sistance of liquid hydrogen sulfide, three runs were made, in one of which a mere trace of water was added, in the second about 1% and in the third 5%. Table II shows the results.

Table II

Effect of Water on the Resistance of Hydrogen Sulfide

	Galvanometer readings			
Voltage	Dry	Trace H_2O	1% H_2O	5% H_2O
1.5	15	12	11	8
3.0	26	20	19	13
6.0	49	34	33	25
9.0	73	52	53	38

Conclusions

1. The specific conductance of liquid hydrogen sulfide determined at $-78.5°$ is 3.7×10^{-11} reciprocal ohms.

2. The presence of even small amounts of water increases the resistance a great deal.

Ames, Iowa

[Contribution from the Laboratory of Physical Chemistry of the University of Upsala]

THE STATE OF DISPERSION OF CELLULOSE IN CUPRAMMONIUM SOLVENT AS DETERMINED BY ULTRACENTRIFUGE METHODS

By Alfred J. Stamm[1]

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Very little is known about the state of dispersion of cellulose in cellulose solvents because hitherto there have been lacking adequate methods for determining the particle size or the molecular weight of coarsely dispersed materials. The usual osmotic pressure methods for determining the molecular weight of solutes of high molecular weight are of little value here, because of the high electrolyte content of the solvents. Even in the case of cellulose derivatives in organic solvents, this method is questionable, because the derivatives themselves cannot be sufficiently purified.

The diffusion experiments of Herzog and Krüger[2] furnish the only available information on the nature of cellulose dispersions in cellulose solvents. Applying Einstein's diffusion law these investigators have calculated the average particle size. Unfortunately, they did not carry their diffusion experiments to low enough concentrations to be sure that they were dealing with free diffusion, and their method of taking only a few samples for analy-

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[1] Fellow of the Rockefeller Foundation. Chemist on leave from the U. S. Forest Products Laboratory, Madison, Wisconsin.

[2] (a) Herzog, *Pulp and Paper Mag. Can.*, **24**, 699 (1926); (b) Herzog and Krüger, *Kolloid-Z.*, **39**, 250 (1926); (c) *J. Phys. Chem.*, **33**, 179 (1929).

sis was not adequate for definitely proving the constancy of their calculated diffusion constant, which is a criterion of a monodisperse system. Herzog and Krüger's work, though of considerable interest, comes far from properly characterizing the cellulose solutions.

It appeared to the author that the ultracentrifuge methods developed by Professor Svedberg in this Laboratory, and so successfully applied in the study of protein solutions, would furnish just the tool necessary for quantitatively studying the nature of cellulose dispersions. It was with the hope of thus furthering the knowledge of cellulose solutions that this research was undertaken.

The Ultracentrifuge

Sedimentation Velocity Method.—In the study of the sedimentation velocity the oil turbine centrifuge capable of developing centrifugal forces from 8000 up to 110,000 times the force of gravity was used.[3] The solution to be studied is placed in a 5° sector shaped cell 12 mm. thick with quartz windows on the two opposite faces. This cell with its steel collar and appropriate fittings is clamped into a drilled slot in the disk-shaped rotor (15 cm. in diameter and 6 cm. thick) of the centrifuge in such a way that the cell windows are parallel to the faces of the rotor. The rotor case is provided with shutter windows so that the dispersed system in the cell can be illuminated and photographed while the centrifuge is in motion. Further details as to the drive, balance and temperature control of the centrifuge, which are of extreme importance, can be found in detail in the other publications.[3]

The rate of settling of the dispersed material is followed photographically during the course of the centrifuging either by the old method of recording the changes in light absorption, or the new method, to be described more fully later, of following the changes of the index of refraction of the sedimenting system. From the change of the position of the sedimentation boundary with time the specific sedimentation velocity of the settling material can be calculated according to the equation

$$s = \frac{1}{\omega^2 x} \times \frac{dx}{dt} \qquad (1)$$

where ω is the angular velocity of the centrifuge, x is the distance from the axis of rotation to the sedimentation boundary, and t is the time. The diffusion constant D can also be determined for a monodisperse material from the extent of spreading of the sedimentation boundary with time. From these two quantities, s and D, together with V, the partial specific volume of the sedimenting material, and ρ, the density of the solvent, the molecular weight of the sedimenting material can be calculated independently of Stokes' law of settling, thus

$$M = \frac{RTs}{D(1 - V\rho)} \qquad (2)$$

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[3] (a) Svedberg and Nichols, This Journal, **49**, 2920 (1927); (b) Svedberg, *Z. physik. Chem.*, **127**, 51 (1927); (c) "Colloid Chemistry," The Chemical Catalog Co., Inc., New York, **1928**, 2d ed., pp. 146–167.

where R is the gas constant and T the absolute temperature, by merely assuming the equality of the frictional forces that determine both s and D.

Determination of Concentration Gradients in the Sedimenting Systems.—The concentration gradients in the cellulose solutions cannot be determined by the ordinary light absorption method, which has been used in the study of all of the proteins, because cellulose, like other carbohydrates,[4] shows no light absorption even in the short wave length ultraviolet. For this reason a new method, developed by Ole Lamm in this Laboratory, was used and found to be satisfactory. Lamm's method[5] consists in determining the changes in the concentration gradient by following the changes in the index of refraction of the dispersed system. This is done by photographing a small uniform transparent scale which is mounted in the centrifuge casing behind the cell. The light from the scale in passing through the cell is refracted differently in passing through the different concentrations along the length of the sedimenting system. This differential bending of the light causes a distorted image of the scale, as is indicated in Fig. 1.

