The Mercerisation of Cellulose

II. A Phase Transition Study with X-Ray Diffraction

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Reference has already been made to earlier work on the mercerisation of cellulose with sodium hydroxide solutions in a preceding paper¹. The process as a phase transition problem — the transition of *Cellulose I* to *Cellulose II* — has been investigated mainly with gravimetric, titrimetric, and X-ray methods. The gravimetric and titrimetric methods include measurements of the swelling of the fibres or the caustic soda uptake by the cellulose and the sorption of water on the cellulose before and after its transition (*cf.* a review by Valko²). Methods of this kind are indirect since they are based on the assumption that the quantities measured are related to the phase transition. X-ray diffraction, however, is a direct and absolute method. It is used throughout in this investigation. In a following paper (Part III) an analogous study using electron diffraction will be described.

The mercerisation of cellulose is of interest as a well-defined phase transition. A thermodynamic interpretation of the process has been proposed in a preceding paper¹. The reaction of cellulose with lye has been studied extensively, not only in connexion with mercerisation³. Furthermore, it is well known that cellulose samples of different origin require different minimum caustic soda concentrations for mercerisation⁴, but the reason has not been explained.

The main purpose of this investigation is to study the mercerisation of cotton and wood cellulose and thus obtain information on the transition mechanism and the possible difference in fine structure between these celluloses. This study is based mainly on the results obtained by Calkin⁵, Sisson and Saner⁶, and Katz and Seiberlich⁴. Parts of Katz and Seiberlich's results were supported by Jörgensen and Ribí⁷. During the course of the work, papers by Woods *et al.*⁸ on the mercerisation of bast fibres were published.

EXPERIMENTAL

Cellulose samples. For this study three cotton and three wood cellulose samples were used.

A. *Egyptian cotton* (supplied by Borås Väfveri AB., Borås, Sweden, as raw cotton, free from dark particles), boiled for 6 hours with 2 per cent caustic soda in an atmosphere of nitrogen, washed free from alkali and extracted in a Soxhlet apparatus with ethanol, benzene, and ether (for 6 hours each). Total loss in weight 9 per cent.

B. *Linters cellulose* (from British Bemberg Ltd., Doncaster, England), used for cuprammonium rayon production, bleached, α -cellulose 98.9 per cent, pentosan 0.5 per cent, viscosity (1 per cent cellulose in cuprammonium, Tappi 206 m) 62 cp.

C. *Linters cellulose* (from AKU, Arnhem, Holland), used for viscose rayon production, bleached, α -cellulose 98.3 per cent, pentosan 0.4 per cent, viscosity 17.1 cp (Tappi 206 m).

D. *Holocellulose* prepared from spruce chips with sodium chlorite solution (pH = 4.2, HAc—NaAc-buffer, 60° C, three treatments, each followed by washing with warm and cold water), yield 67.0 per cent of the wood (extracted with alcohol and benzene), pentosan 8.6 per cent, practically no lignin *).

E. *Sulphate pulp* (produced from pine), prehydrolysed and bleached, used for viscose rayon production, α -cellulose 93.4 per cent, pentosan 3.2 per cent, viscosity 14.4 cp (Tappi 206 m).

F. *Sulphite pulp* (SSS, produced from spruce by Billeruds AB., Säffle, Sweden), bleached and hot alkali refined acetylation grade pulp, α -cellulose 95.5 per cent, pentosan 1.2 per cent, viscosity 20.5 cp (Tappi 206 m).

These samples were used both in their original state and after hydrolysis with boiling dilute sulphuric acid (2.5 N H₂SO₄, 11.4 per cent). The purpose of the hydrolysis was to depolymerise the cellulose and break up the fibers into a powder. In the first experiments, hydrolysis was continued for only short lengths of time (2 min. and 30 min.), followed by treatment with caustic soda and washing out the lye on glass filters in the usual way. This method proved impractical since 50 per cent or more of the hydrolysed cellulose was lost in the alkali treatment. When the sodium hydroxide was removed by dialysis through cellophane against distilled water, only a few per cent were lost even after prolonged hydrolysis. Only the experiments with samples hydrolysed for 4 hours and dialysed after the caustic soda treatment have been described in this paper. The hydrolysed samples have been denoted AH, BH, CH, EH, and FH. No hydrolysed sample was prepared from the holocellulose (D) as the amounts of the substance available were too small.

