	Experiment title: Swelling and dissolution mechanisms of cellulose in concentrated acid solutions at low temperature.	**Experiment number**:
Beamline:	**Date of experiment**: from: 17/02/2022 to: 21/02/2022	**Date of report**:
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Report:

1. Background

Mineral acids, such as sulfuric and phosphoric acid, are essential reagents for processing cellulose materials. They are widely-used hydrolysis and swelling agents of cellulose. Concentrated mineral acid solutions are also direct solvents of cellulose. Despite their importance, the molecular interactions between cellulose and acid molecules has not been well explored compared to other solvent molecules such as alkalis and amines. This situation is largely due to the lack of solvated crystal structures of cellulose and acids that would provide high-resolution information of such information. We recently reported the cellulose-sulfuric acid complex as the first cellulose-acid crystallosolvate.[1] The complexation between cellulose and sulfuric acid occurs only at low temperatures, and cellulose molecules adopt a rare five-fold helical conformation in the complex structure. The complexation was likely driven by the deficiency of water around sulfuric acid molecules to form a stable, hydrated structure. This finding prompted us further to explore the complexation behavior of cellulose and mineral acids. In this study, we extended a similar approach to concentrated phosphoric acid.

2. Experiments

X-ray scattering measurements were carried out at the D2AM beamline at the European Synchrotron Radiation Facility (ESRF) using an X-ray beam of 16 KeV and hybrid pixel detectors (D5 and WOS). Bundles of well-aligned flax fibers were packed in glass capillaries and immersed in 83 wt% H_3PO_4 aqueous solution at room temperature. The specimens were then mounted on a low-temperature specimen holder and placed under a vacuum. The diffraction patterns were acquired at temperatures ranging from -40°C to room temperature

with an exposure time of 3 seconds. The background scattering from the solvent in the patterns was subtracted numerically using in-house programs.

3. Results

Figure 1A shows X-ray fiber diffraction diagrams of flax fiber immersed in 83 wt% H_3PO_4 at room temperature (20 °C) for 15 minutes. The room-temperature diagram shows characteristic reflections of cellulose I, namely equatorial 1-10 and 110, and meridional 004. Thus, the room-temperature immersion in 83 wt% H_3PO_4 did not affect the crystal structure of flax cellulose for at least 15 min.

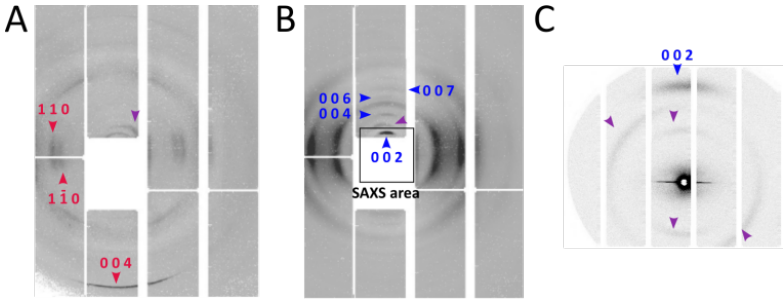

Figure 1: X-ray fiber diffraction patterns of flax cellulose immersed in 83 wt% phosphoric acid solution at different temperatures: (A) room temperature and (B, C) -40 °C. Panel (C) corresponds to the small angle area indicated in panel (B). Reflections indicated by purple arrowheads correspond to the Kapton window used in the low-temperature vacuum cell.

When cooled down to -40 °C (Fig. 1B and 1C), the diagram showed diffraction features different from those of cellulose I, indicating the crystalline complex formation of cellulose and phosphoric acid. The diffraction pattern of the cellulose-phosphoric acid complex is poorly resolved, with only a few strong reflections in the observed wide-angle area. The meridional pattern indicates that the fiber repeat of the complex crystal is 37 Å, increased from 10 Å of cellulose I. The long 37-Å fiber repeat suggests cellulose molecules likely adopt a seven-fold helical conformation in the complex.

We refined the unit cell based on 11 independent reflections indicated in Fig. 2. The refined unit cell is orthorhombic with the cell parameters of a = 6.19 Å, b = 6.95 Å, and c = 37.05 Å. Considering the unit cell volume, 1594 $Å^3$, this unit cell accommodate one cellulose molecular chain in a seven-fold conformation with four phosphoric acid molecules and four water molecules. The tentative packing model is shown in Fig. 3. In this model, cellulose chains in a left-handed 7_3 helical conformation are at the corners of the unit cell, leaving room for phosphoric acid molecules at the center of the cell. Four phosphoric acid molecules stack along the fiber axis in this central space.

This structure is the second known cellulose-acid complex and the first crystal structure consisting of cellulose molecules in a seven-fold helical conformation. The occurrence of the seven-fold conformation in this complex structure highlights the conformational flexibility of cellulose in its solvated states. Together with our previous report on the sulfuric acid complex, the current study indicates that the concentrated acids significantly perturb the molecular conformations of cellulose at low temperatures.

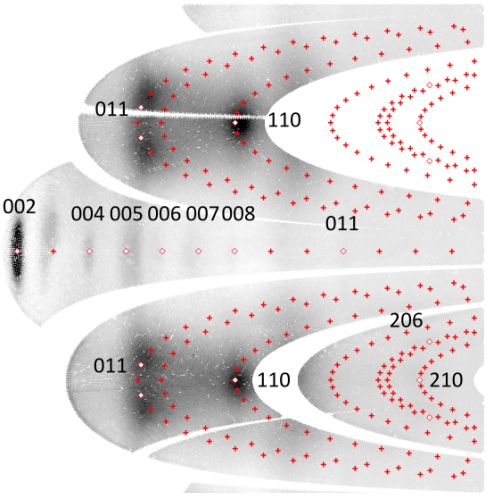

Figure 2. X-ray diffraction pattern of flax cellulose immersed in 83 wt% H3PO4 in polar coordinates. Reflection positions predicted based on the refined orthorhombic unit cell parameters are indicated by red crosses.

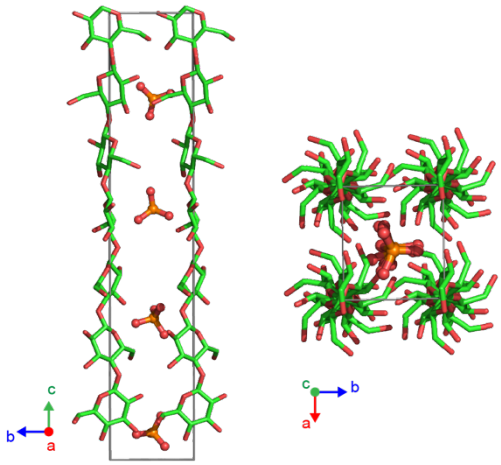

Figure 3. Molecular packing model of the cellulose-phosphoric acid complex.

Reference.

1. Li, Wei, et al. "Fivefold Helical Cellulose Trapped in a Sulfuric Acid Framework." *Crystal Growth & Design* 22.1 (2021): 20-25