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Phase-separation of cellulose from ionic liquid upon cooling: preparation of microsized particles

Introduction

Cellulose has been processed with dissolving and regeneration in ionic liquids. Organic electrolyte solutions (OESs), that are binary mixtures of an ionic liquid and a polar aprotic co-solvent, show even better dissolution capacities for cellulose than the pure ILs. Here we use OESs consisting of tetraalkylphosphonium acetate ILs and dimethyl sulfoxide (DMSO) or γ-valerolactone (GVL) to observe cellulose regenerating. Cellulose is first dissolved in these OESs at 120 °C and then regenerated upon cooling to observe micro and macro phase-separation. This phenomenon much resembles the upper-critical solution temperature (UCST) type thermodynamic transition. This UCST-like behavior allows for the controlled regeneration of cellulose into colloidal dispersions of spherical microscale particles (spherulites) with highly ordered shape and size.

Phase diagram of cellulose in $[P_{4444}][OAc]$-based OESs

We observed the phase separation of cellulose in OESs by means of turbidity measurements. We built a phase-diagram for the UCST-type phase transition of cellulose in $[P_{4444}][OAc]$:DMSO (70:30 w/w) with concentration of cellulose 2-8.5 wt%. Thermodynamic quality of cellulose solution at 120 °C is good, but it becomes poorer with decreasing temperature (cooling rate 1°C/min). Below the cloud point temperature (T_{cp}), cellulose chains associate, grow larger with time and eventually form micro-sized particles that can be detected with an optical microscope. Formation of particles in solutions of 1-4wt% concentrations is more probable. Above c*, cooled solutions are less cloudy with increasing cellulose concentration. This suggests a typical feature of homogeneous gels or gels with some inhomogeneities.

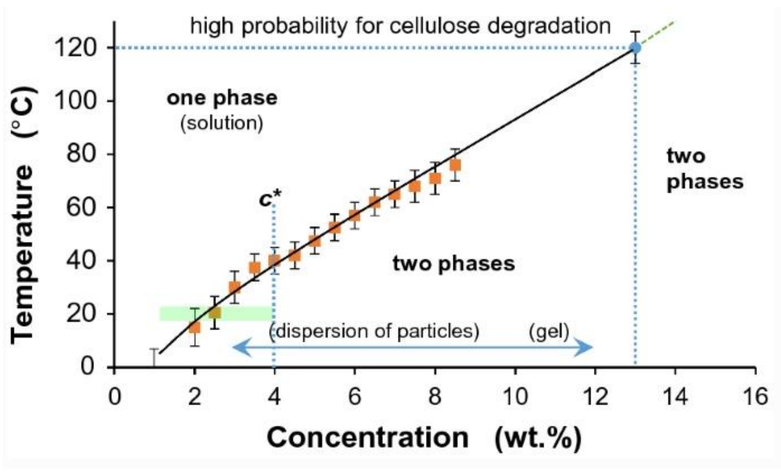
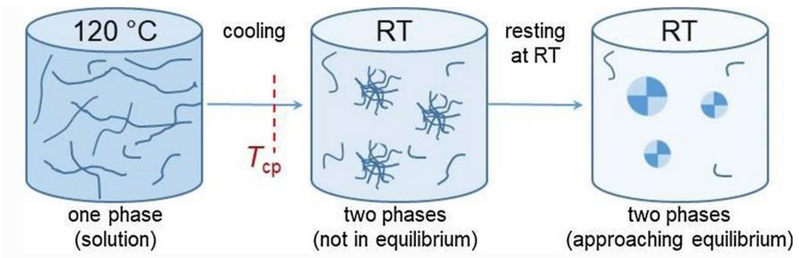


Figure 1. The phase diagram of cellulose.

Micro particles by regeneration from $[P_{4444}][OAc]$:DMSO (70:30 w/w)

Cellulose solutions with concentration of 1-4 wt% in [P4444][OAc]:DMSO (70:30 w/w) were dissolved in 120 °C then cooled down to room temperature (RT) and equilibrated for 18 h for particles regeneration. The hypothetical mechanism is shown in Scheme 1. Optical microscopy was used for observing the regenerated cellulose after equilibration (Figure 2) as well as for visualization of the particle growth (Figure 3).



Scheme 1. A hypothetical mechanism of cellulose regeneration upon cooling

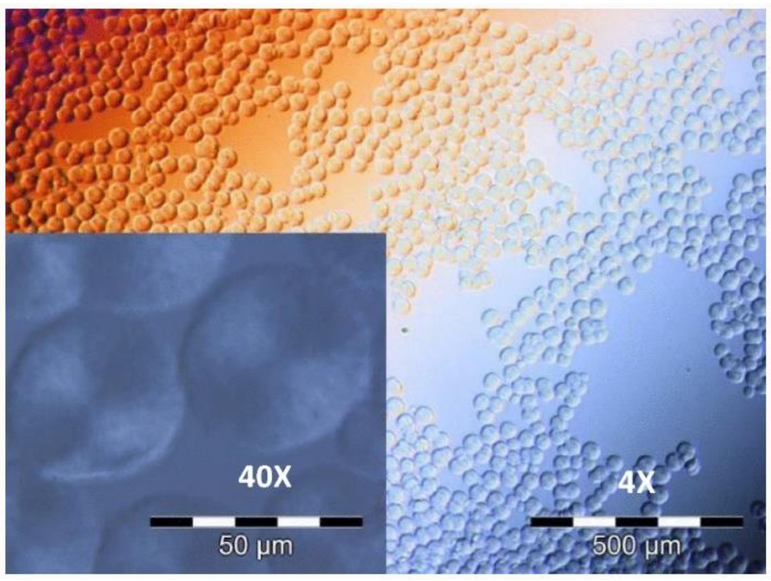


Figure 2. Micro-sized particles regenerated from a cellulose-OES mixture upon cooling