The degree of polymerisation of nitrates of these samples has been determined viscosimetrically in acetone solution using a capillary viscosimeter. The nitrogen contents were determined by the Dumas' method. The K_m -constants at the measured N-contents are according to Jullander (ref. 9, Table 36, p. 101). The results have been collected in Table 1.

Alkali treatment. Solutions of sodium hydroxide (EKA, analytical grade) were prepared in concentrations ranging from 4 to 16 per cent by weight, in increments of about one half per cent (determined by titration with methyl red — methylene blue as indicator).

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Table 1. *Intrinsic viscosity $[\eta]$, nitrogen content, and degree of polymerisation (Z) for the nitrates of samples A–F.*

Sample	$[\eta]$	N-content per cent	$K_m \cdot 10^3$	Z
A	32.1	13.55	9.4	3 410
AH	1.45	13.35	8.9	163
B	16.3	13.82	10.5	1 550
BH	1.49	13.92	11.4	131
C	9.1	13.45	9.1	1 000
CH	1.45	13.45	9.1	159
D	17.7	12.87	7.7	2 300
E	8.0	13.79	10.4	770
EH	1.19	13.70	10.0	119
F	10.5	13.82	10.5	1 000
FH	1.38	13.71	10.0	138

Data of viscometer: length of capillary 9.0 cm, volume of bulb 1.0 ml, and time of flow for pure acetone 119 sec. The $[\eta]$ -values have been extrapolated from $(\log \eta_{sp}/c, c)$ -diagrams by straight lines. c is in g/100 ml.

As Sørensen lye (50 %) and fresh-boiled distilled water were used, the carbonate concentrations were lower than 0.5 per cent of the caustic soda. The treatments were performed in Erlenmeyer flasks in an ice bath for 1 hour with 1 g (or 0.5 g) of air-dry cellulose in about 30 ml of lye. When equilibrium was reached (10–15 min.), the cellulose-lye suspension had a temperature of 0.1–0.2° C. The treatment was stopped by introducing double the amount of ice-cold water, sucking off the dilute lye on glass filter (Jena G 2) and washing with distilled water, 2 per cent acetic acid, and again with distilled water until neutral reaction.

In concentrations at which mercerisation occurs the hydrolysed celluloses form fairly homogeneous and clear, viscous suspensions. It has already been mentioned that it was not possible in these cases to remove the lye by filtration. When the samples had been diluted with pre-cooled, distilled water to a concentration lower than 4 per cent, most of the lye was removed by dialysis through cellophane membranes into distilled water (one day), and the residue removed by centrifugation with distilled water, 2 per cent acetic acid and distilled water until neutral reaction. The water was then removed by freeze-drying to prevent lump formation.

Sorption measurements. The sorption of water was measured for all samples in an atmosphere of 65 % relative humidity (in a desiccator over 36.3 per cent sulphuric acid by weight, according to ¹⁰). The measurements were always made on the adsorption isotherm, starting with samples in equilibrium with the laboratory air (about 40 per cent R. H.). When equilibrium at 65 per cent R. H. was reached (3–5 days), the samples were dried at 105° C to constant weight (3–6 hours).

X-Ray diffraction. The air-dried samples were analysed by X-ray diffraction (Copper $K\alpha$ -radiation, filtered through Nickel foil, $\lambda = 1.54$ Å, from a Philips' fused tube) using a Debye-Scherrer powder camera (radius = 6.5 cm) with pressed rods of the samples (without glass capillary tubes) and of a diameter of 0.75 mm and containing 0.40 ± 0.05 mg cellulose per mm length. The exposures were all two hours with the same

Fig. 1. X-ray diffraction diagrams (Debye-Scherrer) of cotton cellulose (sample C), treated with 7.74 (97), 8.85 (98), and 11.75 (101) per cent NaOH. No. 98 contains both patterns (I and II).

