CCCLXIII.—*Studies of a Bredig Silver Hydrosol.*

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It has been established by several workers (Rebière, *Compt. rend.*, 1909, **148**, 354; Beans and Eastlack, *J. Amer. Chem. Soc.*, 1915, **37**, 2667; Pennycuick, J., 1927, 2600; Pennycuick and Best, J., 1928, 551) that an electrolyte is formed in addition to the metal hydrosol in the Bredig sparking method, but the actual nature of the electrolyte has not been investigated to any great extent, although in the case of platinum it has been shown to consist of a hydroxyplatinic acid (Pennycuick, J., 1928, 2108). It is now shown that the electrolyte produced during the preparation of silver sols by this process consists essentially of silver hydroxide.

Stable silver sols have been prepared by Bredig's method in water of specific conductivity 2—3 $\times 10^{-6}$ mho (Burton, *Phil. Mag.*, 1906, **11**, 425; Rebière, *loc. cit.*). On the other hand, Pauli and Perlak (*Kolloid-Z.*, 1926, **39**, 195) were unable to prepare a stable silver sol in water of specific conductivity 2×10^{-6} mho, but the addition of small quantities of foreign electrolytes, notably metallic hydroxides, rendered the preparation possible (see also Woodard, Diss., Columbia Univ., 1925). By controlling the temperature and the time of arcing, we have now produced stable silver sols in water of specific conductivity 0·4—0·5 $\times 10^{-6}$ mho.

EXPERIMENTAL.

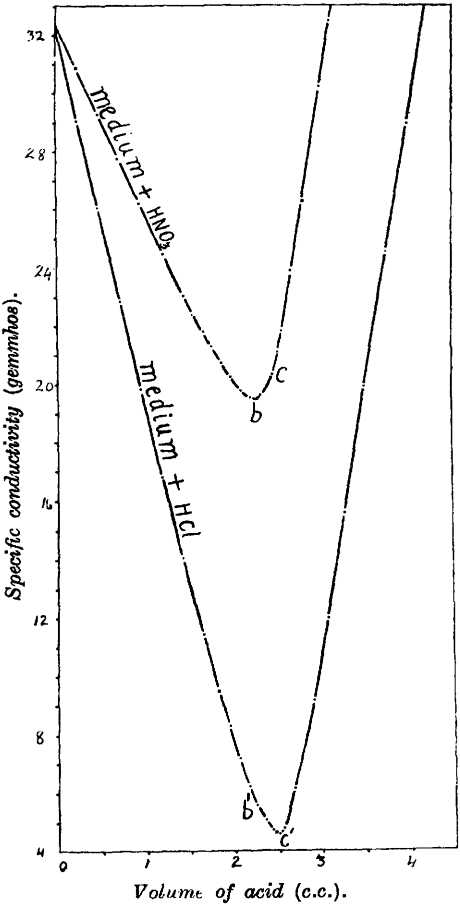
Preparation of the Sols.—In accordance with the experience of Woodard (*loc. cit.*), it was found that a sol on exposure to air absorbed carbon dioxide and cleared at the surface, the exposure sometimes causing the precipitation of an otherwise stable sol. This absorption in a test case (for the sol medium) was found to cause a change in the p_H value from 10 to 7·4 during 6 hours' exposure, and precautions were therefore taken to exclude carbon dioxide throughout. Siphoning of the conductivity water to the cell, and of the sol to the conductivity vessels, in a carbon dioxide-free atmosphere was carried out on this account.

Direct current of 5—6 amps. at 200 volts was found most suitable, and the apparatus used was essentially the same as that described by Pennycuick (*Aust. J. Exp. Biol.*, 1927, **4**, 106).

The stability of the sols was found to depend on temperature and time of arcing, the best results being obtained when the temperature of the water was kept within the limits 15—40°, the time of arcing being 40—55 minutes. In the case of too short or too prolonged arcing, the sols remained stable only for a few hours or at most a few days. Under the conditions described, sols which remained stable over the period of 10 months during which the observations were made were obtained in 80% of the trials.

In some trials the sols were precipitated visibly after 10 minutes' arcing, but when the arcing was continued, a stable sol was obtained. Pauli and Perlak (*loc. cit.*) consider that a minimum concentration of 6×10^{-6} *N*-silver hydroxide is necessary for a stable silver sol to be prepared in this medium. As the soluble silver present in the clear supernatant liquid of our preparations after 10 minutes' arcing was found to correspond with more than this amount of hydroxide, it is to be expected that further arcing will produce a stable sol unless the precipitating concentration is reached or exceeded. The sols are brownish-grey by reflected and brownish-yellow by transmitted light. Cataphoresis experiments show the particles to be negatively charged.

FIG. 1.



