Studies on Ionic Solutions in Diethyl Ether

II. Silver-Silver Ion Potentials and Solubility Products of Silver Halogenides in LiClO₄-Ether Medium

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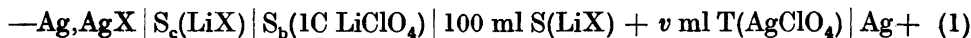*Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm, Sweden*

Berglund and Sillén [1] have suggested that the method of measuring ionic concentrations by emf methods, which has proved so useful for aqueous solutions, can also be applied to ionic solutions in diethyl ether. If, for example, a high and constant concentration of LiClO₄ is maintained in the ether, the activity factors of other ions present in small amounts will be almost constant, and thus the potentials of reversible electrodes giving the ions in question should follow Nernst's formula. The validity of this assumption was proved by measurements of cells with Ag, AgBr electrodes in ether solutions containing 2 C LiClO₄ and small amounts of LiBr.

After this first success, we tried to measure the concentrations of Mg²⁺ and Zn²⁺, dissolved as perchlorates in LiClO₄-ether, using electrodes of pure Mg or Zn metal, or of their liquid amalgams. However, certain difficulties were met with, which were finally traced to minute amounts of oxidizing substances such as oxygen still present in the ether. Steps are now being taken to remove the last traces of these impurities, after which the experiments on Mg and Zn compounds will be started again.

In the meantime, however, experiments have been made on the behaviour of the Ag⁺/Ag electrode in ether solutions, since silver electrodes were assumed to be less sensible to oxidizing agents. It was thought desirable to prove that it is possible in principle to measure the concentration of positive ions in ether also. This end was achieved. Moreover a few equilibrium constants were obtained for our solvent, namely the solubility products of AgCl and AgBr, and approximate values of the solubility product of AgI and the complex product of AgI₂⁻.

PRINCIPLES

The cells used were of the following types (X = Cl, Br or I):

$$-\text{Ag,AgX} \mid S_c(\text{LiX}) \mid S_b(\text{1C LiClO}_4) \mid 100 \text{ ml } S(\text{LiX}) + v \text{ ml } T(\text{AgClO}_4) \mid \text{Ag}+ \quad (1)$$

All the solutions —S_c, S_b and T—contained so much LiClO_4 that $[\text{X}^-] +$ $[\text{ClO}_4^-] = 1$ C. During a titration the halide concentration of S_c at the reference electrode (left) was kept constant. Thus the electrode potential on an arbitrary scale, e_{ref}, was also constant. At the right electrode there is at first an excess of X^- ions. During the titration they are gradually precipitated as AgX. When the equivalence point is passed there is a large increase in $[\text{Ag}^+]$, and a decrease in $[\text{X}^-]$. If the reversible emf is measured, and if our assumption that the activity factors remain constant is valid, then the electrode potential e will follow the formula

$$e = e_{0\text{AgX}} - 58.86 \ \log \ [\text{X}^-] = e_{0\text{Ag}} + 58.86 \ \log \ [\text{Ag}^+] \quad (2)$$

where $e_{0\text{AgX}}$ and $e_{0\text{Ag}}$ are constants.

Of course, at least one of $[\text{Ag}^+]$ and $[\text{X}^-]$ is always very small.

From (2) it follows immediately

$$e_{0\text{Ag}} - e_{0\text{AgX}} = -58.86 \ \log \ [\text{Ag}^+][\text{X}^-] = -58.86 \ \log \ k_s \quad (3)$$

where k_s is the solubility product of AgX in the LiClO_4-ether solvent.

If the liquid junction potential can be neglected, the emf E of the cell is the difference between the electrode potentials:

$$E = e - e_{ref} \quad (4)$$

In the definition of the electrode potential there is always an arbitrary constant which, however, need not concern us here since it cancels out in (4).

From the measured data we can then calculate

$$e_{0\text{Ag}} - e_{ref} = E - 58.86 \ \log \ [\text{Ag}^+] \quad (5)$$

or

$$e_{0\text{AgX}} - e_{ref} = E + 58.86 \ \log \ [\text{X}^-] \quad (6)$$

according to which of $[\text{Ag}^+]$ or $[\text{X}^-]$ is in excess and thus known from the analytical data.