X-ray intensity (~ 18 mA, 40 kV) and the film (Kodak Ultra-Speed, Code 3) developed for 5 mins. at $20-22^{\circ}\text{C}$ in the same developer (Kodak, X-Ray). To demonstrate the resolving power obtained, the diffraction diagrams of native, partly mercerised and mercerised cotton linters (sample C) are shown as positive prints in Fig. 1 and the corresponding photometer curves in Fig. 2. Due to the strong back-ground of the Debye-Scherrer diagrams, it was found necessary to use a wide slit in the photometer, giving poor resolution in the curves. In this paper the term diffraction "pattern" refers to a particular pure component (*Cellulose I* or *II*) while the term diffraction "diagram" refers to a given specimen, containing one or more components. Neither the high tension nor the emission current of the X-ray tube were stabilized. Adjustments of the heating current were made occasionally during the exposures to maintain the emission current at 18 ± 1 mA. Variations as high as 2 mA were sometimes observed. The high tension transformer was kept at the same setting (40 kV) during the experiments.

Control experiments for some samples (comp. Figs. 7 and 8) were made using Guinier powder cameras, built by Prof. G. Hägg (Cu K α -radiation, $\lambda = 1.5387 \text{ \AA}$, made monochromatic and focussed with a bent quartz crystal). The cameras were calibrated using sodium chloride.

RESULTS

Yield after the alkali treatment. Part of the substance is dissolved in the sodium hydroxide solutions. The yield has been determined at three different lye concentrations (below mercerising, partly mercerising, and mercerising) with the samples B, C, E, and F. The results calculated for samples dried at 105°C have been collected in Table 2.

The hydrolysed samples, from which the lye was removed by dialysis through cellophane, gave yield values which are not comparable to those of

Table 2. Yield after treatment with sodium hydroxide solutions.

Sample	Caustic conc. per cent	Yield per cent	Sample	Caustic conc. per cent	Yield per cent
B	7.0	96.4	E	5.0	97.4
	9.0	96.2		7.0	91.1
	12.0	96.6		10.0	93.7
C	7.0	96.0	F	5.0	94.7
	9.0	88.9		7.0	91.2
	12.0	91.0		10.0	86.2

the original samples (Table 2). The values were quite high — 95–98 per cent for sample BH and CH and 93–97 per cent for EH with 10 and 7 per cent lye respectively — and rather insignificant because losses were made due to adsorption on the cellophane.

The samples were used for the further sorption and X-ray studies without introducing any corrections for the losses (Table 2). Such corrections are doubtful since both low molecular cellulose and impurities as other carbohydrates are dissolved in the alkali treatment.

Fig. 2. Photometer curves of the diagrams of Fig. 1.

Figs. 3 and 4. Sorption of water on cellulose samples (in per cent of the dry cellulose), treated with different NaOH-concentrations. The holocellulose sample (D) was investigated also after drying at 105° C.

Sorption measurements. The sorption of water at 65 per cent relative humidity (over 36.3 per cent sulphuric acid) for the different samples has been plotted in Figs. 3 and 4. Such sorption curves have a typical shape with one sharp sorption increase within a limited NaOH-range, starting at 7 and ending at 10–11 per cent sodium hydroxide for cotton celluloses (Fig. 3) and at about 2 per cent lower NaOH-values for the corresponding wood celluloses (Fig. 4).

Sample D (holocellulose) has an abnormal water sorption curve, because of its high content of hemicellulose, partly extracted with increasing NaOH-concentration. It is characteristic that the rapid sorption increase starts at 7.0 ± 0.5 per cent NaOH for the cotton cellulose and at 5.0 ± 0.5 per cent NaOH for the wood cellulose, both original and hydrolysed samples.

X-Ray diffraction analysis. In the X-ray analysis, diffraction diagrams were obtained, the general type of which is shown in Figs. 1 and 2. The hydrolysed samples showed similar diffraction diagrams during the transition. Photometer curves of the diagrams for a hydrolysed wood cellulose (sample FH)

Fig. 5. Photometer curves of diffraction diagrams (Debye-Scherrer). Hydrolysed wood cellulose (sample FH), treated with 5.50 (211), 6.92 (212), and 8.00 (213) per cent NaOH.

are plotted in Fig. 5. As a general rule, mercerised samples give diagrams with stronger back-ground and more diffuse reflections than native samples.

