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Five-Fold-Helical Cellulose trapped in Sulfuric Acid Framework

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ABSTRACT: Sulfuric acid aqueous solution effectively dissolves cellulose at a concentration of 64 wt% when it is pre-cooled at -20 °C. Although this low-temperature acid solution has a high potential as an aqueous cellulose solvent, the molecular detail of its swelling and dissolution mechanism is not known. In this study, we followed the swelling behavior of cellulose in sulfuric acid using X-ray diffraction and found a crystalline complex of cellulose and sulfuric acid at -20 °C. In this structure, the sulfuric acid molecules are organized in a similar manner to those in its tetrahydrate crystal. Cellulose molecules adopt a rare five-fold helical conformation, and their hydroxyl groups participate in the hydration of sulfuric acid. This complexation is acid-concentration dependent and occurs only above 62 wt%, indicating that the deficiency of the number of water molecules around sulfuric acid to form tetrahydrate drives the sulfuric acid to recruit cellulose hydroxyl groups. It swells and opens the cellulose structure without completely destroying the crystalline order as can be confirmed by the partial reversibility to regenerate cellulose I.

Dissolving cellulose is one critical step to bring homogeneous modifications or for analytical purposes. There are limited choices since cellulose is insoluble in most common solvents, each of which has its advantages and disadvantages.¹ Be it aqueous or non-aqueous solvents, all cellulose solvents share in common that at least one component strongly interacts with the hydroxyl groups of cellulose, otherwise cellulose tend to form crystals with regular hydrogen bond networks. The strong interactions and the regularity of cellulose chains often result in crystalline complex involving solvent constituents.^{2, 3} Crystal structures of these so-called crystallosolvates have been extensively studied to understand solute-solvent interactions at the atomic resolution. Among such “complexable” molecules are ammonia⁴ and ethylenediamine⁵ that are the major ingredients in the historical cellulose solvents, cuprammonium hydroxide and cupriethylenediamine hydroxide. They are receiving strong hydrogen bonding from the hydroxymethyl groups of cellulose leading to highly stable complexes even above the boiling temperature of the solvents.⁵ Sodium hydroxide, a promising aqueous solvent of cellulose is known to form a variety of complex crystals with cellulose depending on concentration and temperature.^{6, 7} Both *N*-methylmorpholine *N*-oxide used in Lyocell process and a new ionic liquid solvent, 1-allyl-3-methylimidazolium chloride, form complex crystals with cellulose.^{8, 9} Even non-solvents of cellulose such as water and alcohol can be trapped in the crystalline lattice to form intercalated crystals.^{10, 11}

Concentrated mineral acids such as sulfuric acid and phosphoric acid are another class of cellulose solvents well-known for more than a century.¹² Sulfuric acid swells paper to obtain parchment-like substance as already mentioned in 1844¹³ and is

able to make a highly concentrated cellulose dope without much degradation if the temperature is kept low.¹⁴ However, to date, no complex structure of cellulose with any acid has been reported. Recently, Huang and co-workers reported that sulfuric acid solution precooled at -20 °C dissolves cellulose at a lower concentration (64 wt%) compared to that of the room-temperature system (i.e. 72 wt%).¹⁵ Based on this observation, we followed the structural evolution of cellulose immersed in sulfuric acid under temperature perturbation using X-ray scattering, and found the existence of a new type of cellulose crystalline complex at low temperature.

We put well-aligned dry flax fiber in glass tube, and added 64 wt% sulfuric acid solutions, then eliminated the trapped air bubble by centrifugation. The tubes were horizontally mounted on a temperature-controlled sample holder (Linkam Scientific instruments, UK) for diffraction measurements with an X-ray beam of 16 keV ($\lambda = 0.77489 \text{ \AA}$) at the SWING beamline of SOLEIL synchrotron facility (Paris, France). The specimens were cooled from the ambient temperature (23 °C) to -20 °C, then kept at -20 °C for 1 hour, and warmed up back to the ambient temperature. Two-dimensional wide-angle X-ray diffraction patterns were recorded on a hybrid pixel detector (EigerX4M, Dectris, Switzerland) every five minutes through the entire temperature process. The obtained 2D diffraction patterns were processed using in-house programs for further analyses.

