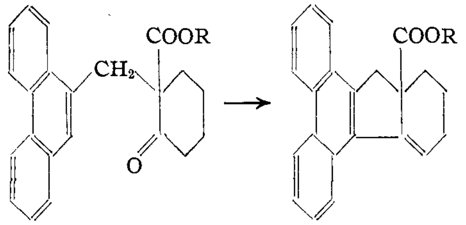

(VI) (VII)

occurred to a negligible extent only.

9-Phenanthrylcarbinol[18] (14 g.) (from benzene as needles, m. p. 150°) is mixed with dimethylaniline (12 g.) and benzene (40 cc.) and treated at 0° with thionyl chloride (7 cc.). The crystalline cake formed is kept for ten hours at room temperature and then heated to 100°, until the evolution of sulfur dioxide ceases. On addition of water and ether, part of the 9-chloromethylphenanthrene separates spontaneously; the remainder was obtained by evaporation of the ethereal layer. From light petroleum the m. p. is 98°; it is useful to induce crystallization by scratching; yield 12 g.[19]

Ethyl 2-(9'-Phenanthrylmethyl)-cyclohexanone-2-carboxylate (VI).—9-Chloromethylphenanthrene (3.7 g.) was added to ethyl sodio-cyclohexanone-2-carboxylate (from 0.4 g. of sodium and 3.1 g. of the ester, b. p. 119° (26 mm.)) in toluene (25 cc.) and the whole boiled for six hours. After treatment with dilute sulfuric acid, the toluene was evaporated and the oily residue triturated with methanol and acetone. It gave 2.5 g. of the desired product, which was recrystallized from light petroleum as dimorphous white needles and yellow stout prisms; m. p. 118–119°. (*Anal.* Calcd. for $C_{24}H_{24}O_3$: C, 80.0; H, 6.7. Found: C, 79.3; H, 6.)

Cyclization VI ⟶ VII.—The foregoing ester (10 g.) was heated at 140° for twelve hours with water (100 cc.) and concentrated sulfuric acid (55 cc.). The organic material was extracted with ether and benzene and distilled *in vacuo.* At 230° (0.03 mm.) a viscous, nearly colorless oil distilled and on treatment with glacial acetic acid gave a crystalline mass (2.9 g.). It consisted almost completely of the starting material, which was recovered by recrystallization from propyl alcohol. A small amount of material proved insoluble in this solvent and was subsequently recrystallized from ethyl malonate. The analysis of the prisms, m. p. 250°, so obtained, was consistent with (VII). (*Anal.* Calcd. for $C_{24}H_{22}O_2$: C, 84.2; H, 6.4. Found: C, 83.8; H, 6.2.) From the glacial acetic acid mother liquor no homogeneous material could be isolated, even after dehydrogenation with platinum black at 320–340°.

Summary

The three hydrocarbons, previously obtained from 9-phenanthrylmagnesium bromide and cyclopentanone, are now identified as 1,2-cyclopentenotriphenylene, 9(?)-methyl-3,4-benzpyrene and 1,2,3,4-dibenzfluorene, respectively.

1,2-Cyclopentenotriphenylene was synthesized from the addition product of 9-cyclopentenylphenanthrene and maleic anhydride by dehydrogenation and subsequent stepwise decarboxylation.

For the synthesis of 1,2,3,4-dibenzfluorene, dicyclohexenyl was condensed with indene and the addition product dehydrogenated by means of selenium. The attempt to apply Ruzicka's chrysene synthesis to the case of 1,2,3,4-dibenzfluorene was unsuccessful.

REHOVOTH, PALESTINE RECEIVED MAY 3, 1938

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[18] Bachmann, THIS JOURNAL, **56**, 1363 (1934).

[19] Compare v. Braun, *Ber.*, **70**, 984 (1937).

[CONTRIBUTION FROM THE CELLULOSE DEPARTMENT, CHEMICAL FOUNDATION, BOYCE THOMPSON INSTITUTE FOR PLANT RESEARCH, INC.]

