

Aqueous Colloidal Solutions of Cellulose Micelles

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In 1920^{1,2} it was postulated from X-ray investigations that native cellulose fibres contain crystalline areas or micelles, and more recently, attention has been concentrated on the dimensions, shape and position of these micelles in the cell wall. From X-ray diffraction measurements^{3,4} a width of approximately 60 Å and a minimum length of 600 Å have been calculated for such micelles. They have now been obtained in aqueous colloidal solution, and have been observed as isolated morphological units by means of the electron microscope. A brief report on this work was given by Svedberg⁵ in a recent lecture and a more comprehensive paper will shortly be published by Rånby and Ribí⁶.

After considerable degradation of the wood or cotton cellulose fibres, the sols are prepared by peptization. This degradation may be performed by boiling with 2.5 *N* sulphuric acid⁷ for 1–8 hours and then washing out the acid in a preparative centrifuge with distilled water. The first 2–3 portions of wash liquid (pH < 2) are almost clear, then peptization begins at pH ~ 3 with maximum opacity (maximum cellulose concentration in the sol) occurring at pH ~ 4. Concentrations of 0.5 % have been obtained with a peptization of 25–40 % of the hydrolysed cellulose sample. A similar peptization can also be obtained from the alkaline side, if the cellulose is immersed in 0.1 *N* sodium hydroxide after hydrolysis, in which case maximum opacity occurs between pH 8.5 and pH 7.

After sterilization by heating to 100° C. the cellulose sols are stable for several weeks if their pH values lie between 3.5 and 9.5. Outside this pH range the sol

coagulates. The pH is controlled by means of 0.01 *N* hydrochloric acid and 0.01 *N* sodium hydroxide. The sols are also coagulated by very small amounts of neutral electrolytes, e. g., 4 · 10⁻⁴ *N* sodium chloride caused coagulation in a few seconds and 1 · 10⁻⁴ *N* in about two hours. Thus, the cellulose sol is definitely *hydrophobic*. The stability of such a sol, prepared as above, is probably due to the protective action of a substance of low molecular weight, possibly oxydized oligosaccharides, which are dissolved during the peptization process. When dialysed against distilled water, the sols coagulate in about half an hour. Only dilution 5–10 times causes a slow coagulation. Other protective substances are being sought among the polyuronides.

The peptized cellulose has a rather high content of carboxyl groups (3–5 milliequivalents/100 g cellulose) which give it a negative charge in aqueous solution.

This colloid particles have been extensively studied morphologically in the electron microscope and structurally by X-Ray and electron diffraction, all in cooperation with Ribí⁶. From this work the following results can be quoted. After suitable hydrolysis an accumulation of rodlike particles having the same dimensions as the micelles, earlier calculated from X-ray diffraction diagrams^{3,4} of cellulose fibres, has been found. The particles are free or in resolvable aggregates. They are very well crystallized — as shown by their X-ray and electron diffraction patterns — and they have exactly the same structure and lattice dimensions as the fibre cellulose⁶. Undoubtedly, the rodlike particles are identical with the earlier postulated micelles of the cellulose fibre. The micelles are well-defined, fundamental morphological units of the cell walls.

The colloidal cellulose has a high electrophoretic mobility (~ 10⁻⁵ cm/sec. volt), a high sedimentation constant (500–700

S), a low intrinsic viscosity ($\lim_{c \rightarrow 0} \eta_{sp}/c \sim 0.3$, c in g/100 ml) and a high turbidity and light scattering. It seems to be a useful model substance for such physico-chemical measurements. The sorption of water by isolated micelles is lower than that of native cellulose⁸. Chemical reactions have also been carried out with the colloidal cellulose.

It is of interest to note that Herzog⁹ in 1925 and Meyer and Mark¹⁰ in 1928 made the assumption that cellulose and cellulose derivatives generally were dissolved as micelles. This assumption could not be proved by later experiments, and only now, more than twenty years later, has it been shown that such micellar cellulose solutions can be produced.

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A New Type of Copper Acetylene Compounds

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When acetylene is introduced into a sufficiently concentrated aqueous solution of cuprous chloride and potassium or ammonium chloride, yellow or orange crystalline precipitates appear. These compounds have hitherto been regarded as addition complexes, *i. e.* as containing acetylene with retained hydrogen together with cuprous and potassium (or ammonium) chloride. For the potassium complex Chavastelon¹ gives the formula $C_2H_2(CuCl)_8(KCl)_2$. Tzyrikh and Ginzberg² state the formula $C_2H_2(CuCl)_6(NH_4Cl)_3$ for the ammonium complex.

Investigations concerning the conditions for the formation and dissolution of these compounds were performed at this laboratory in 1945, and the conclusion drawn was that the complexes must have some composition other than that suggested by the quoted formulas. A complete analysis however encounters many difficulties. *E. g.* the mother liquor which contains a considerable portion of the inorganic compounds cannot be completely removed without altering the precipitate. It is necessary to perform the analysis in such a way (determination of all components in one and the same sample, parallel analysis of the mother liquor) that the contributions from the mother liquor can be calculated. The result will include a cumulative error, for potassium estimated to be $\pm 5\%$, and for chlorine $\pm 2\%$. The data for copper and carbon (determined as acetylene after conversion with cyanide³) are but slightly influenced by the correction. The table shows the results of some analyses.

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