# CLXXIX.—The Properties of some Silver Organosols.

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COMPARATIVELY little is known about the stability and constitution of colloidal solutions in non-aqueous dispersion media. This is due largely to the fact that so many of the systems studied have been of unknown chemical constitution, and that where more simple systems such as metallic alcosols have been investigated sufficient attention has not been directed to the conditions obtaining during the formation of the sol. In most cases, quite large quantities of unknown impurities have been present.

The stability of hydrosols has been shown to be due either to some process analogous to ionisation (the proteins, soaps, etc.), to the adsorption of ions from an electrolyte present in the system (Lottermoser's silver halide sols), or to some process which may be considered intermediate between the two. The investigation described in this communication is an attempt to determine how far the stability of silver organosols is due to such phenomena.

Silver sols in alcohol have been investigated to a considerable The method of preparation most frequently used has been extent. the arc dispersion method, the presence of reagents necessary for a reduction method thus being avoided. On the other hand, a certain amount of decomposition of the medium is inevitable. Carbon and tarry impurities which have an unknown effect on the stability of the sol are always produced, sometimes in considerable quantities. Svedberg ("Formation of Colloids," p. 25) has carried out an extensive investigation of this method. According to one arrangement of his, the arc was protected by enclosing it in a small quartz tube, the silver vaporised in the arc being carried in a stream of nitrogen into the alcohol which surrounded the tube. The decomposition of the medium was undoubtedly reduced by this device; but a new impurity was introduced, silica from the protecting tube being vaporised by the arc and carried into the dispersion medium. As much as 40 per cent, of the disperse phase in one dispersion was silica. Another impurity probably present was rubber. The quartz tube was held in position by rubber tubing. Some rubber from this was almost certainly extracted by the alcohol or other solvent, such having been found to be the case during preliminary experiments in this investigation.

Silver alcosols have been obtained by other methods giving purer products, still, however, containing unknown impurities. Thus Svedberg (op. cit., p. 80; Kolloid Z., 1910, 6, 129) has obtained silver alcosols by electrolysis and with the use of X-rays. Nordenson (Kolloid Z., 1911, 7, 91) has shown that in all these cases an intermediate compound is formed between the silver and the alcohol. The sol therefore always contains this unknown compound.

Burton ("Physical Properties of Colloidal Solutions," p. 148) prepared sols of various metals in alcohol and ethyl malonate, using the arc dispersion method. His sols were probably rather impure.

From the work of these investigators it appears probable that stable silver sols cannot be prepared in the pure state, and that, as in hydrosols, the presence of some stabilising agent is essential.

The first object of the investigations here recorded was to determine the nature and concentration of the stabilising agents necessary to give stable sols. Before doing so, in view of the nature of the apparatus used by Svedberg, it was thought advisable to confirm Burton's results as to the instability of pure silver alcosols.

The apparatus used, shown in the figure, is a modification of Svedberg's enclosed arc apparatus. In this case, neither the arc nor the alcohol comes into contact with anything but silver. Two

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silver tubes are soldered together, one in front of the other in the form of a cross, their interiors communicating through a small hole. This cross was soldered to a cylindrical cooling jacket as shown. Two brass T-pieces fit tightly in the ends of the horizontal silver tube. Glass tubes carrying silver wires are fixed inside these T-pieces by rubber bungs. The vertical silver tube is fitted at the bottom with a brass tap, silvered inside, and at the top with an ordinary cork and outlet tube. The nitrogen is led in at the side tubes of the brass T-pieces, passes through the small hole in the two silver tubes, carrying the silver vapour with it, and bubbles up through the alcohol, which is placed in the vertical silver tube.



The arc was operated by hand; about 6 amperes and 60 volts were used.

Having been prepared in this apparatus, the sol was run out into a specially cleaned test-tube, and observations of its stability were made for about a week. A large number of sols were prepared with absolute alcohol, aqueous alcohol, and alcohol containing various slight additions as dispersion media.

In absolute alcohol, no stable sols were obtained, Burton's results thus being confirmed. The addition of about 15 per cent. of water before dispersion resulted in practically every case in the production of a stable sol. It is impossible to ascertain with greater accuracy the concentration of water necessary to confer

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stability, since it is extremely difficult to distinguish between a slowly settling precipitate and a moderately stable sol. The criterion of stability employed was the absence of sedimentation after two days. Stability also depends on other uncontrollable conditions, for example, concentration. The percentage of water is quite large and the mechanism causing stability is probably the same as in ordinary aqueous sols and is ionic in nature.

