The Solubility of Silver Iodide in Aqueous Solutions of Silver Perchlorate

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The reaction between solid silver iodide and silver ions (*vide* formula (2) below) was studied at 25° C and at an ionic strength of 4 M by saturating 4 M solutions of silver perchlorate and sodium perchlorate and mixtures of these two solutions with silver iodide. The concentration of silver perchlorate in the mixtures ranged from 10^{-5} M to 3 M. The solubility of silver iodide in aqueous solutions of silver salts has been determined by previous authors only at rather high silver ion concentrations (for literature, *vide* Sillén [1]).

Solubilities above 5×10^{-4} M (molar silver ion concentration, $[Ag^+]$, > 0.5) were determined by diluting the saturated solutions with hot water to a silver ion concentration of 0.025 M, where the solubility ($\sim 2 \times 10^{-6}$ M at 25° C) of silver iodide is negligible compared with the solubility at those high silver ion concentrations. The silver iodide, precipitated by the dilution, was filtered off from the solution after cooling and then weighed. The method was controlled by dissolving known (~ 0.1 g) amounts of silver iodide in a 4 M solution of silver perchlorate, which was then diluted as mentioned above. Three such experiments were made and the difference between the weights of silver iodide dissolved and recovered was in all three cases less than 0.05 %. It was determined by analyses that no solid phases other than AgI were formed by contact with any of the silver perchlorate solutions.

In the range $10^{-5} < [Ag^+] < 10^{-1}$ the solubilities were determined by using silver iodide labelled with [131]I (from Harwell). Radioactive silver iodide was prepared by mixing an aqueous solution of carrier-free iodide [131] with a solution of inactive sodium iodide to a known concentration of iodide, say 10^{-2} M, and precipitating the silver iodide with silver perchlorate. Before the precipitation a small part of the active solution of sodium iodide was diluted 10^3 or 10^5 times (with inactive iodide), so that its activity could be conveniently determined in a 10-ml G. M. tube for liquids (Type M6 from 20th Century Electronics Ltd., combined with a Predetermined Count Scaler PW 4035 from Philips). The precipitate of labelled silver iodide was washed carefully first with water and then with the solution, in which its solubility was finally de-

Table 1. The solubility of silver iodide in silver perchlorate solutions. Ionic strength 4 M (NaClO₄). Concentrations in M.

c_{AgClO_4}	$l_{exp.}$	$l_{calc.}$
0	$(9 \pm 3) \times 10^{-9}$	13×10^{-9}
10^{-5}	$(7 \pm 1) \times 10^{-9}$	6×10^{-9}
10^{-4}	$(6 \pm 1) \times 10^{-9}$	6×10^{-9}
10^{-3}	$(8 \pm 1) \times 10^{-9}$	8×10^{-9}
10^{-2}	$(8 \pm 1) \times 10^{-8}$	9×10^{-8}
10^{-1}	$(12 \pm 1) \times 10^{-6}$	11×10^{-6}
0.5	$(62 \pm 1) \times 10^{-5}$	64×10^{-5}
1	$(427 \pm 1) \times 10^{-5}$	4.3×10^{-3} *
2	$(298 \pm 3) \times 10^{-4}$	28×10^{-3} *
3	$(951 \pm 3) \times 10^{-4}$	85×10^{-3} *
4	0.2137 ± 0.0003	0.15 *

* These four values are calculated for the silver ion concentrations 0.99, 1.91, 2.78, and 3.37, respectively, which would be the values of [Ag⁺], if all complexes formed contain only one iodide atom.

termined by shaking in a thermostat. About 10 mg precipitate were used to prepare 100 ml of solution. Samples were taken from the solution after 8, 24, and 48 hrs and filtered under pressure at 25° C through a collodion filter in a Thiessen apparatus. During this time no other change of the activity of the saturated solution could be detected than that depending on the decay of [131]I (half-life 8.0 days), although the silver iodide darkened obviously in a few hours and was quite black after 2 days. The specific activity of the solid silver iodide had to be at least 100 millicuries per gram, when the lowest solubilities were measured. Further experimental details are given elsewhere [2].

