
[OH$^-$] $= 10^{-1.70}$ M, [ClO$_4^-$] $= 10^{0.474}$ M				
0.584	5.079	7.078	1.999	2.693
0.584	4.650	6.978	2.328	3.022
0.806	5.198	6.681	1.483	2.621
0.806	4.767	6.480	1.713	2.851
		mean value: $\log \varphi = 2.80 \pm 0.20$		
[OH$^-$] $= 10^{-1.37}$ M, [ClO$_4^-$] $= 10^{0.472}$ M				
0.584	5.349	7.280	1.931	2.627
0.584	5.057	7.133	2.076	2.772
0.584	4.765	6.960	2.195	2.891
0.584	3.967	6.277	2.310	3.006
0.584	3.599	5.346	1.747	2.443
0.584	3.338	5.663	2.325	3.021
		mean value: $\log \varphi = 2.79 \pm 0.23$		
[OH$^-$] $= 10^{-1.06}$ M, [ClO$_4^-$] $= 10^{0.464}$ M				
0.584	4.813	5.947	1.134	1.838
0.584	3.956	5.113	1.157	1.861
0.584	3.731	4.856	1.125	1.829
0.584	3.610	4.851	1.241	1.945
0.637	6.052	6.835	0.783	1.593
0.637	5.777	6.798	1.021	1.831
0.637	5.368	6.427	1.059	1.869
0.637	4.974	6.242	1.268	2.078
0.637	4.692	5.730	1.038	1.848
0.637	4.530	5.760	1.230	2.040
		mean value: $\log \varphi = 1.87 \pm 0.16$		
[OH$^-$] $= 10^{-0.594}$ M, [ClO$_4^-$] $= 10^{0.438}$ M				
0.584	5.861	6.012	0.151	0.881
0.584	5.643	5.861	0.218	0.948
0.584	4.281	4.543	0.262	0.992
		mean value: $\log \varphi = 0.94 \pm 0.07$		
[OH$^-$] $= 10^{-0.363}$ M, [ClO$_4^-$] $= 10^{0.409}$ M				
0.584	6.570	6.408	0.162	0.597
0.584	6.348	6.087	0.261	0.498
0.584	6.114	5.771	0.343	0.416
0.584	5.553	5.256	0.297	0.462
0.584	4.401	4.239	0.162	0.597
0.584	4.376	4.169	0.207	0.552
0.584	4.358	4.109	0.249	0.510
		mean value: $\log \varphi = 0.45 \pm 0.06$		

Table 3. The solubility of Ag_2O in 3 M $Na(ClO_4,OH)$ measured radiometrically at 25°C with [110m]Ag. Determination of log K_{s2} = log $[Ag(OH)_2^-][OH^-]^{-1}$ for $[OH^-] > 0.1$ M.

log $[OH^-]$	log $[Ag]_{total}$	log $[Ag]_{total}[OH^-]^{-1}$
−1.42	−5.08	(−3.66)
−1.04	−4.76	(−3.72)
−0.883	−4.65	−3.77
−0.827	−4.60	−3.77
−0.578	−4.50	−3.92
−0.461	−4.30	−3.84
−0.248	−4.06	−3.81

mean value: −3.82 ± 0.06

log $[Ag]_{total}$ for $-\log \varphi [OH^-]$. The value of $[OH^-]$ of the solubility minimum of Ag_2O is thus given by

$$- 2 \log [OH^-]_0 = \log K_1K_2 \tag{3'a}$$

The constants in these equations may found by fitting normalized curves to the data [3].

RESULTS

Distribution data. The data on the distribution of silver between solutions of quinoline in benzene and 3 M $NaClO_4$-NaOH solutions, with varying amounts of NaOH are given in Table 2 and plotted in Fig. 1. The two curves in Fig. 1
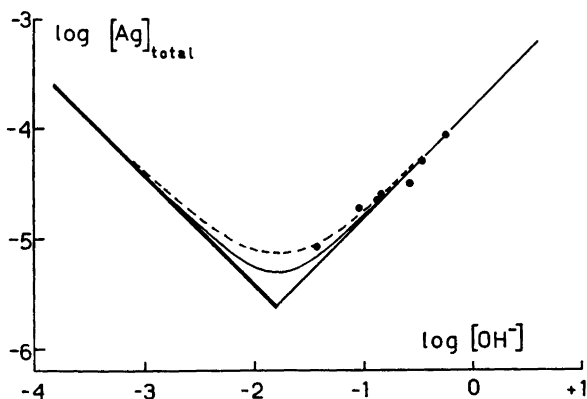

Fig. 2. The solubility of Ag_2O in 3 M $Na(ClO_4, OH)$ as a function of $[OH^-]$. The data are given in Table 3. The equations for the curves are given in the text and are the same as for the curves in Fig. 1. The full-drawn curve has been calculated for $K_1 = 0$ and the dashed curve for $K_1 = K_2$. The position of the left-hand asymptote with slope −1 is given by the solubility product, K_{s0}. The point of intersection of the two asymptotes gives log K_1K_2 = 2 (1.80 ± 0.04) = 3.60 ± 0.08.

correspond to the assumptions $K_1 = 0$ (full-drawn curve) and $K_1 = K_2$ (dashed curve). In spite of the rather large limits of error it can be said that $K_1 < K_2$. The point of intersection of the two asymptotes at log [OH$^-$] = = -1.75 ± 0.05 gives

$$\log K_1 K_2 = 3.50 \pm 0.10$$

There is no evidence of a third complex below 0.5 M NaOH. The equilibrium constant K for the reaction

$$\text{Ag}^+ \text{ (aq)} + 2 \text{ Q (org)} + \text{ClO}_4^- \text{ (aq)} \rightleftharpoons \text{AgQ}_2\text{ClO}_4 \text{ (aq)}$$
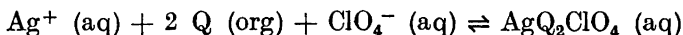
can be calculated from Table 1 ([ClO$_4^-$]) = 3 M, [OH$^-$] $\approx 10^{-7}$ M) to be log $K = 3.23 \pm 0.02$. This constant determines the left-hand asymptote in Fig. 1 rather accurately.

