CLXXIX.—*The Viscosity of Cellulose in Cuprammonium Hydroxide Solution. Part I. The Determination of the Viscosity.*

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IN all technical work connected with cellulose an accurate determination of its viscosity in cuprammonium hydroxide (Schweitzer's reagent) is of importance, for it is largely the viscosity of the cellulose which determines the viscosity figure of solutions of the nitrocellulose or acetylcellulose made therefrom. If, for example, a nitrocellulose is required which will dissolve in acetone to give a high viscosity, a cellulose must be taken which will give a high viscosity in Schweitzer's reagent.

The determination of the viscosity of cellulose presents several difficulties, the chief one being due to the rapid action of oxygen on the solution, resulting in a lowering of the viscosity. These

difficulties were recognised by Gibson, Spencer, and McCall (T., 1920, 117, 484) and a method was developed of dissolving the cellulose in the reagent so that the effect of the oxygen could only be a small one, whilst their method of using the falling-sphere viscometer greatly simplified the actual determination of the viscosity. As, however, widely varying results were sometimes obtained with one and the same cotton by the above method, the whole question of the viscosity of the cellulose in cuprammonium hydroxide was re-investigated. A modification in making up the cellulose solutions was developed, a different method for the preparation of the Schweitzer reagent being used, and the effect on the viscosity of varying the concentration of the cellulose, the copper, and the ammonia was investigated. The cellulose used in this work was cotton sliver which had been kiered with 3 per cent. sodium hydroxide for a length of time depending on the viscosity required. The viscosity throughout is given in seconds for a fall of a 1/16" diameter steel ball through 15 cm. of a solution in a tube of 1.0 cm. diameter at a temperature of 20°. To obtain the absolute viscosity, the time in seconds is multiplied by 0.52.

Method for the Preparation of the Cuprammonium Solutions.

The method adopted for the preparation of the cuprammonium solutions was not that used in the above-mentioned paper, but the solutions were simply made by bubbling air through a mixture of copper turnings and strong ammonia. This procedure requires no attention, and concentrated solutions containing more than 30 grams of copper per litre can be obtained. The copper must be clean, and it was found that the addition of a small amount of sucrose, about 1 gram per litre, hastened the dissolution of the copper.

The effect of the addition of substances such as sucrose on cuprammonium hydroxide has been investigated by W. Traube (Ber., 1921, 54, [B], 3220). He found that a solution of ammonia saturated with copper hydroxide took up more copper hydroxide on the addition of glycerol, sucrose, etc. The concentration of sucrose used here was only about 1/50th that used by Traube, and any extra copper dissolved owing to combination with sugar would not be available in dissolving cellulose. It seemed probable that with sucrose the copper remained cleaner than without it, and therefore permitted the reaction to go forward. It was found that after standing for four weeks, a solution containing 25.6 grams of copper with a little sucrose was unaltered, whilst the copper content of the one without sucrose fell to 20 grams per litre. A solution containing 36 grams of copper per litre remained unaltered for three

weeks, and owing to its high copper content dissolved as much as 90 grams of cellulose per litre. The estimation of the copper in these solutions is simply carried out by evaporating a definite volume to dryness and weighing the copper oxide left. The ammonia is estimated in the usual way, and then the solution can be made up to the desired concentration of copper and ammonia.

The cuprammonium solution made by the above method contains a certain amount of nitrite. The best way of estimating this nitrite was to add the solution slowly to a definite volume of standard permanganate, strongly acidified, until the colour of the permanganate disappeared. By the above method it was found that the amount of nitrite in a freshly prepared solution was about 1 gram per litre calculated as nitrous acid. Solutions of cuprammonium hydroxide combine slowly with oxygen on standing, whilst when shaken with oxygen the reaction is much faster. With a solution containing 13 grams of copper per litre the amount of nitrite ultimately found was 4.4 grams calculated as nitrous acid, whilst the concentration of nitrite rose to 10 grams per litre with a solution containing a high concentration of copper.

It was found that cuprammonium solutions made by the above method gave practically the same viscosities with cottons of widely varying viscosities as the solutions made by dissolving well-washed copper hydroxide in ammonia.

