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ACCESSIBILITY OF HYDROGEN BONDS IN CELLULOSE

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Abstract

Cellulose derives most of its functional properties from its hydroxyl groups: derivatives are formed by reactions with the hydroxyl groups, when cellulose is dissolved it is usually as a complex of the hydroxyl groups with ions or polar groups, and the physical properties of cellulose in the solid state are to a large extent a function of the hydroxyl groups.

It is known from infrared analysis that practically all hydroxyl groups in dry solid cellulose, both native and regenerated, are not free but engaged in hydrogen bonds of some kind. The proton donor group is always a hydroxyl group with another hydroxyl group or an oxygen group as acceptor. The accessibility of the hydrogen bonded hydroxyl groups has been measured by a combination of deuterium exchange (OH to OD groups) in heavy water and infrared analysis. Accessible OH groups are largely in amorphous (disordered) cellulose. The OH groups in crystalline (well ordered) cellulose are gradually made accessible by swelling with caustic soda solutions of increasing strength.

In regenerated cellulose a large fraction (usually about 80%) of the hydroxyl groups is accessible to the exchange in heavy water. Complete accessibility is obtained with 12 to 16% aqueous caustic soda. Intrachain hydrogen bonds along the cellulose chains are more resistant than interchain bonds

between adjacent chains. By certain treatment the crystallinity of regenerated cellulose can be increased substantially. It has been found that the packing density of amorphous cellulose also can be increased by these treatments. Special crystallization processes from dilute solution give cellulose crystals of high order and low accessibility.

Native cellulose has a morphology of rather well defined microfibrils, containing parallel and partly crystallized cellulose chains. The accessibility is usually much lower (30 to 50%) than in regenerated

OH and CH stretching frequencies from about 3600 to 2700 cm^{-1} in wave numbers. For free hydroxyl groups (not engaged in hydrogen bonds), the infrared absorption is at about 3640 cm^{-1} . The recording in Fig. 2 shows that there is only a minute absorption in this band which demonstrates that there is only a trace (maybe 1 per cent) of free hydroxyl groups. The CH stretching frequencies are at 2900 cm^{-1} . Deuterium exchange in heavy water vapor shifts the infrared absorption to longer wave lengths. The accessible OH groups are transformed to OD groups with their stretching frequency absorption band at 2500 cm^{-1} . The remainder of the OH stretching frequency band is well resolved into peaks referring to inaccessible OH groups, hydrogen bonded in the crystal lattice. According to the present interpretation (3), the first two absorption peaks (No. 1 and 2) refer to intrachain hydrogen bonds between $\text{OH}_{(s)}$ in one glucose unit and the ring oxygen ($\text{O}'_{(s)}$) in the next unit. (II) The following two bands (No. 3 and 4) refer probably to interchain hydrogen bonds. It is apparent

Fig. 1. Schematic cross-sections at right angles to the chains of the unit cell of native (N, Cellulose I) and regenerated or mercerized cellulose (M, Cellulose II).

Fig. 2. Infrared spectra of regenerated cellulose membranes before (I) and after deuteration (II) in heavy water vapor, respectively (2).

from these measurements that a large part (actually about 80%) of the OH groups in regenerated cellulose are in accessible hydrogen bonds which are easily opened and exchanged to OD groups in heavy water. The CH groups are not exchanged.

By treatment with caustic soda solutions of increasing strength, the cellulose lattice is expanded by formation of alkali cellulose, and all OH groups are gradually made accessible to deuterium exchange. The intrachain hydrogen bonds (No. 1 and 2) are more resistant than the interchain bonds (No. 3 and 4) as shown in Fig. 3 from the relative intensities of the bands at different levels of residual non-accessible OH groups. These caustic soda treatments were made with NaOD solutions in heavy water of a strength from 4 to 16 per cent.

It is well known that repeated treatments of regenerated cellulose with caustic soda solutions can increase the crystallinity, as demonstrated in Fig. 4. The conditioning increases the X-ray crystallinity from 35 to 47 per cent and decreases the accessibility to heavy water from 81 to 69 per cent. These results are summarized in Table I where the data give a coherent picture of the effects of the caustic soda conditioning with one interesting deviation. If the density is used for calculation of crystallinity, based on accepted values for crystalline (1.59) and amorphous cellulose (1.49 g/ml), the conditioning is found to increase it from 35 to 74 per cent. This is of course an abnormal result in comparison with the X-ray and infrared measurements. The result has been interpreted to mean that the conditioning also increases the density of the amorphous cellulose (2). This interpretation is supported

Fig. 3. Intensity ratios (h/h_0) of infrared absorption bands for OH stretching frequencies in regenerated cellulose at different accessibilities (2).