Figure 1 shows fiber diffraction diagrams of flax cellulose in 64 wt% sulfuric acid solution at 23 °C (Fig. 1a) and -20 °C (Fig. 1b). The isotropic background scattering was numerically subtracted,¹⁶ which originated mainly from the sulfuric acid

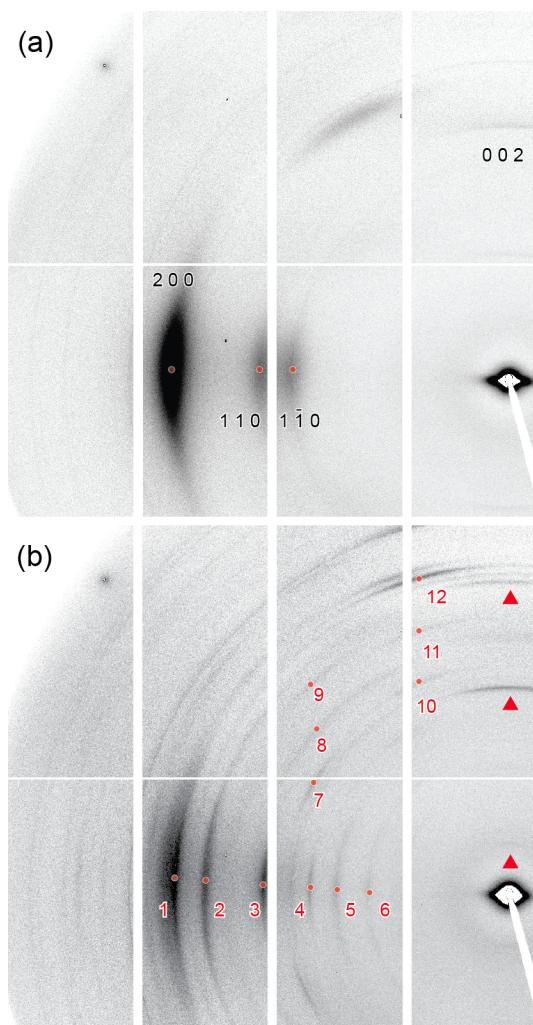


Figure 1. Fiber X-ray diffraction patterns of flax cellulose fibers in 64 wt% sulfuric acid aqueous solution at (a) 23 °C and (b) -20 °C. Arrowheads in (b) indicate meridional reflections. Numbered reflections in (b) are used in the exhaustive search of the unit cell parameters.

solution. The diagram at 23 °C shows a diffraction pattern of native cellulose allomorph, cellulose I, with three characteristic equatorial reflections and one meridional reflection, 0 0 2, at d -spacing of 2.6 Å.¹⁷ The diagram was taken approximately 15 mins after the flax fiber was immersed in the acid solution, so the room temperature immersion did not affect the cellulose crystal. The cooling gave rise to a series of new sharp reflections (Fig. 1b). These reflections have similar azimuthal angular intensity distributions to those of the original cellulose crystals, implying that the structure causing them has a comparable orientation along the fiber direction to the flax cellulose. The d -spacings of observed reflections do not match to those of known sulfuric acid crystals. The new reflections were significantly sharper than the original crystals. The full width at half maximum (FWHM) value is roughly half the value of the flax cellulose but does not correspond to typical mineral crystalline diffractions that are even sharper. These observations indicate that the observed new structure is a complex of cellulose and sulfuric acid but not one of sulfuric acid hydrates.