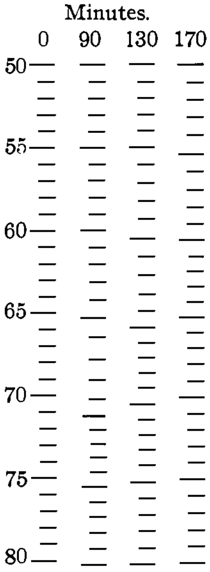

Fig. 1.—Diagrammatic representation of the photographs of the scale for a typical sedimentation velocity run on a 0.10% solution of cotton linters α-cellulose.

The mathematics of the method are so completely developed by Lamm[5] that no attempt will be made to duplicate it here. The fundamental equation on which the measurements are based

$$Z = Gab\frac{dn}{dx} = f\frac{dc}{dx} \qquad (3)$$

gives the relationship between the photographic scale displacement Z and the rate of change of the index of refraction n with changes in height, x. G is the photographic enlargement, a the thickness of the sedimenting layer in the cell and b the optical distance between the scale and the center of the cell. The photographic scale displacement Z is further proportional to the rate of change of the concentration c with changes of the height x, when the refractive index is a linear function of the concentration.

The scale used in this research had one hundred divisions 0.0201 cm. apart; a was in all cases 1.2 cm., b was either 10.2 or 12.4 cm. and for one run it was 25.2 cm., G was 0.473 when b was 10.2 cm., l the optical distance between scale and the lens was 302 cm. when b was 10.2 cm.

The mercury vapor lamp used in the protein researches[3] was used for illumination. The city current instead of the storage batteries was used as the source of current, as great constancy of the light intensity is *not* needed for this method, as *is* the case with

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[4] Kwiecinski and Marchlewski, *Bull. intern. acad. Polonaise,* [A] 271 (1928).

[5] Lamm, *Z. physik Chem.,* (a) **138,** 313 (1928); (b) **143,** 177 (1929).

the light absorption method. The cuprammonium solution served as its own filter, the 435 mμ wave length line being the only intense wave length emitted from the lamp that was not absorbed by the cellulose solvent.

The lens used was a Zeiss F/12.5 lens with a 100-cm. focal length. Diaphragm stops F/44, F/61 and F/88 were used, F/44 when the concentration gradients were small, just at the start and at the end of the runs and F/61 and F/88 for moderate and steep concentration gradients, respectively. In many cases pictures were taken with all three stops, and only the sharpest were used for the measurements. Imperial Process plates, 9 × 12 cm., were used for the exposures; 36 exposures could be taken on each plate. The times of exposure used for the stops F/44, F/61 and F/88 were 7.5 sec., 15 sec. and 30 sec., respectively. The plates were developed for two minutes in hydroquinone–potassium metabisulfite hard developer.

A micro comparator made in this Laboratory using a Johansson screw (Eskilstuna, Sweden) was used for measuring the displacement of the lines on the photographic plates. A Leitz No. 3 objective and a No. 2 ocular giving a magnification of 60 times were used for reading. The comparator drum could be read to 0.0001 cm. and check settings could usually be made to 0.0002 cm. A careful examination of the screw showed it to be accurate to 0.0001 cm.

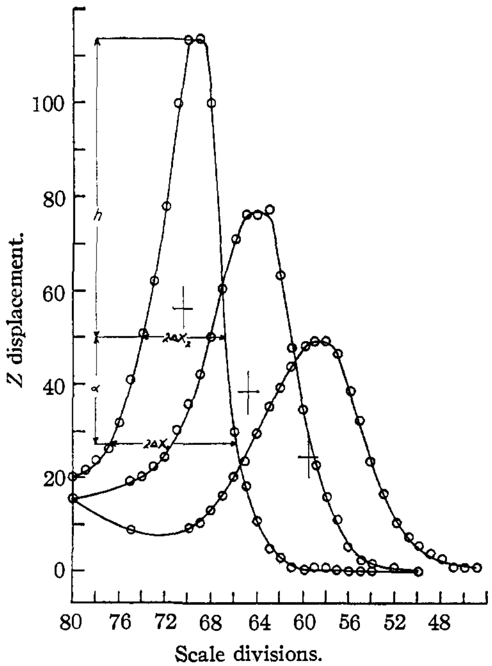

Fig. 2.—Photographic scale displacements for a typical sedimentation velocity run on a 0.10% solution of cotton linters α-cellulose.