Silver Hydroxide as the Electrolyte in the Sol Medium.—The sols and the clear supernatant liquid (sol medium) obtained on precipitating the colloid gave an alkaline reaction. The hydrogen-ion activities of the sol media, determined colorimetrically, varied over the range p_H 8—10, but were mostly near the higher value. Conductimetric titrations with hydrochloric and nitric acids were therefore carried out on portions of the same sol medium, and the results are set out in Table I and plotted in Fig. 1. The cell used was the same as that described by Pennycuick (*loc. cit.*). The titrations were carried out on the day of its preparation on 50·0 c.c. of sol medium at 30·0°, the acids being made up with conductivity water and added from a micro-burette. The flat portions in the curves (see p. 2730) became almost negligible under these conditions.

TABLE I.

Titration of 50·0 c. c. of the sol medium at 30·0° with

(i) 0·0025N-HNO_3.						(ii) 0·0025N-HCl.			
Acid added, c.c.	$\kappa \times 10^6$. obs.	$\kappa \times 10^6$. calc.	Acid added, c.c.	$\kappa \times 10^6$. obs.	$\kappa \times 10^6$. calc.	Acid added, c.c.	$\kappa \times 10^6$.	Acid added, c.c.	$\kappa \times 10^6$.
—	32·4	—	1·96	20·2	18·4	—	32·2	2·29	5·29
0·23	30·9	30·8	2·08	19·8	17·5	0·23	29·05	2·33	5·05
0·46	29·3	29·2	2·18	19·55	16·8	0·46	26·1	2·42	4·75
0·69	27·7	27·6	2·30	19·6		0·71	22·9	2·50	4·62
0·93	26·2	25·9	2·44	20·4		0·95	19·9	2·54	4·81
1·20	24·5	24·0	2·54	21·9		1·19	16·8	2·66	6·13
1·43	23·1	22·3	2·65	23·9		1·41	14·09	2·89	9·18
1·54	22·4	21·5	2·80	26·3		1·64	11·47	3·06	12·03
1·66	21·8	20·7	3·00	30·2		1·82	9·50	3·26	15·57
1·74	21·3	20·0	3·11	32·5		1·93	8·31	3·50	19·90
1·85	20·7	19·2				2·05	7·20	3·75	24·5
						2·16	6·23	3·98	28·9
						2·20	5·90	4·21	33·3
						2·24	5·62		

The steep slope of the curves strongly suggests that they represent the neutralisation of a hydroxide, and if it is assumed that the electrolyte is completely ionised silver hydroxide, then the conductivity at any point along the hydroxide slope may be calculated from the neutralisation equation, $\mathrm{Ag}^{\cdot} + \mathrm{OH}' + \mathrm{H}^{\cdot} + \mathrm{A}' \longrightarrow \mathrm{Ag}^{\cdot} + \mathrm{A}' + \mathrm{HOH}$, by applying the relationship

$$\text{Fall in } \kappa = \text{Vol.} \times \text{normality of acid} \times 10^3\left(\frac{\Lambda_{\infty\,\mathrm{AgOH}}}{v_1} - \frac{\Lambda_{\infty\,\mathrm{AgA}}}{v_2}\right)$$

where v_1 is the initial volume of the solution, and v_2 its volume after titration. (Values for $\Lambda_{\infty\,\mathrm{AgOH}}$ and $\Lambda_{\infty\,\mathrm{AgA}}$ were computed from the figures given in Taylor's "Treatise on Physical Chemistry," Vol. 1, p. 541, by applying the appropriate temperature coefficients.) The agreement between such calculated values and the experimental results with nitric acid in Table I clearly indicates that the electrolyte is silver hydroxide and that at the concentrations considered it is almost completely ionised. The divergence of the observed from the calculated values in the neighbourhood of the minimum is probably due to hydrolysis of the silver carbonate (see p. 2730). In the case of the titration with hydrochloric acid, calculation is rendered valueless on account of the uncertainty attached to the correction to be applied for the solubility of silver chloride, especially in the freshly precipitated condition. Values calculated without applying this correction show a divergence from the observed values which is of the order to be expected.

The normality, N (equivs./l. of original medium), of silver hydroxide in the sol medium may be calculated (*a*) from the initial conductivity, $N = \kappa \times 10^3/\Lambda_{\infty \mathrm{AgOH}}$; (*b*) from the first turning point of the titration curves; or (*c*) from the p_H value (which, being based on a colorimetric method, must be regarded as less exact). The close agreement between the values calculated by these three methods, *viz.*, $N \times 10^4$ = 1·12, 1·125, and 1·26, respectively, taken in conjunction with the previous evidence, leaves little doubt as to the identity of the electrolyte.