Optical Properties of Cellulose Dispersed in Cuprammonium Hydroxide Solution[1]

BY JACK COMPTON

The current concept regarding the nature of the colloidal solutions resulting from the dispersion of cellulose by cuprammonium hydroxide solution, Schweizer's reagent, depends on the theories of cellulose fiber structure, namely, the continuous, or macromolecular, theory, and the discontinuous, or micellar, theory.

The continuous, or macromolecular, theory, developed by Staudinger on the basis of viscosity measurements, may be summed up in the following statement:[2] "Accordingly cellulose and its derivatives are molecular colloids and on the length and form of their macromolecules depends the colloidal behavior of their solutions." The macromolecules in cellulose fibers are considered regularly lined up under the influence of covalent forces in a direction parallel to the fiber axis.

The discontinuous, or micellar, theory, postulated by von Nägeli[3] and extended to cellulose by Karrer[4] in 1921, assumes that the micelle of cellu-

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[1] Presented before the Division of Cellulose Chemistry at the 94th meeting of the American Chemical Society, Rochester, N. Y., Sept. 9, 1937.

[2] H. Staudinger, *Ber.* **70**, 2514 (1937).

[3] C. von Nägeli, "Die Stärkekörner," Friedrich Schulthess, Zurich, 1858.

[4] P. Karrer and F. Widmer, *Helv. Chim. Acta*, **4**, 174 (1921).

lose is formed by the union, or bundling, of many molecules of the elementary substance. Hess and co-workers,[5] in applying the law of mass action to the optical behavior of cellulose dispersed in cuprammonium solution, obtained results that were best explained when the cellulose molecule was assumed to be $C_6H_{10}O_5$. To explain the high viscosity of cellulose in cuprammonium solution on the basis of so small a unit, he assumed that the $C_6H_{10}O_5$ groups are associated to form a larger molecular aggregate. Later Hess[6] concluded that the cellulose fiber should be regarded as a physical aggregation of small units and Meyer and Mark[7] postulated that the cellulose micellae were formed from primary valence chains held together by "micellar forces." Recently, Lieser,[8] in summing up his results, writes: "It may be stated as most important that cellulose in viscose and ammoniacal copper oxide forms micellar solutions, in organic bases and inorganic acids solutions with a not yet clearly definable character. It was further shown that all celluloses regenerated from solution are of micellar structure." The dimensions of the micelle in cellulose fibers have been estimated[9] to be approximately 50 Å. diameter and over 500 Å. long.

The observations of Farr and Eckerson[10] that cotton fibers are composed of microscopic, ellipsoidal, cellulose particles of uniform size (1.1 × 1.5 μ), arranged with their long axis parallel to the fiber axis and held together by an intercrystalline "cementing" material, are of fundamental importance. Cellulose particles obtained from cotton fibers possess all the properties recognized as characteristic of native cellulose other than high viscosity in cuprammonium solution. The low viscosity of the separated particles is attributed by Farr[11] to the removal, or destruction, of the viscosity producing "cementing" material. Qualitative examination of cuprammonium dispersions of cotton fibers with the slit ultramicroscope, or working carefully with the stage microscope, revealed the presence of the apparently unchanged cellulose particles. Upon regeneration, these dispersions yielded a product containing randomly distributed particles similar to the original aggregates. From a study of the X-ray diffraction patterns of cellulose particles, Sisson[12] has concluded that a microscopic unit of cellulose particle dimensions (1.1 × 1.5 μ) adequately satisfies the fundamental requirements of the micelle, with the exception of size.

Since it is commonly accepted that the micelles are composed of macromolecules of cellulose, the theories of cellulose fiber structure do not necessarily conflict. There are, however, many divergent views as regards the nature of the cellulose dispersions in reagents such as cuprammonium solution. The purpose of the present investigation is: first, to investigate the entire cuprammonium viscosity range of cotton fiber to determine if, at any time, a relation exists between the viscosity and optical rotation of the cuprammonium dispersions; second, to determine in general the contribution of each component of native cotton fiber, *i. e.*, crystalline cellulose particles and the intercrystalline phase, to the phenomena of viscosity and optical activity of cuprammonium dispersions; third, to study quantitatively the effect of varying the concentration of differently treated celluloses dispersed in cuprammonium solution on the microscopic particle count, using the slit ultramicroscope; fourth, to study the mechanism of the dispersion phenomenon of crystalline cellulose particles by cuprammonium solution.