A quantitative estimate of the amount of *Cellulose I* and *II* in the diffraction diagrams was obtained by visual comparison of the intensity of the reflections 101 and $10\bar{1}$ of pattern I with that of 101 of pattern II (Figs. 2 and 5). For pure native and mercerised cellulose respectively, the ratio of the intensities is 2 : 1. It was possible, after some practice, to estimate the relative intensities of these three reflections using a scale with ten intervals. When the reflection 101 of pattern II first appeared visible, its intensity was estimated to one tenth or one twentieth of the 101 and $10\bar{1}$ of I.

It is impossible, without the help of a separate investigation of the phase transition using an independent method, to assume a simple proportionality between the intensity of the X-ray patterns and the relative amounts of the phases. In this case a relative intensity number I_r was defined

$$I_r = \frac{2 I_{II}}{I_I + 2 I_{II}}$$

where I_I and I_{II} ($I_I + I_{II} = 1.0$) are the estimated intensities of the reflections mentioned. I_r is 0.0 for a pure native cellulose sample and 1.0 for a pure mercerised sample. Intermediate I_r -values indicate partial mercerisation.

Fig. 6. Photometer curves of diffraction diagrams for hydrolysed cotton (CH), containing 10, 50, and 90 per cent mercerised cellulose respectively (mixed samples). Guinier powder camera G 2, exposed for 6 hours (45 kV, 25 mA), total amounts of cellulose 95.2, 109.8, and 108.1 mg resp.

Test experiments were made using samples containing known amounts of native and mercerised cellulose (mixtures of sample CH, original and treated with 12.0 per cent NaOH). The photometer curves of Guinier diagrams for samples with 10, 50 and 90 per cent mercerised cellulose are shown in Fig. 6. The estimated I_r -values were 0.1, 0.55 and 0.90—0.95 respectively. Analogous results were obtained using the Debye-Scherrer powder camera.

The relative intensity numbers I_r , as a function of the NaOH-concentration have been plotted in the diagrams of Figs. 7 and 8. The phase transition starts at 8.0—8.5 per cent for the cotton celluloses (A, B, C) and at 6.0—6.5 for the wood celluloses (D and F). The influence of hydrolysis is very slight upon the NaOH-range which initiates transition (comp. the H-samples), but promotes the completion of the transition within a short interval. This effect is very marked for sample A, which is not completely mercerised even with 17.8 per cent NaOH and is still considerable for sample B and E, but small for sample C and F.

Figs. 7 and 8. The transition of Cellulose I $\rightarrow$ II for cotton and wood cellulose samples as I_r -values vs. concentration of NaOH in per cent. Double points refer to Guinier exposures (control).

The transition properties are given in Table 3. The I_r -value 0.1 is reached at 8.3–8.7 per cent NaOH for the cotton and 6.3–6.6 per cent for the wood celluloses with the exception of sample E (not hydrolysed) with 7.1 per cent. The transition intervals are in general agreement with earlier measurements^{4,6,7}.

DISCUSSION

The increase in water sorption is not a simple function of the phase transition as can be concluded from the X-ray diagrams. The rapid increase starts at about 1 per cent lower NaOH-concentration than the mercerisation. In fact the increase in water sorption is about 25 per cent of the total increase

Table 3. Transition intervals (in per cent NaOH) for the cotton and wood celluloses.

Sample	Concentration of caustic soda in per cent giving the I_r -values		
	0.10	0.50	0.90
A	8.7	9.8	12.6
AH	8.4	9.0	10.0
B	8.4	9.4	11.3
BH	8.5	9.2	9.9
C	8.3	8.9	10.3
CH	8.3	8.9	9.5
D	6.3	6.6	8.5
E	7.1	7.6	9.0
EH	6.6	7.2	7.8
F	6.3	6.8	7.4
FH	6.3	6.7	7.1

when mercerisation is first observed in the X-ray diagrams. Furthermore 50 per cent increase does not correspond to an I_r -value 0.5; the difference is 0.5—1.5 per cent NaOH according to the diagrams of Figs. 3, 4, 7, and 8.

It is not possible to interpret the sorption phenomenon quantitatively. For native cellulose, the sorption is probably a surface phenomenon, as no effect on the lattice parameters is observed. It is not known, if the increase in water sorption, before transition is observed, is caused by a swelling of the fibres which results in larger surfaces of the micelle strings becoming available, or by a reaction on these surfaces. For a mercerised cellulose, water is both adsorbed on the surfaces of the micelle strings and absorbed into the lattice. Unbleached cotton (sample A), which is not completely mercerised, has a low water sorption.

