	Experiment title: **Ordering of cellulose microcrystals dispersed in polar and non-polar medium**	**Experiment number**: 02 01 705
Beamline: D2AM	**Date of experiment**: from: 06 04 06 to: 07 04 06	**Date of report**:
Shifts: 3	**Local contact(s)**: Cyrille Rochas	*Received at ESRF:*

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Report:

The aim of the study was to measure and understand the ordering behavior of cellulose microcrystals dispersed in water and organic solvents.

Suspensions of cellulose microcrystals from cotton and algal origins (tunicin and *Glaucocystis*) were sealed in either glass 1.5 mm o.d. glass capilaries or in circular sample holders equipped with 0.25 mm-thick mica windows (for a total path length of 1 mm). An energy of 15 keV was used. Scattered intensities were recorded during 1 to 100 s exposures on a CCD detector placed at 1.65 m behind the sample.

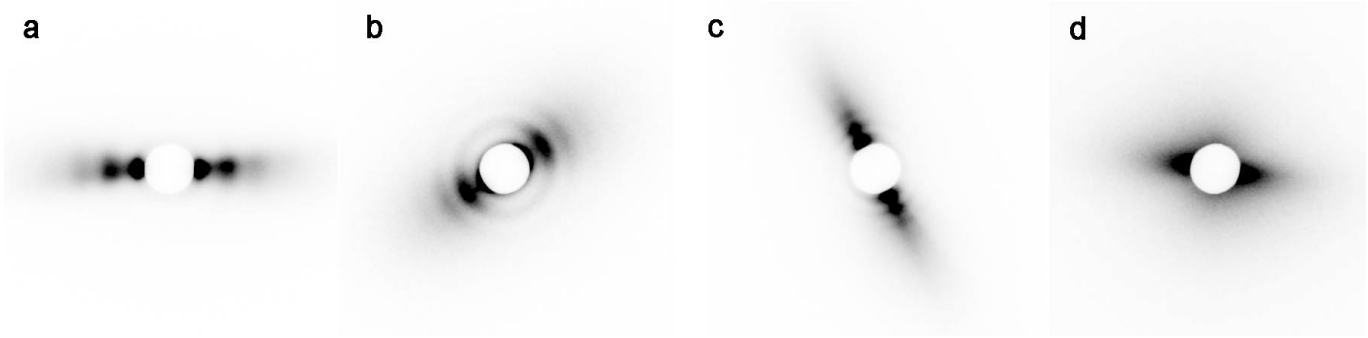

Figure 1. Small-angle scattering patterns of aqueous suspensions of cellulose microcrystals from *Glaucocystis* with solid contents of : a) 4%, b) 2.5%, c) 1.25% and d) 0.95%.

Two dimensional colloidal crystal of cellulose whiskers

Among different conditions studied, we observed hexagonal arrangements and axial orientation extending through the whole scattering volume when microcrystals from *Glaucocystis* or tunicin were used and when salts were removed with ion exchange resins (**Figure 1**). Compared to other cellulosic sources such as cotton or wood, it is known from elecron microscopy observation that the particles from the two algal origins have larger aspect ratio and homogeneous cross section with a whisker-like morphology .

The lattice constant of the colloidal crystals changed as a function of cellulose content down to 1.25% and the axial orientation persisted even when Bragg peaks due to the two-dimensional hexagonal arrangement could no more be observed (**Figure 1d**), indicating a relatively sharp transition to a nematic phase at around 1%.

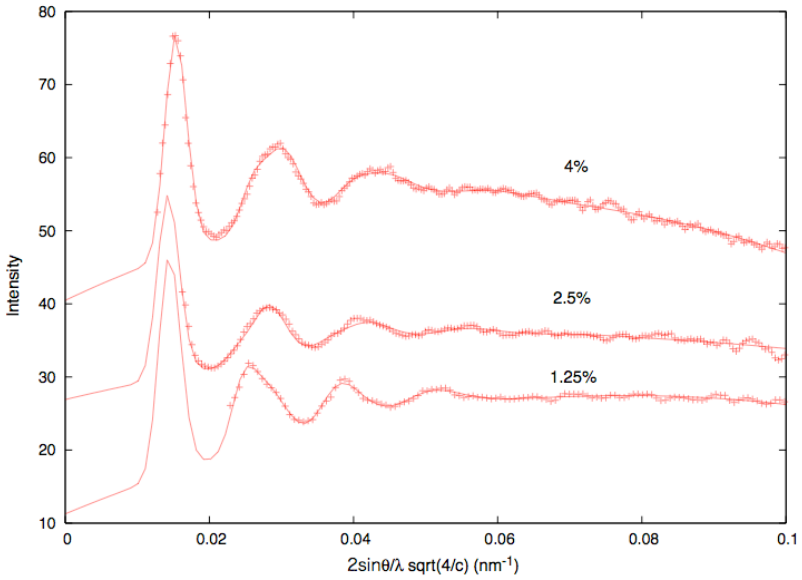

Figure 2. Small-angle scattering profiles of cellulose whisker suspensions at different concentrations (cross) and their fit (solid line) assuming a two dimensional hexagonal arrangement with limited crystal size and paracrystallinity.

Figure 2 shows the intensity profile of the small-angle scattering patterns shown in **Figure 1**, normalized with the intensity profile of the nematic phase (**Figure 1d**). When the scattering vectors were multiplied by the squared root of concentration, the peak positions almost coincided, indicating that the organization could be interpreted purely as a two dimensional close packing of strongly repelling particles. The whole intensity profiles were fitted using a series of gaussian peaks and a second order polynomial background function. Each peak had the following form :

$$f_i = A_i \exp\left(-4\ln 2\left(\frac{x - b_i}{(1/t + b_i^2 c_p)}\right)^2\right)$$

where t is a global parameter corresponidng to the crystal size, c_p a paracrystallinity parameter. The peak position b_i is generated from the global lattic constant a. A_i is the peak height.

At 4 % cellulose content, the hexagonal lattice constant was a = 75.5 nm. Assuming a square cross section and using the density of cellulose (1.6 g/cm^3), a crysal width of 14 nm estimated by Scherrer analysis of wide-angle diffraction peaks, the lattice constant would be 82 nm if the whole volume was crystalline. The density in the colloidal crystals is probably higher because of the voids due to the polydispersity of the whiskers. In fact, the lattice of colloidal crystals expanded more than estimated by dilution and approached theoretical values, probably because the system was more relaxed and the voids were filled.

The crystal size was about 300 nm, and the paracrystallinty parameter was almost constant for the whole dilution when the crystal size was fixed. Since the 100 peak was hidden behind the beamstop for diluted suspensions, the crytal size and paracrystallinity could not be estimated independently.

A small quantity of ions due to the dissolution of carbon dioxide during the preparation shifted the phase transition to much higher concentrations, and thus we could not modulate the ionic strength systematically.

Conclusion and perspectives

We confirmed the existence of hexagonal phase in cellulose whisker aqueous system and found a phase transition from hexagonal to nematic phase by dilution. It would be of interest to further focus on the concentration range close to the phase transition to see whether a better organization and growth of colloidal crystal can be achieved with the system.