Since three visible meridional reflections appeared at multiples of $d^* = 0.04 \text{ \AA}^{-1}$, we assigned these peaks, from the

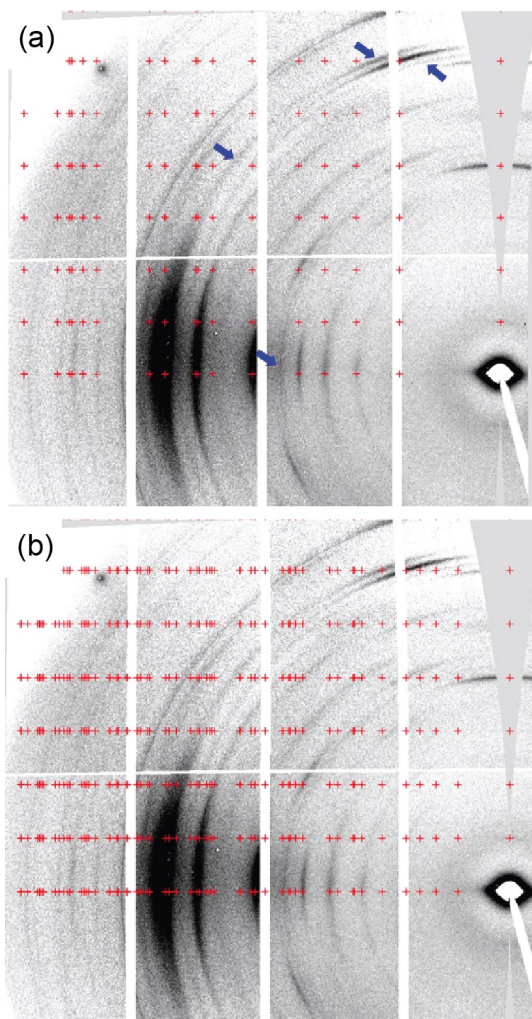


Figure 2. Predicted reflection position superimposed on the diffraction pattern of the cellulose-sulfuric acid complex remapped in cylindrical reciprocal space coordinate. (a) $a = 9.12 \text{ \AA}$ and $b = 12.99 \text{ \AA}$, $c = 25.05 \text{ \AA}$ (b) $a = 18.24 \text{ \AA}$, $b = 25.98 \text{ \AA}$, $c = 25.05 \text{ \AA}$. Blue arrows indicates the observed reflections that are not predicted by the unit cell.

innermost to the utmost, to 0 0 1, 0 0 4 and 0 0 6 with the c -axis being 25.08 Å. Then, we searched for a unit cell by an exhaustive approach, assuming an orthorhombic unit cell ($\alpha = \beta = \gamma = 90^\circ$) and using d -spacings of 12 strong and well-separated reflections marked in Figure 1b. The detailed procedure of this exhaustive search is described in the supporting information. The obtained parameters were $a = 9.12 \text{ \AA}$ and $b = 12.99 \text{ \AA}$. The reflection positions calculated using this unit cell are superimposed on the diffraction pattern remapped in cylindrical reciprocal space coordinate (Figure 2a). They are generally in good agreement, while there are four observed reflections, including a strong one on the sixth layer line, that are not predicted from the unit cell.

The lattice constant along the fiber axis, $c = 25 \text{ \AA}$, corresponds to five times the length of glucose residue, 5 Å. On the meridian, the strongest reflection is 0 0 4, indicating the presence of a periodicity of 6.27 Å along the fiber axis. Such a periodicity is not expected from the cellulose structure, but sulfuric acid tetrahydrate crystal has a tetragonal unit cell with a lattice constant of $c = 6.35 \text{ \AA}$.¹⁸ This length corresponds to a

