Reports

Metallic Colloids in Molten Salts

Abstract. *Gold, silver, and silver iodide sols were prepared in mixed nitrate melts. Electron micographs of the gold and silver sols show particles smaller than 1 micron. The gold sols exhibit conventional absorption and scattering spectra. Both gold and silver sols show unusual stability.*

The possibility that small particles in molten salts exhibit colloidal behavior in the sense that the particles are stabilized by mutual repulsion has been considered; but it has not been given a great deal of credence because of lack of experimental (*1*) or theoretical (*2*) evidence. We have found it comparatively easy to prepare colloids in molten salts. However, although colloids can be readily prepared in concentrated media (*3–5*), none of these media is as highly conducting as molten salts are. There are reports of "pyrosols" (*6*) in molten salts but their colloidal properties have not been well characterized.

The gold sols were prepared by cautious addition of 5 to 200 μl of $AuCl_3$ solution (concentration, 6 g/liter) to 10 cm^3 of a eutectic consisting of molten $LiNO_3$ and KNO_3 or of $NaNO_3$ and KNO_3. A colloid formed immediately because of reduction of the Au^{+++} with residual nitrite. This sol was violet in transmitted light and brick-orange in reflected light. The gold could be redissolved by addition of HCl solution to the melt and reprecipitated again by addition of nitrite or by electrolytic reduction. Reduction with 5 percent H_2 in He at high temperature (400°C) gave large particles which settled rapidly. Varying the temperature, nitrite concentration, and the water concentration and agitation through helium bubbling apparently did not change the spectrum enough to lead us to believe that changing these conditions alters the particle size. These colloids usually lasted a day; even after a week there was usually still some unsettled colloidal gold in the solution. Raising the temperature by 150°C did not measurably hasten the coagulation.

The absorption spectrum of the gold colloid in $LiNO_3$-KNO_3 eutectic showed a peak of 5750 Å which, when corrected for the difference in the velocity of light of the two media, corresponds to a wavelength in water of 5250 Å. The wavelength of this absorption remains very nearly constant at 5250 Å in water systems for particles of less than 400 Å in diameter (*7*). In such a situation, only the absorption coefficient would change, and we could not measure this accurately enough to determine our particle size (*8*). Therefore two representative preparations were cooled and dissolved in water, the gold was separated by centrifugation, and electron micrographs were made after redispersion with an ultrasonic stirrer (Fig. 1). Admittedly these are now redispersions of water-washed coagulations of the original molten salt colloids, but their particle size distribution is consistent with the optical properties of the molten salt preparation. The gold particles from the $LiNO_3$-KNO_3 eutectic formed at 150°C had a mean diameter of about 350 Å, and they were quite uniform in size and spherical. The particles of the colloid formed from the eutectic of $NaNO_3$ and KNO_3 at 255°C were larger (on the average) and less uniform in size and shape. Occasionally triangular or hexagonal particles could be detected. The mean particle size was about 600 Å. Electrolytically reduced gold was much coarser and more irregular.

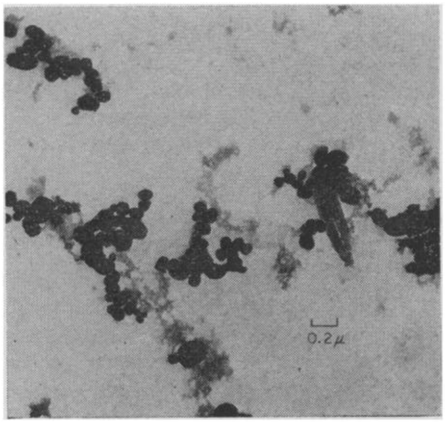

Fig. 1. Colloidal gold from a eutectic consisting of $NaNO_3$ and KNO_3.

Silver colloids were prepared with a 125-watt medium-pressure mercury arc, by photolysis of silver nitrate dissolved in a KNO_3-$NaNO_3$ eutectic. The rate of formation and of disappearance was monitored with a Beckman spectrophotometer modified to serve as a high-temperature Tyndallometer (Fig. 2). We have not yet been able to produce silver colloids by γ-irradiation of molten nitrates or chlorides or by photolysis of the $LiNO_3$-KNO_3 melt.