In water as solvent, the most efficient stabilising ions are the hydrogen- and the hydroxyl-ion. The effect of small additions of acid or alkali was therefore investigated. Caustic soda, aniline, chloroacetic acid, and stearic acid were added in small amounts and found to have no effect. Svedberg states (*Nova Acta Soc. Sci.*, 1907, 2, No. 1) that sols of such metals as silver in alcohol can be stabilised by the addition of bromobenzene. The addition of 0.8 per cent. of this compound was found to have no stabilising effect on sols prepared in this apparatus. The stabilising effect obtained by Svedberg was probably due to decomposition of the bromobenzene, some compound of silver being formed.

From this it appears that the ions most effective in stabilising aqueous colloids have no corresponding effect in alcohol; also, that the effect attributed to bromobenzene is not real. On the other hand, in preliminary experiments it was found that when the solvent came in contact with rubber stoppers or tubing, stable sols resulted. This effect was quite definitely shown to be due to the presence of rubber, thus proving that these sols can be protected by even small quantities of colloids of the emulsoid type.

# Silver Sols in Stearic Acid.

As a result of the preparation of certain sols by the arc method Burton (op. cit., p. 151) considered that only substances containing a mobile hydrogen atom could give stable sols of such metals as silver. He suggested using organic acids, but did not carry the investigation any further. Assuming his view to be correct, it appeared to the authors that the most convenient substance to use would be an acid of high molecular weight. An attempt was therefore made to prepare silver sols in stearic acid. The apparatus already described was not found convenient for this purpose. If a sol of silver in stearic acid can exist, it should be formed by reduction of silver stearate in stearic acid with hydrogen—an extension of Kohlschütter's method of preparing silver hydrosols. This method is superior to an arc dispersion method, as decomposition of the medium is prevented.

Preliminary experiments using silver oxide in place of silver stearate indicated that a sol was formed. Reduction took place slowly at 100° and rapidly at 180°, a red liquid being formed in each case. Ultramicroscopic examination of this red substance showed the presence of a large number of fine particles. In all subsequent work, silver stearate was used. It was prepared from silver nitrate and stearic acid by double decomposition in alcoholic solution. In the latter part of the work, ammoniacal silver nitrate was used. The percentage of silver in the silver stearate was found to be 27.50, compared with a calculated value of 27.58.

When prepared from pure stearic acid, silver stearate is colourless and stable to light. Impure stearic acid gives a product which rapidly turns violet on exposure to light. Below  $100^{\circ}$ , silver stearate is almost insoluble in stearic acid. Above  $100^{\circ}$ , the solubility increases rapidly; thus, at 83° and at 180°, the solubility is about 0.005 per cent. and about 50 per cent., respectively.

# Reduction with Hydrogen.

When hydrogen was passed through a solution of silver stearate in stearic acid at  $180^{\circ}$ , the solution rapidly turned dark red with a beautiful purple or blue sheen, and also began to froth. After hydrogen had been passed for some time, the colour of the sol changed from red to dirty mustard colour and finally became grey. This grey mixture settled completely when the current of hydrogen was stopped

It seemed probable that the sol of silver in stearic acid is stabilised by silver stearate, and becomes unstable when the last trace of this is reduced. To test the accuracy of this hypothesis, analyses were made to determine the course of the reduction. Portions of the sol were removed at intervals and weighed, the stearic acid was extracted with hot absolute alcohol, and the mixture of silver stearate and silver weighed in a Gooch crucible. The total silver was then estimated by solution in nitric acid and titration with ammonium thiocyanate. When silver stearate is dissolved in stearic acid at  $180^{\circ}$ , the solution turns somewhat orange. It was thought that this might indicate some decomposition of the silver stearate, but an analysis of such a solution showed the presence of 99.5 per cent. of the quantity of silver stearate dissolved, and therefore very little decomposition had taken place.

The results of one reduction experiment are as follow:

Stearic acid, 40 grams ; silver steara	te, 2 g	rams; te	mperat	ure $180^{\circ}$
Time (hours)	5	10	16	23.5
	84-9	86-2	91-2	100

After twenty-three hours, a change was observed in the sol; the colour was grey and frothing had ceased. After twenty-four hours,

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the stearic acid, when solidified, was as white as the original stearic acid. These results indicate that a very small amount of silver stearate is sufficient to stabilise the sol, but that this small amount is essential. Very much more concentrated sols than this can be obtained. One was prepared which contained 10 per cent. of free silver.