Method of Dissolving the Cellulose and Filling the Viscosity Tubes.

Viscosity measurements of low or medium viscosity cottons, by the method developed by Gibson, Spencer, and McCall, give satisfactory results, but solutions of high viscosity cottons gave trouble, especially in the filling of the viscosity tubes. At the same time their method has obvious disadvantages, for air has to be admitted to the solution before the viscosity is determined, and on inverting the bottle the air passes through the solution. This has two disadvantages. Some of the air obviously must react with the cotton, and when the solution is very viscous it is not easy to get the solution into the tubes free from bubbles. These bubbles gradually move up the viscosity tube, and on many occasions it was evident that part of the solution through which the bubble had travelled was less viscous than the other part. The method of making up the solutions and the filling of the tubes were therefore modified in the following manner. Instead of using an ordinary bottle for making up the solution, a glass tube (*B*, Fig. 1), 10 cm. long and 5 cm. wide, drawn out at each end to a narrow tube 0.7 cm. wide and 3 cm. long, is used. The correct weight of cotton

FIG. 1.

In making up a solution, the vessel *B* which contains the cotton is connected with the filling apparatus, the screw clip being shut. *B* is evacuated and *E* is turned off, so that by opening *H* the solution in *A* is allowed to enter *B*. *H* is closed and *E* opened and shut three times to get all the air out of the cotton. The screw clip *F* is shut and the vessel *B* is disconnected and well shaken until solution is complete. It is then kept under water in an upright position. In filling the viscosity tube *D*, *B* is connected as before with *E* and also with *D*, by means of the glass tube *C* and rubber tubing. The tap *E* is opened and air or any other gas is allowed to flow in and then, on opening *G* and *S* and applying a slight pressure, the tube is easily filled. Several tubes may be filled from the same bottle, if necessary. With this arrangement the time taken for making up a solution is very little more than with the old method, but the filling of the viscosity tubes is quicker, easier, and is free from any objection. The viscosity tubes, being open at both ends, are easier to clean and dry than those closed at the lower end.

Cotton sliver which had been boiled with normal sodium hydroxide for four hours was dissolved in a cuprammonium solution containing 11.8 grams of copper and 192 grams of ammonia per litre, according to the Gibson, Spencer, and McCall method and to the above method. At the same time samples of the sliver were placed under water in an evacuated vessel in order to free them thoroughly from air, then as much as possible of the water was squeezed out, thus leaving about the same weight of water as of cotton. These air-free celluloses were dissolved according to the new method. The dilution caused by the water in the cellulose would be therefore about 2 per cent. and hence by taking a correspondingly less amount of Schweitzer reagent the change in viscosity caused by diluting by this amount may be neglected. The solutions were made up in triplicate, and two tubes were filled from each bottle.

The results were as follow :—

TABLE I.

Comparison of the viscosity in seconds of a cotton as determined by the three methods, by the fall of a 1/16 in. steel ball through 15 cm.

Two grams of cellulose in 100 c.c. of solvent.

G. S. and M.'s method.	New method.	New method with air-free cotton.
3240	4230	4020
3180	4050	3900
3735	4035	4065
3600	3975	3975
3600	4050	4035
—	—	3975

It is observed that there is an increase of about 12 per cent. on the viscosity of the solution made up by the new method, and that freeing the air from the cellulose beforehand makes no difference.

It will be seen that in the duplicate determinations the viscosity of the solution in the second tube is 1 to 2 per cent. less than that of the solution in the first tube. In blowing out the solution no great care was taken, and mixing of the air and the solution may have taken place. As in the above determinations air was employed to drive the solutions into the viscosity tubes, an experiment was carried out to see whether the presence of air affected the results. One hundred and fifty c.c. of solution were made up and successive tubes were carefully filled at intervals of two minutes until the bottle was empty, and the time of fall was taken for each 5 cm. of the tubes. The viscosity of the solutions in each tube is generally given by the time of the fall for the last three 5 cm. distances.

TABLE II.

Effect of air-blowing on the viscosity.

