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).

cellulose are identical, it does not exclude either the possibility of difference in the degree of association of the fundamental building units or the further possibility of difference in the manner in which these units are put together. The facts should be made evident from a quantitative study of the degree of dispersion of the celluloses dissolved in a cellulose solvent.

The ultracentrifuge technique, developed and applied to the study of pure cotton linters α-cellulose in the previous research,[3] was also used for the study of several different wood celluloses as well as other cotton celluloses.

Materials Used.—The solvent used for all of the measurements was the previous stock cuprammonium solution (1.28% Cu and 22.0% NH_3). Three different forms of cotton cellulose and four of wood cellulose were used. The cotton linters α-cellulose was the same as that studied in the previous research. The α-cellulose content was 99.6%, the copper number 0.17 (Braidy method) and the ash content 0.031%. The absorbent cotton was a long staple, extracted, non-medicated cotton with an α-cellulose content of 99.2%. The filter paper was a high-grade paper made from cotton linters stock that had not been subjected to acid treatment. The α-cellulose content was 97.2%. The aspen cellulose obtained from the wood by the Cross and Bevan method had an α-cellulose content of 71.2%. The white spruce cellulose was obtained by the same method. Unfortunately the sample was not sufficiently large for an α-cellulose determination to be made. The α-cellulose from spruce sulfite pulp was prepared by the Stora Kopparbergs Bergslags Aktiebolag in Falun, Sweden. The α-cellulose content was 96.1%, copper number 0.98 (Braidy method), and ash content 0.08%. The bleached sulfite pulp was an ordinary spruce pulp. The α-cellulose content was 81.4%.

Cotton Cellulose.—Table I gives a comparison of the specific sedimentation velocities and the diffusion constants obtained from runs made

TABLE I

SUMMARY OF RESULTS ON 0.10% SOLUTIONS OF DIFFERENT CELLULOSES DISSOLVED IN CUPRAMMONIUM SOLVENT (1.28% CU AND 22.0% NH_3) SOLUTIONS ONE-HALF HOUR OLD

Material	α-Cellulose, %	Cu no.	Rel. visc. of soln.	Constituent A		Constituent B		Approx. proportion of A and B	Constituents of still finer dispersion
				$s_{20} \times 10^{13}$	$D_{20} \times 10^{7}$	$s_{20} \times 10^{13}$	$D_{20} \times 10^{7}$		
Cotton linters α-cellulose	99.6	0.17	2.12	4.18	2.68	..	..	....	Very sl.
				4.29	2.79	..	..	....	
Absorbent cotton	99.2	..	2.09	4.28	2.64	..	..	....	Somewhat more
Cotton linters filter paper	97.2	..	1.83	3.94	2.83	small amount		....	Still more
Cross and Bevan aspen wood cellulose	71.2	..	1.98	4.28	2.70	2.73	3.53	2A:1B	Considerable of about 1/8 normal mol. wt. and finer
Cross and Bevan white spruce cellulose	..	..	..	4.05	2.80	2.79	3.87	2B:1A	Same
Sulfite pulp α-cellulose	96.1	0.98	1.97	4.10	2.84	2.74	3.38	2A:1B	Same
Bleached sulfite pulp	81.4	..	1.80	4.28	2.72	2.73	3.67	3B:1A	Same

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[3] Stamm, THIS JOURNAL, **52**, 3047 (1930).

at a concentration of 0.10% on the three different cotton celluloses. The results show that practically the same conditions of dispersion must exist for each of the three celluloses. The *Z* displacement curves for the absorbent cotton are almost identical with those for the cotton linters α-cellulose given in Fig. 2 of the previous paper, except that the deviation from symmetry at the extreme left is somewhat greater. This indicates the presence of a little more material of a much finer state of dispersion. The curves for the cotton linters filter paper show the presence of still more of this material of relatively fine dispersion, together with a small amount of materials of perhaps only half of the molecular weight of the major part. Though the amount of this latter material present is not enough to cause a definite break in the curves, as will be shown to be the case with the wood celluloses, still it is present in sufficient quantities to give a slight decrease in the average sedimentation velocity and a corresponding increase in the calculated diffusion constant. This increase in the calculated diffusion constant is caused by a slight spreading of the sedimentation boundaries of the two constituents.[4] The results indicate that the three cotton celluloses are practically monodisperse with only relatively small amounts of material of finer dispersion present. The amount of this material of relatively fine dispersion present seems to decrease with an increase in the α-cellulose content.

