[A CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF IDAHO]

Preparation and Properties of Silver Sols by Reduction of Silver Halides with Formaldehyde

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An analysis of some Bredig silver sols showed them to be unsuitable for some investigations recently begun. The precipitated colloid was found to contain from 26 to 44% of silver oxide depending, among other things, on the amount and kind of electrolyte used for stabilizing. Approximately a liter of the gases given off during the preparation of Bredig silver sols was collected and analyzed. The gases consisted of 22.1% oxygen and 77.9% hydrogen by volume. There was, therefore, an equivalent of 11.2% oxygen united with the silver to form silver oxide.

A silver colloid comparable in constitution and properties to Zsigmondy gold sols seemed desirable, so a method of reduction with formaldehyde without the use of a protective colloid was developed.

Experimental

It is well known that silver halides formed in excess of silver nitrate or alkali halide form stable positive and negative colloids, respectively. The angle of attack chosen was the reduction of these colloidal silver halides. The halide sols prepared with excess silver nitrate were reduced immediately forming a stable negative sol while those with excess halide were reduced only slowly and formed no stable sol.

Though the amounts of the reagents theoretically necessary were calculated, the solution to the problem was best found by trial and error

TABLE I

EFFECT OF VARYING AMOUNTS OF REAGENTS ON STABILITY AND PROPERTIES OF THE SILVER SOLS

Cc. of 0.1 *N* $AgNO_3$ (diluted to 250 cc.)	Cc. of 0.1 *N* KBr (diluted to 250 cc.)	Cc. of 2% Formaldehyde	Cc. of 0.3 *N* NaOH	Stability and properties of sol
10	9	20	0	No reduction
			3	Reddish-purple, cloudy, unstable
			10	Ruby-red, stable
			30	Dark, unstable
10	9	5	10	Dark, unstable
		10		Ruby-red, stable
		30		Ruby-red, stable (no effect)
10	0	10	10	Bluish-gray, unstable
	0.1			Bluish-gray, unstable
	.2			Straw-yellow, stable
	.3			Straw-yellow, stable
	1.0			Reddish-yellow, stable
	5.0			Reddish-yellow, stable
	9.0			Ruby-red, stable

methods. Table I gives a brief summary of the results as the amounts of the different substances were varied.

The procedure finally adopted for the preparation of a highly dispersed silver sol by this method is briefly summarized as follows. Dilute 10 cc. of 0.1 *N* silver nitrate to 250 cc. and add slowly with vigorous stirring 1 cc. of 0.1 *N* potassium bromide diluted to 250 cc. Add to the resulting mixture 10 cc. of 2% solution of formaldehyde; then add quickly with vigorous stirring 100 cc. of 0.03 *N* sodium hydroxide. Reduction takes place immediately after addition of the sodium hydroxide and the sol changes from a brownish-yellow by reflected light to a straw-yellow in about an hour. It then has a clear reddish-yellow color by transmitted light.

Hydroquinone was used with equal success but it has the disadvantage of giving a brown-colored oxidation product. A stable sol could not be prepared by replacing potassium bromide with potassium chloride, but potassium iodide worked equally well. A comparison of the properties of these sols, all prepared by the same method, is best given in Table II.

TABLE II

ANALYSIS AND PROPERTIES OF SOLS PREPARED FROM HALIDES

Halide salt, cc.		Color of sol	Stability	Silver, %	Precipitation value mml. $NaNO_3$ per liter	Cataphoretic velocity $\times 10^5$ cm./sec./volt/cm.
KCl	1	Bluish-gray	Unstable	99.44	..	..
	9	Bluish-gray	Unstable	99.46	..	..
KBr	1	Reddish-yellow	Stable	99.03	40.0	42.2
	9	Ruby-red	Stable	98.26	12.0	41.7
KI	1	Brownish-red	Stable	82.75	44.0	41.7
	9	Bright ruby-red	Stable	4.32	88.0	39.9

The percentage of silver was determined by dissolving the silver in the precipitated sol with warm nitric acid. The residues in the cases of potassium bromide and potassium chloride were completely soluble in ammonia. Silver iodide is insoluble in ammonia. Warm ammonia poured over another precipitated sol made with 1 cc. of potassium bromide dissolved only 0.46%, indicating that silver bromide was dissolving from the surface, but may have been some silver oxide or silver hydroxide. At most, then, there is only very little, if any, silver oxide in the sol.

The precipitation values were made by diluting varying volumes of 0.1 *N* sodium nitrate to 15 cc. and mixing quickly with 10 cc. of the sol. The color change at the precipitation point is almost as marked as it is with Zsigmondy gold sols. The amount of electrolyte which causes complete precipitation within twelve hours causes the sols to change to a definite green within three to five minutes. The color changes by transmitted light after addition of precipitating electrolyte are as follows: orange-yellow ⟶ reddish-yellow ⟶ ruby-red ⟶ greenish-yellow ⟶ green ⟶ bluish-green ⟶ blue ⟶ bluish-lavender ⟶ purple ⟶ purple-gray ⟶ gray.