Calculation of the Specific Sedimentation Velocity.—In Fig. 2 the photographic scale displacements Z in thousandths of a mm. are plotted against the scale division numbers for the enlarged representation of the photographic image shown in Fig. 1. That is, the rate of change of concentration with height in the sedimenting system is plotted against the height. The positions of the maxima in these first derivative of concentration curves correspond to the inflection points in the simple concentration curves obtained by the light absorption method, which, in turn, corresponds to the photographic position of the sedimenting boundary. The Δx values from the curves, distances between the maxima, or better, the vertical bisectors of the areas of the curves for two successive exposures taken Δt time apart, have to be corrected to the basis of actual cell distances by multiplying by the actual distance between scale divisions, 0.0201 cm., and by the factor $(l - b)/l$ to change from scale distances to distances in the cell. There is also a slight shift in x position due to the curvature of a light beam in passing through the solution. This curvature varies directly with the steepness of the concentration gradient at the point under consideration. The correction for the position of the sedimentation boundary is $-\Delta Z_{\text{max.}}/2G$ in the direction of increasing concentration when the sedimentation is calculated from a point at half the height of the vertical bisector. The absolute corrected distance between the maxima on two successive exposures, $\Delta X_{\text{corr.}}$ is thus

$$\Delta X_{\text{corr.}} = \frac{l - b}{l}\left(0.0201\,\Delta x - \frac{\Delta Z_{\text{max.}}}{2G}\right) \tag{4}$$

where Δx is in scale division units. The sign of the correction is plus as Z decreases with increasing time.

As the exact position on the scale corresponding to the position of the meniscus of the solution in the cell cannot be directly determined from the photographs, the distance from the center of rotation to the sedimenting boundary has to be determined in a roundabout way. From the average value of $\Delta X_{\text{corr.}}/\Delta t$, and the time elapsed up to the first exposure, the position of the sedimenting boundary at zero time, which corresponds to the position of the meniscus of the solution, can be calculated. From exposures taken with the camera focused on the cell rather than on the scale, the exact height of the solution in the cell can be measured with the comparator. Knowing the distance from the center of rotation to the bottom of the cell, the distance from the center of rotation to the sedimenting boundary can be calculated. The specific sedimentation velocity can then be calculated using Equation 1.

Calculation of the Diffusion Constant.—The diffusion constant can be calculated for a monodisperse system from the extent of spreading of the sedimentation boundary with changes in the time, that is, from the breadth of the curves of Fig. 2. If there were no diffusion taking place at the sedimentation boundary the concentration gradient would be infinite right at the boundary and zero to each side. The sedimentation curve would then be represented by a straight vertical line.

Only the method of determining D from the curves will be given here. For the theoretical considerations and the development of the equations the reader is referred to Lamm's publication.[5b] Let $2\,\Delta x_1$ represent the breadth of the curve at any height and $2\,\Delta x_2$ the breadth of the curve at such a height that $\Delta x_1^2 = 2\,\Delta x_2^2$. Let α represent the Z distance between the x_1 and the x_2 lines, and h the Z distance from the x_2 line to $Z_{\text{max.}}$ as indicated in Fig. 2. Then the diffusion constant

$$D = \frac{0.1086\,\Delta x_2^2}{t\log_{10}(h/\alpha)} \tag{5}$$

where t is the diffusion time. The value of Δx_2 determined from the curves must be corrected to absolute units and from the scale to the cell position as before by multiplying by 0.0201 and $(l - b)/l$.

Materials Used.—Cuprammonium solution was chosen for the cellulose solvent as chemical studies have shown that it is the nearest approach to a true physical solvent of all of the cellulose solvents. Further it is of considerable importance because of the cuprammonium artificial silk industry, and because this is the chief solvent used for viscosity comparisons of different grades of cellulose.

The cuprammonium solution was prepared by drawing carbon dioxide-free air slowly through a tall cylinder containing concentrated ammonia (sp. gr. 0.91) and strips of electrolytic copper foil for from six to eight hours. A large stock solution was prepared for all of this work, and kept in a tightly stoppered bottle in the dark. The copper concentration was determined by evaporation of 2-cc. portions, igniting and weighing as the oxide. The ammonia concentration was determined by titrating a diluted portion against 0.1 *N* hydrochloric acid using methyl orange as an indicator. The stock solution contained 1.28% of copper and 22.0% of ammonia.

All of the measurements reported in this paper were made on a cotton linters α-cellulose. The α-cellulose content was 99.6%, the copper number 0.17 (Braidy method) and the ash 0.031%.

A heavier lubricating oil, Vacuum Oil Co., Mobile B, was used as a seal over the surface of the cuprammonium solution in the centrifuge cell than was used in the protein researches, as greater precautions against evaporation are necessary here on account of the high vapor pressure of the ammonia. Careful examination showed that no ammonia evaporated through the oil layer.

Experimental

The new index of refraction method of measuring the concentration gradients, and the accompanying method of calculating the specific sedimentation velocity and diffusion constant have been tested by making runs on a number of proteins by this method and by the old light absorption method by both Lamm[5b] and the author.[6] The agreement was found to be quite satisfactory.

Specific Volume.—The partial specific volume of the pure cotton linters α-cellulose was determined pycnometrically at 19.8°. Measurements were made at three different concentrations in two different solvents, as shown in Table I.

TABLE I

PARTIAL SPECIFIC VOLUME OF COTTON LINTERS α-CELLULOSE IN CUPRAMMONIUM SOLVENT OF DIFFERENT CONCENTRATIONS AT 19.8°

Cellulose concn., %	Solvent concn. Cu, %	NH$_3$, %	V
0.568	1.28	22.0	0.645
.764	0.83	16.2	.637
1.029	1.28	22.0	.643

The values for the specific volume are constant within experimental accuracy, which unfortunately is not as great as might be desired due to

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[6] Svedberg and Stamm, THIS JOURNAL, 51, 2170 (1929).

the high vapor pressure of the solvent. The results show, however, that the specific volume is not affected to any appreciable extent by the cellulose concentration or the concentration of the solvent.