The constancy of the expressions (5) and (6) during each titration, and of $(e_{0Ag} - e_{0AgX})$ when several titrations are compared, should be a measure of the validity of our fundamental assumptions. With iodine certain complications were met with, which will be discussed below.

A number of the bromide titrations were made by a reverse process, with $AgClO_4$ in S, and LiX in T; the calculations are, of course, analogous.

REAGENTS

Diethyl ether, lithium perchlorate and *lithium bromide* were obtained as described by Berglund and Sillén [1].

Lithium chloride of Baker's make (BPC) was kept for 40 hours at 200° C in a current of dry air (apparatus as in Part I [1]). We tried to dissolve the product in ether, but the solubility was so low that Cl^- could not be detected with Ag^+. Since we had previously observed that LiBr is more soluble in $LiClO_4$-ether than in pure ether, the dry LiCl was digested with 1 C $LiClO_4$-ether, which proved to dissolve about 20 mC LiCl.

Silver perchlorate: A mixture of $AgNO_3$ and a slight excess of 70 % $HClO_4$ was evaporated to dryness. The $AgClO_4$ formed was dried for 40 hours at 160° C in a current of dry air and digested with ether; the solution contained about 100 mC $AgClO_4$.

Lithium iodide (Baker's BPC) was dried and dissolved in ether, which gradually became yellow because free iodine was formed. The colour was barely visible after one hour. LiI is more soluble in ether than LiCl and LiBr.

APPARATUS

The apparatus was mainly the same as that used by Berglund and Sillén[1].

The experiments were performed in a thermostat room at a temperature of 23.5 ± 0.2 °C. The cell was kept in an oil bath at the same temperature (23.5 ± 0.1 °C). The emfs were measured by means of a valve potentiometer (Radiometer PHM 3 g). The thermostat room was screened off from external electric fields by an earthed metallic network in the walls and ceiling.

The Ag,AgX electrodes were prepared by Brown's method [2]. Silver electrodes were prepared in four different ways:

1) A Ag,AgBr electrode was first prepared by Brown's method and then the AgBr washed away by treatment with concentrated $Na_2S_2O_3$ solution. The electrode was finally washed free from salts by boiling repeatedly with distilled water.

2) A Pt coil was silvered and then coated with a thin layer of Ag_2O, which was decomposed by keeping it at 475 °C for 7—8 hours, leaving a porous layer of metallic silver (Brester [3]).

3) Silver was deposited on a Pt coil by electrolysis of $KAg(CN)_2$ solution for 17—18 hours with 0.2—0.3 mA (Brown [2]).

4) A silver wire of 1 mm diameter was used without further treatment.

The preparation of electrodes by method 2) proved rather difficult, since the silver layer is brittle and liable to peel off. Moreover, when the composition of the solution was changed it took a long time — several hours — for the electrode to reach the new equilibrium potential; perhaps this inertia was due to the slowness of diffusion through the pores.

Electrodes of type 1), 3) and 4) gave steady emfs within 10—15 minutes. Since it was easier to prepare, type 3) was preferred to type 1), and was used in most of our experiments. Only one titration was performed with an electrode of type 4).

ANALYSES

Lithium perchlorate was determined by evaporating 5 ml of solution to dryness, dissolving in water, and passing the solution through an ion exchanger saturated with H^+. The content of H^+ liberated (equivalent to the Li^+ of the sample) was determined by titration with NaOH. — It was checked from time to time with Ag^+ that the stock solution (3.6 C $LiClO_4$) did not contain any Cl^-.

Silver perchlorate was determined by titration with 10 mC KSCN, and the *lithium halides* by Volhard titration.

The solutions S, T, etc. were prepared by transferring with burettes calculated amounts of the stock solutions of $LiClO_4$ and LiX or $AgClO_4$ to a measuring flask, and diluting to the mark with ether. The determination of $LiClO_4$ was made with the stock solution, the titrations for Ag^+ and X^- with the mixed solutions.

In an emf titration as described below the equivalence point usually occurred at the volume of T calculated from the analyses for Ag^+ and X^-. When a divergence occurred — usually only one or a few 0.1 % — the halide concentration was assumed to be accurate, and the concentration of the silver solution was corrected.

