Summary

1. Measurements of the cells, $H_2 \mid KOH(m_1), KCl(m) \mid KOH(m_1) \mid H_2$ containing potassium hydroxide at 0.01 and 0.1 M concentrations, have been presented.

2. The activity coefficients of the hydroxide in the mixtures have been calculated.

3. The activity coefficient of potassium hydroxide in a potassium chloride solution is greater than that of sodium hydroxide in a sodium chloride solution when the hydroxides and salts are at the same strength.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE NEW JERSEY COLLEGE FOR WOMEN]

THE PREPARATION AND PROPERTIES OF SOME PROTECTED SILVER SOLS

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In 1839[1] Wöhler obtained a brown, soluble mass by the reduction of dry silver citrate or silver mellitate with hydrogen at 100°. This was the first recorded preparation of colloidal silver. Since then many experimenters have prepared the metal in the colloidal state by some modification of one of the two general methods: (a) the reduction of a silver compound in solution,[2] or (b) the dispersion of the massive metal by an electric arc,[3] by ultra-violet light,[4] or by simply boiling the metal in water.[5,6] The reduction method has been most widely employed and reducing agents in great variety have been recommended by different authors.

That metallic sols were stabilized by the addition of certain organic substances had been known for many years, but no considerable investigation of the phenomenon was made until that of von Meyer and Lottermoser[7] in 1897. Since then this protective effect has been investigated from several angles by Zsigmondy,[8] Groh,[9] Rideal,[10] Iredale,[11] and Friend and Vallance.[12]

Many concentrated, protected silver sols have been made, but they are

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[1] Wöhler, *Pogg. Ann.*, (2) **46,** 629 (1839).

[2] Lea, *Am. J. Sci.*, (III) **37,** 476; **38,** 47, 129, 237 (1889).

[3] Bredig, *Z. Elektrochem.*, **4,** 51 (1898).

[4] Svedberg, *Ber.*, **42,** 4375 (1910).

[5] Traube-Mengarini, *Z. Chem. Ind. Kolloide,* **10,** 113 (1912).

[6] Nordenson, *Kolloidchem. Beihefte,* **7,** 91 (1915).

[7] Von Meyer and Lottermoser, *J. prakt. Chem.*, (2) **56,** 241 (1897).

[8] Zsigmondy, *Z. anal. Chem.*, **40,** 697 (1902).

[9] Groh, *Z. physik. Chem.*, **88,** 414 (1914).

[10] Rideal, THIS JOURNAL, **42,** 749 (1920).

[11] Iredale, *J. Chem. Soc.*, **119,** 109 (1921); **121,** 1536 (1922).

[12] Friend and Vallance, *ibid.*, **121,** 466 (1922).

usually commercial products, and the method of preparation is seldom given with sufficient detail for execution. They are, in general, protected with some protein material.

The present paper describes the preparation of silver sols with a carbohydrate or related substance as the protecting agent. Accordingly, agar agar, dextrin and gum arabic were chosen as protectors and formaldehyde and glucose were used as reducing agents.

Reagents and Procedure

The silver nitrate and sodium hydroxide used were of the usual C. P. grade. The formaldehyde was a fresh stock of 37% U. S. P. formalin. The glucose was a highly purified white powder. The agar agar and gum arabic were white, high grade commercial samples and the dextrin was a white powder (N. F. IV).

The procedure was essentially the same in every case. Stock solutions of silver nitrate of 0.1 *N* and *N* concentrations, sodium hydroxide of the same concentrations, and 0.4% and 0.8% glucose were made up. Agar agar was prepared in a concentration of 15 g. in a liter and the gum arabic and dextrin dispersions each contained 20 g. in a liter.

In making a sol., a definite volume of the protective dispersion was first added to a measured volume of the silver nitrate solution. The reducing solution was added and then water to a given volume such that the final concentration of silver ion was brought to some definite value by which the sol is described, as for example, a 0.01 *N* silver-agar sol. Finally a volume of sodium hydroxide solution equivalent to the silver nitrate was added. The mixture was then stirred with a mechanical stirrer for 20 minutes.