Preparation of Cellulose Solutions.—The cellulose solutions were made up in small glass-stoppered vials of 8-cc. total capacity by pipetting 5 cc. of the solvent into the vial, dropping in the weighed cellulose sample, and immediately stoppering, then gently rotating until the cellulose was dissolved. By this method the sample was not prepared entirely free from oxygen, so for comparison a few samples were made up by first warming the solvent to 60° in the vial, opening for one-half minute for the air to be displaced by the ammonia, which has a vapor pressure of 2.5 atm. at this temperature, then dropping in the weighed cellulose sample, stoppering and holding at the elevated temperature for fifteen minutes. After standing at room temperature for the length of time indicated, a sample was quickly pipetted into the centrifuge cell and sealed with a layer of lubricating oil.

Colloidal Nature of Solvent.—A run was made on the pure cuprammonium solvent to determine if it contained any sedimentable material. The results showed the presence of some polydisperse material, which is most likely colloidal copper hydroxide.[7] The sedimentation velocity ranged from 5×10^{-12} cm./sec. per cm./sec.^{2} to 10 to 100 times this value. The particles thus range in size from 6.5 mμ in diameter to more than 20.0 mμ, using Stokes' law for the calculations and taking the density of copper hydroxide as 3.37. Unfortunately the percentage of the total copper concentration that is colloidally dispersed cannot be determined definitely without knowledge of the relationship existing between the sol concentration and the refractive index. It is very likely less than 10% of the total copper concentration, however.

The sedimentation velocity of this colloidal copper hydroxide is fortunately 10 to 100 times greater than that of the cellulose so its presence does not interfere with the work of the present investigation. It is merely necessary to avoid making measurements near the bottom of the cell where this material becomes concentrated.

Sedimentation Velocity Results

Table II gives the results of a typical sedimentation velocity run made on a 0.10% cellulose solution. The data for the first three exposures are given in Fig. 1, and the diagrammatic representation thereof in Fig. 2. The table shows not only a constant value for the sedimentation velocity but also for the diffusion constant, indicating that the material under investigation is monodisperse. This is further indicated by the general symmetry of the curves of Fig. 2. The slight deviation from symmetry

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[7] Bhatnagar, Goyle and Prasad, *Kolloid-Z.*, **44**, 79 (1928).

at the extreme left, which is caused by a slight displacement near the meniscus of the solution, indicates the presence of relatively small amounts of a material of a much finer state of dispersion. This effect was in all cases very small for the runs made on pure cotton linters α-cellulose.

TABLE II

RESULTS OF A TYPICAL SEDIMENTATION VELOCITY RUN MADE UPON A 0.10% SOLUTION OF COTTON LINTERS α-CELLULOSE

Copper concn. of solvent, 0.64%; NH_3 concn. of solvent, 22.0%; $V = 0.642$; $\rho = 0.9356$; rel. visc. of solvent, 1.365; age of solution at time of starting run, 0.5 hr.; length of column of solution, 1.16 cm.; thickness of column, 1.20 cm.; average speed, 44,900 r. p. m.; time interval between exposures, 40 min.; average temperature, 20.7°.

Sedimentation

ΔX, scale div.	$\frac{\Delta Z_{\max.}}{2G}$, cm.	$\Delta X_{\text{corr.}}$, cm.	X mean, cm.	$\omega^2 \times 10^{-7}$	s_{20} cm./sec. per cm./sec. $\times 10^{13}$
5.7	0.0038	0.1136	4.91	2.22	4.29
5.5	.0029	.1088	5.01	2.21	4.03
6.0	.0015	.1174	5.12	2.20	4.28
				Av.	4.20

Diffusion

Time, sec.	$2\Delta X_2$, scale div.	$\Delta(X_{2\text{corr.}})^2$, cm.^{2}	h, cm. $\times 10^3$	α, cm. $\times 10^3$	D_{20}, cm.^{2}/sec. $\times 10^7$
5,160	7.7	0.00552	6.35	2.30	2.58
5,160	6.4	.00381	5.10	2.45	2.48
7,560	8.5	.00672	3.40	1.60	2.88
7,560	7.2	.00482	2.65	1.50	2.75
9,960	11.2	.01165	2.75	1.05	2.98
9,960	9.0	.00752	2.00	1.05	2.87
12,360	11.5	.01230	1.40	0.60	2.89
				Av.	2.77

Table III gives a summary of all of the sedimentation velocity runs. Part A shows the effect of varying the concentration of the solvent. For the purpose of comparison both the specific sedimentation velocity and the diffusion constant have been corrected to the basis of sedimentation and diffusion in the most concentrated solvent. The specific sedimentation velocity depends inversely upon the viscosity of the solvent, and directly upon the difference in density between that of the particle and of the solvent, and the diffusion depends inversely upon the viscosity of the solvent. The results show that the specific sedimentation velocity is practically independent of the copper and of the ammonia concentration over the range tested. The diffusion constant is also unaffected by the changes in copper concentration, but it is affected by appreciable reductions in the ammonia concentration. This latter may be due to an increased gel tendency.