# Electrical Condition of the Particles.

As there now seemed no doubt that the red mixture did consist of a silver sol in stearic acid, experiments were made to determine if the particles were electrically charged and, if so, the sign of the charge. Four cataphoresis experiments were carried out at about 80°. Only slight and variable changes in the level of the sol were observed. In order to increase any slight effect that might have been produced, a much smaller U-tube was then used, the distance between the electrodes being only 6 cm. This again gave a negative result.

As no motion was observed in the cataphoresis experiments, an attempt was now made to find if the medium and the sol would conduct at all. It was found at once that the conductivity was far too low to be measured by the method ordinarily used for aqueous solutions. A direct-current method employing a mirror galvanometer was therefore used. With an E.M.F. of 200 volts, measurable although very small deflections were obtained. The specific conductivities of pure stearic acid, of a solution of silver stearate in stearic acid, and of the sol were measured and found to be of the same order, about  $2 \times 10^{-11}$  rec. ohm.

Edser ("Fourth Report on Colloid Chem.," p. 313) examined two colloidal solutions in non-conducting media, rust in paraffin and stannic oxide in toluene, and observed no cataphoresis. He assumed, therefore, that the particles were uncharged. This does not necessarily follow. According to Helmholtz (Memoir of the London Physical Soc., 1888), cataphoresis and endosmosis can only occur in a liquid which conducts electricity. If charged particles, suspended in an insulating medium, are subjected to an electric field, a displacement of the components of the double electric layer will take place; but it will stop at a point where the attraction by the external field is balanced by the attraction between the two layers themselves. The fact therefore that a sol does not show cataphoresis does not prove the absence of an electric charge. If the two electrically charged layers are perfectly symmetrical, no displacement at all will take place when the electric field is applied. It is also possible that a double electric layer might be formed, the two charges residing in the extremities of a polar molecule such as silver stearate. Conductivity determin-

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ations, on the other hand, show definitely that if there is any charge it is not due to the adsorption of ions and therefore that the stabilising effect of silver stearate is not similar to that of ferric chloride on a ferric hydroxide sol.

## Surface Tension and Viscosity.

As previously mentioned, it was noticed that when a mixture of stearic acid and silver stearate was being reduced with hydrogen, after about five minutes or less a froth of very stable bubbles was formed. This frothing continued until all the silver stearate had been reduced and the sol became unstable. It therefore seemed probable that the silver stearate lowered the surface tension of the stearic acid. Measurements of surface tension were made and it was hoped that if the effect was sufficiently great the surface tension might be measured from time to time during a reduction, and the relation between composition, surface tension, and the stability of the sol investigated. At the same time, it was thought of interest to see if the viscosity of the stearic acid was affected by the presence of silver stearate or silver sol.

The surface tension was determined by the rise in a capillary tube at 138°, this temperature being maintained by means of boiling xylene. The results obtained were :

	Surface tension.	Density.
Stearic acid	22.7	0.8019
Stearic acid $+ 2\%$ silver stearate	22.6	0.8070
Silver sol in stearic acid	21.0	(0.8070)

These results show that the presence of 2 per cent. of silver stearate does not appreciably lower the surface tension of stearic acid. No accurate value could be obtained for the sol, owing possibly to the silver being deposited in the capillary tube. A considerable lowering, however, was observed.

The viscosity determinations were made in an ordinary Ostwald viscometer, heated in a bath of the vapour of boiling xylene. The reading for pure stearic acid was first taken and then silver stearate was added to give a 2 per cent. solution. Readings were taken for this solution, which was then reduced in the viscometer with a current of hydrogen, and the time of flow of the sol noted. The following results were obtained :

ſ	ime of flow	•	
Temperature 138°.	(mins.).	Density.	t d.
Stearic acid	179.5	0.8019	144.0
2% silver stearate	183.0	0.8070	147.7
Silver sol	179.0	(0.8070)	144.4

It will be observed that t d, which is proportional to the viscosity, is slightly increased by the addition of 2 per cent. of silver stearate.

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This increase, about 3 per cent., is more comparable with the increase produced by crystalloids than by colloids such as soap in water. The silver sol is seen to have practically the same viscosity as the pure medium.