Experimental

Apparatus.—The equipment of the Leitz slit ultramicroscope included a micro cell and an eyepiece micrometer ruled in 1.0-mm. squares. In all counts reported in Table II, a 6L objective and a 10X eyepiece were used.

The optical rotations were determined in a Schmidt and Haensch Polariscope with an 85-watt capillary mercury arc lamp as the light source. A combination of monochromatic glass filters (No. 7) recommended by the Corning Glass Works was used to transmit only the 0.4358 μ blue mercury line.

Viscometers of the type recommended by Clibbens and Geake,[13] slightly modified by the addition of ground glass stoppers in place of the rubber stoppers previously specified were used in determining the viscosities of the celluloses dispersed in cuprammonium solution.

Preparation of the Cuprammonium Solution.—The cuprammonium solution prepared by the method of Clibbens and Geake,[13] containing 15 g. of copper, 240 g. of ammonia and 1 g. of sucrose per liter was satisfactory for determining the viscosity, optical activity, and particle

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(5) (a) K. Hess and E. Messmer, *Ann.*, **435**, 7 (1923); *Kolloid Z.*, **36**, 260 (1925); (b) K. Hess, E. Messmer and N. Ljubitsch, *Ann.* **444**, 315 (1925).

(6) K. Hess, "Die Chemie der Cellulose," Leipzig, 1928, p. 301.

(7) K. H. Meyer and H. Mark, *Ber.*, **61**, 607 (1928).

(8) T. Lieser, *Ann.*, **528**, 291 (1937).

(9) J. Hengstenberg and H. Mark, *Z. Krist.*, **69**, 271 (1928).

(10) W. K. Farr and S. H. Eckerson, *Contrib. Boyce Thompson Inst.*, **6**, 309 (1934).

(11) W. K. Farr, "Disintegration of Cellulose Membranes." Paper presented before the Division of Cellulose Chemistry of the American Chemical Society, Pittsburgh, Penna., Sept. 7, 1936.

(12) W. A. Sisson, *Textile Research*, **5**, (3), 119 (1935).

(13) D. A. Clibbens and A. Geake, *J. Textile Inst.*, **19**, 79T (1928).

counts of the various cellulose dispersions. It was possible to carry out all three determinations on one dispersion when necessary.

Preparation of Cellulose Samples Used in Studying the Effect of Various Treatments on the Viscosity, Optical Rotation, and Particle Count after Dispersion in Cuprammonium Solution.—Raw cotton (*Gossypium hirsutum* L.) was extracted with alcohol–benzene (1:1) in a Soxhlet extractor for twenty-four hours, thoroughly washed with water, and air-dried at room temperature. This material was used in the experiments listed below.

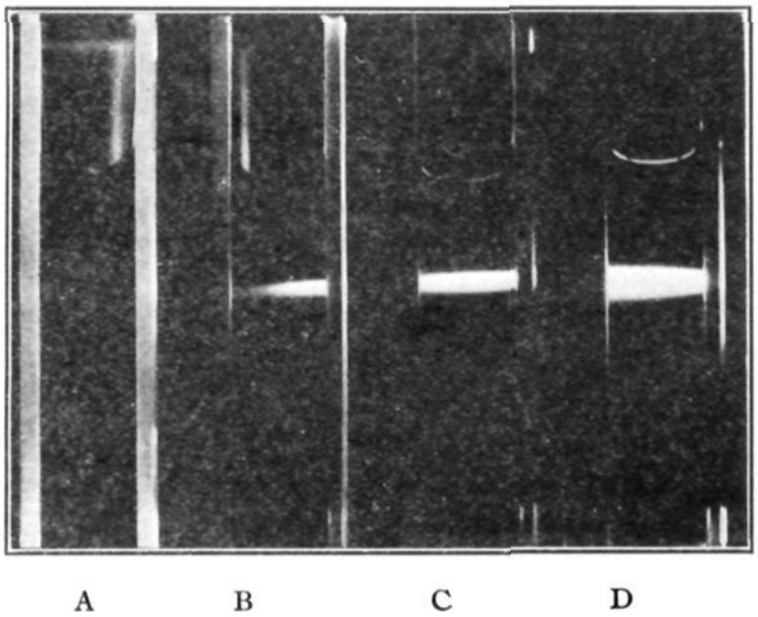

Fig. 1.—Effect of increase in concentration of cellulose dispersed in cuprammonium solution on the Tyndall phenomenon: (A) cuprammonium solution, control; (B) 0.5%, (C) 1.0%, and (D) 2.00% dispersions of cellulose particles in cuprammonium solution.