The initial rate of formation appears to be a linear function of lamp intensity, independent of silver-ion concentration. The temperature dependence, if one uses the initial slope of the formation curves, showed an activation energy of 2.7 kcal. The photolysis showed an induction period which can be quite long (Fig. 2). Water, added by bubbling with wet helium, discouraged the formation of metallic silver and produced a long induction period but did not inhibit silver formation entirely. When the illumination ceased, a limited dark reaction sometimes followed.

We are convinced of the identity of the particles. When the colloid was allowed to stand, a silver ring sometimes formed on the glass at the solution interface. The particles were also examined by electron microscopy and electron diffraction and showed the diffraction pattern of silver. They agglomerate in blobs about 200 Å across. A fine structure of tiny blobs about 10 to 15 Å across can sometimes be detected.

Silver iodide sols were prepared much as they are prepared in water solutions. Dilute aqueous silver solution was added to the nitrate melt (50 μl of an 0.75*M* solution to 10 cm^3 of molten salt), the resulting turbidity was cleared with a bit of nitric acid, the solution was swept with helium to remove the resulting water and nitric oxides, and then a nearly equivalent amount of potassium iodide solution was added. The sol was quite yellow, with a marked scattering peak at 5000 Å and an absorption in the transmission spectrum at the same wavelength. The colloid was not excessively stable; the turbidity as measured with the

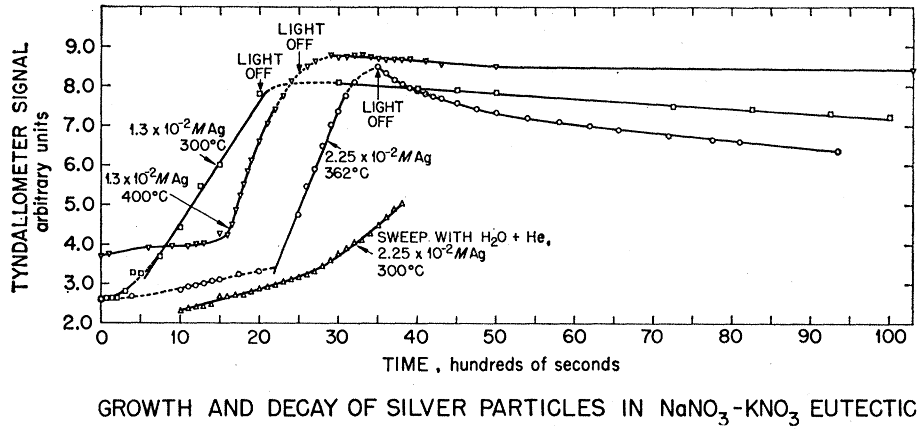

Fig. 2. Rate of formation of colloidal silver from photolysis of $NaNO_3$-KNO_3 eutectic that also contains $AgNO_3$.

Tyndallometer decreased to half its initial value on standing overnight. When the colloid was heated to 400°C, it dissolved and did not re-form on cooling.

Experiments to determine how these colloids are stabilized have been inconclusive. Electrophoretic plating of the gold sol gave negative results. None of the sols absorbed fluorescein dye (the staying power and ionization of this material in molten nitrates is also open to question). Mixing aged silver iodide sol, containing excess Ag^+ or excess I^-, with gold sols did not give mutual flocculation (*9*), as one would expect for these sols in a water system. However, addition of gold chloride to the silver iodide sol did reduce the amount of silver iodide scattering; thus there must be some interaction of the freshly formed gold sol with the silver iodide. However, since gold sol and silver iodide sol can coexist in the same solution, their interaction is not complete as it is in water solution.

The apparent stability of these colloids is not well understood. Both Voet (*3*) and Burkard (*5*) invoke a tightly bound layer of solvent molecules as a stabilizing influence on their sols. Indeed, Burkard (*5*) found that removing all solvents (for example, CS_2 from As, CS_2 from Se, C_6H_6 from P) from the glacial acetic acid sols caused them to precipitate rapidly. Such a picture could also be applied to these molten salt colloids; it is preferred to the alternative, proposed by Ostwald and Wannow (*4*), which calls for low conductivity in concentrated solutions and is thus clearly inapplicable here. Kreyger, Kirslis, and Blankenship (*10*) observed a change in the contact angle between molten salts and metal or graphite, depending on whether the salts contained water. This indicates a change in the affinity of salt for the metal interface induced by the presence of water, because of the adsorption and reaction of water itself. That the water in association with the solvent salt molecules then assumes an image charge due to the contact potential of the metal, or assumes a charge due to preferential cation hydration, then seems reasonable. The observation of ion-exchange phenomena in molten salt solutions also indicates that some sort of charge layer can occur in molten salts; but again, water or some form of bound water is a prerequisite for this ion exchange (*11*). A serious drawback to the model is that in view of the high conductivity of the molten salt solution, the repulsion from such a charge layer could operate only through a small distance (one or two atomic layers) unless further ordering of quasi-lattice structures by these surface charges is possible in the molten salt.