The results are listed in Table 1. The accuracy (*vide* Table 1) of the radio assay method is rather low, mainly because of the low specific activity of the solutions, which corresponded to 10 to 30 cpm for the lowest solubilities, measured with a 30 cpm background count.

The solubility, l can be described by the equation

$$l = \sum_{n=-1}^{N} K_n [Ag^+]^n \qquad (1)$$

if the activity constants maintain constant values in all the solutions, and if the silver iodide is dissolved according to the reactions

$$m \ AgI(s) + n \ Ag^+ \rightleftharpoons Ag_{m+n}I_m^{n+} \qquad (2)$$
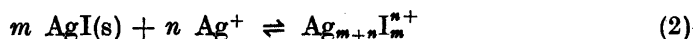
i. e., to produce species with the charges n (*cf.* Ref. [3]). By graphical methods or by trial and error the following constants are easily calculated ($N = 3$): $K_0 = 6 \times 10^{-9}$, $K_1 = 10^{-6}$, $K_2 = 7 \times 10^{-4}$, $K_3 = 3.7 \times 10^{-3}$. For K_{-1} the value 4.5×10^{-17} has been used, which is the value of the solubility product of silver iodide in a 4 M solution of sodium perchlorate, as determined in this laboratory by e.m.f. measurements. The experimental values of the solubility
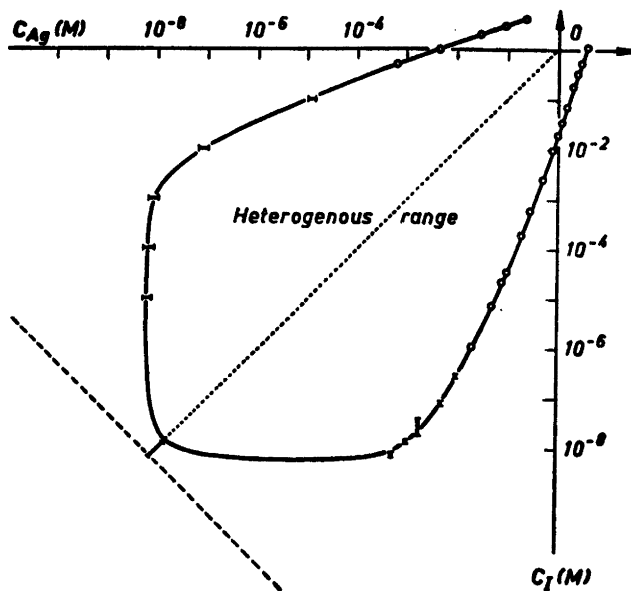
Fig. 1. The solubility of silver iodide in aqueous silver perchlorate and sodium iodide at 25° C. Ionic strength 4 M (NaClO₄).

are compared with those computed from eqn. (1) in Table 1. The concentration of free silver ions may be considered to be equal to the concentration of silver perchlorate in the solvent except for the pure sodium perchlorate, where the value $\sqrt{K_{-1}}$ has been used, and for the last four determinations in Table 1. In these latter cases the solubility can be neglected no longer, when compared with the contents of silver perchlorate. For the calculation of [Ag⁺] of these four solutions the constants K_n have been used, and it has been assumed that every complex contains only one iodide atom, i. e., that the dominating species are Ag_4I^{3+} and Ag_3I^{2+}. As is seen from Table 1 the solubility is described well by eqn. (1) in all solutions except three, viz., those of pure sodium perchlorate and 3 and 4 M silver perchlorate. In sodium perchlorate the reproducibility is also less than elsewhere, being dependent perhaps on the difficulty in washing away the silver perchlorate from the precipitate so carefully that its remaining concentration becomes small compared with 10^{-8} M. In the two last solutions with high silver ion concentrations the lack of success in describing the results with eqn. (1) can depend on any or all of the following reasons: (a) changes of activity factors, as most of the sodium perchlorate is here substituted by silver perchlorate; (b) formation of complexes with charges higher than 3, i. e., $N > 3$ in eqn. (1), which would then contain more than five terms; (c) formation of complexes with several iodide atoms, e. g. $Ag_6I_3^{3+}$ instead of Ag_4I^{3+}, which would cause a smaller decrease of the free silver ions of the silver perchlorate than that calculated at the bottom of Table 1 and hence higher values of l_{calc}.