Table I. Crystallinity, accessibility and density of regenerated cellulose before (A) and after conditioning (D) by caustic soda treatment (2).

	Type A		Type D
	Bulk	Film	Bulk
X-ray crystallinity (dry), %	35	—	47
Density (dry), g./ml.	1.517	—	1.557
Crystallinity from density (dry), %	(35) ^a	—	74
Infrared accessibility (wet), %	81.5	87	69
Infrared crystallinity (wet), % ^a	27.5	19	40

^a The data obtained refer to wet samples (D_2O exchange), although the subsequent infrared measurements are made on dried samples.

^b Assumed value according to the X-ray data.

Fig. 4. X-ray diffractograms of unconditioned regenerated cellulose (A) and of the gel conditioned sample (D) after repeated treatments with 20 per cent caustic soda solutions (2).

by our infrared work (Fig. 5). The OD band of deuterium exchanged samples before (A) and after conditioning with caustic soda solutions (D) shows a shift towards longer wavelengths, i.e. shorter hydrogen bonds, as a result of the treatment. This means a denser packing of the amorphous cellulose. Using the known relations between wavenumber and bond length ($-O-H-O-$) for hydrogen bonds we have calculated that the OD bands shift observed could mean an increase in density of about 2 per cent for the amorphous cellulose. A density correction of this magnitude would bring the crystallinity values derived from density measurements well in line with the data from other methods.

It is likely that such changes in the packing density of amorphous cellulose are more important than the degree of X-ray crystallinity, e.g. for the properties of commercial rayon fibers.

The assignment of the infrared absorption bands to specific hydrogen bonds in the crystalline Cellulose II structure is still only tentative. The 101 planes are assumed to be the most intensely hydrogen bonded planes in Cellulose II. Two systems of hydrogen bonds have been proposed for these planes as shown in Fig. 6. The main difference between the two systems is that Mann and Marrinan assign some of the $OH_{(b)}$ groups to intrachain hydrogen bonds in addition to the $OH_{(g)}$ groups. Whichever of the two systems is the correct one, it is likely

Fig. 5. The O-D-O band in the infrared spectrum of regenerated cellulose before (A) and after conditioning (D) with caustic soda solutions (2).

that the first two infrared bands refer to intrachain hydrogen bonds. These bonds are the weakest according to their infrared shifts. The reason that they show the highest resistance towards deuterium exchange would then be a cooperative effect: due to the chain stiffness, caused by the intrachain hydrogen bonds, and the lattice order, several of these rather weak bonds have to be broken at the same time to make the OH groups accessible to exchange into OD groups.

2. The accessibility of native cellulose microfibrils. (6)

The properties of native cellulose are very different from those of regenerated cellulose as described in the previous section (1). First of all the native cellulose has a morphology of rather well defined microfibrils, about 100 Å wide, containing parallel and partly crystallized cellulose chains. A schematic cross-section of the probable arrangement of the microfibrils, forming a bundle in a plant cell wall,

Fig. 7. Schematic cross-section of a bundle of cellulose fibrils in a secondary plant cell wall(1).

is shown in Fig. 7. The microfibrils are flat with the 101 planes oriented largely parallel with the plane of the cell wall. There is accumulated evidence that the cellulose microfibrils are biologically formed entities and not a result of secondary aggregation of cellulose chains (5). An important question is, to what extent the microfibrils are crystalline when they are first formed, and what changes do occur when the native cellulose is isolated and purified.

We have studied freshly grown cellulose membranes, formed by cultures of *Acetobacter* (6), using the combination of deuterium exchange and infrared analysis as previously described. The cellulose was purified by repeated treatments (7×1 day) with 1% caustic soda solutions at 25°C. The membranes were washed in distilled water until neutral and stored in distilled water under refrigeration. The purified membranes were investigated by deuterium exchange in never-dried form and after drying at room temperature, respectively.

From the work with regenerated cellulose membranes, it was known that treatments of gel cellulose with caustic soda solutions decreased the accessibility irreversibly. Therefore, some samples were purified in heavy water. The freshly formed gel cellulose membranes were immersed in heavy water, then purified with caustic soda solutions (1%) in heavy water and never allowed to be exposed to water or water vapor to prevent reexchange of OD groups to OH groups. It is assumed that this procedure will give the total accessibility of the native gel cellulose in its original unchanged state before any treatment.