Results

With 0.001 *N* silver nitrate, a green fluorescent sol was formed in the presence of the gum arabic and glucose, and a brown one with the agar agar, but the dextrin gave a dark brown precipitate. Both the agar agar and gum arabic sols were readily reversible after evaporation to dryness on a water-bath. This experiment was repeated with the gum arabic and a final concentration of 0.001–0.002% formaldehyde, and a reversible sol was likewise produced. Other sols were made in a similar way with 0.01 *N* and 0.1 *N* silver nitrate. As was to be expected, the color became darker with increasing concentration of silver. Since the dextrin afforded very little protection, it was not tried with later preparations. The gum arabic sols were purified by dialysis through a collodion bag against distilled water until the dialyzate showed a negative test for silver and sodium ions. The inner solution was then evaporated to dryness on a water-bath and found to be readily reversible.

Two sols were made of such concentration that the residue after dialysis and evaporation contained from 30 to 35% of silver. One was protected with gum arabic and the other with agar agar. Both were purified by dialysis until the dialyzate showed no test for silver. These sols were then evaporated to dryness and dispersions made from the dried product for further experiment.

A 10% solution of each and also of a commercial sol was made up and its bactericidal activity determined as follows: The 10% dispersions were each diluted with distilled water to concentrations of 1–50, 1–100, 1–200, 1–500 and 1–1000. A beef tea culture of *Staphylococcus aureus* was incubated for 24 hours after which 0.1 cc. was added to each of the dilutions and the mixtures were left for ten minutes. Then a loopful from each was added to beef tea and incubated for 24 hours. The results of the 1–100 commercial preparation and 1–50 agar sol were checked by inoculation of an agar slant. Both the gum arabic and the agar agar sols prevented the bacterial growth in the 1–50 dilution, but growth continued in all the others. The commercial sol inhibited growth in the 1–100 dilution.

The sols of lower silver concentration still showed no appreciable sediment at the end of 14 months. The 10% agar agar sol which was used in the bactericidal test solidified, and because of this tendency, only the gum arabic sols were used in most of the remaining experiments. The gum arabic 10% sol had deposited some sediment at the end of a year, but this could be dispersed again in water.

A closer study was made of the preparation of a sol by the use of gum arabic. It was found that the gum arabic used gave considerable reduction of an alkaline copper tartrate solution, and that when no glucose was added the method gave a brown dispersion of silver oxide which changed slowly into a silver sol on long standing, or immediately if heated. The addition of glucose or formaldehyde gave the same result without heating. Very little silver was removed by dialysis since most of that which was unreduced was in the form of colloidal silver oxide. The tendency of the sol to settle increased with the silver content and decreased with an increase in the gum arabic.

Electrophoresis experiments showed that both the gum arabic and the agar agar sols were negatively charged.

Attempts were made to determine the stability of gum arabic-silver sols in the presence of certain ions. Sodium, potassium, ammonium, barium, stannic and aluminum chlorides, potassium bromide and iodide, barium nitrate, potassium sulfate, ammonium disodium phosphate and sodium carbonate all failed to give a complete precipitation over a wide range of concentration. Likewise, nitric, acetic and sulfuric acids were ineffective. Many of these reagents gave a gradual color change or some precipitation, but none of them gave a change with quantitative possibilities.

The sols were found to reduce permanganate and a solution of iodine in potassium iodide. With gold, antimony, bismuth and mercuric chlorides, the sol reacted with the production of metallic gold, antimony and bismuth and mercurous chloride sols, respectively. The reaction with cupric chloride to give a mixed dispersion of metallic copper and silver chloride gave a sharp color change from green to a violet-red and so this reaction was used to measure relative stability.

