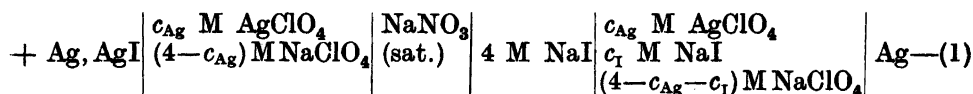# A Potentiometric Study of the Complex Formation between Silver and Iodide Ions

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The e.m.f. of the cell (1) below was measured at 25° C in the range $0.003 < c_{Ag} < 0.08$ and with enough sodium iodide (<4 M) to prevent solid silver iodide from being precipitated. In this range the solutions contained significant amounts of four silver iodide species, *viz.* AgI_2^{-}, AgI_4^{3-}, $Ag_2I_6^{4-}$, and $Ag_3I_8^{5-}$. The corresponding equilibrium constants were computed (Table 2) and the solubility product of silver iodide at the given ionic strength 4 M (NaClO$_4$) was determined.

The following cell, e. m. f. E mV, was measured at 25° C. All concentrations throughout the paper are given in gram formula weight per litre (M)

$$+ \text{ Ag, AgI} \left| \begin{array}{l} c_{Ag} \text{ M AgClO}_4 \\ (4-c_{Ag}) \text{ M NaClO}_4 \end{array} \right| \begin{array}{c} \text{NaNO}_3 \\ (\text{sat.}) \end{array} \left| 4 \text{ M NaI} \right| \begin{array}{l} c_{Ag} \text{ M AgClO}_4 \\ c_I \text{ M NaI} \\ (4-c_{Ag}-c_I) \text{ M NaClO}_4 \end{array} \right| \text{Ag---(1)}$$

The solutions of the right hand half-cell were obtained by mixing an original solution in the electrode vessel, containing c_{Ag} M AgClO$_4$ and $(4-c_{Ag})$ M NaI, with a solution from a burette containing c_{Ag} M AgClO$_4$ and $(4-c_{Ag})$ M NaClO$_4$. Portions of this latter solution were added until silver iodide was precipitated in the vessel. In some cases E was determined by measuring the two halves of the cell above against a reference electrode, Hg,Hg$_2$Cl$_2$ | 4 M NaCl | NaNO$_3$ (sat.). The silver electrodes consisted of silver plated platinum wires, from which the silver-silver iodide electrodes were produced by anodic oxidation in a solution of sodium iodide acidified with hydrogen perchlorate (*cf.* Brown[1]). The sodium iodide was of *pro analysi* quality. Other chemicals used are described elsewhere (Ref. [2,3]), and here also the experimental details may be found.

The results of the measurements are given in Table 1. If the concentration of uncomplexed silver ions in the right hand solution of cell (1) is [Ag$^+$], Nernst's formula gives

$$E = 59.16 \log \frac{c_{Ag}}{[\text{Ag}^+]} \tag{2}$$

Table 1. The potentiometric measurements.