(1) Treatment of Cotton Cellulose with 0.01 *N* Hydrochloric Acid Solution at 75°.[14]—Ten grams of cotton cellulose was placed in 1 liter of 0.01 *N* hydrochloric acid solution previously heated to 75° and after vigorous stirring and shaking samples were removed at stated intervals of time, Table I. The sample was rendered neutral immediately after removal by plunging it into a large volume of ice-cold sodium bicarbonate solution. After agitating for ten minutes the sample was washed thoroughly with distilled water and air-dried at room temperature.

(2) Treatment of Cotton Cellulose with Concentrated Hydrochloric[10] Acid (d. 1.18) at 25°.—Cotton cellulose (10 g.) was placed in concentrated hydrochloric acid (250 cc.) at 25°. The removal and treatment of samples was effected in the manner described above (1). After twenty-two hours, slight pressure on the cover glass of a microscopic slide of this material destroyed the fiber structure completely. Many free cellulose particles could thus be disengaged from the fragments of fibers.

(3) Treatment of Cotton Cellulose with 0.04 *N* Sodium Hypochlorite[15] Solution of *p*H 9 at 25°.—Ten grams of cotton cellulose was treated with two liters of 0.04 *N* sodium hypochlorite solution containing 1.42 g. of available chlorine per liter, the solution being buffered at *p*H 9. Samples were removed at definite intervals of time, Table I, immediately washed with water, and given the standard acid wash. After again thoroughly washing in water the samples were air-dried at room temperature.

(4) Treatment of Cotton Cellulose with Excess Hydrogen Peroxide in the Presence of 4% Sodium Hydroxide Solution.[14]—Five grams of cotton cellulose was placed in 200 cc. of 4% sodium hydroxide solution and heated to boiling during the portion-wise addition of 3% hydrogen peroxide solution over a period of ten hours. The fiber structure could be disrupted completely by pressure at the end of this time, yielding microscopic cellulose particles. The fine white powder was washed with water, dilute acetic acid, and with water until neutral. After final washings with alcohol and ether, the material was allowed to air-dry at room temperature. The fluffy white material was then pulverized by light grinding in a mortar.

(5) Preparation of Cellodextrin (Biosan).—Cellodextrin was prepared according to the procedure of Hess and Friese.[16] Analysis of this material confirmed the observation[17] that it has a chain length of from eight to twelve glucose anhydride units.

Method Employed in the Dispersion of Cellulose in Cuprammonium Solution.—The method employed in the dispersion of the various cellulose samples listed in Tables I and II, and Fig. 2, was essentially the same as that described by Clibbens and Geake.[13]

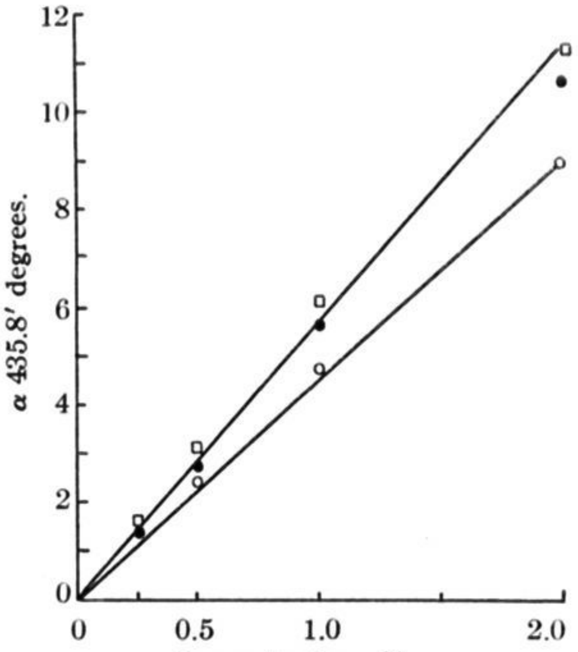

Fig. 2.—Effect of increase in concentration on the optical rotation of: ○, cellodextrin (biosan); ●, cellulose particles, expts. (2) and (4); □, kiered and bleached cotton, dispersed in cuprammonium solution.