A larger error may have been caused by the high viscosity of the strong $LiClO_4$ solutions, which made them flow very slowly out of burettes and pipettes. (One reason for our choosing 1 C $LiClO_4$ instead of 2 C $LiClO_4$ (as in Part I [1]) was that the viscosity of the solutions is lower at lower concentrations). The $LiClO_4$ concentration may sometimes have differed from 1.00 C by as much as 0.01; as we shall see later, the corresponding error in the emf is however rather small.
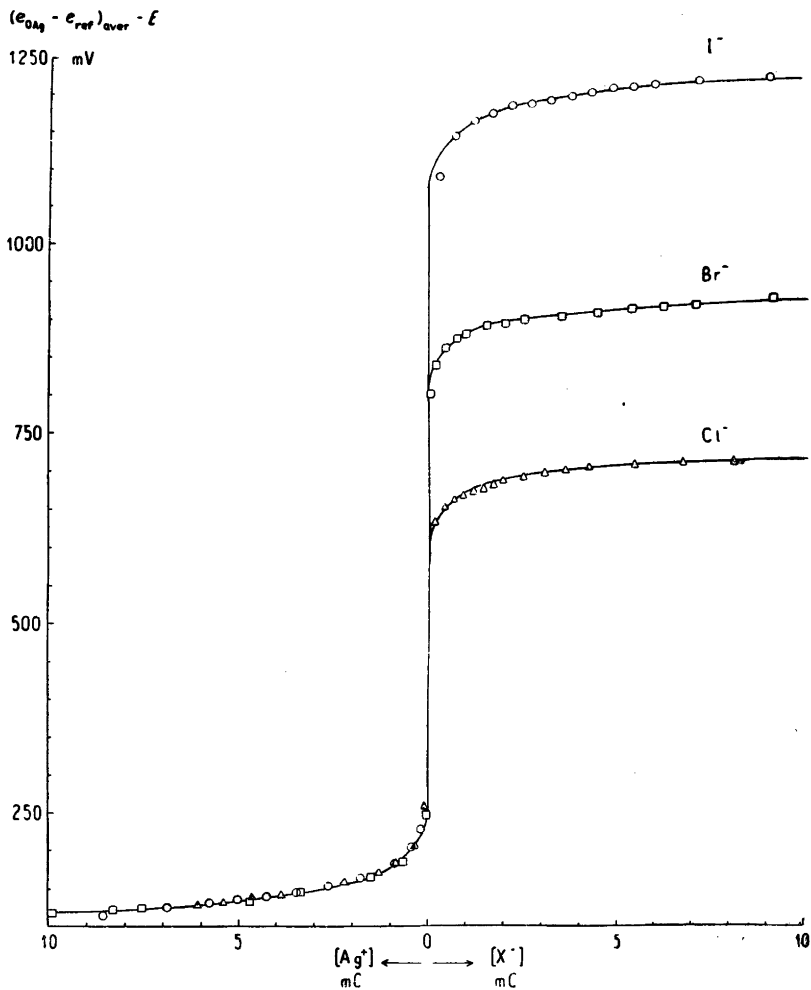
Fig. 1. Electrometric titration of Ag^+ with halide ions X^- in $LiClO_4$ — ether medium.

PROCEDURE AND EXPERIMENTS

The solutions were prepared and transferred to the electrode vessels in the same way as described by Berglund and Sillén[1]. Usually two Ag electrodes of different types were inserted in the same solution, and the emf measured between each of them and the reference electrode. Before the emf measurements began, a few ml of T [X⁻] were added to S so that AgX precipitated. After one hour of stirring — in order to get temperature

equilibrium and allow the AgX to form larger grains — the measurements began. After each new addition of T, we waited till the emf had been constant for 5 minutes, which generally took 10—15 minutes. It was essential to have the stirrer working all the time, so that AgX was kept suspended in the solution.

