The Mercerisation of Cellulose

III. A Phase Transition Study using Electron Diffraction

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Electron diffraction has been applied as a tool for structure investigation mainly in three fields: a) the molecular structure of gases and vapours, b) the structure of thin films and surfaces and c) the structure of polycrystalline materials.

Brockway¹ and Glasstone² have reviewed the first field, and Finch, Quarrell, and Wilman³ the second. Applications in the third field are scarcer, since most of the work on the structure of small crystals is done using X-rays (powder diagrams). However, fast electron beams offer important possibilities, which have as yet not been fully realized. The scattering of fast electrons is due chiefly to the interaction of the electrons and the electrostatic fields of the atomic nuclei. X-rays are scattered mainly by the extra-nuclear electrons of the atoms. Furthermore, the angle of incidence tolerance which is only a few minutes for X-rays, is several degrees for the Bragg reflections of the electrons. The resulting diffracted electron beams are intense even from a crystalline layer containing few lattice planes. The diffracted intensity is usually sufficient to produce visible patterns on a fluorescent screen, allowing consequently short exposures (generally less than one second) on normal photographic plates. The significant factor in the study of surface structures using fast electrons is the tremendous power of even small amounts of material in scattering the electrons. This is also important in the analysis of small crystals containing light atoms. The strong scattering decreases the penetration, however, which restricts the use of crystals of larger dimensions and aggregates from study with fast electrons.

I. CALIBRATION EXPERIMENTS

According to de Broglie's wave theory, the wave length λ of charged particles is related to the accelerating potential V by

$$\lambda = h / \sqrt{2 m e V} \quad (1)$$

For electrons, with the numerical values of charge (e), and mass (m_0) according to Birge ⁴, the relation is (λ in Å, and V in Volts)

$$V = 150.0/\lambda^2 \quad (2)$$

No corrections according to relativity mechanics are introduced in equ. (2).

According to the diffraction theory the conditions for ordinary Bragg reflections are

$$n \lambda = 2 d \sin \Theta/2 \quad (3)$$

where n is an integer, d the distance between the lattice planes, and $\Theta/2$ the angle which the incident or diffracted beam makes with the lattice planes. The electron diffraction diagram of a polycrystalline substance forms a system of concentric rings on the screen or the plate. The mean radius R of the rings corresponds to the angle Θ between the primary (incident) and the diffracted beam. For $n = 1$ (first order) and L the distance from specimen to plate equ. (3) is transformed and approximated into

$$\begin{aligned} \lambda &= 2 d \sin \Theta/2 = 2 d \cdot \operatorname{tg} \Theta/2 \cdot \cos \Theta/2 \simeq \\ &\simeq 2 d \frac{R}{2 L} \cdot \cos \Theta/2 \simeq d \cdot \frac{R}{L} \end{aligned} \quad (4)$$

As the distance L is about 60 cm and the ring radius never exceeds 2 cm in the following experiments, the maximum approximation in equ. (4) is 0.015 per cent.

The wave length λ of the electron beam was determined from the diffraction diagrams of substances containing known lattices.

The electron diffraction exposures were made using a Siemens electron microscope (Type 1939 Û M 100, hot cathode) with the diaphragm of the objective lens and the pole pieces of the projection lens removed. The high tension transformer was kept at a constant setting (P 3, ~ 100 kV) and the emission current as low as possible (~ 0.03 mA). The distance between specimen and photographic plate was 58.20 cm within 0.02–0.03

Fig. 1. Electron micrograph of magnesium oxide smoke, shadowed with Gold-Manganese (Magnification $25\,500\times$). Exp. by G. Eklund.

Fig. 2. Electron diffraction diagram of magnesium oxide (original size). The (220) — ring has the diameter 3.1 cm.

cm. A special type of specimen holder was used: circular discs of Platinum foil (0.10 or 0.15 mm) with one hole (diameter 0.15–0.20 mm) drilled in the center. The specimen holders were covered with a thin carrier membrane (zapon laquer) cast on a water surface in the usual way.

Two reference substances were used: *magnesium oxide* (MgO, prepared directly on the carrier membranes as a fine-grain powder from magnesium oxide smoke), and *graphite*

Figs. 3 and 4. Electron micrographs of diffraction specimens (micelles) from native and mercerised wood cellulose, shadowed. (Magnification $85\,000\times$).

Figs. 5 and 6. Electron diffraction diagrams of cellulose micelles from native (P) and mercerised (MP) wood cellulose (original plate magnified $2 \times$).