Samples of celluloses were taken to yield dispersions of the per cent. actual cellulose concentration specified when dissolved in a volume equal to that of the calibrated viscometers. The material was finely divided, and, in the case of cotton fibers, the material was cut across with scissors into lengths not greatly exceeding a sixteenth of an inch (1.6 mm.). The samples were conveniently weighed

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[14] R. A. Joyner, *J. Chem. Soc.*, **121**, 2395 (1922).

[15] D. A. Clibbens and B. P. Ridge, *J. Text. Inst.*, **18**, 135T (1927).

[16] K. Hess and H. Friese, *Ann.*, **450**, 40 (1926).

[17] K. Freudenberg, *Ber.*, **62**, 383 (1929).

TABLE I

THE VISCOSITIES AND OPTICAL ROTATIONS[a] OF THE CUPRAMMONIUM DISPERSIONS OF COTTON CELLULOSE AFTER TREATMENT WITH VARIOUS REAGENTS

Length of treatment, min.	(1) Action of 0.01 *N* HCl at 75°		(2) Action of concd. HCl (d. 1.18) at 25°		(3) Action of 0.04 *N* sodium hypochlorite at *p*H 9, 25°	
	η, cp.	α	η, cp.	α	η, cp.	α
0	46.0	−3.00°	46.0	−3.00°	46.0	−3.00°
5	–	–	3.4	3.12	–	–
10	35.3	3.01	2.7	3.09	–	–
15	–	–	–	–	22.5	3.06
30	28.6	3.06	2.2	3.06	18.4	–
60	25.3	3.01	2.0	3.02	16.3	3.02
180	17.1	3.02	1.9	3.04	12.1	3.03
240	14.4	3.01	–	–	–	–
270	–	–	–	–	10.4	3.03
480	10.3	3.01	–	–	–	–
510	–	–	–	–	7.9	3.06
22 hrs.	–	–	1.9	3.02	5.0	3.01
32 hrs.	4.5	3.04	–	–	–	–
Action of excess H_2O_2 in presence of 4% NaOH at 100°; 10 hrs.					1.9	3.06

[a] All viscosities and optical rotations were determined with cellulose concentration of 0.5% (0.5 g. subs. in 100 cc. soln., moisture-free basis); the former at 25°, the latter in mercury light (435.8) at 32° in a 0.5-dm. tube, η, cp., cuprammonium solution 1.2.

TABLE II

VARIATION OF PARTICLE COUNT WITH CONCENTRATION OF DIFFERENT CELLULOSES DISPERSED IN CUPRAMMONIUM SOLUTION

		Number of particles observed in volume of soln. 2.02 × 10^{-9} cc.				
		Cotton cellulose particles				
Concn., %	Theoretical no.[a] of particles in volume 2.02 × 10^{-9} cc.	Cellodextrin (biosan) (5)	Prepd. by action of HCl (2)	H_2O_2 in presence of 4% NaOH 100° (4)	Wood pulp (Kipawa)	Kiered and bleached cotton
0.00	0.0	0.0	0.0	0.0	0.0	0.0
.25	3.5	.0	2.8	2.8	3.6	3.4
.50	7.0	1.8	6.3	5.5	5.7	7.5
1.00	14.0	3.2	13.8	9.4	8.8	13.2
2.00	28.0	3.7	–	–	–	22.2

[a] Calculation made on basis of uniform cellulose particle, 1.1 × 1.5 μ, with density 1.5.

on a small watch-glass and quantitatively transferred to the viscometers. A moisture content of 4% was assumed, previous experiments having shown that this figure was a representative average value.