Since dialysis changed the concentration of the sols by an unknown amount, undialyzed sols were used for comparison of the degree of protection. Sol 11 which was made in the usual way gave no filterable residue after standing overnight. It contained 0.32% of silver and 0.6% of gum arabic. Sol 14 was madei n the same way and contained 0.32% of silver but only 0.3% of gum arabic. Sol 13 was similarly made and contained 0.16% of silver and 0.6% of gum arabic. To samples of these three sols in test-tubes were added varying amounts of 0.1 *M* cupric chloride, and the concentration necessary for a complete reaction within ten minutes was determined. Five cc. of No. 11 required 1.9 cc.; when diluted to twice its volume with water it required 2.6 cc., and when diluted to four times its volume required 3.0 cc. No. 13 which contained half as much silver as No. 11 required 1.3 cc. No. 14 which contained half as much gum arabic as No. 11 required 1.8 cc. of cupric chloride to effect the change.

In order to secure a more accurate comparison of the two sols containing the same amount of silver and different amounts of gum arabic, a set of experiments involving the time required for a given amount of cupric chloride to effect the change in color, was made with the results recorded in Table I.

TABLE I

RELATIVE PROTECTION BY DIFFERENT PROPORTIONS OF GUM ARABIC

Sol	Gum arabic %	Cc. of sol	Cc. of water	Cc. of 0.1 *M* $CuCl_2$	Time in minutes
11	0.6	5.0	..	2.2	3.0
14	.3	5.0	..	2.2	1.0
11	.6	5.0	2.5	2.5	4.0
14	.3	5.0	2.5	2.5	1.5
11	.6	5.0	11.0	4.0	3.5
14	.3	5.0	11.0	4.0	1.5

The commercial sol that was used for comparison in the bactericidal test was coagulated by the cupric chloride before any important amount of the copper was displaced. It was likewise coagulated by gold chloride, but with greater displacement.

Discussion of Results

Of the various reagents tried as coagulants, alcohol alone was reasonably effective, since none of the ionogens produced complete settling even after several hours' standing, and such coagulation as did occur was too gradual and indefinite to admit of quantitative measurement. Alcohol in a final concentration of 65% caused complete coagulation and settling of Sol 13 in less than an hour, while a 0.6% solution of gum arabic alone showed no coagulation at an alcoholic concentration of 85%.

The reaction of the silver sol with cupric chloride gave a double sol of copper and silver chloride; the latter settled to a large extent on standing, and carried some of the copper with it. The cupric chloride required in this reaction is not the stoichiometric equivalent in the most concentrated solution used and a greater amount is required in more dilute solutions although the concentration required then is less. Thus the amount of cupric chloride required depends on both the actual weight of silver present and the concentration of the salt.

From the time required for the reaction to take place, it is clear that 0.6% of gum arabic is a much better protector for silver than a 0.3% solution, and this is also true with various dilutions of the original sol.

Summary

1. A silver sol can be prepared by heating a dispersion of silver hydroxide containing gum arabic, or by allowing the mixture to stand.
2. A method is given for the preparation of a reversible silver sol protected with gum arabic, that is stable within wide limits of concentration and in the presence of high concentrations of electrolytes.
3. Silver sols protected with gum arabic react with chlorides of antimony, bismuth, copper, gold and mercury to give other sols.
4. The rate of the reaction between cupric chloride and a protected silver sol may be used to measure the extent of the protection.
5. The bactericidal activity of silver sols protected with agar agar or gum arabic is of the same order as that of a commercial preparation protected with protein.

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[Contribution from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, No. 167]

THE ACTIVITIES OF STRONG ELECTROLYTES. III. THE USE OF THE FLOWING JUNCTION TO STUDY THE LIQUID-JUNCTION POTENTIAL BETWEEN DILUTE HYDROCHLORIC ACID AND SATURATED POTASSIUM CHLORIDE SOLUTIONS; AND THE REVISION OF SOME SINGLE-ELECTRODE POTENTIALS

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Introduction

One of the outstanding problems in the theory of electrolytic solutions is the determination of the activity of individual ions, in particular that of the hydrogen ion. Individual ion activities have usually been calculated through one of the three following assumptions: (a) that, for a uni-univalent electrolyte, the activities of the two ions are equal; (b) that Assumption (a) holds in the particular case of potassium chloride, and

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