On titrations of Ag^+ in S with Cl^-, Br^- or I^- in T, the titration curves E versus v were of the same type as obtained in aqueous solutions (Fig. 1); if desired the equivalence points could be determined very accurately. In Fig. 1 $[(e_{0Ag} — e_{ref})_{average} — E]$ has been plotted against the excess concentration of Ag^+ or X^-. If (5) is valid, this expression should be equal to $— 58.86$ log $[Ag^+]$. In fact, the experimental points with excess of Ag^+ are seen to coincide with the theoretical curve (black line). With excess of X^-, the points for the different halides are widely separated. The highest values are obtained for I^-, which indicates that the solubility product increases in the order AgI, AgBr, AgCl, just as for aqueous solutions.

In Tables 1, 3, and 5 are given the figures for one titration with each of Cl^-, Br^-, and I^-. The values of $e_{0Ag} — e_{ref}$, and $e_{0AgX} — e_{ref}$, calculated by means of (5) and (6), spread slightly but show no definite trend. Thus, as far as each individual titration is concerned, Nernst's law seems to be valid for the concentrations of Ag^+, Cl^-, Br^- and I^-.

Tables 2, 4 and 6 give a survey of the results of different titrations; the largest number of experiments was made with Br^-, which was used in all the preliminary experiments. (In the average values, the experimental points with $[Ag^+]$ or $[X^-]$ less than 1 mC have not been taken into account.)

Although $e_{0Ag} — e_{ref}$ and $e_{0AgX} — e_{ref}$ are generally constant within ± 5 mV for each titration, the variations between different titrations are larger, sometimes amounting to ± 20 mV. On the other hand, the difference, $e_{0Ag} — e_{0AgX}$ varies less, by ± 6—8 mV. From the averages we calculated the following values for the solubility products in 1 C $LiClO_4$-ether at 23.5° C (maximal deviations are given):

$$AgCl : e_{0Ag} — e_{0AgCl} = 841.6 \pm 6.5 \text{ mV} \quad \log k_s = — 14.30 \pm 0.11$$
$$AgBr : e_{0Ag} — e_{0AgBr} = 1045.0 \pm 8.4 \text{ mV} \quad \log k_s = — 17.75 \pm 0.14 \qquad (7)$$
$$(AgI : e_{0Ag} — e_{0AgI} = 1330.5 \pm 6.4 \text{ mV} \quad \log k'_s = — 22.60 \pm 0.11)*$$

Since we always tried to keep the same concentration, 0.1 C X^-, in the reference electrode solution (S_c), one might expect $e_{0AgX} — e_{ref}$ to be constant, even if the Nernst equation value ($— 58.86$ mV) cannot be·expected to apply at such high $[X^-]$ as 0.1 C. As causes of the variations one might suggest:

* See »Complications with I^-» below.

Table 1. Titration $Cl^- + Ag^+$.

$S\ =\ 0.0161\ C\ LiCl;\ 0.98_{39}\ C\ LiClO_4\ (62.2\ ml)$.
$T\ =\ 0.0425\ C\ AgClO_4;\ 0.95_{75}\ C\ LiClO_4\ (v\ ml)$.
$S_b\ =\ 1.00\ C\ LiClO_4$.
$S_c\ =\ 0.010\ C\ LiCl;\ 0.990\ C\ LiClO_4$.

Electrodes: Ag-electrode using method 3).
Ag; AgCl using Brown [2].

E mV	v ml	$10^3[Cl^-]$	log $[Cl^-]$	$e_{0AgCl} - e_{ref}$
112.6	16.1	4.032	— 2.3945	— 28.4
119.5	17.1	3.445	— 2.4628	— 25.5
124.0	18.1	2.873	— 2.5417	— 25.7
126.3	18.6	2.592	— 2.5864	— 26.0
130.8	19.1	2.314	— 2.6356	— 24.4
133.3	19.6	2.039	— 2.6906	— 25.1
139.0	20.1	1.768	— 2.7525	— 23.1
144.0	20.6	1.500	— 2.8239	— 22.3
149.4	21.1	1.235	— 2.9083	— 21.8
154.1	21.6	0.9737	— 3.0116	— 23.2
158.0	22.1	0.7153	— 3.1455	(— 27.2)
189.9	23.1	0.2075	— 3.6830	(— 27.0)