Fig. 6. Proposed intra- and interchain hydrogen bonds in the 101 lattice planes of Cellulose II (3, 4).

The infrared spectra of bacterial cellulose membranes in the OH and CH stretching vibration region are shown in Fig. 8. The never-dried and the dried membranes were treated in heavy water and then dried in a stream of dry nitrogen for recording of the infrared spectra. The same membranes were then treated with distilled water for reexchange of the accessible OD groups to OH groups, then dried and analyzed.

Fig. 8. Infrared spectra of never-dried and dried bacterial cellulose membranes after deuterium exchange in heavy water (solid line) and after a subsequent reexchange in distilled water (dotted line) (6).

Fig. 9. The OH stretching frequency bands in the infrared absorption spectra of dried bacterial cellulose membranes (6).

The initial drying causes apparently a lowering of the accessibility. Furthermore, we can observe that a cycle of deuterium exchange followed by hydrogen reexchange causes a trapping of certain OD groups as a result. The most interesting part of the infrared spectrum is the OH stretching frequency bands (Fig. 9). There is no measurable absorption at 3640 cm^{-1} indicating that no free hydroxyl groups are present. The composite band contains four peaks: the strongest at 3350 cm^{-1} , two weaker peaks symmetrically on both sides (at 3405 and 3305 cm^{-1} , respectively) and a fourth peak at 3245 cm^{-1} . Deuterium exchange has a different relative effect on the four bands, i.e. the accessibility varies when measured from the intensity ratios in the four bands. The assignment of the four bands to specific hydrogen bonds was pioneered by Tsuboi (7) but is still not complete (3). The strongest band at 3350 cm^{-1} is assigned to an intrachain hydrogen bond ($\text{OH}_{(3)}\cdots\text{O}'_{(6)}$) in the 002 planes of the lattice. The two weaker bands at 3405 and 3305 cm^{-1} are assigned to interchain hydrogen bonds in the $10\bar{1}$ and 101 planes, respectively. The fourth band at 3245 cm^{-1} is probably related to an interchain hydrogen bond, but it is not yet assigned.

The total accessibility to deuterium exchange is calculated from the integrated intensity ratio of the composite absorption bands after and before deuterium exchange. The results in Table II show that the

Table II. Total accessibility of bacterial cellulose membranes in heavy water, measured by infrared analysis (6).

	A Total 'accessibility %	B Total amount of resistant OD%	A-B %
Membranes purified in heavy water	44.7	12.2	32.5
Never-dried membranes	39.9	6.9	33.0
Dry membranes	31.4	4.4	27.0
Dry membranes (Deuteration for 15 hr.)	32.2	—	—

(A-B) represents amount (in %) of reexchangeable OD groups.

total accessibility of the membranes is indeed a function of the pretreatment, decreasing in the order: untreated (44.7%), purified never-dried (39.9%) and dried membranes (31.4%), respectively. The amount of trapped (resistant) OD groups decreases in the same order. The amount of reexchangeable OH groups does not change by the purification procedure but decreases sharply as a result of drying. Prolonged treatment in heavy water from 25 min. (5×5 min.) to 15 hr. (8 washings) showed only a small effect, an increase in accessibility from 31.4 to 32.2%.

From these data it is concluded that bacterial cellulose microfibrils most probably are synthesized directly in partly crystalline form. Purification and drying increase the crystallinity further, in general agreement with earlier findings for regenerated cellulose.

Swelling with caustic soda solutions gradually increases the accessibility. The treatments of the bacterial cellulose membranes were made with NaOD solutions in heavy water at 27°C, washing with heavy water and drying with a stream of dry nitrogen. The infrared spectra showed clearly the gradually higher accessibility (Fig. 10) from the exchange of OH groups to OD groups. There is no ex-

Fig. 10. Infrared spectra of dry bacterial cellulose (dotted line) and deuterated (15 hr) bacterial cellulose (solid line), treated with heavy water and 12% NaOD as indicated (6).

Fig. 11. The total accessibility of OH groups (solid line) and the amount of reexchangeable groups (dashed line) as a result of treatments with NaOD solutions in D_2O for 1 and 15 hr., respectively (6).

ange in the CH groups. The swelling of cellulose with NaOD solutions is a slow process, especially at high NaOD concentrations (Fig. 11). Even treating times of 15 hr. may be too short for equilibrium, measured as total accessibility of the OH groups. The membranes started to disintegrate after about 1 hr. in 16% NaOD solution.