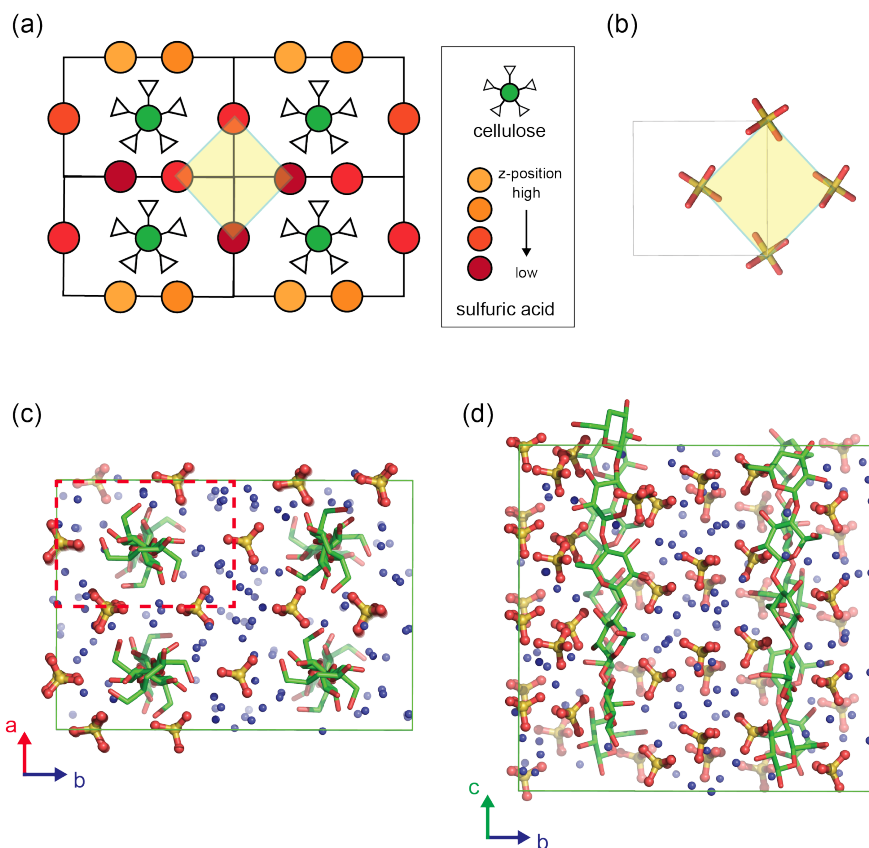


Figure 3. (a) Schematic packing model of the cellulose-sulfuric acid complex in *ab* projection. Circles with different colors denote sulfuric acid molecules in different *z*-position (along *c*-axis). A yellow rhomb indicates the quadruplet formation of sulfuric acid. (b) Organization of sulfuric acid molecules in the tetrahydrate crystal. Water molecules are removed for clarity. (c, d) Molecular model of the cellulose-sulfuric acid complex in (c) *ab* and (d) *bc* projections.

distance between two sulfuric acid molecules. Considering the similar spacings between 0 0 4 of this complex and *c*-axis of the tetrahydrate, sulfuric acid molecules in this complex are likely organized along the fiber axis similarly to those in the tetrahydrate crystal. In the 64 wt% sulfuric acid solution, the molar ratio between sulfuric acid and water is 1:3. To form a tetrahydrate-like organization, hydroxyl groups of cellulose would replace one hydration site of sulfuric acid tetrahydrate structure in the complex.

The stoichiometric ratio between each component in the complex is thus glucose residue: sulfuric acid: water = $5n: 4m: 12m$. The volume of the unit cell is 2971 \AA^3 and those of each component are 164 \AA^3 for glucose residue based on cellulose I β crystal structure,¹⁹ 88 \AA^3 for sulfuric acid based on its density at 0°C , and 30 \AA^3 for water. When *n* and *m* are 1 and 3, the sum of the component volumes is 2956 \AA^3 , reasonably close to the unit cell volume. Thus, the unit cell contains one cellulose chain, 12 sulfuric acid molecules and 36 water molecules, yielding a density of 1.46 g/cm^3 .