$c_{Ag} = 0.08$			●		$c_{Ag} = 0.02$			○	
c_I	$[I^-]$	E	$10^{14} \times F_4$	$-\log [Ag^+] -2\log [I^-]$	c_I	$[I^-]$	E	$10^{14} \times F_4$	$-\log [Ag^+] -2\log [I^-]$
3.92	3.63	987.1	2.75	16.66	3.98	3.90	988.3	2.19	17.23
3.63	3.34	979.4	2.88	16.60	3.69	3.61	979.9	2.14	17.14
3.38	3.09	972.5	3.02	16.56	3.43	3.35	972.8	2.19	17.09
3.16	2.87	966.2	3.16	16.51	3.21	3.13	966.0	2.24	17.04
2.80	2.52	954.9	3.44	16.44	3.02	2.94	960.0	2.30	16.99
2.58	2.31	947.7	3.64	16.39	2.84	2.76	954.3	2.35	16.95
2.39	2.12	941.2	3.98	16.35	2.62	2.54	946.0	2.35	16.88
2.23	1.97	935.8	4.37	16.33	2.43	2.36	939.1	2.40	16.82
2.09	1.83	930.2	4.68	16.30	2.26	2.19	931.9	2.46	16.77
1.92	1.67	923.7	5.25	16.27	2.12	2.05	926.1	2.58	16.74
1.78	1.53	916.8	5.83	16.22	1.95	1.87	918.5	2.70	16.68
1.66	1.42	911.9	6.47	16.21	1.81	1.74	911.5	2.76	16.63
					1.66	1.59	904.3	3.03	16.59
1.61	1.39	911.3	$L = 4.4 \times 10^{-17}$		1.53	1.46	897.2	3.25	16.54
1.56	1.34	910.7	$L = 4.3 \times 10^{-17}$		1.42	1.35	891.2	3.48	16.50
1.51	1.29	910.5	$L = 4.2 \times 10^{-17}$		1.31	1.24	883.6	3.64	16.45
					1.28	1.21	881.6	3.73	16.43
From the solutions below the lines silver iodide has been precipitated. Hence the solubility product, L, can be computed from the values of E, measured in these solutions.					1.17	1.10	874.2	4.08	16.40
					1.08	1.01	868.0	4.48	16.36
					0.996	0.93	863.6	$L = 4.7 \times 10^{-17}$	
					0.926	0.86	862.2	$L = 4.6 \times 10^{-17}$	

●, ○, □, +: These signs are used in Figs. 1 and 2 to distinguish the four titration series.

As the variation of $c_{Ag}/[Ag^+]$ is about 1000:1 within a titration series, it is more practical to use the function (*cf.* Ref.[3])

$$F_4 = \frac{c_{Ag}}{[Ag^+]\,[I^-]^4} \qquad (3)$$

for the graphical representation as the range of variation of F_4 is only 3:1 at most. F_4, drawn as a function of $1/[I^-]$, gives some of the equilibrium constants more directly than does a logarithmic representation.

To calculate F_4 and on the whole to analyse the data of Table 1, it is necessary to compute the concentration of the f r e e iodide ions of the solution. This has been done (*cf.* columns c_I and $[I^-]$ of Table 1) by reducing c_I with the small term of correction $\bar{n} \cdot c_{Ag}$, where $\bar{n}$, defined by the well-known eqn. (4), is the mean number of iodide ions bound per silver ion in the solution.

$$[I^-] = c_I - \bar{n} \cdot c_{Ag} \qquad (4)$$

Table 1. Continued.

c_I	[I⁻]	E	$10^{14} \times F_4$	$-\log [Ag^+] -2 \log [I^-]$	c_I	[I⁻]	E	$10^{14} \times F_4$	$-\log [Ag^+] -2\log [I^-]$
	$c_{Ag} = 0.01$			□		$c_{Ag} = 0.00333$			+
3.99	3.95	988.8	2.14	17.52	4.00	3.99	989.7	2.10	18.01
3.69	3.65	980.7	2.14	17.46	3.45	3.44	974.5	2.10	17.88
3.44	3.40	973.7	2.14	17.40	3.23	3.22	967.9	2.14	17.82
3.22	3.18	966.7	2.14	17.34	3.03	3.02	961.2	2.10	17.76
3.02	2.98	960.6	2.20	17.30	2.86	2.85	954.6	2.10	17.71
2.63	2.59	946.5	2.24	17.17	2.63	2.62	946.6	2.14	17.64
2.43	2.39	939.0	2.30	17.11	2.44	2.43	939.7	2.19	17.59
2.27	2.23	932.4	2.35	17.06	2.27	2.26	932.2	2.20	17.53
2.12	2.08	925.9	2.40	17.01	2.13	2.12	926.1	2.24	17.48
1.96	1.92	917.6	2.40	16.94	1.96	1.95	918.1	2.30	17.44
1.81	1.77	910.4	2.52	16.89	1.82	1.81	911.2	2.35	17.38
1.66	1.62	902.9	2.64	16.84	1.67	1.66	902.3	2.35	17.31
1.60	1.56	898.7	2.64	16.80	1.60	1.59	898.6	2.46	17.27
1.53	1.49	895.4	2.76	16.79	1.54	1.53	894.7	2.40	17.23
1.43	1.39	888.8	2.82	16.74	1.43	1.42	887.8	2.52	17.19
1.29	1.25	879.2	3.03	16.67	1.29	1.28	878.2	2.58	17.11
1.17	1.13	871.5	3.31	16.62	1.08	1.07	861.3	2.76	16.98
1.08	1.04	863.0	3.32	16.56	1.00	0.99	854.1	2.82	16.93
0.998	0.963	857.0	3.56	16.52	0.909	0.897	845.4	3.03	16.86
0.907	0.873	849.2	3.90	16.47	0.833	0.822	837.9	3.17	16.81
0.832	0.798	842.9	4.37	16.44	0.769	0.758	831.2	3.40	16.77
					0.667	0.656	818.4	3.72	16.68
					0.615	0.614	811.7	3.72	16.57
0.798	0.766	841.0	$L = 4.6_5 \times 10^{-17}$						
0.768	0.736	839.5	$L = 4.7_5 \times 10^{-17}$		0.533	0.522	803.2	$L = 4.6 \times 10^{-17}$	