Tube No.	Time of exposure in min.	Viscosity in sec. for each 5 cm. of tube.				Viscosity for last 15 cm.
		1st.	2nd.	3rd.	4th.	
1	0	1230	1215	1215	1234	3664
2	2	1215	1230	1215	1215	3660
3	4	1185	1260	1260	1230	3750
4	6	1260	1230	1200	1215	3645
5	8	1080	510	165	90	765

This shows that the air effect is confined to the top layer of the solution in the bottle and that therefore it is permissible to expel the solution by means of air.

When cellulose solutions were made up as above, they did not alter in viscosity by more than 2 per cent. after being kept for eight days under water and in the dark.

It was found eventually that the cause of great variations in the value of the viscosity of a particular batch of cotton was due to the difficulty in taking a representative sample. It was found necessary to pick over and open out every piece of cotton in a sample and then to mix them thoroughly.

Effect of Dissolved Substances on the Viscosity of Cellulose in Cuprammonium Hydroxide Solution.

The effect of dissolving sucrose, sodium chloride, and sodium sulphate in the cuprammonium hydroxide solution before adding the cellulose was investigated, and the results are given in Table III.

TABLE III.

The effect of the addition of sucrose, sodium chloride, and sodium sulphate on the viscosity of a cellulose. Concentration of cellulose 2 grams per 100 c.c. of solvent.

Grams of material added per litre.	0	5	10	17	20	40	50	80
Viscosity when addition was :								
Sucrose	240	235	395	—	488	—	Cell. insol.	—
	225							
	240							
	245							
Sodium chloride	„	—	252	350	Cell. insol.	—	—	—
			248	366				
Sodium sulphate	„	—	240	—	228	485	—	Cell. insol.

It will be seen that the addition of small amounts of the above substances has little or no effect on the viscosity, whilst the addition of larger amounts raises the viscosity and then renders the cellulose insoluble in the solvent. The effect of the addition of much sucrose is similar to that found by Traube (*loc. cit.*). He attributed the action to the sucrose combining with the copper and rendering it unavailable for the solution of the cellulose. The gradual increase in viscosity with smaller concentrations of sucrose confirms this.

The effect brought about by the addition of the salts cannot be due to this cause. It may be due to a salting-out action, similar to the effect of salts on soap solution.

The Effect of the Concentration of Copper on the Viscosity of Cellulose in Cuprammonium Hydroxide Solution.

In carrying out these experiments a well mixed cellulose was used, allowance always being made for the moisture content. The amount of ammonia in the reagent was always 210 grams per litre. The effect on the viscosity of the cellulose concentration was determined, and also the effect of diluting a cellulose cuprammonium hydroxide solution both with ammonia containing 210 grams per litre and with water. The results are given in Tables IV, V, VI, and VII, whilst the relationship between the copper content of cuprammonium hydroxide solutions and their absolute viscosity as found by the Ostwald viscometer is shown in Table VIII.

The results of Table IV are shown graphically on Fig. 2. The curves *aa'*, *bb'*, *cc'*, *ee'*, and *ff'* show the relation between the concentration of copper, in grams per litre, and the logarithm of the viscosity of solutions which contained quantities of cellulose varying from 0.5 gram to 3.0 grams per 100 c.c. of solvent. These curves are all of a hyperbolic nature, which shows that there is a limit to the effect produced by the concentration of the copper which lies in the neighbourhood of 30 grams per litre.

TABLE IV.

Effect of varying the concentration of copper on the viscosity of cellulose in 100 c.c. of cuprammonium hydroxide solution.

Ammonia 210 grams per litre.

Copper concentration. Grams per litre.	Grams of cellulose per 100 c.c. of solvent.					
	0.5	1.0	1.5	2.0	2.5	3.0
	Viscosity (sec.).					
29.4		5.5		103	330	900
25	0.9		29.4			
24				113,110		
22.8					373	
20.0						1310
18				159,154	530	
16				180,182		2160
15				198,190		
14					980	3300
13		6.6		240,238		
12					*1500	
11.8						
11.5				316,310		
10.5				396,408		
10			59.4	505,517		
9	1.0					
8.5			90			
8.0		11.0	76.75			
7.0		*11.4				
6.0	1.1	* 8.9				

* Solution incomplete.