Part B of Table III gives the effect of varying the cellulose concentration for solutions one-half and sixteen hours old, respectively. In each case

TABLE III

SUMMARY OF RUNS MADE ON COTTON LINTERS α-CELLULOSE

A. Effect of Varying the Solvent Concentration, Cellulose Concn. 0.10%. Age of Solutions at Time of Starting Runs, 0.5 hr.

No.	Solvent Cu, %	Concn. NH_3, %	Density of solvent	Rel. visc. of solvent	Av. r. p. m.	s_{20}, cm./sec. per cm./sec. $\times 10^{13}$	D_{20} cm.^{2}/sec. $\times 10^7$	Basis of concn. Solvent s_{20} $\times 10^{13}$	D_{20} $\times 10^7$
1	0.32	22.0	0.9297	1.350	44,800	4.27	2.80	4.03	2.72
2	0.64	22.0	.9356	1.365	44,900	4.20	2.77	4.05	2.72
3	1.28	22.0	.9474	1.390	43,400	4.18	2.68	4.18	2.68
4	1.28	22.0	.9474	1.390	36,000	4.29	2.79	4.29	2.79
5	1.28	18.4	.9583	1.330	42,700	4.28	2.63	4.17	2.52
6	1.28	14.8	.9692	1.275	45,000	4.23	1.76	4.03	1.62

B. Effect of Varying the Cellulose Concentration and the Age of the Solution. Solvent Concn., 1.28% Cu, 22.0% NH_3

No.	Cellulose concn., %	Age of soln., hours	Av. r. p. m.	s_{20}, cm./sec. per cm./sec.^{2} $\times 10^{13}$	D_{20}, cm.^{2}/sec. $\times 10^7$
1	0.50	0.5	41,900	2.31	0.237
2	.20	0.5	44,800	3.72	0.540
3	.10	0.5	43,400	4.18	2.68
4	.10	0.5	36,000	4.29	2.79
5	.05	0.5	45,000	4.38	4.52
6	.025	0.5	42,800	4.32	5.15
7	.50	16.0	42,800	2.56	0.640
8	.50	16.0	42,900	2.47	.673
9	.20	16.0	43,100	3.41	2.14
10	.12	16.0	43,100	3.99	3.51
11	.10	16.0	43,200	3.95	4.07
12	.07	16.0	43,100	4.13	5.10
13	.05	16.0	43,100	3.92	5.58
14	.025	16.0	43,200	3.65	5.90
15	.10	7 days	45,100	4.28	4.00
16	.10	0.5	45,200	4.26	2.77[a]
17	.10	16.0	43,000	4.24	2.73[a]
18	.10	0.5	43,000	4.43	1.27[b]

[a] Heated to 60°. [b] Added 0.10% glucose.

the specific sedimentation velocities increase slightly with a decrease in concentration in a linear manner as is indicated in Fig. 3. The deviation between the two lines is practically within the range of experimental error. The diffusion constants, on the other hand, increase at a greater rate with a decrease in concentration, and the values from the fresh solutions are considerably smaller than for the solutions sixteen hours old.

This slight increase in the sedimentation velocity and a relatively large increase in the diffusion constant with a decrease in concentration has also been obtained by Svedberg and Chirnoaga[8] for the protein, hemocyanin from *Helix pomatia*. The protein has a molecular weight of 5,000,000. The molecules are approximately spherical with a diameter of about 24 mμ. The diffusion constant for a 3% solution of this protein is approximately

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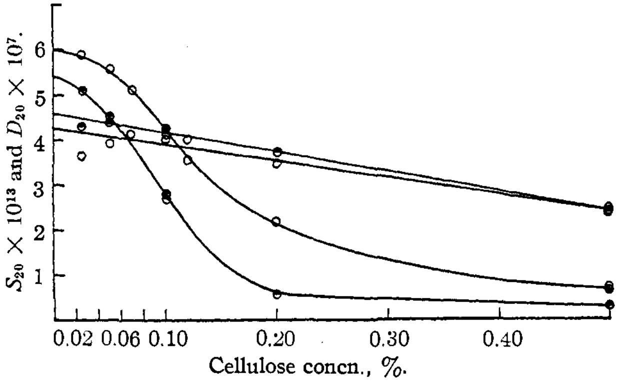
[8] Svedberg and Chirnoaga, THIS JOURNAL, 50, 1407 (1928).

one-third of its value for an infinitesimal concentration. The calculated average distance between the surface of adjacent molecules in the 3% solution is only about one and a half times the molecular diameter. The proximity of the molecules to each other for this concentration is very likely the cause of the low diffusion constant, the intermolecular action appreciably hindering free diffusion.

In the case of the 0.5% cellulose solutions the diffusion constant differs from the value for free diffusion by a still greater amount than in the case of the 3% solution of the hemocyanin, thus indicating that the intermolecular action must be still greater. The concentration effect in this case is very likely due to the rod shape of the molecules rather than their mass. From measurements of the width of the x-ray diffraction bands, Mark and Meyer[9] have estimated the length of the cellulose molecule or micelle in the solid crystal lattice to be 50 mμ. If the molecules in solution are of this same order of length, the marked decrease in the diffusion constant can well be accounted for on the basis of the intermolecular forces which come into play when any part of one molecule comes within the range of action of another. Sedimentation, on the other hand, involves directed motion and should be affected far less by concentration changes, as is the case.



●, Solutions 0.5 hour old; ○, solutions 16 hours old.