To understand the molecular organization in the complex crystal, we first built a packing model based on the unit cell dimensions and the stoichiometry (Fig. 3a). Along the *c*-axis, four sulfuric acid molecules stack up as in the tetrahydrate crystal. According to the structure of sulfuric acid tetrahydrate, the distance between sulfur atoms should be around 6 \AA .¹⁸ A way to place three molecular stacks of sulfuric acid in the *a*-*b*

projection while leaving space for the cellulose chain would be to place them on the border, two on the long *b*-axis and one on the short *a*-axis. This will leave space in the middle of the unit cell to host a cellulose chain. These molecular stacks should be shifted to each other along the *c*-axis, so the inter-sulfur distance is kept around 6 \AA . This indicates that the real unit cell should be larger than the current cell. Doubling both *a* and *b* dimensions allows accommodating all the stacks in the different *z*-positions, resulting in the unit cell dimensions of $a = 18.24 \text{ \AA}$, $b = 25.98 \text{ \AA}$, $c = 25.05 \text{ \AA}$. This unit cell provides a better prediction of diffraction positions compared to the smaller one (Fig. 2b). In this packing model four sulfuric acids between cellulose chains are organized in a similar way to two center and two corner molecules in the tetrahydrate crystal, as indicated with squares in Figs 3a and 3b. Thus, the orientation of sulfuric acid molecules in this quadruplet presumably conforms to that of the tetrahydrate.

Based on the above-mentioned consideration, we constructed a molecular model shown in Figures 3c and 3d. The 25-\AA periodicity along the fiber axis implies an occurrence of a five-fold helical conformation of cellulose molecules. This is the first example of cellulose adapting this conformation since, so far, the five-fold conformation has been reported only for one cellulose derivative crystal, cellulose trinitrate, among known cellulosic crystal structures.^{20, 21} The inter-sulfur distances in this structure are maintained approximately at 6.1 \AA , similar to

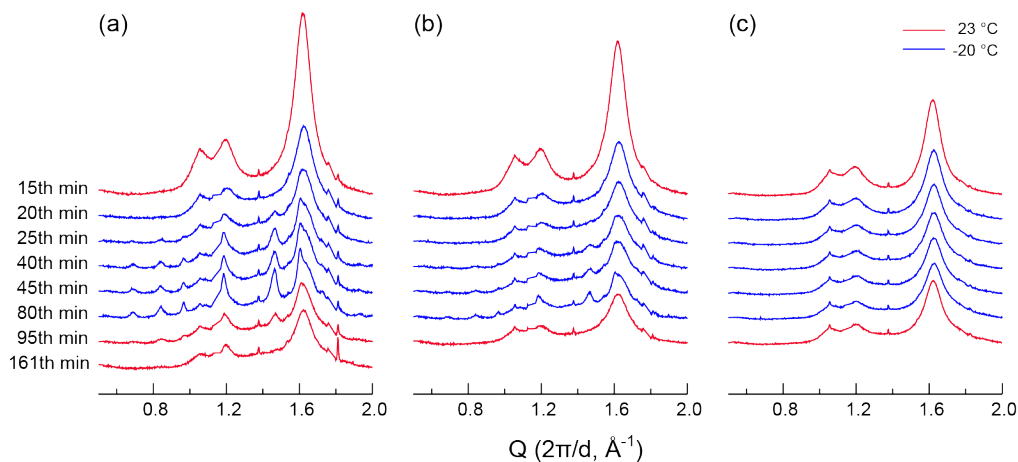


Figure 4. Equatorial X-ray diffraction profiles of flax cellulose fibers in (a) 64, (b) 62, and (c) 60 wt% sulfuric acid aqueous solution during the cooling and warming temperature process.

those of the tetrahydrate crystal. The orientation of sulfuric acid molecules is determined according to their organization in the tetrahydrate crystal. Each SO_4^{2-} ion is surrounded by three water molecules and one hydroxyl group of cellulose. The intermolecular distance between cellulose chains is 9 Å, which is slightly more than twice the initial intermolecular distance in cellulose I, 3.9 Å.¹⁹ This indicates that the peak sharpening upon complexation, where FWHM of the diffraction peak becomes about a half, is mainly due to this swelling effect rather than crystal growth or co-crystallization.