A sufficiently accurate value of $\bar{n}$ can be deduced from Bodländer's formula, approximated to (*cf.* Ref.[4])

$$\frac{\varDelta E}{\varDelta \log c_I} = 59.16 \; \bar{n} \qquad (5)$$

where $\varDelta E$ and $\varDelta c_I$ are the differences between two consecutive values of E and c_I in a titration series of Table 1. Though this approximation is certainly far from accurate, especially as the solutions contain polynuclear complexes, it gives values of [I⁻] from eqn. (4), which agree in all cases to within 1 % with the final values computed below. Hedström [5] has recently given an exact and general method to calculate the concentration of free ligands of a complex system, but in the present case a sufficient number of titration series has not been measured in order to make it possible to carry out the graphical integration necessary in Hedström's method.

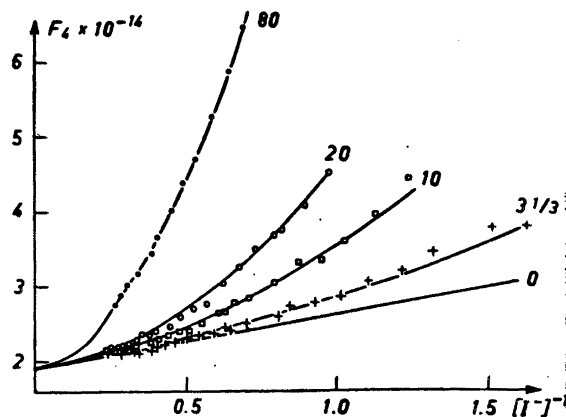The complex formation can be described by the equilibria

$$m \; Ag^+ + n \; I^- \rightleftharpoons Ag_m I_n^{m-n} \qquad (6)$$
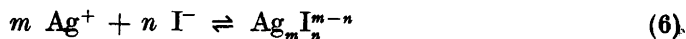
Fig. 1. F_4 *as a function of* $1/[I^-]$. *The numbers at the curves denote* $10^3 \times c_{Ag}$. *The ordinates of the points are obtained from the experiments by means of eqn. (3). The curves are calculated from the values of* $\beta_{m,m+n}$ *in Table 2 with the aid of eqns. (11) and (12).*

with the over-all complexity constants $\beta_{m,n}$. The law of mass action then gives ($\beta_{1,0} = 1$)

$$c_{Ag} = \sum_{m=1}^{M} \sum_{n=0}^{N} m\ [Ag_m I_n^{m-n}] = \sum_{m=1}^{M} \sum_{n=0}^{N} m\beta_{m,n}[Ag^+]^m[I^-]^n \qquad (7)$$

and hence F_4 can be written as

$$F_4 = \sum_{n=0}^{N} \beta_{1,n}[I^-]^{n-4} + \sum_{m=2}^{M} \sum_{n=1}^{N} m\beta_{m,n}[Ag^+]^{m-1}[I^-]^{n-4} \qquad (8)$$

where the first sum of the right hand member originates from the mononuclear and the double sum from the polynuclear species. Obviously

$$\lim_{c_{Ag} \to 0} F_4 = F_4^\circ = \sum_{n=0}^{N} \beta_{1,n}[I^-]^{n-4} \qquad (9)$$