Fig. 3.—Variation of the specific sedimentation velocity and of the diffusion constant with cellulose concentration.

Degradation of Solutions by the Oxygen of the Air.—The increase of the diffusion constant with an increase of the age of the solution (see Table IIIB) is worthy of a closer examination. Is the effect due to the inherent aging of the solution or to a chemical change caused by the slight amount of oxygen present? The following viscosity measurements (see Table IV) give some insight into this matter. A solution was prepared

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[9] Mark and Meyer, *Z. physik. Chem.*, **2B**, 115 (1929).

containing 0.050 g. of cellulose in 50 cc. of cuprammonium solvent (1.28% Cu and 22.0% NH_3). Portions of 5 cc. each were quickly pipetted into the 8-cc. vials. The vials were immediately stoppered and allowed to stand for various lengths of time at room temperature (approximately 18°). Sample 6 was opened to the air for two hours the day before the determinations were made. Sample 7 was kept in the big bottle in contact with a large volume of air. Samples 8 and 9 were prepared by the previously mentioned technique for exclusion of oxygen of the air. The viscosity determinations were made in a 53-second Ostwald viscosimeter at 19.8°. The table shows that exclusion of the oxygen of the air prevents a change in the viscosity of the solution with time. The small amount of air ordinarily present in the vials, where no precautions for its exclusion were taken, shows a definite effect upon the viscosity. The presence of oxygen causes a decrease in the viscosity of the solution with time. Presumably when the oxygen is used up the viscosity remains constant. Allowing more oxygen to enter the vial, however, causes a further reduction in viscosity. Sedimentation velocity measurements (Nos. 16 and 17, Table IIIB) further show that exclusion of the oxygen of the air also prevents a change of the sedimentation velocity and of the diffusion constant with time. The previously observed change, therefore, must be due to the effect of the oxygen of the air on the solution and not to any inherent aging of the solution.

TABLE IV

EFFECT OF THE AGE OF 0.10% CELLULOSE SOLUTIONS IN CUPRAMMONIUM SOLVENT (1.28% CU, 22.0% NH_3) ON THE VISCOSITY OF THE SOLUTION

No.	Age of soln., hours	Viscosity relative to H_2O at 19.8°	Remarks
	...	1.39	Of solvent
1	1.5	2.12	Access to O_2 in vial
2	18.5	1.95	Access to O_2 in vial
3	43.0	1.94	Access to O_2 in vial
4	121.0	1.91	Access to O_2 in vial
5	309.0	1.91	Access to O_2 in vial
6	309.0	1.66	Opened to air for 2 hrs.
7	309.0	1.58	Access to large volume of O_2
8	0.5	2.13	O_2 free
9	16.0	2.14	O_2 free

A run was made on a solution twenty-two days old that had been kept in a big bottle with a large volume of air to act on the sample. The solution was so completely decomposed that with the highest centrifugal force obtainable no maximum in the Z displacement could be obtained though a Z displacement near the meniscus was quite evident. This shows that the dispersion of the degraded cellulose was so fine that it could not be studied with the centrifugal forces available, but part of it at least was still much coarser than the simple glucose units.

From the results of the above run, where the large volume of air present caused a breaking down of the cellulose particles, it seems quite probable that a similar effect has resulted in the case of the sixteen-hour old solutions only to a much smaller extent. The degradation has made itself noticeable to a very slight extent in the case of the sedimentation velocity, but quite appreciably in the case of the diffusion constant. Such a slight decrease in the sedimentation velocity and a more appreciable increase in the diffusion constant can be caused by the presence of small percentages of a material of a somewhat finer state of dispersion. The fact that the diffusion constant does not increase from exposure to exposure in a single run, however, indicates that the material cannot be appreciably heterodisperse.

A run was made on a 0.10% cellulose solution to which 0.10% glucose had been added (see Table IIIB). The sedimentation velocity was normal, but the diffusion constant was quite low. The viscosity of the solvent was increased by only a fraction of a per cent. by the addition of the glucose, so this cannot account for the reduction of the diffusion constant. The viscosity of the solution, however, was considerably higher than that of a 0.10% cellulose solution without the glucose present (2.49 rel. visc. instead of 2.12). The decreased diffusion constant must then be due to an increased gel tendency caused by the presence of the glucose.

Molecular Weight of the Dispersed Cellulose.—From an extrapolation of the curves of Fig. 3 for the change of the sedimentation velocity and of the diffusion constant with concentration, the ideal sedimentation velocity and diffusion constant for an infinitesimal concentration can be obtained. For the undegraded solutions $s_{20} = 4.6 \pm 0.2 \times 10^{-13}$ and $D_{20} = 5.4 \pm 0.5 \times 10^{-7}$. Using the average value of $V = 0.642$ and $\rho = 0.947$, then according to Equation 2, $M = 53{,}000 \pm 7000$.

