

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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Table 1. Results of analyses.

	Moles/8.00 moles of Cu			Cu+K -Cl
	C	Cl	K	
I	2.08	8.00	2.00	2.00
II	2.16	8.01	2.22	2.21
III	2.20	8.11	1.93 (?)	1.82
IV	2.14	8.20	2.33	2.13
V	2.11	7.96	2.17	2.10

Approximate composition of solutions (molarities):

1.5 m CuCl, 4 m KCl, 0.06 m C₂H₂
 Preparations: I 1.45 m CuCl, 3.80 m KCl, 0.07 m C₂H₂; II Do. but 0.10 m C₂H₂; III Do. but 0.06 m C₂H₂; IV 1.40 m CuCl, 4.00 m KCl, 0.2 m KAc, 0.05 m C₂H₂; V 1.60 m CuCl, 3.90 m KCl, 0.10 m LiCl, 0.04 m C₂H₂.

More accurate results can be achieved by use of a marking method involving addition of a small known amount of a tracer. Determination of tracer in the sample gives the quantity of mother liquor present. Work on this is continuing.

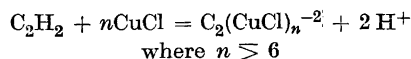
The last column of the table shows a kation surplus well corresponding to the content of acetylenic carbon. Thus the hydrogen atoms of the acetylene must be substituted by metal. That the compounds are *carbide* is proven also by the fact that an amount of acid, approximately equivalent to the acetylene introduced, is liberated on their formation. The analyses also show that the complexes contain an *equal number* of copper and chlorine atoms. To suggest an unambiguous formula is however difficult. Best corresponding with the results is the formula C₂(CuCl)₈K₂. There is however a systematic deviation: the acetylene content is somewhat too high (4–10 %). The potassium values may also be too high, but the greater possible error in this analysis makes a decision difficult. The results and the appearance indicate that the main body of the precipitate has the formula stated, but that it also contains varying amounts of another com-

pound, possibly also of the type C₂(CuCl)_nK₂, but with $n < 8$.

If the carbide nature of the compound is to be stressed the formula could be written C₂Cu₂(CuCl)_{n-2}(KCl)₂. So far however it seems preferable to regard the molecules of cuprous chloride as equivalent.

A liquid phase in equilibrium with a solid compound of this type is yellow. The dissolved colouring copper acetylene compound has a very high molar extinction. In a solution composed of 2.3-molar cuprous chloride, 5.75-molar ammonium chloride and 0.10-molar ammonia, where we have reason to assume that the acetylene absorbed (if the concentration is low) is quantitatively combining as the dissolved yellow complex, the acetylene concn. necessary for a visible yellow coloration amounts only to a 10⁻⁵ solution. For spectrophotometric measurements solutions have been used giving no precipitates even at an acetylene pressure of 1 atm. (*e. g.* 0.6-molar CuCl, 3.8-molar KCl, 0.2-molar HCl). The concn. of the dissolved yellow compound is low, but optically measurable. The main part of the acetylene entering the solution is present in the form of a dissolved colourless addition complex containing 1 mole of copper per mole of acetylene. (Its existence has been demonstrated by Manchot⁴.)

Computations from the measurements have been carried out under the assumption that there exists only one compound contributing to the extinction. The assumption is unproven but supported by the fact that the colour curves are identical in all measurements. The *results* which are sketched under a)–c) indicate a close relationship between the dissolved yellow compound and the solid yellow precipitate, and that the concentration of the former is determined by an equilibrium which can be expressed as



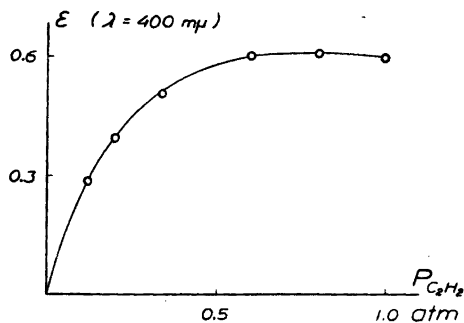


Fig. 1. Concentration of dissolved yellow complex at different acetylene pressures.

a) Variation of hydrochloric acid concn. at a constant concn. of cuprous chloride and chloride ion and constant acetylene pressure (the CuCl-activity of the solution and the concentration of the simple addition complex remaining unchanged) gives values of extinction proportional to $(\text{H}^+)^{-2}$.

b) Variation of the cuprous chloride concn. at constant potassium chloride and hydrochloric acid concns. (the relative depression of the CuCl-activity through formation of the simple addition complex remaining unchanged) gives extinction values proportional to the cuprous chloride concn. raised to its 6th–8th power.

c) According to the formula there should be a linear relation between acetylene pressure and extinction, but variations of the acetylene pressure over the same solution give the results illustrated by the figure.

The concentration of the yellow complex thus initially increases rapidly with the acetylene pressure, but then approaches a flattened maximum. The shape of the curve can be completely explained by considering that an increasing acetylene pressure indirectly causes a decrease in the CuCl-activity by augmenting the formation of the simple addition complex. Although the reduction of the CuCl-activity is moderate — 22 % at the highest

acetylene pressure in the experiment illustrated by the curve — it considerably influences the concn. of the yellow complex, since the CuCl-activity enters the equilibrium to such a high power. An adjustment of the results to a common CuCl-activity, utilizing an equilibrium constant for the simple addition complex (determined through solubility experiments) gives a linear relation between the concn. of yellow complex and acetylene pressure.

A structural similarity seems likely between these copper acetylene compounds containing the group $\text{C}_2(\text{CuCl})_n^{2-}$ and the silver compounds³ of the type $\text{C}_2(\text{Ag}^+)_n$. (There exists a solid nitrate where $n = 8$, $\text{C}_2\text{Ag}_3(\text{NO}_3)_6$. In both cases a large number of metal atoms — eight or less, but perhaps preferably eight — is bound to the C_2 -group. The dissimilarity between the compounds may depend on the fact that the copper atoms, unlike silver, do not become coordinatively saturated, and thus every copper atom brings a chloride ion into the complex. When $n = 8$ the silver complex thus becomes a hexavalent kation but the cuprous chloride complex a bivalent anion.

In solutions containing cuprous chloride and an alkali chloride polymerization of acetylene to monovinylacetylene occurs⁵. Kinetic investigations on this process (performed as 'flow experiments' in stationary state) indicate that the catalytically active agent should be the ions of the dissolved yellow complex. At a constant acetylene pressure the polymerization rate seems approximately proportional to the concn. of the dissolved yellow complex.

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