The Presence of Silver Carbonate in the Sol Medium.—The regions marked *bc* and *b′c′* in the curves of Fig. 1 are flatter than the usual type of neutralisation curve, but the deviation may be neglected for ordinary purposes. The flattening might be traced to an oxide–hydroxide complex with a high Ag/OH ratio, but it is more probably due to the presence of a small amount of silver carbonate. This was directly tested by exposure of the sol medium to ordinary air, whereupon the absorption of carbon dioxide lowered both the p_H value and the conductivity, and the flatter portions of the titration curves became more marked, the effects being more pronounced the longer the time of exposure. As was to be expected, formation of carbonate did not affect the position of the minimum in the hydrochloric acid titration curve which occurs at the same volume of added acid as before; the minimum in the nitric acid curve, however, occurs earlier, but the second turning point, *c*, becomes more marked and occurs at the same volume of added acid as before exposure. It is clear that the volume of acid equivalent to the carbonate present in a solution is directly obtained from the difference in added acid at the minima of the hydrochloric and nitric acid titration curves. In the actual titrations, a slight downward drift in the conductivity values, presumably due to the removal of carbon dioxide by the air stream used for stirring, follows the immediate drop after the addition of acid along *bc* and *b′c′*. Values recorded in Table I and plotted are the final values of the conductivity after the drift.

Slight flat portions still persist in the graphs even when rigorous precautions have been taken to exclude carbon dioxide, and these can be traced to the gas contained in the conductivity water used. Assuming that the conductivity of the water in excess of the theoretical is due to carbon dioxide, one of the authors has calculated (*Aust. Jour. Exp. Biol.*, 1929, 6, 107) that water of specific conductivity 0·4 × 10^{-6} mho and 0·5 × 10^{-6} mho at 18° would respectively contain $0{\cdot}53 \times 10^{-5}$ and $0{\cdot}79 \times 10^{-5}$ mol. of carbon dioxide per litre; hence the water used, which had $\kappa = 0{\cdot}44 \times 10^{-6}$, would contain $0{\cdot}625 \times 10^{-5}M$-carbon dioxide, which corresponds with the quantity of silver carbonate deduced from the curves.

Effect of Freezing the Sols.—On freezing the sols the colloidal matter is precipitated, and if the supernatant liquid formed by thawing is separated, it is found to have a lower conductivity at 30° than the original sol. The fall varies in the case of different preparations, depending on the amount of silver in true solution, and appears to be due to the decreased solubility of the electrolyte at the freezing point, since when the solution after thawing is allowed to remain in contact with the precipitated colloid at 30°, the conductivity rises and *exceeds the original value determined in the case of the sol.* This behaviour can best be explained by assuming that the colloidal particle itself splits off some silver hydroxide, and the following example may be quoted as typical of a number of determinations showing the recovery in the conductivity and the increase in the amount of silver in true solution.

A preparation which before freezing had $\kappa = 27{\cdot}4$ gemmhos and contained 14·9 mg./l. of silver in true solution, on standing in contact with the colloidal matter after freezing gave $\kappa = 20{\cdot}3$, 22·4, and 35·3 gemmhos after periods of 16, 22, and 40 hours respectively. In the same times, the amount of silver in true solution determined by conductimetric titrations was found to be 11·8, 16·1, and 22·7 mg./l., respectively. From this behaviour, it follows that the colloidal particle contains in its complex either silver hydroxide or silver oxide, which gives rise to the increased amount of electrolyte formed. This is in agreement with the work of Rebière (*Compt. rend.*, 1912, **154**, 1540), who, after analysis of a number of flocculated silver sols, which on ignition gave up oxygen and lost weight, showed that the complex consisted of metallic silver with silver oxide (silver hydroxide would also fit the facts) in proportions varying from 29 to 68% of the latter.

In the conductimetric titrations carried out in the above connexion it was observed that the amounts of silver carbonate present were greater than that found in a freshly prepared sol. This is doubtless due to diffusion of carbon dioxide through rubber, but does not affect the main result.

Conductivity of the Sols.—From a number of preliminary determinations, it would appear that the conductivity of a sol varies on standing, and two types of change have been observed. In most cases there was a rise in conductivity followed by a fall, and finally a slow rise to a steady value. In a typical case the conductivity after definite times was as follows:

Time (hours)	0·5	18	40	67	72	89	94	96	143	237
$\kappa \times 10^6$	56·1	62·9	62·2	59·1	59·3	59·8	60·0	60·2	61	61

On the other hand, a few weak sols showed a general fall in conductivity, gradually decreasing to a steady value. The exact cause of these changes is still being investigated. A general explanation that suggests itself in the light of Donnan's hypothesis (*Phil. Mag.*, 1901, **1**, 647) is that the colloidal complex attains its " critical size " by either building up or breaking down, involving a change in the concentration of the electrolyte.

Summary.

1. Stable silver sols have been prepared in water of initial specific conductivity 0·4—0·5 × 10^{-6} mho.

2. The electrolyte formed during the process has been identified as silver hydroxide by means of conductimetric titration.

3. It has been shown that the clear liquid obtained by thawing a frozen sol contains more silver hydroxide than the original sol.

4. The cause of a slight irregularity in the titration curves has been traced to the presence of a small quantity of silver carbonate resulting from interaction of the hydroxide, formed during the sparking, with carbon dioxide initially present in the conductivity water.

5. Changes in the conductivity of the sols with time are recorded and briefly discussed.

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