## Stability of the Silver-Stearic Acid Sol to Change of Solvent.

The behaviour of the sol when its dispersion medium was changed from stearic acid to a solution of stearic acid in various solvents was investigated. The following results were obtained when approximately equal weights of the sol were dissolved in the same volume of the solvents :

Solvent.	
Paraffin wax	Quite stable.
Ligroin Hexane Toluene	Stable. A slight black deposit gradually formed. Stability greater than 14 days.
Benzene	Fairly stable. Settled completely in a week. Black ppt.
Xylene	Settled completely in 1 day. Black ppt.
Ethyl alcohol	Settled in a few minutes. Black ppt.
Amyl alcohol	Settled in 1 day. Red ppt.
Amyl acetate	Deep red sol. Very opaque and stablo.
Acetone	Slight black deposit after 10 days. This sol was found to be negatively charged. The sol at first appeared quite unstable and a black deposit formed. After about 4 hours this coordination and and
Ether	the remaining sol became quite stable. It was found to be negatively charged. Unstable. The sol settled completely in 1 day. The ppt. was white.

These results are discussed in the conclusion.

#### Coagulation.

The sol coagulated when heated strongly with sodium chloride. Sodium sulphate had no such coagulating effect. This seemed to suggest that the precipitation was due to a reaction between the salt and the silver stearate giving silver chloride and sodium stearate. Hydrogen chloride gas was found to coagulate the sol much more quickly and at a lower temperature than sodium chloride. Analyses of the sol before and after coagulation indicated that the hydrogen chloride rapidly attacked first the silver stearate and then, gradually, the free silver. It also quickly coagulated a solution of the sol in benzene at room temperature.

#### Silver Sols in other Dispersion Media.

The method of preparing a colloidal solution of silver in an acid which proved successful in the case of stearic acid was tried with other fatty acids in order to find out what effect variation in the length of the carbon chain has on the stability of the sol.

Acetic Acid.—Special care was taken to dry the acetic acid. After being purified by partial solidification, it was heated for some time with a few drops of acetic anhydride and distilled directly into a flask containing silver acetate. A current of hydrogen was then bubbled through the mixture. Reduction took place gradually at  $80^{\circ}$ . A brown stain was formed on the glass, and a coarse suspension in the liquid. It was observed that sols could be formed, although they were not stable, by heating acetic acid with silver acetate; the mixture, which was colourless initially, became yellow, then reddish-brown, and finally green. At whatever stage the action was stopped the sol rapidly coagulated.

Valeric, n-Octoic, Lauric, Palmitic, and Margaric Acids.—The silver salts of these acids were prepared by the action of an ammoniacal solution of silver nitrate on an alcoholic solution of the acid (Found: Ag = 51.81; 42.92; 35.14; 29.2; 28.4 per cent. for the respective silver salts in the order given above).

In each case, a current of hydrogen was passed through a mixture of the acid with a small quantity of the silver salt heated at  $100^{\circ}$ ; a reddish-brown sol was formed, most rapidly in the case of valeric acid. When an intensely coloured sol had been formed (two minutes for valeric, ten minutes for *n*-octoic, thirty to sixty minutes for the other acids), the current of hydrogen was stopped and the sol kept at  $100^{\circ}$  for observation of stability. The sol in valeric acid showed definite signs of coagulation in five minutes and was completely coagulated in about ten minutes. In the case of *n*-octoic acid, the first signs of coagulation appeared in ten minutes, and it was complete after twenty-five minutes. The sols in lauric, palmitic, and margaric acids were quite stable and showed no signs of coagulation. Frothing was observed during the production of each of the sols as in the case of stearic acid.

It was desired to find the effect of substituting a phenyl group for the fatty hydrocarbon chain. A suspension of silver benzoate in benzene was therefore treated with hydrogen, benzoic acid not being suitable as a dispersion medium. A red sol was formed. It coagulated, however, completely in about an hour.

The effect of the presence of two carboxyl groups was investigated in the case of sebacic acid. No sign of sol formation was observed.

# Conclusion.

From a consideration of previous work on this subject and of the results of this research, it seems that, as a rule, a stable organosol can be formed only when there is present, besides the dispersion medium and the disperse phase, a polar compound containing radicles similar to those in each of the two phases.

First with regard to alcohol: stable alcosols of zinc, tin, and lead have been prepared by Burton (op. cit., p. 147), but he could not obtain stable alcosols of silver, gold, or platinum. It seems probable that the positive metals form ethoxides or hydroxyethoxides, whereas the noble metals do not. Again, in both cases in which purer silver alcosols have been prepared—by electrolysis and by illumination of a silver plate in alcohol by ultra-violet light—it has been shown, as already mentioned, that some silver compound is formed.