Fig. 7. Electron micrograph of diffraction specimen (micelles) from native cotton cellulose (Sample B), shadowed. (Magnification $85\,000 \times$).

Fig. 8. Electron diffraction diagram of cellulose micelles from wood cellulose (E), treated with 6.53 per cent sodium hydroxide, partly mercerised. (Magnified $2 \times$). Note that the strong inner reflections are of about equal intensity.

(powdered pure graphite, chemical grade, prepared on the carrier membranes from a water surface). The cubic, face-centered lattice of MgO is known with high precision⁵. X-ray diffraction has given the parameter $a = 4.204 \pm 0.004$ Å and electron diffraction 4.190 ± 0.010 Å. This difference may be due to a contraction effect in ionic crystals of small dimensions predicted by Lennard-Jones⁶ and discussed by Finch and Wilman^{3,p.418}. The electron diffraction value $d_{220} = 1.481$ Å was used for the calibration. The hexagonal lattice of graphite has the axes $a = 2.458$ Å and $c = 6.701$ Å determined with electron diffraction, in close agreement with X-ray determinations^{3,p.418}. The length of the a-axis, referred to the C—C distance in the hexagon layers ($d_{200} = 1.229$ Å), was used for the calibration.

An electron micrograph and a diffraction diagram of magnesium oxide are shown in Figs. 1 and 2. The ring diameters were measured directly on the plates using a microcomparator with an accuracy of 0.001 cm or better. As the rings were slightly distorted (length ratio of extreme diameters 1.002—1.004), it was necessary to measure along four directions (45°) and use the average value. The wave lengths of the electron beam were calculated from the calibration exposures according to equ. (4). The average wave length λ during the investigation was $= (3.926 \pm 0.008) \cdot 10^{-2}$ Å which corresponds to the high tension $V = 107\,600 \pm 500$ Volt (equ. (2)).* The variation in λ during the course of one day was usually smaller. The maximal variation observed during the whole period was $\pm 0.014 \cdot 10^{-2}$ Å.

II. NATIVE AND MERCERISED CELLULOSE

There are a few references to electron diffraction studies of cellulose in the literature, describing investigations of thin cellulose membranes, precipitated from cuprammonium^{7a} or prepared from nitrocellulose by denitration^{7b}.

When cellulose particles of colloidal dimensions (micelles) were isolated as sols⁸ it was easy to obtain useful specimens for electron diffraction. The first diffraction experiments using cellulose sols were referred to by Svedberg⁹ in a lecture. Investigations on cellulose particles from viscose¹⁰ and cuprammonium rayon¹¹ have also been reported.

The test experiments with pure native and mercerised cellulose were made using the wood cellulose sols (samples P and MP), the colloidal properties of which recently were described by Rånby¹².

The cellulose sols were centrifuged (15 min., field 1 000 g) and treated with ultrasonic waves (90 min., 22 kc, ca. 1 W/cmsq) to decrease the aggregation. The electron diffraction

* This value is calculated with the relativistic correction in the electron mass $m = m_0 / \sqrt{1 - \beta^2}$ introduced, where m_0 is the mass at rest, $\beta = v/c$, v the velocity of the electron and c the velocity of light (cf. Finch and Wilman³, p. 393).

tion specimens were prepared from the aqueous sols directly on the specimen holders covered with carrier membranes. Diffraction diagrams with resolved lines and a minimum of background scattering were obtained from specimens containing only a thin ("mono-particle") layer of cellulose micelles, aggregated as little as possible (Figs. 3 and 4). The amounts of substance giving diffraction diagrams clearly visible on the fluorescent screen are of the order of magnitude $5 \cdot 10^{-10}$ g as calculated both from the volume and the concentration of the cellulose sols and directly from the structure of the specimen observed in the electron microscope. The specimens were exposed for 0.5–1 sec. and the plates (Ilford Process) developed for 2–3 min. in a dilute metol-hydroquinone developer (Ilford ID-2).

As a comparison, X-ray powder diagrams were obtained from specimens containing 1–10 mg cellulose and exposed for one hour or more (the X-ray diffraction diagrams are invisible on the fluorescent screen). This demonstrates the very high intensity of the diffracted electron beam compared to that of the X-ray.

A serious drawback of electron diffraction is the rapid destruction of the cellulose lattice, probably due to heat. After exposure in the beam for 5–10 sec., the diffraction rings gradually become fainter and generally they disappear after 15–20 sec. To avoid long exposures of the specimen in the electron beam, the high tension was switched on first and the cathode heating current 1–2 min. later, when the dark current (leak) was constant. After about 2 sec., when the emission current was constant, the plate was exposed.