The above value for the molecular weight is, of course, the molecular weight of the cellulose cuprammonium complex, whether it is a definite stoichiometric combination of 1 Cu:1$C_6H_{10}O_5$ according to Hess[10] or whether the copper complex is merely absorbed according to Bauer.[11] In the case of the stoichiometric combination, the copper content would be 28.0%. From Bauer's adsorption isotherm $X/m = 0.386$ g. of copper per g. of cellulose for the solvent containing 1.28% copper and $X/m = 0.260$ g., for the solvent containing 0.32% copper. The ratio of the molecular weights in the two solvents would be 1.10, and the ratio of the sedimentation velocities 1.065, as $s_1/s_2 = (M_1/M_2)^{2/3}$. The experimental ratio is 1.04. The deviation is well within the range of experimental error. In the case of the solvent containing 1.28% copper, the complex contains

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[10] Hess, *Ann.*, **435**, 1–144 (1923); *Z. angew Chem.*, **37**, 993 (1924); *Kolloid-Z.*, **36**, 260 (1925).

[11] Bauer, *Kolloid-Z.*, **36**, 257 (1925).

27.8% copper, which is practically the same as Hess's value for a stoichiometric combination. On either basis, then, the molecular weight of the uncombined cellulose would be 38,000 ± 5000.[12] The dispersed cellulose particles must then be made up of from 200 to 260 of the simple $C_6H_{10}O_6$ units.

It is of interest to compare the molecular weight of the cellulose–copper complex with that calculated from Herzog and Krüger's diffusion results for cuprammonium solutions.[2b] Applying Einstein's diffusion equation

$$D = \frac{RT}{N} \times \frac{1}{6\eta\pi r} \qquad (6)$$

the average radius of the cellulose particle is found to be 5.0×10^{-7} cm. Using the expression for the molecular weight

$$M = \frac{4}{3}\pi r^3 \rho_p N \qquad (7)$$

where r is the radius of the particle, ρ_p, the density of the particle, and N, Avogadro's number, M is found to be 495,000, which is just about ten times the value reported in this paper. The discrepancy seems to be due to the fact that Herzog and Krüger did not extend their diffusion measurements to sufficiently low concentrations to get entirely free diffusion. Their investigation also involves the assumption that the particles are spherical, which is most likely far from the truth.

Sedimentation Equilibrium Method.—Two runs were made on the cellulose solutions using the sedimentation equilibrium method so as to determine the molecular weight of the dispersed cellulose independently of measuring the sedimentation velocity and the diffusion constant. With this method a centrifugal force of only sufficient magnitude is applied to give a readily measurable constant concentration gradient after a reasonable duration of time that represents the attainment of equilibrium between the backward diffusion of the dispersed material and the outward sedimentation. The molecular weight is given by the relation[13,3c]

$$M = \frac{2RT \ln (c_2/c_1)}{(1 - V\rho)\omega^2(x_2^2 - x_1^2)} \qquad (8)$$

where c_1 and c_2 are the concentrations at the distances x_1 and x_2 from the center of rotation, and the other symbols have the same significance as previously. The index of refraction method, however, does not give the concentrations directly, but rather a function which is proportional to the rate of change of concentration with height. A mathematical analysis by Lamm has shown the following relationship to be valid

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[12] Mark and Meyer, *Z. physik. Chem.*, [Abt. B] **2**, 115–45 (1929). These investigators have determined the approximate molecular weight of cellulose in the fiber form from the width of the x-ray diffraction lines obtained in their crystallographic studies. $M = 10^5$ to 10^6. This is in fair agreement with the above results.

[13] (a) Svedberg and Fåhraeus, THIS JOURNAL, **48**, 430 (1926); (b) Svedberg and Nichols, *ibid.*, **48**, 3081 (1926).

$$\frac{c_2}{c_1} = \frac{(\mathrm{d}n/\mathrm{d}x)_2\, x_1}{x_2\, (\mathrm{d}n/\mathrm{d}x)_1} = \frac{Z_2\, x_1}{Z_1\, x_2} \qquad (9)$$

Applying this relationship in Equation 8 for the concentration ratio, the molecular weight can be readily calculated by merely measuring the Z displacements for two different heights in the equilibrium system. The x values have to be corrected, as previously described, for the slight bending of a light beam in passing through the solution $\Delta Z/G$, and for the change from scale distances to cell distances $(l - b)/l$.

The measurements were made in the new low speed centrifuge (2000 to 12,000 r. p. m.) driven by a Siemens-Schuckert motor generator set. The centrifuge is completely described in a recent publication from this Laboratory.[14] The scale was mounted in an adjustable tubular holder placed between the prism and the shutter. A horizontal reference cross hair was mounted across the outside face of one of the cell windows. From the shadow cast by this line on the photographic image of the scale, and from its actual position with respect to the bottom of the cell, the point in the cell corresponding to any of the scale divisions can be definitely determined.

A preliminary run was first made with only the cuprammonium solvent in the solution cell and in the standard cell. The scale divisions became quite regular after several hours, except near the bottom of the cell. This shows that the colloidal copper hydroxide is completely removed even at this lower speed. The exact distance from one of the lines that was superimposed on the standard cell image to each of the scale division lines, that were superimposed on the solution cell image, was determined. Runs were then made with the cellulose solution in the solution cell. The exact distance of each of the lines from the same reference line was again determined, and the Z values were calculated from the differences. This method of determining the Z displacements proved to be far more accurate than that used in the first part of this research.

The results of one of the equilibrium runs made on a 0.50% cellulose solution are given in Table V. The molecular weight values obtained at the different heights are quite uniform, again showing that the cellulose is monodisperse. This run required one hundred and sixty hours for the system to come to equilibrium. The time is considerably greater than that required in the study of any of the proteins.[3c,13] This is due to the high viscosity or gelation of the solution, which manifested itself in the sedimentation velocity study by giving abnormally low diffusion constants in solutions of this concentration.