We further investigated the formation and stability of the cellulose-sulfuric acid complex in terms of time, temperature and acid concentration. Figure 4 shows equatorial diffraction profiles of flax cellulose in sulfuric acid at a concentration of 60, 62 and 64 wt% during the cooling and warming temperature schedule as described above. At room temperature, the equatorial profiles at all concentrations remain identical to that of cellulose I after 15 min of immersion in the solutions. In the 64 wt% solution, the complexation occurred about 5 min after the specimen temperature reached $-20\text{ }^\circ\text{C}$. At the 25th minute, reflections of the complex became visible at $q = 1.19$ and $1.47\text{ }\text{Å}^{-1}$, while the intensity of cellulose I reflections became weaker. Sharp reflections of the complex became stronger over time. A minor part of the cellulose crystal might still exist as cellulose I after 1 hour at $-20\text{ }^\circ\text{C}$ since the $2\ 0\ 0$ reflection was seen as a shoulder peak in the profile at the 80th min. A similar but much slower complexation was observed in the 62 wt% solution, where the features of the crystallosome appeared only after the 40th minute. The reflections of the complex were weaker compared to those of the 64 wt% specimen. A greater portion of cellulose I remained unswollen in the 62 wt% solution as the $2\ 0\ 0$ reflection of cellulose I ($q = 1.6\text{ }\text{Å}^{-1}$) was visible at $-20\text{ }^\circ\text{C}$. On the other hand, the complex did not form in the 60 wt% solution. Although the reflection intensities became weaker at the low temperature, all the reflection of cellulose I was present and no trace of complexation was observed during the cooling experiment. Upon warming to room temperature, the reflections of the complex immediately disappear in the 62 wt% solution, while in the 64 wt % solution, the trace of them remained for more than 1 hour at room temperature. The intensities of cellulose I reflections became weaker after warming in all the samples, indicating partial dissolution or amorphization of

cellulose. This trend is more pronounced in the higher concentrated solutions: the intensity of $2\ 0\ 0$ decreased by about 70 % in the 64 wt% solution, 50 % in the 62 wt% solution, and 30 % in the 60 wt% solution, respectively. These observations show that the formation of cellulose-sulfuric acid complex occurred at the low temperature and with a critical concentration of 62 wt%.

This observed acid-concentration and temperature dependence reflect the mechanism behind the complexation. The crystallization of sulfuric acid tetrahydrate occurs in aqueous sulfuric acid solution below $-36\text{ }^\circ\text{C}$.²² Thus, the tetrahydrate-like molecular organization of sulfuric acid is favored in the current system upon cooling. When the number of water molecules is sufficiently low compared to that in the tetrahydrate structure (sulfuric acid concentration is 57.6 wt% in the tetrahydrate crystal), the hydroxyl groups of cellulose would be necessary for hydration of sulfuric acid to form a stable tetrahydrate-like hydration state. Such a water-lacking situation would lead to effective swelling of cellulose fibers and the complexation between sulfuric acid and cellulose. This implies that complexation with different hydration numbers of sulfuric acid might be possible by exploring a wider acid concentration range.

After complexation in 64 wt% sulfuric acid solution at $-20\text{ }^\circ\text{C}$, we washed the swollen flax fibers with cold water. The washed flax fibers were subjected to lab-source X-ray diffraction and solid-state ^{13}C NMR spectroscopy. As shown in figure S2 in the supporting information, the X-ray diffraction patterns of both wet and dry fibers show blurry scattering, indicating the amorphous nature of cellulose in the sample. The solid-state NMR spectrum also shows features of low crystalline cellulose, in accordance with the X-ray diffraction results. This is distinctive from cellulose-alkali complexes which convert to crystalline cellulose II upon water rinsing and drying.²³ This different behavior suggests, on one hand, that cellulose chains are likely in parallel chain arrangement in the complex as in cellulose I. On the other hand, complexation with cellulose II might provide a similar crystal structure but with cellulose molecules in an anti-parallel chain arrangement.