Electron diffraction diagrams of micelles from the samples P (native) and MP (mercerised cellulose) are reproduced in Figs. 5 and 6. The main reflections were measured, the corresponding d -values (= distances between the lattice planes) calculated, and the results collected in Table 1. The d -values are compared with recent X-ray determinations by Kiessig¹³ and electron diffraction values by Ribl¹⁰. The accuracy in these determinations is better than 0.5 per cent.

The relative intensity of the cellulose reflections is not the same for X-ray and electron diffraction. This is partly due to the orientation of the micelles in electron diffraction exposures (most of the micelles form a right angle to the beam). This effect will be treated in a forthcoming publication.

III. PHASE TRANSITION OF COLLOIDAL CELLULOSE

In a previous paper¹⁴ the phase transition of cotton and wood cellulose (as fibres and as powder after hydrolysis) was studied using X-ray diffraction. Because of the influence of the fibre morphology, it was of interest to perform an analogous investigation on colloidal cellulose particles (micelles) using electron diffraction.

Table 1. Lattice plane distances (d in Å) for native and mercerised cellulose micelles.

Native cellulose						
Index			(021)		(103)	(110)
Plate	(101)	(10 $\bar{1}$)	(120)	(002)	(311)	(011)
132	—	—	4.349	3.939	2.584	2.008
137	5.975	5.290	4.362	3.937	2.584	2.005
144	5.905	5.209	4.338	3.925	2.580	2.002
Average	(5.940)	(5.250)	4.350	3.934	2.583	2.005
Kiessig ¹³	5.941	5.358	4.32	3.901	—	—

Mercerised cellulose						
Index			(130)	(040)	(10 $\bar{3}$)	
Plate	(10 $\bar{1}$)	(002)	(031)	(12 $\bar{2}$)	(14 $\bar{1}$)	(061)
126	4.431	4.023	3.116	(312)	(20 $\bar{2}$)	1.683
127	4.452	4.036	3.126	(311)		1.695
128	4.423	4.021	3.112			1.682
Average	4.435	4.027	3.118	2.576	2.218	1.687
Kiessig ¹³	4.432	4.052	—	—	—	—
Ribi ¹⁰	4.42	4.04	3.12	2.57	2.20	—

The indices are according to H. Mark, *Physik und Chemie der Cellulose*, pp. 154—155, 166—167, Verlag Springer, Berlin (1932).

The electron diffraction plates have been measured by Miss Anna-Lisa Nörling and Mrs Els Pärkma.

A. Samples prepared

Cellulose sols from three samples (B, E, and F, ref. 14) were investigated:

B. Bleached cotton linters (chemical grade).

E. Prehydrolysed, bleached, sulphate pulp (rayon grade).

F. Bleached, hot alkali refined sulphite pulp (acetylation grade).

Sample F is identical with sample P in sect. 3 of this paper ^{Cf. 12}.

The aqueous cellulose sols were prepared according to Rånby ¹² by peptization after hydrolysis of cellulose in a boiling 2.5 *N* sulphuric acid (11.4 per cent) for 16 hours (fresh acid after 6 hours). The concentration of the peptized sols was brought to 0.01 g/100 ml by dilution. The sols were treated with ultrasonic waves (22 kc, ca. 1 W/cmsq.) for 90 min. Sol portions of 15.0 ml in centrifuge tubes were flocculated by adding 0.5 ml 0.1 *N* sodium chloride. After half an hour the precipitates (voluminous clouds) were centrifuged down and the supernatant removed. The cellulose gel had a volume of 0.25—0.5 ml in each tube, containing less than 0.5 per cent cellulose. The same series of sodium

hydroxide solutions with increasing concentrations, as described in the previous paper¹⁴, were used for the alkali treatments. 15.0 ml of caustic soda was added to each tube at room temperature (20–22°C) and the gel was dispersed in the lye by stirring. The amount of gel was weighed before adding the lye and the exact alkali concentration calculated. The suspensions were poured into Erlenmeyer flasks, which were then stoppered and cooled in an ice-bath for 1 hour. The minimum caustic concentration to form a clear (or slightly turbid) suspension was observed. The treatment was stopped by introducing 30 ml ice-cold water and the alkali was removed by dialysis through cellophane bags against distilled water over-night, against 0.5 per cent acetic acid until the cellulose flocculated (4–5 hours), and against water again over-night. The flocculated cellulose was collected and washed with water by centrifuging, and suspended in 15 ml water. To obtain homogeneous sols for diffraction specimens, the suspensions were treated with ultrasonic waves for 1–2 hours. A typical specimen of sample B (cotton) is shown in Fig. 7. Its diffraction diagram is very similar to that of wood cellulose micelles.