E mV	v ml	$10^3[Ag^+]$	log $[Ag^+]$	$e_{0Ag} - e_{ref}$
603.1	24.1	0.2885	— 3.5398	(811.5)
628.0	25.1	0.7732	— 3.1117	(811.2)
643.1	26.1	1.247	— 2.9041	(814.1)
656.0	27.1	1.471	— 2.8324	822.8
662.4	28.1	1.926	— 2.7153	822.3
667.2	29.1	2.370	— 2.6252	821.8
671.2	30.1	2.805	— 2.5521	821.5
679.2	32.1	3.645	— 2.4383	822.8
683.4	34.1	4.454	— 2.3512	821.8
687.0	36.1	5.227	— 2.2817	821.3
689.4	38.1	5.971	— 2.2239	820.3
692.0	40.1	6.685	— 2.1749	820.1

Average values:

$e_{0Ag} - e_{ref} = 820.9 \pm 1.3$
$e_{0AgCl} - e_{ref} = -24.7 \pm 3.3$

Table 2. Summary of results for $Ag^+ + Cl^-$.

Electrodes acc. to	$e_{0Ag} - e_{ref}$	$e_{0AgCl} - e_{ref}$	$e_{0Ag} - e_{0AgCl}$
Method 3)	814.9 ± 2.5	− 23.3 ± 5.3	838.2
»	820.9 ± 1.3	− 24.7 ± 3.3	845.6
»	814.4 ± 1.2	− 32.0 ± 2.6	846.4
»	806.8 ± 1.4	− 26.7 ± 2.7	833.5
»	808.5 ± 1.6	− 36.1 ± 3.9	844.6
Method 4)	792.4 ± 1.6	− 49.0 ± 5.2	841.4

Average: $e_{0Ag} - e_{0AgCl} = 841.6 \pm 6.5$

$$pk_s = \frac{e_{0Ag} - e_{0AgCl}}{58,86} = 14.30 \pm 0.11$$

1) The liquid junction potential S_c/S_b varies for different experiments according to the way the junction has been formed.

2) The silver halides AgX precipitate in forms (*e. g.* very fine-grained) of varying activity, higher than that of the equilibrium form, and are transformed to the latter only very slowly.

3) Small variations in the concentration of $LiClO_4$ cause large variations in the emf (*e. g.* because of changes in the liquid junction potential or in the activity factors).

The third possibility, at least, could be ruled out by the experiments described in Tables 7 a and b. There the ionic strength has been varied in the titration vessel, whereas the concentration of Ag^+ (Table 7 a) or Br^- (Table 7 b) has been kept constant. The emf shifted by about — 8 mV in the first case, and about + 25 mV in the second when the ionic strength I was increased from 0.5 to 1.2 C. The changes are in both cases in the direction corresponding to a lowering of the activity factor with increasing ionic strength. The changes in the liquid junction potential between S + T and S_b cannot give the chief contribution, since in such case the shift would have had the same sign and approximately the same magnitude in the experiments with Ag^+ and Br^-.

COMPLICATIONS WITH I^-

The titrations with I^- differed in one respect from those with Br^- and Cl^-. According to (2) the quantity $(e_{0AgX} - e_{ref})$ should be equal to 58.86 log $[X^-]$ at the reference electrode; since the concentration of X^- was always 0.1 C, one would expect a negative value, though may be numerically somewhat less

Table 3. Titration Br⁻ + Ag⁺.

S = 0.02 C $AgClO_4$; 0.98 C $LiClO_4$ (50 ml).
T = 0.0533 C $LiBr$; 0.94_{67} C $LiClO_4$ (v ml).
S_b = 1.00 C $LiClO_4$.
S_c = 0.10 C $LiBr$; 0.90 C $LiClO_4$.

Electrodes: *Ag-electrode using method 3);*
Ag; AgBr using Brown [2].