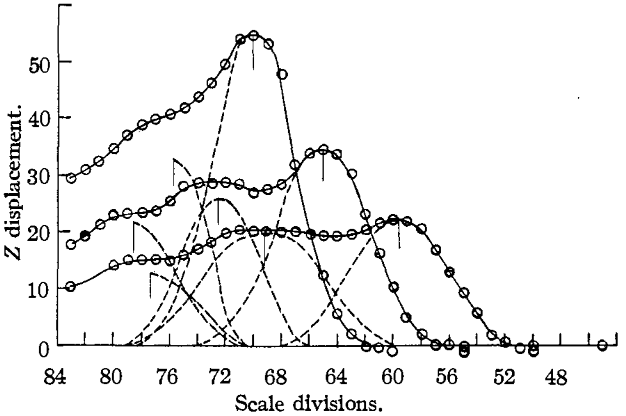

Fig. 1.—Photographic scale displacements for a run on Cross and Bevan aspen cellulose.

Wood Cellulose.—Figure 1 gives the results for the Cross and Bevan aspen cellulose. The curves are quite different from those for cotton cellulose (Fig. 2 of previous paper). Instead of being symmetrical with but one maximum, the curves are decidedly unsymmetrical and show at least three maxima. The right-hand maxima correspond very closely to the positions

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[4] Svedberg and Stamm, This Journal, **51**, 2170 (1929).

of the sedimenting boundaries of the molecular species found to be present in the cotton celluloses, as is shown by the sedimentation velocity values calculated from these maxima (see constituent A, Table II). Further, if the diffusion is calculated from the sections of the curves to the right of these maxima, values comparable with the diffusion values for cotton cellulose are obtained (see constituent A, Table II). If then the curves representing the molecular species present in cotton cellulose are completed by making the left-hand section symmetrical with the right-hand section (represented in the figure by the dotted lines), it is then possible to obtain the curve which, combined with the one just constructed, will give the experimental curve. In this way the curve for the second constituent (B in Tables I and II) is constructed. The sedimentation velocity calculated for constituent B is practically equal to the two-thirds power of the sedimentation velocity of constituent A, which indicates that it has a molecular weight of just half that of constituent A.

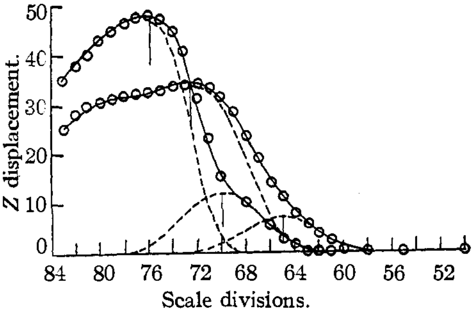

Fig. 2.—Photographic scale displacements for a run on bleached sulfite pulp.

$$M_A = M_B\,(s_A/s_B)^{3/2}$$

This is further confirmed from the values of the diffusion constant calculated from the corresponding curves, as

$$s_A/D_A = 2s_A/D_B$$

It is difficult to apply this analysis further to get the molecular weight of the materials of still finer dispersion. There are indications of a material of one-eighth of the normal molecular weight being present, together with still finer dispersed material. A material of one-fourth of the normal molecular weight may also be present. The overlapping of the individual curves, which become closer and closer together as the size of the particles decreases, makes it impossible to determine just what constituent curves really make up the experimental composite curve in this zone.

Figure 2 gives the results for the bleached sulfite pulp. An analysis of the data indicates that both constituents A and B are present, together with still more finely dispersed material. The proportions of constituent A and constituent B are, however, quite different from the proportions present in the aspen Cross and Bevan cellulose. Unfortunately, the base line of the curves cannot be determined with sufficient accuracy so as to obtain the exact proportions of the various constituents from the relative areas under each of the curves. The approximate proportions are given, however, in Table I.