With regard to silver and stearic acid, the case is quite clear. At one time, the authors were of opinion that in dispersion media in which the molecules were long chains adsorption of these molecules stabilised the sol, no intermediate substance being present. But this is evidently not the case. The presence of a little silver stearate is essential to the production of a stable sol, whilst on its removal the sol becomes quite unstable. This behaviour is comparable in some respects with that of ferric hydroxide hydrosols, for the stability of which a small quantity of a ferric salt is necessary. In this case, the stability is definitely an ionic effect. The colloidal complexes acquire a positive charge, whilst the corresponding negative chlorine ions remain free in the liquid. Conductivity determinations show conclusively that this cannot be the case with the silver-stearic acid sol, and it becomes necessary to postulate a non-ionic mechanism of the stabilising action of silver stearate. The most probable explanation is adsorption by the metallic silver particles and consequent lowering of the surface tension between them and the dispersion medium. The work of Langmuir, Harkins, and others has shown that, at interfaces, polar molecules of the type of stearic acid tend to arrange themselves so that the ends of the molecule are directed towards the phase they more strongly resemble. In the case under consideration, the silver atom would be attached to the colloidal silver particle, whilst the hydrocarbon chain would be extended into the stearic acid. This arrangement would considerably decrease the tendency towards coagulation; each silver particle, being covered with a layer of fatty acid, would behave as a large (associated) stearic acid molecule.

It appears to be an established fact ("Fourth Report on Colloid Chemistry," p. 49) that molecular attraction extends to a considerable distance and that it is not only the contiguous molecule or atom that is affected. We should expect, therefore, that the stability of an organosol of the type silver-AgX-dispersion medium would be dependent on (i) the similarity between X and the dispersion medium, and (ii) the length of the X group.

(i) The results recording the effect of change of medium on the stability of the silver-stearic acid sol illustrate the importance of this factor. Paraffin wax gave the most stable sol. Ligroin and hexane, which still resemble the radicle  $C_{17}H_{35}$  quite closely, gave sols nearly as stable. Of the remainder, benzene gave a fairly stable sol, and ethyl alcohol, amyl alcohol, and ethyl ether did not give stable sols. In the cases of acetone and amyl acetate, ionic complications arose and stable, negatively charged sols resulted.

(ii) The effect of this factor is seen in the different stabilities of the sol in various fatty acids. In acetic acid, very transitory sols only were formed. In valeric and *n*-octoic acids, sols were formed which quickly coagulated. In lauric, palmitic, margaric, and stearic acids, stable sols were formed. Benzene and silver benzoate gave a sol the stability of which was intermediate between those of the *n*-octoic and the lauric acid sols.

It is impossible to say definitely whether in these solutions the silver salts are molecularly dispersed or are present in the colloidal state. They apparently show a definite solubility, which is a characteristic of true solutions, but, on the other hand, concentrated solutions show a tendency to gel on cooling. Very possibly sols are only formed when the solubility of the silver salt is suddenly reduced by cooling. The stabilising action of the salts runs parallel with the molecular weight and therefore with the tendency to form colloidal solutions, but in the very small concentration necessary for stability it is probable that they are present as crystalloids as in the case of aqueous soap solutions.

It is interesting to consider one case of protection in the light of this hypothesis. Very stable silver, gold, and platinum organosols can be made by a method described by Amberger (Kolloid Z., 1915, 11, 97, 100). A concentrated solution of silver nitrate is mixed with lanoline, and caustic soda added. The mass is left exposed to daylight for some time, when it will dissolve in an organic solvent to give a silver organosol. Lanoline consists chiefly of cholesterol,  $C_{27}H_{45}$ °OH, a complex alcohol containing a terpene ring and the group  $>C = CH_2$ ; on oxidation, this yields various complex acids. In the preparation of the sol, the silver salts of these acids are formed by the oxidising action of silver oxide. They are then adsorbed by the free silver which is also produced, the great length of the hydrocarbon residue making it a very efficient stabilising agent. A very large number of protective agents are acids of high molecular weight, for example, the proteins

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and their decomposition product, lysalbic acid, so that a great many protective actions may have a similar explanation. Further investigations on this point are in progress, in the course of which it is proposed to study the formation of silver sols in glycerol in the presence of silver mannonate, which, according to the hypothesis outlined above, should be an effective stabilising agent.

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