A small amount of the cuprammonium solution was drawn up into the capillary end of the viscometer and closed off by folding over the attached rubber tube. The tube was fixed in an upright position, 0.7 cc. of clean mercury run in from a 1-cc. pipet, and the cellulose transferred to the viscometer by means of small tweezers and tapping the conical-shaped paper which holds it. The tube was then half filled with cuprammonium solution and the cellulose stirred in the solvent for a few seconds to remove entangled air. The viscometer was filled with the solvent to within an inch (2.5 cm.) of the top, the rod being washed at the same time. Finally, the viscometer was filled completely with cuprammonium solution and the stopper inserted, so that the excess liquid, displacing all air, overflowed through the top capillary and rubber tube, which was then folded over and made tight with a rubber band; the ground-glass stopper was fastened in place by use of steel springs. The viscometer was fastened securely in a box and placed in an apparatus constructed so as to make four revolutions per minute. The end over end motion of the instrument and the resulting motion of the mercury produced an agitation in the liquid which was continued until a homogeneous dispersion was obtained. A uniform period of eighteen hours was sufficient for complete dispersion of the high viscosity celluloses prepared above. The mixture was maintained at a temperature of 4° during dispersion by placing the whole apparatus in a cold room thermostatically controlled.

To measure the viscosities of the resulting dispersions, the viscometers were removed from the box and immersed[13] in a thermostat at 25°. After standing for thirty minutes, the stopper was removed from the viscometer and the solution allowed to flow freely through the capillary. The time in seconds necessary for the liquid meniscus to fall from the top to the bottom ring was noted with a stop watch.

In determining the optical rotations and particle counts, Tables I and II and Fig. 2, after viscosity measurements, the dispersions were stoppered and centrifuged (1800 r. p. m.) to remove any entangled mercury droplets. The apparently clear homogeneous dispersions thus obtained were transferred to the polarimeter tube and the micro cell of the ultramicroscope and the optical rotations and particle counts determined.

Effect of Increasing the Concentration of Cellulose in Cuprammonium Solution on the Tyndall Phenomenon.—A typical example of this effect is shown in Fig. 1. Cellulose particles (Expt. 2 above) were dispersed in cuprammonium solution in the manner previously described, and a strong beam of light focused into the solutions.

Method Used in Making Particle Counts on Cuprammonium Dispersions of Cellulose Using the Slit Ultramicroscope.—Refinement of the Tyndall phenomenon by use of the slit ultramicroscope enables one to arrive at a quantitative estimate of the number of cellulose particles present in a definite volume of the dispersions. The cuprammonium dispersions of the various cellulose samples were introduced into the micro cell and sealed immediately with a cover glass to prevent evaporation and formation of hydrated copper oxide. The light was then properly focused into the cell and the number of particles in a unit area counted. The average of ten counts at various positions of the field were taken, and this value checked similarly by an independent observer. Controls were run on the cuprammonium solution alone and corrections applied to the particle counts. Cuprammonium solutions containing more than one-tenth of a particle in the unit volume were rejected. Knowing the focal depth, and the calibration of the eyepiece micrometer for the microscopic lens system used, the unit volume in which the particle counts are made can be calculated. The dimensions of the unit volume were: focal depth (2.4 μ) × unit area on eyepiece micrometer (29 × 29 μ) = 2018.4 $\bar{\mu}^3$, or 2.018 × 10^{-9} cc. The results obtained are recorded in Table II.

To calculate the theoretical number of particles that should be present in the unit volume at a definite concentration, it is necessary to know, first, the average volume of the cellulose particle and, second, the total volume of cellulose dispersed in the solution. The volume of the cellulose particle, V_1, may be calculated from the dimension $1.1 \times 1.5\ \mu$ by substituting in the equation for the volume of a prolate spheroid, $V_1 = 4/3\pi ab^2$, where a and b are the major and minor semi-axes, respectively. Thus, $V_1 = 4.189 \times 0.75\ \mu \times (0.55\ \mu)^2 = 0.95\ \overline{\mu}^3$, or 9.5×10^{-13} cc. For a 0.5% (0.5 g. cellulose in 100 cc.) dispersion of cellulose the actual cellulose volume, $V = 0.5$ g./1.5, density of cellulose $= 0.33$ cc. In the unit volume, 2.018×10^{-9} cc. there would be, accordingly, a cellulose volume, V_2, of 6.66×10^{-12} cc. The theoretical number of cellulose particles, N, in the unit volume is obtained from the formula $N = V_2/V_1$. Thus, N[18] $= 6.66 \times 10^{-12}$ cc./9.5×10^{-13} cc. $= 7.0$, for a 0.5% soln. The corresponding values for other concentrations may be calculated in a similar manner.

