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Crystallosolvate formation between cellulose and concentrated phosphoric acid at low temperature

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ABSTRACT:
Concentrated mineral acids, such as phosphoric and sulfuric acid, are important reagents for cellulose processing including dissolution and hydrolysis. A better understanding of cellulose-acid interactions is therefore crucial to optimize such processes. We recently discovered the first crystalline complex of cellulose and an acid [1]. Complexation occurred when flax cellulose was immersed in concentrated sulfuric acid at -20 °C. In this complex structure cellulose molecule adapts a rare five-fold helical structure, while the sulfuric acid forms a tetrahydrate-like structure. In the present work, we extended our approach to another concentrated mineral acid, phosphoric acid and found the second cellulose/acid crystallosolvate.

We performed synchrotron X-ray diffraction experiments to monitor the changes in the crystalline structure of flax cellulose immersed in concentrated phosphoric acid at temperatures ranging from -40 °C to room temperature. A simple immersion of flax cellulose in 83% phosphoric acid barely affected the crystal structure of flax cellulose (Fig. 1a). When cooled to -40 °C, new strong diffraction peaks appeared, as seen in Figure 1(b), indicating the formation of a novel cellulose-phosphoric acid complex. This complex has a fiber repeat of 37 Å, making it the first example of crystal structure with cellulose molecules in a seven-fold helical conformation. The crystal has an orthorhombic unit cell with lattice parameters: a = 6.19 Å; b = 6.95 Å; c = 37.05 Å. Furthermore, unlike the cellulose-sulfuric acid complex, the cellulose-phosphoric acid complex remained stable when warmed up from -40 °C to room temperature.

We then studied the effect of the complexation on the cellulose chain arrangements. Flax fibers were immersed in 83% phosphoric acid at -20 °C or at room temperature and subsequently regenerated in water at 0 °C or 65 °C. X-ray diffraction and FT-IR revealed that the swelling and regeneration generally result in the amorphization of cellulose regardless of the conditions. However, when flax cellulose was swollen at -20 °C, a minor fraction of cellulose I was discernible in the regenerated cellulose implying the parallel packing of cellulose molecules in the complex structure.

Solid-state ^{13}C NMR spectroscopy suggests the conformational change of hydroxymethyl groups from *tg* to *gg* conformation when swollen by phosphoric acid solution according to the empirical relationship of the C6 chemical shift and O6 conformation (66 ppm and 62 ppm for *tg* and *gg* respectively) [2]. This conformation remains *gg* after removal of the acid.

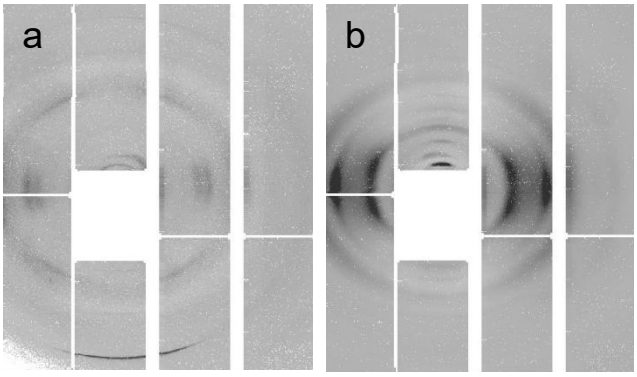

Figure 1: X-ray fiber diffraction patterns of flax cellulose immersed in 83% phosphoric acid at (a) 20 °C and (b) -40 °C

KEY WORDS: Cellulose, concentrated phosphoric acid, crystallosolvate, X-ray diffraction

References

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