COLLOIDS IN GLACIAL ACETIC ACID. I

ELEMENTS, CHLORIDES, SULFIDES, AND SULFATES

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Most of the recent work done using glacial acetic acid has dealt largely with salt solubilities (1, 2), phase studies (3, 6), electrometric work (8), and activity coefficients of salts (4, 5, 7, 10). Weiser and Mack (13) list numerous examples of colloidal dispersions in other organic solvents. Voet (11, 12) discusses colloidal solutions in concentrated electrolytes and he has prepared some sols in mixtures of concentrated sulfuric and acetic acids. Since the completion of this investigation Ostwald and Wannow (9) have reported the preparation of arsenic trisulfide in glacial acetic acid and have noted its very great stability.

COLLOIDAL ELEMENTS

Arsenic

The yellow, metastable form of arsenic is slightly soluble in carbon disulfide. Some of this solution was added to glacial acetic acid and the arsenic was dispersed in the colloidal state. The glacial acetic acid was prepared in a pure and anhydrous condition by refluxing with 1-2 per cent chromic oxide and the calculated amount of acetic anhydride and then carefully distilled. Only that acid with melting point of 16.5°C. or above was used in the experimental work. The yellow sols which formed varied in intensity according to the concentration of arsenic present.

One stable arsenic sol was prepared by dissolving 0.120 g. of arsenic in 333 ml. of carbon disulfide and then pouring this solution into 667 ml. of glacial acetic acid. Somewhat higher concentrations of arsenic can be used. Attempts were made to stabilize arsenic sols further by the use of gum mastic and gum dammar in concentrations of approximately 0.1 g. per liter. Instead of stabilizing the sols, the opposite effect was noted. Attempts were made to remove the carbon disulfide by dialysis and by heating, but each resulted in decreasing the stability of the sol.

Selenium

Red selenium was dissolved in carbon disulfide and this solution was added in varying amounts to glacial acetic acid. The color of the sol depended upon the concentration of selenium present, some being red, others pink, and some having a yellowish tinge. By transmitted light all the sols were nearly colorless. These sols were stable for about three days. No satisfactory protective agents were found. Sixteen sols were prepared varying in selenium concentration per liter from 0.00179 to 0.4470 g. The carbon disulfide concentration was varied from 0.2 to 50.0 per cent by volume.

Sulfur

White to yellow sulfur sols, depending upon the amount of sulfur dissolved in carbon disulfide, were prepared by adding the glacial acetic acid slowly from a buret to the sulfur dissolved in carbon disulfide. These sols were not very stable. A sol containing 0.0762 g. of sulfur, 0.0452 g. of gum mastic, 168 ml. of carbon disulfide, and 832 ml. of glacial acetic acid contained no precipitate after seven hours, but had precipitated in one day.

Sulfur sols were also prepared by dissolving sulfur monochloride in glacial acetic acid and passing dry hydrogen sulfide into this solution. The yellow sols which formed were not very stable. It is interesting to note that these sols, immediately after formation, could be poured into large volumes of water without the sulfur precipitating.

Phosphorus

Better phosphorus sols were prepared by dissolving yellow phosphorus in benzene than in carbon disulfide. If glacial acetic acid is added very slowly to the benzene containing the phosphorus, very stable sols are formed. In some instances it was necessary to seed with a small amount of another phosphorus sol. Dialysis through cellophane to remove the benzene eventually caused complete precipitation of the sol. If the phosphorus sol is poured into water, the sol fumes and smells strongly of burning phosphorus.

Two typical stable phosphorus sols were prepared as follows: (1) 0.02995 g. of phosphorus was dissolved in 2 ml. of benzene and 998 ml. of glacial acetic acid was added and (2) 2.96 g. of phosphorus was dissolved in 200 ml. of benzene and 800 ml. of glacial acetic acid was added. Many phosphorus sols of other ratios of phosphorus:benzene:acetic acid have been prepared.

Gold, platinum, silver, and copper

Platinic and auric chlorides are not soluble in acetic acid. If dry hydrogen chloride gas is passed into suspensions of these salts in glacial acetic acid, the soluble complexes H_2PtCl_6 and $HAuCl_4$ form. Small amounts of phosphorus dissolved in benzene added to the solution of chloroauric acid in glacial acetic acid produced a beautiful change in color from a pale yellow to red and finally brown. A precipitate soon forms, so these sols cannot be considered as being very stable. With chloroplatinic acid a similar reaction took place, the final product being a black precipitate. It was found possible to reduce chloroplatinic acid with gum dammar. No satisfactory stabilizing agent was found.

Silver nitrate and silver acetate dissolved in glacial acetic acid were immediately reduced to unstable red sols by the addition of yellow phosphorus dissolved in benzene.

Copper acetate dissolved in glacial acetic acid was slowly reduced by phosphorus, but it always precipitated as a reddish brown deposit.

SULFIDES

Many elements which form insoluble sulfides in water also form insoluble sulfides in glacial acetic acid. Soluble acetates are very desirable for the preparation of sulfide sols, because the secondary product is acetic acid. Oxides are not desirable because water is formed. Some sulfides, such as arsenious sulfide, antimony trisulfide, and nickel monosulfide in the presence of a large excess of ammonium ion, tend to be colloidal in acetic acid as well as in water.

Colloidal sulfides containing Pb⁺⁺, Hg⁺⁺, Cu⁺⁺, Ni⁺⁺, Co⁺⁺, As⁺⁺⁺, Sn⁺⁺⁺⁺, and Ag⁺ have been prepared by bubbling hydrogen sulfide into acetic acid solutions of lead acetate, mercuric chloride, cupric acetate and ammonium acetate, nickel acetate and ammonium acetate, cobaltous chloride, arsenic trichloride, stannic chloride, and silver nitrate, respectively. Arsenic, cobalt, and copper sols have been prepared which have been stable for about a month. The others were not as stable. Gum mastic was a satisfactory stabilizing agent.

Very stable arsenic trisulfide and antimony trisulfide sols were prepared by bubbling hydrogen sulfide into acetic acid solutions containing arsenic trioxide and antimony trioxide. Since water is a product of this reaction, the system is no longer non-aqueous.

COLLOIDAL CHLORIDES

Attempts were made to prepare colloidal silver, lead, mercurous, and thallous chlorides by passing dry hydrogen chloride gas into silver nitrate, lead acetate, and thallous nitrate. None of these sols was stable for more than a few hours. Mercuric chloride was dissolved in glacial acetic acid and a small amount of yellow phosphorus in benzene added. A colloidal solution of mercurous chloride formed, which was stable for about two days.

COLLOIDAL SULFATES

Since nearly all of the inorganic sulfates are insoluble in glacial acetic acid, it is possible to precipitate the sulfates by adding 100 per cent sulfuric acid to a solution of a soluble salt in glacial acetic acid. Barium sulfate formed by adding sulfuric acid to a solution of barium chloride in glacial acetic acid showed a slight tendency to be colloidal. Lead sulfate formed from lead acetate dissolved in glacial acetic acid tended to precipitate immediately. The reaction between copper acetate and sulfuric acid in glacial acetic acid forms a thick gel-like solution when first mixed. Upon standing, the white copper sulfate precipitates, leaving a clear solution. The most stable sulfate sol was prepared from strontium acetate dissolved in glacial acetic acid. A sol which was stable for four days contained 0.62 g. of strontium acetate and 0.376 g. of sulfuric acid per liter.

SUMMARY

Colloidal elements, sulfides, chlorides, and sulfates have been prepared in glacial acetic acid.

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