Effect of Increasing the Concentration of Various Celluloses in Cuprammonium Solution on the Optical Rotation.—The experiments were carried out essentially in the manner described by Hess,[7] with the exception that a cuprammonium solution containing 15 g. of copper, 240 g. of ammonia and 1 g. of sucrose per liter was employed. Dispersion of the various celluloses was carried out as described above. The results obtained are plotted in Fig. 2.

Determination of the "Saturation Point" of Cellulose Particles in Cuprammonium Solution.—The possibility of the existence of a mass action equilibrium between the cellulose–copper complex and cellulose in cuprammonium dispersions has been considered previously.[5,19] In the present experiment cellulose particles (Expts. 2 and 4 above) have been used to determine the point at which the cuprammonium solution could no longer cause permanent dispersion. When the concentration was increased beyond 4.5%, the excess undispersed cellulose could be centrifuged unchanged (1800 r. p. m.) from the permanently dispersed phase. That this saturation point is not connected with the copper content of the cuprammonium solution was shown by the fact that the same "saturation point" occurred when A. C. S. cuprammonium solution (containing 30 g. copper, 165 g. ammonia, and 10 g. sucrose per liter) was used.

Discussion

The two general methods employed for the gradual disintegration of cellulose fibers are: first, the action of dilute acids, and, second, the action of mild oxidizing agents. The disintegrating action of these reagents, which is accompanied by a lowering of the cuprammonium viscosity, Table I, has been interpreted previously as indicating a decrease in the chain length of the cellulose molecules. Based on the dual structure of the cellulose fiber, however, a new interpretation is now placed on this behavior. Since the crystalline phase, or cellulose particles, remains largely intact by these treatments, it follows that the intercrystalline "cementing" material is the phase easily modified or destroyed. The conclusion may also be drawn that this unstable, reactive phase of native cellulose fibers is largely responsible for their high viscosity when dispersed in cuprammonium solution. This interpretation is somewhat similar to that of Joyner,[14] who postulated the existence of a cellulose A with high and a cellulose B with low viscosity in native cellulose fibers.

The high optical activity of cellulose colloidally dispersed in cuprammonium solution was considered by Hess[5] to be due to the uniform formation of an asymmetric complex cellulose–copper compound $[(C_6H_{10}O_5)_2Cu][Cu(NH_3)_4]$. It was further shown that with low viscosity celluloses there was no relation between optical activity and change in cuprammonium viscosity. The present work extends this conclusion to the entire viscosity range possible with cotton cellulose, Table I. Thus, the cellulose particle, or crystallite, seems to be responsible for the high optical activity, for as the viscosities of the cuprammonium dispersions are lowered, indicating removal of the intercrystalline "cementing" material, the rotations remain constant. The high optical activity of celluloses of high viscosity shows that either the rotation of the intercrystalline–copper complex is very similar to that of the cellulose particle–copper complex, or that the intercrystalline phase is present in quantities so minute as to escape detection.

It has long been recognized that cuprammonium is not a true solvent for cellulose[20] but in many researches this fact has been neglected. The Tyndall phenomenon characteristic of colloidal dispersions is exhibited clearly by cellulose dispersed in cuprammonium solution, Fig. 1. The slit ultramicroscope enables one to examine such dispersions in strong light under high magnification. Thus examination of cuprammonium dispersions of disintegrated cotton fibers whose viscosity had reached a constant low value, Table I, showed practically the theoretical possible number of cellulose particles to be present, Table II. The

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[18] Due to the variable values reported for the true density of cellulose [*cf.* A. J. Stamm and L. A. Hansen, *J. Phys. Chem.*, **41**, 1007 (1937)] and allowing for possible slight error in the dimensions of the cellulose particle, the values of N cannot be considered absolute, but do not exceed a possible correction of more than ± 20%.