Going back to the selective accessibility to deuterium exchange in the different infrared bands, the experiments with NaOD solutions have given additional information (Fig. 12). The accessibility measured in the different infrared bands varies with a factor of about 2 with the lowest values at 3350 cm^{-1} assigned to an intrachain hydrogen bond, and the highest values measured at 3405 cm^{-1} assigned to a hydrogen bond in the 101 plane.

The shape of the accessibility curves indicates that the swelling of the cellulose lattice starts at about 8% NaOD. This would mean that about 50% of the OH groups are located in non-accessible, well ordered crystalline regions. The result of treatments with NaOD solutions supports the views that there

is a gradual transition from order to disorder in cellulose.

A better illustration of these relations is given in Fig. 13, where the total accessibility and resistant and reexchangeable OD groups are shown as block diagrams.

Based on these data we may conclude that OH groups in intrachain hydrogen bonds are less accessible, i.e. the bonds are more resistant than other OH groups, both in native and regenerated cellulose. The accessibility of the different OH groups is highly selective, due to the different types of hydrogen bonds in which they are engaged. Accessibility data for cellulose specimens should then refer to the total accessibility, which is an integrated average value, or to a specific OH stretching frequency band in the infrared spectrum.

Fig. 12. The accessibility of OH groups in heavy water (D_2O) and NaOD solutions in D_2O , respectively, measured in different OH bands (6).

Fig. 13. Total accessibility of OH groups in bacterial cellulose as the sum of resistant and reexchangeable OD groups (6).

3. The accessibility of wood cellulose. (9)

The accessibility of wood cellulose cannot be measured by direct application of the deuterium exchange-infrared absorption technique, due to the optical scattering of wood and pulp fiber samples. Instead a tritium exchange method (8) has been worked out. The samples are exposed to tritiated water in liquid or vapor phase. This gives a partial exchange of OH groups to OT groups. The total number of OH groups in the sample, containing cellulose, hemicellulose and lignin, is calculated based on our present knowledge of the chemical structure. The overall accessibility (OA) of the hydroxyl groups is derived from the tritium exchange measurements. The OA values for spruce wood are 61% and for birch wood 53%. These values include 1 and 2% resistant OT groups, respectively. The further treatment of these data for derivation of accessibility values for the cellulose and hemicellulose fractions is rather difficult because we do not know the accessibility of the lignin component. With the assumption that lignin is completely

accessible, we calculate an accessibility value for holocellulose from spruce of about 57 %. Reported accessibilities for purified wood pulp from softwood are about 58% (8). If our measured data are accepted as given here, they would indicate that hemicellulose in the native state in wood, although X-ray amorphous, is only partially accessible to tritium exchange in tritiated water. There are, however, some difficulties in the interpretation of these measurements, and the data will be further treated elsewhere.

4. The accessibility of cellulose crystals(11).

It has recently been possible to obtain small compact crystals of regenerated cellulose by slow saponification of dilute aqueous solutions of water-soluble cellulose acetates (10). The D.P. of the crystallized cellulose is about 50 and it is practically free from acetate groups. The crystals are lozenge-shaped and flat, although somewhat irregular, and they resemble to single crystals from linear polyethylene. When prepared at temperatures from 30 to 90°C., the crystal lattice is Cellulose II. When the crystallization is made at higher temperature under pressure (120 and 150°C., respectively) the lattice formed is Cellulose IV (High-temperature Cellulose). Measured by X-ray diffraction, the cellulose crystals prepared at 120 and 150°C. have a degree of crystallinity of 70 to 80% which makes them comparable with well crystallized native cellulose. The accessibility of these crystals to deuterium exchange in heavy water is, however, as high as 50 to 60%. This would lead to the contention that also the crystalline fraction, as measured by X-ray diffraction, is accessible to a considerable extent (about 40%).

Although the research work on the cellulose crystals is still in progress, the results obtained definitely indicate that cellulose can crystallize to single crystals containing folded chains in principally the same way as linear synthetic polymers like polyethylene and polyamide. This conclusion has important bearings on our concepts of fiber formation. It is likely that rayon fibers prepared by conventional methods for regeneration contain folded cellulose chains. Once the regeneration has occurred, it will be very difficult to unfold the chains due to the many cooperating hydrogen bonds between the chains. In the recently developed methods to produce rayon fibers of high strength and low shrinkage (e.g. polynosic fibers), the regeneration is delayed and the fibers are stretched extensively in the gel state. The fibers produced show a high degree of orientation but usually a lower degree of crystallinity than ordinary rayon fibers. The general methods of preparation and the properties of these rayon fibers indicate that folded cellulose chains are less likely to occur in the new fibers than in the conventional rayon fibers.

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