E mV	v ml	10^3 [Ag^+]	log [Ag^+]	$e_{0Ag} - e_{ref}$
916.9	2.0	17.18	− 1.7650	1020.8
913.2	4.0	14.57	− 1.8365	1021.3
908.5	6.0	12.15	− 1.9154	1021.3
903.0	8.0	9.890	− 2.0048	1021.0
897.2	10.0	7.783	− 2.1088	1021.4
889.6	12.0	5.813	− 2.2356	1021.2
885.6	13.0	4.875	− 2.3120	1021.7
879.9	14.0	3.966	− 2.4016	1021.3
873.7	15.0	3.085	− 2.5107	1021.5
866.2	16.0	2.230	− 2.6517	1022.3
855.0	17.0	1.402	− 2.8532	(1023.0)
828.4	18.0	0.5956	− 3.2250	(1018.3)

E mV	v ml	10^3 [Br^-]	log [Br^-]	$e_{0AgBr} - e_{ref}$
174.8	19.0	0.1855	− 3.7317	(− 44.9)
148.6	20.0	0.9443	− 3.0249	(− 29.5)
132.3	21.0	1.682	− 2.7742	− 31.0
121.1	22.0	2.397	− 2.6203	− 33.2
114.8	23.0	3.096	− 2.5092	− 32.9
110.0	24.0	3.774	− 2.4232	− 32.7
107.0	25.0	4.435	− 2.3531	− 31.6
103.6	26.0	5.078	− 2.2943	− 31.5
101.9	27.0	5.704	− 2.2438	− 30.3
99.7	28.0	6.314	− 2.1997	− 29.8
97.3	29.0	6.909	− 2.1606	− 29.9
95.3	30.0	7.489	− 2.1256	− 29.9

Average values:

$e_{0Ag} - e_{ref}$ = 1021.4 ± 0.7
$e_{0AgBr} - e_{ref}$ = − 31.3 ± 1.2

Table 4. Summary of results for $Ag^+ + Br^-$.

Electrodes acc. to	$e_{0Ag} - e_{ref}$	$e_{0AgBr} - e_{ref}$	$e_{0Ag} - e_{0AgBr}$
Method 3)	1007.1 ± 4.0	-32.5 ± 1.6	1039.6
»	1021.4 ± 0.7	-31.3 ± 1.2	1052.7
»	1035.0 ± 5.6	-10.4 ± 3.0	1045.4
»	1034.0 ± 3.5	-10.5 ± 3.2	1044.5
»	1048.1 ± 3.6	-25.7 ± 0.6	(1073.8)
»	1012.2 ± 1.7	-14.0 ± 3.0	(1026.2)
»	1020.3 ± 4.7	-15.6 ± 3.6	1035.9
»	1033.9 ± 5.0	-15.3 ± 3.5	1049.2
»	1043.2 ± 1.5	-20.2 ± 4.5	(1063.4)
Method 1)	1008.8 ± 3.5	-41.0 ± 0.9	1049.8
Method 2)	1015.2 ± 0.7	-27.4 ± 8.4	1042.6

Average: $e_{0Ag} - e_{0AgBr} = 1045.0 \pm 8.4$

$$pk_s = \frac{e_{0Ag} - e_{0AgBr}}{58, 86} = 17.75 \pm 0.14$$

than — 58.86 mV, because the activity coefficients for X^- cannot be expected to be the same in S_c as in the solution $(S + T)$. For Cl^- and Br^- values between — 20 and — 40 mV were in fact found.

For I^-, however, the quantity $(e_{0AgX} - e_{ref})$ proved to be *positive*. In order to find out the reasons for this unexpected behavior, we carried out a few titrations of Ag^+ with I^- where $[I^-]$ finally amounted to about 100 mC (0.1 C). In order to get about the same relative accuracy in different ranges of I^- we first added a weaker I^- solution and in the last part of the titration a stronger one.

When the solution $(S + T)$ ought to have had the same composition as S_c, E was about 60 mV and not, as expected, in the neighbourhood of 0.

Part of the explanation of these puzzling results came when one of us happened to observe that at the end of a titration the ether solution was quite clear. Thus the precipitate of AgI which had previously been repeatedly observed at lower $[I^-]$ had dissolved in excess of I^-. At the reference electrode all AgI has then certainly dissolved in the 0.1 C LiI solution; the silver concentration at the reference electrode must depend on the amount of AgI originally deposited on the silver.

The most plausible hypothesis is that a complex ion AgI_2^- had been formed. In such case the excess of I^- over Ag^+, X_e, is no longer equal to the concentration of free I^- but

Table 5. Titration $I^- + Ag^+$.

S = 0.010 C LiI; 0.99_0 C LiClO$_4$ (100 ml).
T = 0.0550 C AgClO$_4$; 0.94_{50} C LiClO$_4$ (v ml).
S_b = 1.00 C LiClO$_4$.
S_c = 0.10 C LiI; 0.90 C LiClO$_4$.