TABLE II

RESULTS OF A SEDIMENTATION VELOCITY RUN MADE UPON A 0.10% SOLUTION OF ASPEN CELLULOSE PREPARED BY THE CROSS AND BEVAN METHOD

Copper concn. of solvent, 1.28%; NH_3 concn. of solvent, 22.0%; $V = 0.642$; $\rho = 0.9474$; rel. visc. of solvent, 1.390; age of solution at time of starting run, 0.5 hr.; length of column of solution, 1.26 cm.; thickness of column, 1.20 cm.; average speed, 42,900 r. p. m.; time interval between exposures, 40 min.; av. temp., 20.7°.

Sedimentation. Constituent A

Δx in scale div.	$\frac{\Delta Z \text{ max.}}{2G}$, cm.	Δx corr., cm.	x mean, cm.	$\omega^2 \times 10^{-7}$	s_{20} cm./sec. per cm./sec.$^2 \times 10^{13}$
4.8	0.0076	0.1006	4.81	2.02	4.25
5.0	.0042	.1005	4.91	2.02	4.16
5.5	.0026	.1085	5.02	2.00	4.43
				Av.	4.28

Constituent B

Δx in scale div.	$\frac{\Delta Z \text{ max.}}{2G}$, cm.	Δx corr., cm.	x mean, cm.	$\omega^2 \times 10^{-7}$	s_{20} cm./sec. per cm./sec.$^2 \times 10^{13}$
3.2	0.0024	0.0641	4.82	2.20	2.70
3.3	.0019	.0655	4.88	2.00	2.75
				Av.	2.73

Diffusion. Constituent A

Time, sec.	$2\Delta x_2$ in scale div.	$(\Delta x_2 \text{ corr.})^2$	h	α	D_{20} cm.^{2}/sec. $\times 10^7$
5,160	6.8	0.00430	10.7	5.2	2.83
7,560	8.0	.00594	13.3	6.2	2.52
9,960	8.0	.00594	7.1	4.1	2.66
12,360	7.7	.00550	4.0	2.7	2.78
				Av.	2.70

Constituent B

Time, sec.	$2\Delta x_2$ in scale div.	$(\Delta x_2 \text{ corr.})^2$	h	α	D_{20} cm.^{2}/sec. $\times 10^7$
7,560	6.0	0.00335	3.6	2.6	3.33
7,560	4.4	.00180	2.1	1.8	3.73
9,960	6.8	.00430	2.7	1.9	3.02
9,960	5.0	.00233	1.7	1.45	3.60
12,360	8.2	.00625	1.5	1.1	3.96
				Av.	3.53

Time permitted making comparative measurements on the different celluloses only at one cellulose concentration, namely, 0.10%. It seems highly probable, however, that the increase of the diffusion constant with decreasing concentration of cellulose will be similar to that reported in the previous paper for the cotton linters α-cellulose even in the case of the wood celluloses. No great error can be introduced by making this assumption, as calculations made from the specific sedimentation velocity alone, using Stokes' law, give the same order of molecular weight. As the molecular weight of constituent A from the previous paper is 40,000 ± 5000 on a copper-free basis, then the molecular weight of constituent B should be 20,000 and the number of simple glucose units in a particle should be 100 to 130.

The present data indicate that the difference between isolated wood cellulose and cotton cellulose is largely a difference in the degree of association of the structural building units and perhaps also in the manner in which the fundamental building units are put together. Unfortunately, the author did not have time to carry this work further so as to determine whether these differences between cotton and isolated wood celluloses are inherent differences in the celluloses as they exist in nature, or if the chemical treatment used in isolation has caused a partial dissociation of the wood cellulose. This question and many others of interest might be answered by a continuation of this work. The author hopes to be able to build a centrifuge to continue the work in the United States, but at present he is uncertain whether this will be possible.

The author again 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.

Summary

1. The nature of the dispersion in cuprammonium solvent of several different isolated wood celluloses was compared with that of cotton cellulose with the aid of the ultracentrifuge.

2. The cotton celluloses are monodisperse with but a very small amount of a considerably finer material present.

3. The amount of this more finely dispersed material present seems to decrease with an increase in the α-cellulose content.

4. The isolated wood celluloses show the presence of a material of the same molecular dispersion as that of cotton cellulose together with a material of one-half of this molecular weight, and molecular species of still finer dispersion.

5. The data thus indicate that the difference between isolated wood cellulose and cotton cellulose dissolved in cuprammonium solvent is at least partially a matter of difference in the degree of association of similar structural building units.

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