F_4 is drawn as a function of $1/[I^-]$ in Fig. 1, from which it is seen that the curves for the two series with lowest silver contents coincide for low values of $1/[I^-]$. This gives immediately F_4°, which can be described by a straight line, *i. e.*

$$F_4^\circ = \beta_{1,4} + \beta_{1,3} / [I^-] \qquad (10)$$

for sufficiently high values of $[I^-]$. $\beta_{1,3} = (7 \pm 2) \times 10^{13}$ is obtained as the slope and $\beta_{1,4} = (19 \pm 1) \times 10^{13}$ as the extrapolated ordinate of this line. In Fig. 1 F_4° is drawn as a straight line in all that range, where potentiometric measurements have been made. This could be done, as some measurements of the solubility of silver iodide in aqueous sodium iodide, carried out in this
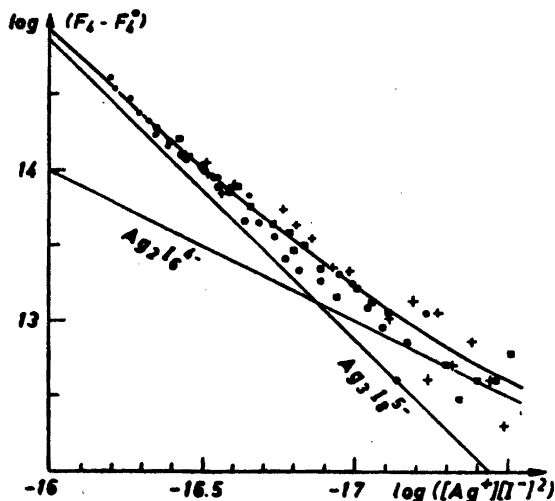
Fig. 2. $(F_4-\overset{\circ}{F_4})$ *is a function of* $[Ag^+][I^-]^2$ *solely for all the four series measured. The straight lines show how* $(F_4-\overset{\circ}{F_4})$ *can be separated into two terms, corresponding to the two complexes marked.*

laboratory, show definitely that the succeeding terms of F_4^0, *viz.* $\beta_{1,2}/[I^-]^2$ and so on, are quite negligible, when $[I^-] > 0.5$.

The polynuclear species and their strength can be obtained by studying the difference $(F_4-F_4^c)$, F_4^0 now being known from eqn. (10). This has been done in Fig. 2, where log $(F_4-F_4^c)$ has been drawn as a function of log $([Ag^+]$ $[I^-]^2)$ (*cf. e.g.* Hietanen and Sillén [6]). In this diagram the points from all the four series measured fall on one single curve. This means that the only terms to be considered in the double sum of eqn. (8) are those of the form $\beta_{m,\,2m\,+\,2}$ $([Ag^+][I^-]^2)^m$, corresponding to one or several of the species $Ag_mI_{2m\,+\,2}^{(m\,+\,2)-}$. At the higher values of $(F_4-F_4^0)$ the curve of Fig. 2 is described rather well by a straight line with slope -2, which means that the species $Ag_3I_8^{5-}$ dominates. At lower values the accuracy is small, as $(F_4-F_4^0)$ is small compared with F_4. At all events it seems obvious that the points here lie over the line mentioned, and hence a term of first degree in $[Ag^+]$ $[I^-]^2$ has been introduced, representing the silver tied up in $Ag_2I_6^{4-}$. Hence the only polynuclear complexes to be considered are $Ag_2I_6^{4-}$ and $Ag_3I_8^{5-}$. The distribution of the silver between those is shown by the two straight lines in Fig. 2. Their positions are settled by the over-all complexity constants $\beta_{2,6} = (5 \pm 3) \times 10^{29}$ and $\beta_{3,8} = (25 \pm 5) \times 10^{45}$, which have been obtained from the straight line resulting, when $(F_4-F_4^0) \cdot [Ag^+]^{-1} [I^-]^{-2}$ is drawn in a diagram as a function of $[Ag^+] [I^-]^2$. From such a diagram the accuracy of the constants can also be judged.