It can also be seen from Table 2 that the value of q (or φ) is independent of the silver concentration at the low amounts of silver used in these experiments. As silver certainly is monomeric in the organic phase (*cf.* φ at [OH$^-$] $\approx 10^{-7}$ M) this proves that no appreciable amounts of polynuclear complexes are present in the aqueous phase.

It was mentioned under "Experimental" that losses of silver occured in the distribution experiments in spite of the purification of the reagents. However, the loss of silver did not seem to correlate with any change in q (or φ). It was also found that the losses could be kept at a minimum using a rather large concentration of quinoline in benzene.

Solubility data. The data in Table 3 are plotted in Fig. 2 as log [Ag]$_{\text{total}}$ against log [OH$^-$]. It was shown above that the same curves as in Fig. 1 then apply to the solubility data too. The position of the left-hand asymptote with slope -1 is given by the solubility product, K_{s0}; log [Ag]$_{\text{total}}$ = log K_{s0} $-$log [OH$^-$]. A value of this constant, log $K_{s0} = 7.42 \pm 0.02$, was determined from potentiometric determinations of [Ag$^+$] and [H$^+$] by Hietanen [7]. The right-hand asymptote is determined by log K_{s2}, which was calculated to be -3.82 ± 0.06 in Table 3. The point of intersection of the asymptotes gives

$$\log K_1 K_2 = 3.60 \pm 0.08$$

This value is not very different from the value determined from the distribution data. Nor do the solubility data provide any evidence of appreciable amounts of AgOH or Ag(OH)$_3^{2-}$; we conclude $K_1 < K_2$ and $K_3 \ll K_2$ in 3 M NaClO$_4$ from these experiments too. It might be pointed out that a study of the solubility of Ag$_2$O in solutions less alkaline than 0.01 M gives rather uncertain values due to the fact that the buffer capacity of such solutions is low.

CONCLUSIONS

The hydrolysis of silver in water, examined at low concentrations of silver in 3 M NaClO$_4$ at 25°C by the distribution and solubility methods described above, can be explained by the following two reactions:

$$\text{Ag}^+ + \text{OH}^- \rightleftharpoons \text{AgOH} \qquad K_1$$

$$\text{AgOH} + \text{OH}^- \rightleftharpoons \text{Ag(OH)}_2^- \quad K_2$$
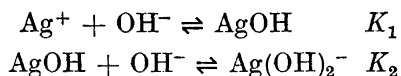
The data indicate that $K_1 < K_2$, *i.e.* that in 3 M Na(ClO$_4$,OH) [AgOH] is never as much as 1/3 of the total silver. The value of log K_1K_2 was determined as 3.6 ± 0.1. The hydrolysis of Ag^+ thus seems to resemble that of Hg^{2+} as determined by Hietanen and Sillén [6]. No evidence is found for the existence of $Ag(OH)_3{}^{2-}$ below [OH$^-$] = 0.5 M.

The distribution method allows a full variation of the concentration of all silver species. However, no influence of the silver concentration on the distribution ratio could be detected at $[Ag^+][OH^-] < K_{s0}$. This does not preclude the possibility that polynuclear hydroxo complexes can be proved to exist in solutions with higher silver concentrations, *e.g.* 1 M AgNO$_3$ or 5 M KOH saturated with Ag$_2$O. In the former case titration with HNO$_3$ in 1 M AgNO$_3$ would reveal any $Ag_m(OH)_n$ and in the second case a potentiometric determination of $[Ag^+]$ (*cf.* Ref.[2]) on dilution with 5 M KOH should reveal any polynuclear species. Results on such solutions will be reported in following papers [7,8].

REFERENCES

1. Bjerrum, J., Schwarzenbach, G. and Sillén, L. G. *Stability Constants*, part II, The Chemical Society, London, 1958, Spec. Publication No 7.
2. Pleskov, Yu. V. and Kabanov, B. N. *Zhur. Neorg. Khim.* 2 (1957) 1807.
3. Sillén, L. G. *Acta Chem. Scand.* 10 (1956) 186.
4. Dyrssen, D., Krašovec, F. and Sillén, L. G. *Int. Conf. on Coordination Chemistry*, London 1959.
5. "*Some laboratory methods* . . ., Department of Inorganic Chemistry, Royal Institute of Technology, Stockholm", manuscript, 1959.
6. Hietanen, S. and Sillén, L. G. *Acta Chem. Scand.* 6 (1952) 747.
7. Antikainen, P. J., Hietanen, S. and Sillén; L. G. *Acta Chem. Scand.* 14 (1960) 95.
8. Biedermann, G. and Hietanen, S. *Acta Chem. Scand.* 14 (1960) *In press.*
9. Biedermann, G. and Sillén, L. G. *Acta Chem. Scand.* 14 (1960) *In press.*