The difference between the original and the hydrolysed celluloses is of the same kind for all samples: it does not affect the start, but it favours the completion of the mercerisation within a short range of NaOH-concentration. The sulphate pulp, sample E, is an exception. Its transition starts with 0.5—1.0 per cent higher caustic concentration. After hydrolysis, which breaks the fibres down into a powder, the transition interval is very similar to the other wood cellulose samples.

The transition mechanism is now assumed to be the following: the caustic penetrates (swells) the native cellulose lattice partially or completely, forming alkali-cellulose, which gives the mercerised lattice, when the alkali is washed out at room temperature ^{Cf. 5 and 11}. If the formation of alkali-cellulose is incomplete, due to bad penetration of the lye or restricted swelling of the fibres, the mercerisation is partial. If these views are accepted, it seems rea-

Fig. 9. Photometer curves of diffraction diagrams (Guinier) for cotton (B) and wood (F) celluloses. Powder camera G 1, exposed for 6 hours, amounts of cellulose 13.9, and 15.8 mg resp.

sonable to assume that the start of the transition is related mainly to the reacting structure elements, *i.e.* the micelles and the micelle strings, while the completion can be hindered by the packing of the elements, *i.e.* the fibre structure. An interpretation along these lines is in agreement with the experiments described in this paper.

The difference between the reacting elements of wood and cotton cellulose is considerable and of fundamental nature: the transition intervals of the samples C and F hardly overlap. It seems reasonable to relate the NaOH-concentration necessary for transition with the water sorption of the original native fibres: both the initiation of the transition and the sorption of water implies a reaction with the hydroxyl groups on the surface of the micelle strings. A cellulose with a transition interval at low NaOH-concentrations is then expected to have a high water sorption. That is true in this case, in agreement with earlier sorption measurements¹². The three cotton samples (A, B, and C) have a water sorption (in equilibrium with air of 65 per cent relative humidity) of 7.50, 7.35 and 7.16 per cent respectively and the wood cellulose samples (E and F) 8.30 and 8.24 per cent. In connexion with other investigations, it is found that the micelle strings of wood cellulose are 10–20 Å thinner than those of cotton cellulose as measured on electron micrographs.¹³ Furthermore, the X-ray diffraction pattern of pure native cotton cellulose (sample B) has sharper and more narrow reflections than pure native wood cellulose (sample F, Fig. 9). All these facts indicate that native wood cellulose has a larger active surface than cotton cellulose. So far it is not possible to decide whether this is an effect of both the dimension and the lattice order of the micelle strings.

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REFERENCES

1. Rånby, G. B. *Acta Chem. Scand.* **6** (1952) 101.
2. Valko, E. I. *Mercerization*, Chapt. III D of Ott, E. (Ed.) *Cellulose and Cellulose Derivatives* (1943) New York.
3. Heuser, E. *The Chemistry of Cellulose* (1944) 116—121. New York.
4. Katz, J. R., and Seiberlich, J. *Pulp & Paper Mag. Can.* **41** (1940) 337.
5. Calkin, J. B. *J. Phys. Chem.* **40** (1936) 27.
6. Sisson, W. A., and Saner, W. R. *J. Phys. Chem.* **45** (1941) 717.
7. Jörgensen, L., and Ribí, E. *Nature* **166** (1950) 148.
8. Sen, M. K., and Woods, H. J. *Biochim. et Biophys. Acta* **3** (1949) 510.
9. Mukherjee, R. R., and Woods, H. J. *Nature* **165** (1950) 818.
10. Jullander, I. *Arkiv Kemi Mineral. Geol.* **A 21** (1945) no. 8, 101.
11. Hodgman, C. D. *Handbook of Chemistry and Physics* (1947) 1926. Cleveland.
12. Legrand, C. *Compt. rend.* **230** (1950) 2185; comp. ref. (5).
13. Cf. Campbell, W. B. *The Cellulose-Water Relationship in Paper-Making* (1933). Forest Service Bull. **84**, Ottawa 1933, and Babbitt, J. B. *Can. J. Research A* **20** (1942) 143.
14. Cf. Rånby, B. G. *Arkiv Kemi* **4** (1952) no. 42.

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