A sol prepared according to the above directions was dialyzed in cellophane bags for 108 hours in running distilled water (average conductance, 4.2×10^{-6}). The effect of the dialysis is given in Table III.

TABLE III

EFFECT OF DIALYSIS ON SILVER SOL

Sol	Cataphoretic velocity cm./sec./volt/cm.	Conductance, mhos	Precipitation value, millimoles of $NaNO_3$ per liter
Undialyzed	42.2×10^{-5}	5.14×10^{-4}	40.0
Dialyzed	40.7×10^{-5}	5.0×10^{-6}	24.0

Further tests on the properties and structure of these silver sols were made by diluting 10 cc. of 0.1 *N* silver nitrate to 500 cc. and reducing with formaldehyde and sodium hydroxide as before. Just as the color reached a milky purple, 2 cc. of 0.1 *N* solutions of various salts were added and their effect on the stability of the silver particles noted at various times. Some settled out comparatively rapidly while others settled only slowly, and some not at all. The apparent order of their stabilizing effect as judged from rate of settling and appearance after twenty-four hours is: unstable, $NaOH$, K_2CO_3, K_2SO_4, KCl, $K_2C_2O_4$, $KMnO_4$, $NaNO_2$; slightly precipitated, K_2CrO_4, Na_2SiO_3, $Na_2HPO_4(PO_4^{=})$, $K_2Cr_2O_7(CrO_4^{=})$, KCN, $KCNS$; completely stable, KBr, $K_3Fe(CN)_6$, $K_4Fe(CN)_6$, $Na_2S_2O_3(S^{=})$, Na_2S, K ethyl xanthate, KI.

The order is essentially that of the solubility of the silver salt normally formed with the anion. Most all anions which normally form a silver salt with a solubility of 0.002 g. per 100 g. of water or less stabilize the silver particles. Apparently at low concentrations of the anion, the more insoluble the silver salt, the greater is its stabilizing effect. The one most definitely out of place is the chloride ion. The true ionic radius of the chloride ion according to Goldschmidt is 1.33 Å. compared with 2.02 Å. for the iodide ion. In general, the smaller the ionic radius, the greater the hydration of the ion. Thus the moles of water per mole of chloride ion is two while for the iodide ion it is only one-half. The greater the hydration of the ion, the less will be the electrochemical attraction of the silver atoms in the crystal surface for that ion. The greater insolubility of the chloride ion is apparently overbalanced by its hydration, thus preventing adsorption of enough ions to give the required potential for stability.

Six liters of sols stabilized as above by chloride, bromide and iodide were prepared and precipitated. The washed and dried coagulum of each was analyzed as before. The warm nitric acid dissolved and carried through the crucible all the silver but enough to react with the halide carried down. The results are given in Table IV.

TABLE IV

ADSORPTION OF HALIDES BY SILVER

Halide sol	Pptd. colloid, g.	Undissolved residue of AgX, g.	Halogen, g.	Total weight of silver, g.	G. atoms of halogen per gram atom silver	Ratio of halogens adsorbed
AgCl	0.8733	0.0026	0.00064	0.8727	0.002243	1
AgBr	.9025	.0076	.0030	.8995	.004478	1.997
AgI	1.0383	.3738	.1604	.8779	.1293	57.66

If a regular stoichiometric chemical reaction of the simple double decomposition or replacement type had taken place on the surface, one would expect equivalent amounts to be carried down after allowing for the differences in solubility. This is definitely not the case. The process seems to be one governed more by the principles of electrochemical adsorption. The differences are readily explainable on the basis of hydration of the ions and insolubility as a measure of the electrochemical attraction between the atoms of the crystal surface and the ion adsorbed. Similar observations were made by Beckley and Taylor[1] on the adsorption of various substances on silver iodide. Besides adsorption in this type of system, however, one must not fail to recognize other types where the system is fundamentally different.[2]

There is a difference in the appearance, stability, and apparent degree of dispersion obtained when the stabilizing substance is added before reduction rather than after. For example, a sol prepared with 1 cc. of potassium bromide added before reduction is a clear reddish-yellow, while it is a milky, brownish-yellow when added after reduction. On adding the potassium bromide to the silver nitrate as directed above, no precipitate or coloration can be seen, but very minute particles of silver bromide must be present which act as reduction and condensation centers. The bromide ions liberated on the reduction of these silver bromide nuclei can then act as stabilizing ions on the surface of the reduced silver.

Summary

1. A method of preparing comparatively pure silver colloids by a reduction process has been described.

2. The properties and probable structure of these sols with analyses of sols prepared with different halides at varying concentrations have been given.

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(1) Beckley and Taylor, *J. Phys. Chem.*, **29**, 942 (1925).

(2) *Cf.* Mukherjee, *Phil. Mag.*, [6] **44**, 338 (1922).