In summary, cellulose formed a crystalline complex with sulfuric acid at $-20\text{ }^\circ\text{C}$ and above the acid concentration of 62

wt%. The complex crystal has an orthorhombic unit cell with dimensions of $a = 18.24 \text{ \AA}$, $b = 25.98 \text{ \AA}$, $c = 25.05 \text{ \AA}$. This large unit cell contains 4 cellulose chains, 48 sulfuric acid molecules and 144 water molecules. The fiber repeat of 25 \AA indicates the rare occurrence of a five-fold helical conformation of cellulose molecules. Sulfuric acid molecules are organized similarly to those in the sulfuric acid tetrahydrate crystal. Hydroxyl groups of cellulose molecules are likely to participate in the hydration of sulfuric acid molecules together with water molecules in the crystalline lattice. The complexation occurs only above the critical acid concentration, 62 wt%. This concentration dependence of crystal swelling indicates that the lack of water molecules in the system drives the complexation to form a stable hydration state of sulfuric acid.

While we have proposed a tentative packing model of the complex crystal structure based on the current diffraction dataset, its crystallographic structure resolution requires more complete, high-resolution diffraction data and extensive modeling efforts. We simulated the diffraction intensities based on the packing model as shown in Fig. S4. The simulated diffraction pattern reproduces the strong 0 0 4 reflection, supporting the presence of the stacking of sulfuric acid molecules along the fiber axis. However, a clear discrepancy is observed on the equator, where two simulated innermost reflections, 0 1 0 and 1 0 0, are absent in the experimental data. Considering its orthorhombic unit cell and parallel chain arrangement, this complex crystal should belong to one of the triclinic and monoclinic Sohncke space groups, $P1$, $P2$, $P2_1$ and $C2$. As mentioned above, the adjacent molecular stacks of sulfuric acid molecules should be shifted along the c -axis, which excludes $P2$ and $C2$ from candidate space groups. Nevertheless, the systematic absence of these low-symmetry space groups does not explain the absence of the innermost reflections. Such an absence can be explained by non-crystallographic symmetry, where there should be structural motifs staggered by half the axis length along both a - and b -axes. Such a structural feature will be considered in a full structure refinement in a future study.

The observed complexation behavior between cellulose and sulfuric acid will serve as a basis for understanding the low-temperature swelling and dissolution of cellulose in concentrated hygroscopic acids as the structural stabilization of acid by solvation. Similar solvent systems such as phosphoric acid should be also investigated for a better understanding of the molecular interactions between cellulose and acids.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures, details of exhaustive search of unit-cell parameters and regeneration experiments of cellulose-sulfuric acid complex. (PDF)

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Author Contributions

The manuscript was written through contributions of all authors.

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Notes

The authors declare no competing financial interest.

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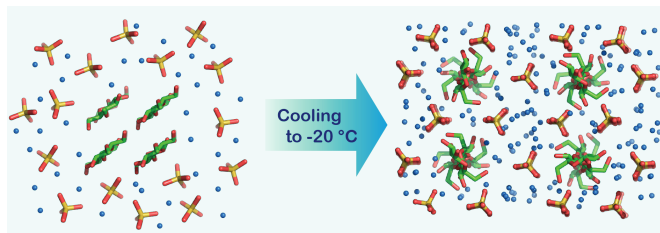
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In this study, we report the occurrence of cellulose-sulfuric acid crystalline complex at $-20\text{ }^{\circ}\text{C}$. In this structure, cellulose molecules adopt a rare five-fold helical conformation, and their hydroxyl groups participate in the hydration of sulfuric acid. The complexation is found acid-concentration and temperature dependent.