[19] D. MacGillavry, *Rec. trav. chim.*, **48**, 18 (1929); E. Valkó, *Kolloid. Z.*, **51**, 130 (1930).

[20] E. Heuser, "Textbook of Cellulose Chemistry," 2d ed. German translation by C. J. West and G. J. Esselen, Jr., McGraw-Hill Book Co., Inc., New York, N. Y., 1924, p. 138.

variable deviations of the observed number of particles from the theoretical with increasing concentration is due to the difficulty of obtaining an absolute estimate from relatively few counts. When the number of counts on the samples was increased, the average value more closely approached the theoretical. The significant fact, however, is the trend toward an increase in particle count with increase in cellulose concentration. Due to the Brownian movement of the dispersed particles and the convection currents set up in the micro cell by heat from the light beam, an accurate count is difficult to obtain on more than one per cent. concentrations of low viscosity cellulose. With high viscosity cellulose, however, such as kiered and bleached cotton, motion in the dispersion is greatly reduced. Wood pulp dispersed in cuprammonium solution showed the same particle count tendency as cotton celluloses, thus indicating that both are composed of the same elementary units.

Inasmuch as cuprammonium dispersions of cellulose contain microscopically visible particles and possess high optical activity, it would appear that the organized units must be able both to transmit and reflect light. In ordinary light without high magnification, these dispersions seem to be true solutions due to even lighting from all directions of the transparent cellulose particle–copper complex.

Cuprammonium dispersions of a cellodextrin such as "biosan" are slightly less optically active than cellulose (Fig. 2). Dilute dispersions are optically void when examined in the slit ultramicroscope, but upon increasing the concentration a few particles are observed, Table II. It thus appears that this cellulose-like substance is dispersed beyond the limits of microscopic visibility. The conclusion thus may be drawn that regardless of the state of aggregation of the cellulose–copper complex, the optical rotation is of the same order of magnitude.

The existence of a definite equilibrium between the permanently dispersed cellulose particle–copper complex phase and the excess undispersed solid cellulose at concentrations exceeding 4.5% is shown by the fact that saturation is reached at this point. The saturation point is independent of the copper concentration and has only been observed with cellulose particles (Expt. 2) as the viscosity of native cellulose is much too high to make the point distinguishable. The excess undispersed cellulose phase may be almost entirely recovered unchanged upon centrifuging cuprammonium dispersions containing more than 4.5% cellulose particles. X-Ray diffraction analysis[21] shows the excess undispersed phase, thus recovered from a more than saturated cuprammonium dispersion, to be native cellulose, whereas the permanently dispersed phase upon regeneration gives a mercerized or hydrated cellulose pattern. Since the undispersed cellulose phase is not combined with the copper or ammonia in any way, it appears that the intermediary formation of the cellulose–copper complex is necessary for the transformation of native cellulose into the mercerized form, or that copper complex compound formation and dispersion of cellulose occur simultaneously.

Summary

1. The successive lowering of the cuprammonium viscosity of native cotton fibers by the action of dilute acids or mild oxidizing agents is not accompanied by a change in the optical activity of the resulting dispersions, a conclusion in agreement with the work of Hess on celluloses of low viscosity.

2. From (1) it follows that the optical activity of cellulose dispersions in cuprammonium solutions is dependent upon the formation of a cellulose particle–copper complex.

3. Quantitative examination of various celluloses dispersed in cuprammonium solutions, using the slit ultramicroscope, reveals the presence of approximately the theoretical number of cellulose particles ($1.1 \times 1.5\ \mu$).

4. Further evidence that cellulose–copper compound formation precedes dispersion of cellulose in cuprammonium solution is presented.

5. Visible cellulose particles ($1.1 \times 1.5\ \mu$) observed in the living cytoplasm, cellulose fibers and dispersions of cellulose in cuprammonium solution possess the essential features, with the exception of size and shape, of the hypothetical micelles.

YONKERS, N. Y.

RECEIVED FEBRUARY 3, 1938

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(21) Prior to the author's independent observation, W. A. Sisson of this Laboratory noted this apparent equilibrium from a qualitative examination of cuprammonium dispersions of cellulose particles.