FIG. 2.

Showing relation between concentrations of copper (grams per litre) and cellulose (grams per 100 c.c. solvent) and the log viscosities obtained.

TABLE V.

Effect of dilution by ammonia on the viscosity of cellulose cuprammonium hydroxide solutions, the ammonia content being constant at 210 grams per litre.

Copper concentration.		Grams of cellulose per 100 c.c. of solvent.					
At start.	After dilution.	0.5	1.0	1.5	2.0	2.5	3.0
		Viscosity (sec.).					
30	—				103		900
29.4	—					330	
—	25.0						
—	22.0			28.0			
20.0	20.0				138		1310
—	16.7					570	
—	15.0		5.4	36			
14.0	—						3300
—	13.3				205		
—	11.7					1500	
—	10.0		7.6	37			
—	9.3				480		
—	7.0	0.9		122			
—	6.7		8.5				
—	5.0	1.1					
—	4.7		36				
—	3.3	1.5					
—	2.3	3.0					

TABLE VI.

Effect of concentration of copper on the viscosity of a solution of cellulose of less viscosity than that used in previous tables. Concentration of cellulose 4 grams per 100 c.c. of solvent.

Ammonia 210 grams per litre.

Copper concentration.	Viscosity in sec.
29.4	7.9
22.8	10.5
18.0	15.2
16.0	38.0*

* Solution incomplete.

TABLE VII.

Effect of the concentration of copper on the absolute viscosity of ammonia solution containing 220 grams of ammonia per litre.

Concentration of copper.	Viscosity in C.G.S.		Log.
Grams per litre.	Density.	units.	viscosity.
30.1	0.9560	0.0165	—1.7825
8.0	0.9293	0.0144	—1.8420
0	0.912	0.0136	—1.8665

With low copper concentration the tendency is for the solutions to have an infinite viscosity, but this is not realised since the cotton

will not dissolve completely in these weak solutions, and the logarithms of the viscosities of the heterogeneous mixtures obtained in these cases obviously do not lie on the respective curves.

On diluting a concentrated cellulose cuprammonium hydroxide solution with ammonia solution such that the concentration of cellulose coincided successively with those for the curves aa' , bb' . . . ff' , it was found that the logarithms of the viscosities, on being determined, lay on these curves. This showed that equilibrium was established at these points, the same result being obtained whether the solution was prepared by directly dissolving cellulose or by diluting a concentrated solution with ammonia. On connecting the points obtained in this way, the curves Aa' , Am , Aa , and Ac (Fig. 2) were obtained. It was found that it was thus possible to obtain cellulose solutions which could not be made directly with very low concentrations of copper, owing to the inability to dissolve the cotton. The latter, however, was not precipitated by dilution of the solution with ammonia. The curves were observed to meet at a point A , which represents the logarithm of the viscosity of a solution of ammonia as determined by the falling-sphere method, and this point is not very different from that obtained with cuprammonium hydroxide. The lowest of the transverse lines, Aa' , represents the viscosities of a saturated solution of cotton in the cuprammonium hydroxide solutions containing copper concentrations represented by the curve, and an ammonia concentration of 210 grams per litre.

It will be seen that the minimum copper concentrations for complete solution of a cellulose are almost proportional to the amount of cellulose present, and that about 2.3 grams of cellulose requires about 1 gram of copper. This means that 162 grams of cellulose, that is, one $C_6H_{10}O_5$ group, requires 70 grams of copper, or about 1 gram-atom. On increasing the ratio of copper to cellulose in solution to three times this value, the least viscous solution is formed.

The effect of a low viscosity cellulose is shown by curve PQ (Fig. 2). The concentration of cellulose is 40 grams per litre, but for high concentrations of copper the curve almost coincides with that of a 10 grams per litre solution of high viscosity cellulose. On reducing the copper concentration with this low viscosity cellulose, the values for the viscosity rapidly increase until separation of cellulose takes place at a copper concentration of 16 grams per litre. This is the approximate value, as extrapolated from the curves for the high viscosity cotton, for the limit of copper concentration, and therefore it suggests that the solubility of a cotton in a cuprammonium hydroxide solution is dependent only on the copper

concentration, provided that there is enough ammonia present, and is independent of the viscosity of the cellulose.