From the discussions above it follows, that only four complexes, *viz.* AgI_3^{2-}, AgI_4^{3-}, $Ag_2I_6^{4-}$, and $Ag_3I_8^{5-}$, are to be considered in the range, where e.m.f. measurements have been carried out. Hence eqn. (7) is simplified in this range to
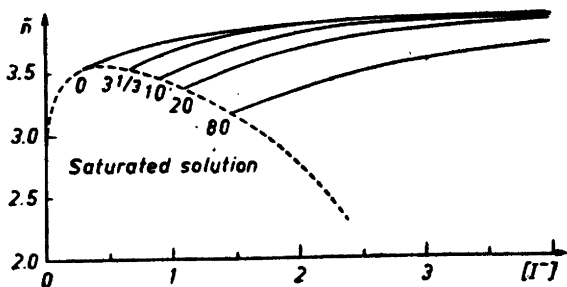
Fig. 3. The mean number, $\bar{n}$, of iodide ions bound per silver ion in unsaturated solutions with total silver contents marked as $10^3 \times c_{Ag}$ at the corresponding curves. The dashed curve is calculated from the solubility of AgI in aqueous solutions of NaI.

$$c_{Ag} = \beta_{1,3}[Ag^+][I^-]^3 + \beta_{1,4}[Ag^+][I^-]^4 + 2\beta_{2,6}[Ag^+]^2[I^-]^6 + 3\beta_{3,8}[Ag^+]^3[I^-]^8 \quad (11)$$

and correspondingly

$$c_I - [I] = 3\beta_{1,3}[Ag^+][I^-]^3 + 4\beta_{1,4}[Ag^+][I^-]^4 +$$
$$+ 6\beta_{2,6}[Ag^+]^2[I^-]^6 + 8\beta_{3,8}[Ag^+]^3[I^-]^8 \quad (12)$$

where the pertinent constants $\beta_{m,n}$ are now known from the graphical computations, described above. Hence $\bar{n}$, representing the value of the right hand member of eqn. (12) divided by the right hand member of eqn. (11), may be calculated for each titration series, by solving for $[Ag^+]$ and $[I^-]$ from eqns. (11) and (12) for some values of c_I. The same values of $[Ag^+]$ and $[I^-]$ have also been used to calculate the F_4-curve of Fig. 1. The corresponding $\bar{n}$-curves are to be seen in Fig. 3, which has been used to calculate the values of $[I^-]$ in Table 1 from eqn. (4). On the whole this computation gives the same result as the first approximation from Bodländer's formula, eqn. (5), and the same values of $[I^-]$ were also obtained by several other approaches, tried by the author to describe the complex formation. The reason for this is of course that c_I is in all cases so much larger than c_{Ag} that even a very rough approximation of $\bar{n}$ gives a rather correct value of $[I^-]$ from eqn. (4).

The two polynuclear complexes found above are formed quite reasonably by the two consecutive condensation reactions

$$2AgI_4^{3-} \rightleftharpoons Ag_2I_6^{4-} + 2I^- \text{ and } Ag_2I_6^{4-} + AgI_4^{3-} \rightleftharpoons Ag_3I_8^{5-} + 2I^- \quad (13)$$
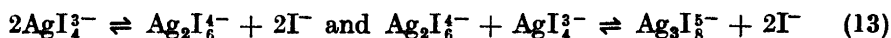
with the equilibrium constants $b_{2,6} = \beta_{2,6} \cdot (\beta_{1,4})^{-2} = 15 \pm 10$ and $b_{3,8} = \beta_{3,8} \cdot (\beta_{2,6} \cdot \beta_{1,4})^{-1} = 250 \pm 150$, respectively. It seems rather probable that analogous condensation reactions continue to produce larger species of the form $Ag_mI_{2m+2}^{(m+2)-}$ with increasing total silver concentrations. It could certainly be possible to draw the curve of Fig. 2 less rectilinear in its upper part and so make room for more highly condensed species at the expense of $Ag_3I_8^{5-}$. Such an increased curvature would be rather arbitrary, however. It is known (Sillén [7]) that the method used in the present paper is "a rather un-