In this method of preparation the cellulose particles in a gel are dispersed in a lye of a certain concentration, which is lowered 0.2–0.4 per cent by dilution by the water of the gel. This dilution does not influence the phase transition of the cellulose particles, however, as the cooling from 20° to 0° C is equivalent to a 2 per cent increase in the caustic concentration according to observations of Katz and Seiberlich¹⁵.

B. Phase analysis

Electron diffraction diagrams of the alkali-treated samples were obtained in the same way as described in Sect. 3, and the phase transition followed by a visual comparison of the diagrams. In the corresponding X-ray diffraction diagrams¹⁴, this comparison was done using the relative intensity of the reflections (101) and (10 $\bar{1}$) of the native pattern (I) and (101) of the mercerised (II). This method was not applicable for electron diffraction because of the strong background scattering close to the primary beam, and it was necessary to use other reflections. In pattern I the intense reflection (002) with $d = 3.93$ Å and the weaker, mixed reflection (120) and (021) with $d = 4.35$ Å form a resolved pair. In pattern II the corresponding pair of reflections is the intense (10 $\bar{1}$) with $d = 4.44$ Å and the weaker (002) with $d = 4.03$ Å (comp. Figs. 5 and 6). It is possible to follow the phase transition by a visual comparison of the intensity of these reflections, but the method is not as accurate as that used in the X-ray diffraction work. No relative intensity numbers were defined. The first shift in the relative intensity of the two I-reflections was recorded as the start of the transition. When the relative intensity of the two II-reflections was identical with that of micelles from pure mercerized cellulose (Fig. 6), the transition was recorded as complete. An electron diffraction diagram of partly mercerised micelles from sample E is shown in Fig. 8.

Table 2. Observations on the turbidity of the cellulose suspensions in sodium hydroxide solutions and the composition of the electron diffraction diagram.

Sample E			Sample F		
NaOH per cent	Turbidity	Diffraction diagram	NaOH per cent	Turbidity	Diffraction diagram
4.66	3	I	4.94	3	I
5.33	3	I	5.48	3	I
5.74	3	I	5.91	2	I(+ II)
6.15	2	I(+ II)	6.34	2	I + II
6.53	2	I + II	6.88	1	((I +))II
6.97	1	(I +) II	7.15	1	II
7.29	1	II	7.92	1	II

Sample B		
NaOH per cent	Turbidity	Diffraction diagram
7.48	3	I
7.90	3	I
8.35	2	I ((+ II))
8.74	2	I + II
9.42	1	(I +) II
9.66	1	((I +))II
10.40	1	II

Singel brackets, for instance (+ II), mean that pattern II is fainter than I, double brackets mean much fainter. Turbidity 1 means clear or almost clear suspension, 2 means turbid without and 3 with lumps.

From Table 2 containing observations on the alkali suspensions and the diffraction diagrams it is obvious that the cotton cellulose sol (sample B) has its transition interval between 8 and 9.5 per cent NaOH and the two wood cellulose sols (samples E and F) between 6 and 7 per cent. The difference between E and F is 0.2–0.3 per cent, *i.e.* of the order of magnitude of the probable error and thus insignificant.

SUMMARY AND DISCUSSION

The phase transition study of *Cellulose I*→*II* with X-ray diffraction, described in the preceeding paper¹⁴, made the assumption of a fundamental difference between cotton and wood cellulose very probable. These views are

supported by the result of the present investigation using electron diffraction. The phase transition of cellulose micelles from wood and cotton cellulose starts at the same NaOH-concentration as that of the corresponding hydrocelluloses. The completion of the transition, however, occurs within a shorter interval of NaOH-concentrations (the difference is 0.5 to 1.0 per cent). This is quite reasonable as the micelles are free or in small aggregates, where hard packing, incomplete penetration and restricted swelling that could hinder the complete mercerisation are not expected. The conclusion is that the difference between wood and cotton cellulose is due not only to the fibre morphology or the possible impurities but also to the properties of the submicroscopic structure elements, the micelle strings, from which the cellulose micelles are derived. The latter difference can be interpreted as a greater active surface of wood cellulose micelles, which might be both a surface area and a surface structure question.

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