A run made on a 0.20% cellulose solution took less than seventy-two hours to come to equilibrium. This run was made at a speed of 8350 r. p. m., and gave an average molecular weight of 54,400.

These results are in very good agreement with those obtained in the sedi-

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[14] Svedberg and Sjögren, THIS JOURNAL, 51, 3594 (1929).

TABLE V

RESULTS OF A TYPICAL EQUILIBRIUM RUN ON COTTON LINTERS α-CELLULOSE

Concentration, 0.50% cellulose; solvent, 1.28% Cu and 22.0% NH_3; $V = 0.642$; $\rho = 0.947$; length of column of solution, 0.63 cm.; thickness of column, 0.4 cm.; distance of outer end of solution from axis of rotation, 5.95 cm.; distance from scale to center of cell, 20.0 cm.; distance between scale divisions, 0.0257 cm.; optical distance between scale and photographic lens, 227.0 cm.; time of exposure, 1 min.; time of centrifuging, 190 hrs.; average speed, 7750 r. p. m.

Distance from center of rotation, cm. X_2	X_1	Photographic scale, displacement in cm. Z_2	Z_1	Ratio of concns., C_2/C_1	Mol. wt.
5.35	5.30	0.00685	0.00573	1.185	58,400
5.40	5.35	.00820	.00685	1.187	58,200
5.45	5.40	.00983	.00820	1.188	58,100
5.50	5.45	.01185	.00983	1.194	59,600
5.55	5.50	.01435	.01185	1.199	60,200
5.60	5.55	.01730	.01435	1.194	58,400
5.65	5.60	.02080	.01730	1.192	57,200
				Mean	58,600

mentation velocity study, and the two taken together quite definitely characterize the nature of the dispersion of pure cellulose in cuprammonium solvent.

Note on Viscose Solutions.—The author was anxious to compare cellulose dissolved in other solvents with the above results, but time was available for only one such run. This was made on a 0.26% viscose solution in 2.2% sodium hydroxide. The viscose was prepared from the above cotton linters α-cellulose. The relative viscosity of the solution was 2.17. The curves were symmetrical with but one maximum, thus indicating that the system is monodisperse. The sedimentation velocity, $s_{20} = 2.8 \times 10^{-13}$ cm./sec. per cm./sec.^{2} and the diffusion constant, $D_{20} = 0.71 \times 10^{-7}$ cm.^{2}/sec. Converted to a basis of sedimentation and diffusion in a solvent with the same density and viscosity as the cuprammonium solvent, $s_{20} = 3.3 \times 10^{-13}$ and $D_{20} = 0.73 \times 10^{-7}$. This sedimentation value is very similar to that for cellulose in the cuprammonium solvent at the same concentration. The diffusion is also of the same order of magnitude as that for the cuprammonium solvent. The molecular weight of the cellulose xanthogenate in the viscose solution must then be very similar to the value given above for the cellulose solutions.

The author wishes to express his sincere thanks to Professor The Svedberg for the use of the ultracentrifuge equipment of this Laboratory, and for the help which he always freely gave toward the carrying out of this research. The author also wishes to thank Mr. Ole Lamm, of this Laboratory, for allowing him to use the newly developed method for determining the concentration gradients, and for the help which he gave in applying this method.

Summary

1. The nature of the dispersion of pure cotton linters α-cellulose in cuprammonium solvent was studied with the aid of the ultracentrifuge.

2. The cellulose is monodisperse and has a molecular weight of 55,000 ± 7000. On a copper-free basis it is 40,000 ± 5000. The particles must be made up of from 200 to 260 of the simple $C_6H_{10}O_5$ units.

3. The specific sedimentation velocity of the dispersed cellulose increases slightly with a decrease in concentration while the diffusion constant increases quite appreciably. This is explained on the basis of the gelation of the system.

4. Oxygen of the air is shown to cause a degradation of the solution by decreasing the particle size.

5. The cuprammonium solvent is shown to contain some colloidally dispersed particles. Their sedimentation velocity ranges from ten to several hundred times that of the cellulose particles. Their size ranges from 6.5 mμ in diameter to more than 20.0 mμ.

6. A single run made on a viscose solution indicates that cellulose xanthogenate dissolved in a dilute alkali solution has approximately the same molecular weight as the above cellulose.

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DIFFERENCES BETWEEN THE STATE OF DISPERSION OF ISOLATED WOOD CELLULOSE AND COTTON CELLULOSE IN CUPRAMMONIUM SOLVENT

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All of the available chemical evidence indicates that there is a definite difference between isolated wood cellulose (Cross and Bevan cellulose) and cotton cellulose. The presence of mannan and pentosans in the wood cellulose has been shown in many cases, but it has never been found possible to remove these impurities completely. Because of this fact, it has not been possible to determine definitely from chemical evidence whether the hypothetically pure wood cellulose differs from pure cotton cellulose. X-ray studies on the other hand show that wood cellulose and cotton cellulose give the same interference bands and the same axial ratios,[2] thus indicating that the fundamental building units are identical. Although this evidence indicates that the hypothetically pure wood cellulose and the pure cotton

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[2] Herzog and Jancke, *Z. Physik*, **3**, 196 (1920).