Electrodes: Ag-electrode using method 3);
Ag, AgI using Sillén-Ekedahl [4].

E mV	v ml	10^3 [I^-]	log [I^-]	$e_{0AgI} - e_{ref}$
141.0	6.5	6.033	$-$ 2.2195	10.3
148.5	7.5	5.465	$-$ 2.2624	15.3
149.2	8.5	4.908	$-$ 2.3091	13.2
155.3	9.5	4.361	$-$ 2.3604	16.3
161.0	10.5	3.824	$-$ 2.4175	18.7
165.5	11.5	3.296	$-$ 2.4820	19.4
171.0	12.5	2.778	$-$ 2.5563	20.5
172.7	13.5	2.269	$-$ 2.6442	17.0
182.0	14.5	1.769	$-$ 2.7523	19.9
191.4	15.5	1.277	$-$ 2.8938	21.0
212.0	16.5	0.7940	$-$ 3.1002	(29.5)
264.5	17.5	0.3192	$-$ 3.4959	(58.7)

E mv	v ml	10^3 [Ag^+]	log [Ag^+]	$e_{0Ag} - e_{ref}$
1126.3	18.5	0.1477	$-$ 3.8306	(1351.8)
1151.8	19.0	0.3782	$-$ 3.4223	(1353.3)
1173.0	20.0	0.8333	$-$ 3.0792	(1354.3)
1184.1	21.0	1.281	$-$ 2.8924	1354.4
1190.4	22.0	1.721	$-$ 2.7642	1353.2
1202.3	24.0	2.581	$-$ 2.5882	1354.7
1210.2	26.0	3.413	$-$ 2.4669	1355.5
1215.3	28.0	4.219	$-$ 2.3748	1355.1
1219.3	30.0	5.000	$-$ 2.3010	1354.8
1223.2	32.0	5.758	$-$ 2.2397	1355.1
1229.3	35.0	6.852	$-$ 2.1642	1356.7
1238.8	40.0	8.571	$-$ 2.0670	1360.5

Average values: $e_{0Ag} - e_{ref} = 1355.6 \pm 3.6$

$e_{0AgI} - e_{ref} = 17.2 \pm 5.3$

Table 6. Summary of results for $Ag^+ + I^-$.

Electrodes acc. to	$e_{0Ag} - e_{ref}$	$e'_{0AgI} - e_{ref}$	$e_{0Ag} - e'_{0AgI}$
Method 3)	1355.6 ± 3.6	17.2 ± 5.3	1338.4
»	1355.7 ± 3.1	17.5 ± 5.2	1338.2
»	1345.6 ± 7.7	19.8 ± 5.3	1325.8
»	1347.0 ± 8.7	21.3 ± 5.6	1325.7
»	1330.5 ± 1.1	4.7 ± 8	1325.8
»	1329.4 ± 1.6	0.5 ± 10	1328.9

Average: $e_{0Ag} - e'_{0AgI} = 1330.5 \pm 6.4$

$$pk'_s = \frac{e_{0Ag} - e'_{0AgI}}{58,86} = 22.60 \pm 0.11$$

Table 7. Variation of E with concentration of $LiClO_4$.

Electrodes: Ag-electrodes using method 3);
Ag, AgBr using Brown[2].
(I is the ionic strength in the titration vessel.)

a)
$S = 0.040\ C\ AgClO_4;\ 0.50\ C\ LiClO_4$
$\quad$ *(50 ml)*
$T = 0.040\ C\ AgClO_4;\ 2.0\ C\ LiClO_4$
$\quad$ *(v ml)*.
$S_b = 1.0\ C\ LiClO_4$
$S_c = 0.10\ C\ LiBr;\ 0.90\ C\ LiClO_4$

b)
$S = 0.020\ C\ LiBr;\ 0.50\ C\ LiClO_4$
$\quad$ *(50 ml)*
$T = 0.020\ C\ LiBr;\ 2.0\ C\ LiClO_4$
$\quad$ *(v ml)*
$S_b = 1.0\ C\ LiClO_4$
$S_c = 0.10\ C\ LiBr;\ 0.90\ C\ LiClO_4$