A group of Italian investigators (*12*) has prepared metallic dispersions of colloidal dimensions in fused sodium chloride. Copper, silver, and nickel were vaporized in the melt by the Bredig arc method (*13*). However, the many differences in their systems and ours, namely the difference in electrophoretic behavior, particle size distribution, temperature, and melt composition lead us to believe that these two groups of colloids have very little in common.

HAROLD W. KOHN
Reactor Chemistry Division,
Oak Ridge National Laboratory,
Oak Ridge, Tennessee 37830
TED E. WILLMARTH
Analytical Chemistry Division,
Oak Ridge National Laboratory

References and Notes

1. M. A. Bredig, in *Molten Salt Chemistry*, M. Blander, Ed. (Interscience, New York, 1964), p. 367.
2. E. J. W. Verwey and J. Th. G. Overbeek, *Theory of the Stability of Lyophobic Colloids* (Elsevier, New York, 1946).
3. A. Voet, *J. Phys. Chem.* **40** (1936).
4. W. Ostwald and H. A. Wannow, *Koll. Z.* **76**(2), 160 (1937).
5. A. L. Elder and P. Burkard, *J. Phys. Chem.* **41**, 621 (1937).
6. C. B. Gill, M. E. Straumanis, A. W. Schlechten, *J. Electrochem. Soc.* **10**, 42 (1955); R. Lorenz and W. Eitel, *Pyrosole* (Akademische Verlag, Leipzig, 1926).
7. G. Mie, *Ann. Phys.* **25**, 377 (1908); M. A. Jeppesen and R. B. Barlow, *J. Opt. Soc. Amer.* **52**, 99 (1962).
8. In this discussion it is assumed that the change in refractive index that occurs when molten salt is substituted for water from the gold-water to the gold-molten-salt system does not sensibly change the shape of the scattering curve. The rigorous (and laborious) recalculation of the absorption spectrum from the Mie scattering theory is outside the scope of this communication.
9. R. H. Bogue, *The Theory and Application of Colloidal Behavior* (McGraw-Hill, New York, 1926), vol. 6, chap. 13.
10. P. J. Kreyger, S. S. Kirslis, F. F. Blankenship, *Molten Salt Reactor Program Annual Report 1964* (Oak Ridge National Laboratory No. 3659, Oak Ridge, Tenn., 1964), pp. 38–42.
11. G. Alberti and S. Allulli, *J. Chromatogr.* **32** (2), 379 (1968).
12. R. Piontelli, G. Lecis Coccia, U. Ducati, *Electrochim. Metallorum* **3**, 171 (1968).
13. G. Bredig, *Z. Angew. Chem.* **1898**, 951 (1898); *Z. Electrochem.* **4**, 515, 547 (1898).

14. Supported by the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation. We thank Dr. Voet for informing us of Refs. (*4*) and (*5*).

27 December 1968

Oxytocin: Crystal Data of a Seleno Analog

Abstract. *The sulfur atom in position 6 of deamino-oxytocin (1-β-mercaptopropionic acid–oxytocin) was replaced by selenium. The crystals of the resulting deamino-6-seleno-oxytocin are similar to those of the "wet" form of deamino-oxytocin, but they are stable upon prolonged exposure to air.*

The major obstacle to x-ray crystallographic analysis of neurohypophyseal principles (*1*) has been the small size of the crystals available.

The replacement of a sulfur atom in the disulfide bridge of deamino-oxytocin by selenium may overcome this difficulty (*2, 3*). Selenium, with its higher electron density, could serve as a heavy-atom marker, thus permitting the analysis of structure from smaller crystals. Biological and conformational studies in soluiton (*3, 4*) indicate that the selenium replacement introduces differences in the parent molecule; but this replacement does not affect the overall molecular conformation.

Crystals of deamino-6-seleno-oxytocin