Effect of the Concentration of Ammonia on the Viscosity of Cellulose in Cuprammonium Hydroxide Solution.

The effect of altering the ammonia content from 60 grams to 250 grams per litre was studied with different concentrations of cotton, using a copper concentration of 13.5 grams per litre. The results are given in Tables VIII, IX, and X.

TABLE VIII.

Showing the effect of varying the concentration of the ammonia on the viscosities of cellulose cuprammonium hydroxide solutions containing 12.5 grams of copper per litre.

Grams of cellulose per 100 c.c.	Grams of ammonia per litre.	Viscosity.	Log. viscosity.
2.0	254	720	2.86
	216	1020	3.01
	184	1500	3.18
	144	2070	3.32
	106	3240	3.51
1.0	58	4980	3.70
	254	16.5	1.22
	184	35	1.54
	106	79	1.90
	58	138	2.14
0.6	252	2.3	0.362
	215	3.2	0.505
	144	4.8	0.681
	62	4.3	0.919

Table IX shows the influence of an increase in the copper concentration of the solution.

TABLE IX.

Effect of varying the concentration of ammonia on the viscosities of cellulose cuprammonium hydroxide solutions containing 24 grams of copper per litre.

Grams of ammonia per litre.	2.0 Grams of cellulose per 100 c.c. of solvent.	
	Sec.	Log. viscosity.
235	576	2.76
177	937	2.97
92	2340	3.37

The results of experiments on a cotton having a lower viscosity than that used above are given in Table X.

TABLE X.

Effect of using 2.0 grams of a cellulose of lower viscosity than that employed in Tables VIII and IX. Copper concentration = 13.5 grams per litre.

Grams of ammonia per litre.	Viscosity. Sec.	Log. viscosity.
212	153.2	2.18
180	220	2.34
170	238	2.38
135	392	2.59
99.2	534	2.77
60.5	870	2.94

The curves obtained from Tables VIII, IX, and X, by plotting ammonia concentration against the logarithm of the viscosity, are shown in Fig. 3, and it will be seen that they form a series of straight

FIG. 3.

Showing the effect of varying the concentration of ammonia on the viscosities of cellulose cuprammonium solutions containing 13.5 grams and 24.0 grams of copper per litre.

- (1) 2.0 Grams of cellulose per 100 c.c. of solvent and 13.5 grams of copper.
 (2) 1.0 " " " " " "
 (3) 0.6 " " " " " "
 (4) 2.0 " " " " 24.0 "
 (5) 2.0 " " " " (low viscosity) 13.5 grams of copper

lines which are all practically parallel, with the exception of curve No. 3, which represents the effect for a very dilute cellulose, namely, 0.6 gram per 100 c.c. From the other curves it is seen that the decrease in the logarithm of the viscosity is directly proportional to the increase of ammonia concentration, and is independent of the viscosity either of the cotton, the amount taken, or the amount of copper in solution. The mean of the results shows that an increase in ammonia concentration of 10 grams per litre decreases the logarithm of the viscosity of the cotton by 0.047. Therefore from the values obtained with solutions containing 1 gram or more of cellulose in 100 c.c. of cuprammonium hydroxide solution of a definite ammonia content, the viscosity for any other ammonia concentration may be calculated.

*Effect of Cellulose Concentration on the Viscosity of Cellulose
Cuprammonium Hydroxide Solutions.*

The effect on the viscosity produced by varying the concentration of the cellulose in solution was determined and it was found that when the logarithm of the viscosity was plotted against the concentration the curve obtained was nearly straight. Accordingly the relationship is best expressed by the Arrhenius formula, which states that

$\log \eta = \theta C$, where η is the ratio viscosity solution/viscosity solvent, C is the concentration, expressed most accurately as grams of solute per 100 grams of solvent, and θ is a constant depending on the nature of the cellulose used and is equal to

$$[\log (\text{viscosity of solution}) - \log (\text{viscosity of solvent})]/C.$$