E mV	v ml	I	E mV	v ml	I
951.6	0.0	0.540	58.3	0.0	0.520
951.6	1.0	0.569	64.7	5.0	0.656
950.4	6.0	0.701	69.0	10.0	0.770
948.1	11.0	0.810	73.2	16.0	0.884
946.5	16.0	0.904	75.0	20.0	0.949
945.6	21.0	0.984	77.2	25.0	1.020
945.0	26.0	1.053	78.2	30.0	1.083
944.5	31.0	1.114	81.0	40.0	1.187
943.9	36.0	1.168	84.6	45.0	1.231
943.3	41.0	1.216			
942.8	45.5	1.255			

$$X_e = [Ag]_{tot} - [I]_{tot} = [I^-] + [AgI_2^-] \tag{8}$$

Introducing the complex product $\varkappa_2$, the equilibrium conditions are, as long as solid AgI is present

$$[Ag^+] \, [I^-] = k_s$$

$$[AgI_2^-] = \varkappa_2[Ag^+] \, [I^-]^2 = \varkappa_2 k_s[I^-] \tag{9}$$

and thus

$$X_e = [I^-] \, (1 + \varkappa_2 k_s) \tag{10}$$

As for the quantity $(e'_{0AgI} - e_{ref})$ and the »solubility product» k'_s for AgI, which were calculated in the same way as for AgCl and AgBr it is easily seen that

$$e'_{0AgI} - e_{ref} = E + 58.86 \log X_e \tag{11}$$

$$\log k'_s = e'_{0AgI} - e_{0Ag} = \log \, [Ag^+] \, X_e \tag{12}$$

$$k'_s = [Ag^+]X_e = k_s \, (1 + \varkappa_2 k_s) \tag{13}$$

Thus k'_s and $(e'_{0AgI} - e_{ref})$ should have constant values as long as solid AgI is present. The value for $\varkappa_2$ can be estimated from measurements at higher X_e, where all AgI has dissolved, since in such cases

$$[AgI_2^-] = [Ag]_{tot}$$

$$[I^-] = [I]_{tot} - 2 \, [Ag]_{tot} = X_e - [Ag]_{tot}$$

As usual, $[Ag^+]$ can be obtained from E,

$$[Ag^+] = \text{antilog} \left[[E - (e_{0Ag} - e_{ref})] \, 58.86^{-1} \right]$$

Thus all concentrations are known that are needed for calculating $\varkappa_2$. From the preliminary experiments we calculated values of $\varkappa_2 = (2 \pm 1)10^{22}$. (If it was instead assumed that AgI_3^{2-} is formed, the spread in the values for $\varkappa_3$ was still larger.) With values of $\varkappa_2$ of this order of magnitude one would calculate $\log k_s = -22.8 \pm 0.3$.

Our experiments with I^- are to be considered as preliminary, since at any rate the presence of small amounts of free iodine may have disturbed the measurements. We intend to repeat them with an ether that is much freer from oxidizing substances.

SUMMARY

The behavior of silver electrodes has been studied during emf titrations of $Ag^+ClO_4^-$ with Li^+Cl^-, Li^+Br^-, and Li^+I^-, using as solvent 1 C $LiClO_4$-diethylether. Titration curves were obtained of the same type as in aqueous solution. When the ionic strength was kept constant, the emfs were found to follow Nernst's law rather well, both with excess of Ag^+ and halide ions. The effect of varying the ionic strength between 0.5 and 1.2 C has been studied.

For the solubility product in 1 C $LiClO_4$-ether at 23.5° C we found: AgCl: $\log k_s = -14.30 \pm 0.11$, AgBr: $\log k_s = -17.75 \pm 0.14$.

With I^- the measurements were complicated by the formation of a soluble complex, probably AgI_2^-, and by the appearance of small amounts of free iodine. Preliminary values: AgI: $\log k_s = -22.8 \pm 0.3$; $\varkappa_2 = [AgI_2^-][Ag^+]^{-1}[I^-]^{-2} = (2 \pm 1) \; 10^{22}$.

The values for $\log k_s$ in water at 25° C are according to Latimer [5]: AgCl -9.77, AgBr -12.48, AgI -16.07.

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