Fig. 1 is a graphical representation of the data of Table 1 and contains also the solubility of silver iodide in solutions of sodium iodide as determined in this laboratory. The curve above the line $c_{Ag} = c_{I^-}$ (dotted in Fig. 1) is calculated from the constants K_n and thus represents eqn. (1). The part of the curve under the same line describes the solubility in sodium iodide solutions. c_{Ag} and c_I are the t o t a l contents of silver and iodide of a system. Every point outside the curve signifies an unsaturated solution, the composition of which is given by the co-ordinates of the point. A point inside the curve signifies a heterogeneous system, containing both solid silver iodide and a saturated solution, the composition of which can be obtained easily from the diagram in the following way. Let Δ be the difference between the known total contents of silver and iodide of the heterogeneous system. Then the intersection of the solubility curve in Fig. 1 and the curve $c_{Ag} - c_I = \Delta$ gives the composition of the saturated solution. It is to be noted that $c_{Ag} - c_I = \Delta \neq 0$ is not a straight line, if drawn in a l o g a r i t h m i c diagram like Fig. 1. The dashed line to the left of Fig. 1 would describe the solubility of silver iodide, if no complexes were formed between silver and iodide ions.

From the constants K_n the distribution of iodide on the different complexes in a saturated solution can be calculated. If α_n is that fraction of the dissolved iodide, which is contained in a species with the charge n, the following expression is valid (*cf.* Ref.[4])

$$\alpha_n = \frac{K_n \ [Ag^+]^n}{l} \qquad (n = 0, 1, 2, \text{ or } 3) \qquad (3)$$

The distribution of iodide as calculated from eqn. (3) is given in Fig. 2, from which the values of α_n at a given silver ion concentration are obtained by drawing a vertical line through the corresponding abscissa. The curves divide this line in parts, each of which is equal to that α_n, whose number n has been written in the area between two curves. A remarkable feature of the distribution diagram is the almost complete predominance of uncharged molecules in a broad range of silver ion concentrations.

From solubility measurements alone it is not possible to conclude, whether the species formed contain one or several iodide atoms (*vide* Ref.[3]). As the solubility of silver iodide is very small in most of the solutions studied, it seems rather probable, however, that the species with the charges 0, 1, 2, and 3 simply are AgI, Ag_2I^+, Ag_3I^{2+}, and Ag_4I^{3+}. If this be the case, the distribution shown by Fig. 2 is also valid for u n s a t u r a t e d solutions containing silver iodide dissolved in aqueous silver perchlorate.
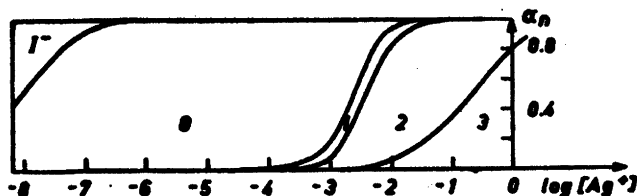

Fig. 2. The distribution of dissolved iodide on species with charges 0, 1, 2, and 3 in aqueous solutions of silver perchlorate saturated with silver iodide. Ionic strength 4 M (NaClO₄).

Obviously silver iodide is a very weak electrolyte. The degree of ionic dissociation of silver iodide in a pure aqueous solution is only about 50 % in spite of the low concentration. (See Fig. 2, which starts to the left with a solution of silver iodide in pure aqueous sodium perchlorate.) The dissociation constant for $AgI \rightleftharpoons Ag^+ + I^-$ (referring to d i s s o l v e d silver iodide) is $K_{-1}/K_0 = 7.5 \times 10^{-9}$, if the silver-iodide molecules are monomeric. The corresponding dissociation constants for silver chloride and silver bromide are about 8×10^{-4} and 4×10^{-5}, respectively (vide Refs.[2,4]).

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