The viscosity of the solvent cannot be found by the falling-sphere method directly, owing to the rate of fall being so great, but by plotting the logarithm of the viscosity of various cellulose solutions against the concentration a series of lines is obtained which meet at a point on the concentration axis giving a value of about -0.8 , similar to the point *A* on Fig. 2. This gives for the viscosity of the solvent a value of about 0.160 sec. or 0.08 *C.G.S.* unit. The value found, using the Ostwald viscometer, is 0.015 *C.G.S.* unit. It would be probably incorrect to use the Arrhenius formula for extrapolating the value for the viscosity of the solvent, but in this case the number obtained gives a constant for θ over considerable differences in concentration and great differences in viscosity. The value -0.8 is accordingly used in determining the value of θ . It is seen that several factors affect the viscosity, for example, the concentration of the copper; as more cellulose is dissolved, more copper is removed from a state of true solution,

and, as shown in Fig. 2, a diminution in the uncombined copper results in increased viscosity of the solution and therefore in an increase in θ . Another factor which may affect the viscosity is hydration of the sol, which may be altered by the concentration of the cellulose.

TABLE XII.

The relationship between the log. viscosity of cellulose solution and its concentration.

Concentration of copper in 1 and 2 = 12 grams per litre.

“ “ “ “ 3 “ 4 = 18 “ “ “

“ “ “ “ 5 = 29 “ “ “

C = wt. of cellulose per 100 c.c. of solvent. η = viscosity in seconds.

Solution 1.				Solution 2.			
C .	η .	Log η .	θ .	C .	η .	Log η .	θ .
1.0	2	0.30	1.08	0.50	2.0	0.30	2.16
1.5	8	0.90	1.12	1.00	34.5	1.54	2.32
2.0	26	1.41	1.09	1.60	324	2.52	1.94
2.5	103	2.01	1.12	2.00	1580	3.20	1.99
3.0	540	2.73	1.17	2.40	6000	3.78	1.90

Solution 3.				Solution 4.			
C .	η .	Log η .	θ .	C .	η .	Log η .	θ .
1.0	1.7	0.23	1.01	2.00	1.2	0.08	0.43
1.5	5.5	0.74	1.01	2.00	5.4	0.73	0.50
1.75	11.0	1.04	1.03	5.00	54	1.73	0.50
2.0	16.8	1.22	1.00	6.00	285	2.45	0.55
2.25	30	1.48	1.00	7.00	Insol.		
2.5	46.5	1.67	0.98				
2.75	99	2.00	1.00				
3.0	192	2.28	1.02				
3.25	292	2.49	1.00				
3.5	402	2.60	0.97				

Solution 5.			
C .	η .	Log η .	θ .
0.50	0.90	1.95	1.46
1.00	5.5	0.74	1.52
1.50	29	1.46	1.50
2.00	103	2.01	1.40
2.50	330	2.52	1.32
2.00	900	2.95	1.24

As regards the best copper concentrations for Schweitzer's reagent, it can be seen that any error in analysis causes the smallest change in viscosity when the concentration is high. It has been noticed, however, that with high copper concentrations, especially when the ammonia content is low, cellulose is gelatinised and then dissolves only slowly. The best concentration for general use is 13 grams of copper per litre with 20 grams of cellulose per litre, the ammonia concentration being 200 grams per litre. However, such a low concentration of cellulose does not differentiate between very low viscosity cottons, and for these a 4 per cent. solution of cellulose should be made in a Schweitzer reagent containing 20

grams of copper per litre, the ammonia concentration being the same as above. Using the Arrhenius formula, the viscosity for a 2 per cent. solution may then be calculated.

Occasionally even a 4 per cent. cellulose solution was not concentrated enough to bring out differences between very low viscosity celluloses, and a 9 per cent. solution of cellulose was made in a cuprammonium hydroxide solution containing 36 grams per litre. Thus, after a certain treatment, a cellulose gave a viscosity in seconds for a 4 per cent. solution of 4.7, whilst in a 9 per cent. solution the viscosity was 120. After further treatment the two viscosities were 2.5 and 30 respectively.

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