favourable case, as $[Ag^+]$ is measured, but the difference $(c_I - [I^-])$ cannot be calculated with enough accuracy to be of much help". Hence there is not much reason to speculate about the higher condensation products. Perhaps it could be said that it is rather probable that the equilibrium constant, $b_{4,10}$, of the next member of the series, $Ag_4I_{10}^{6-}$, is less than $b_{3,8}$, as $b_{4,10} > b_3$ would give a quite pronounced curvature to the upper part of the curve of Fig. 2. The description above of the silver-iodide system is in better agreement with the experimental data than an infinite series of complexes would be, in which all the equilibrium constants $b_{m, 2m + 2}$ have the same value for $m > 2$. There is also the possibility that a reaction, e. g. a ring closure:

$$Ag_m I_{2m + 2}^{(m + 2)-} \rightleftharpoons Ag_m I_{2m}^{m-} + 2I^- \qquad (14)$$
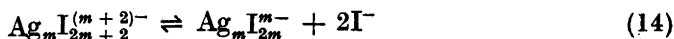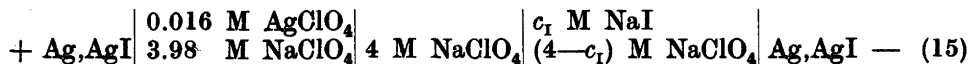
cuts off the series at some step in the postulated continuing condensation.

The results obtained from the e.m.f. measurements agree quantitatively with those from the solubility determinations already mentioned. These latter measurements moreover gave some information about the silver iodide species with negative charges less than —2. They also proved the existence of complexes with negative charges higher than —5 in solutions with silver contents larger than those studied in the present paper.

Table 2. The over-all complexity constants $\beta_{m,m + n}$ for the reaction (6) and $k_{m,n}$ for the reaction (16). $L = 4.5 \times 10^{-17}$.

Complex	$\beta_{m,m + n}$	$k_{m,n}$
AgI_3^{2-}	$\beta_{1,3} = (7 \pm 2) \times 10^{13}$	$k_{1,2} = (3 \pm 1) \times 10^{-3}$
AgI_4^{3-}	$\beta_{1,4} = (19 \pm 2) \times 10^{13}$	$k_{1,3} = (9 \pm 1) \times 10^{-3}$
$Ag_2I_6^{4-}$	$\beta_{2,6} = (5 \pm 3) \times 10^{29}$	$k_{2,4} = (10 \pm 6) \times 10^{-4}$
$Ag_3I_8^{5-}$	$\beta_{3,8} = (25 \pm 5) \times 10^{45}$	$k_{3,5} = (23 \pm 5) \times 10^{-4}$

The solubility product, L, of silver iodide in 4 M sodium perchlorate could be computed from the values of E in those solutions at the end of the titration series (vide Table 1), where solid silver iodide was formed. It was also determined by measuring the e.m.f. of the following cell

$$+ Ag,AgI \begin{vmatrix} 0.016 \text{ M AgClO}_4 \\ 3.98 \text{ M NaClO}_4 \end{vmatrix} 4 \text{ M NaClO}_4 \begin{vmatrix} c_I \text{ M NaI} \\ (4-c_I) \text{ M NaClO}_4 \end{vmatrix} Ag,AgI - \qquad (15)$$

The e.m.f. was 723.8 mV for $c_I = 0.005$ and 801.7 for $c_I = 0.1$, which gives $L = 4.6_6 \times 10^{-17}$, respectively $4.5_0 \times 10^{-17}$. The average of all the determinations is $L = (45 \pm 1) \times 10^{-18}$. This value has been used in Table 2 to calculate the equilibrium constants, $k_{m,n}$, valid for the reactions between solid silver iodide and iodide ions
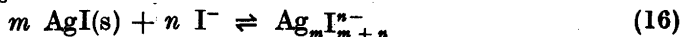
$$m \text{ AgI(s)} + n \text{ I}^- \rightleftharpoons Ag_m I_{m + n}^{n-} \qquad (16)$$

Hence

$$k_{m,n} = L_m \times \beta_{m,m + n} \qquad (17)$$

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