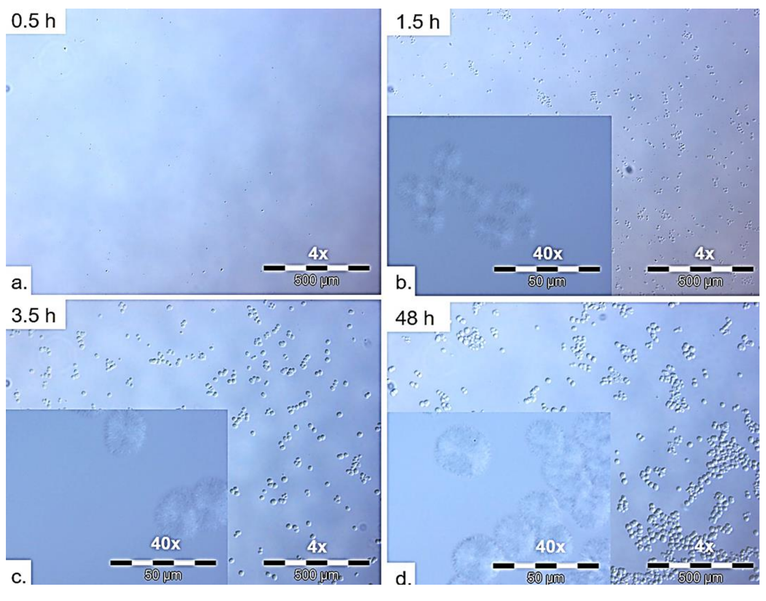


Figure 3. Process of the particles formation in 2.0 wt.% [P4444][OAc]:DMSO inside a 20 ml vial after slow cooling with increasing equilibration time at RT

Preparation of dry particles

A rapid solvent exchange was applied to wash the OESs away: 10 times larger weight of water (non-solvent) were added into the regenerated cellulose solutions. Probe sonication was applied for preventing growth of large agglomerates in the mixture, then the particles were recovered by centrifugation and the process was repeated 3 times.

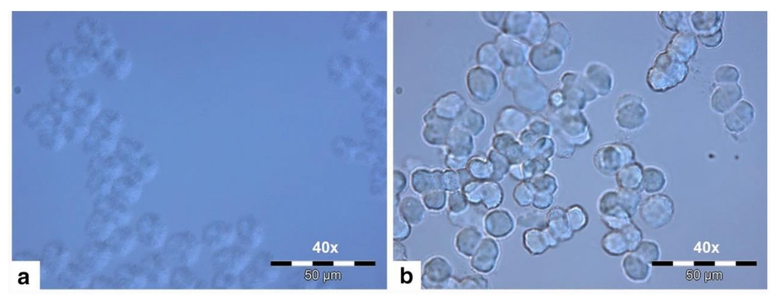


Figure 4. Regenerated particles from 2.0 wt.% cellulose solution in $[P_{4444}][OAc]$:DMSO; before washing (a) and the particles washed and redispersed in water (b)

Dry particles were examined by means of wide angle X-ray scattering (WAXS). The 1D diffraction pattern shown in Figure 5 is typical the Cellulose II. The diffraction pattern also reveals a significant amorphous contribution and crystallinity of Cellulose II is 37.2%.

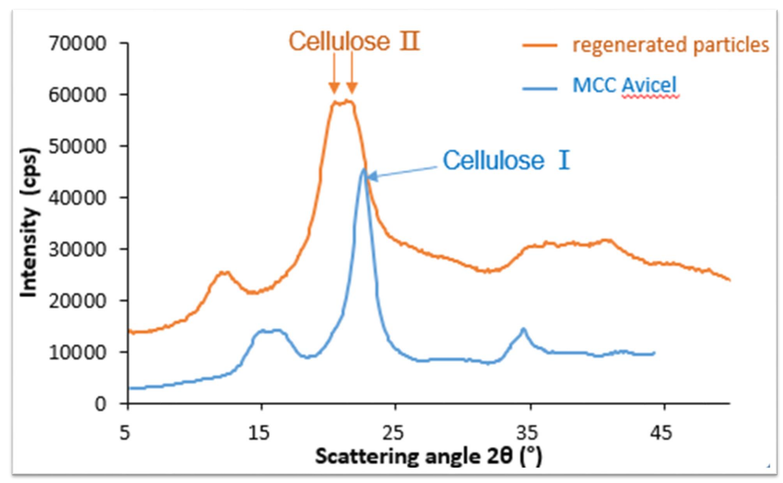


Figure 5. Wide angle X-ray scattering representing freeze dried regenerated cellulose in the form of particles and original MCC (Avicel)

References

Xia, J., King, A.W.T., Kilpeläinen, I. et al. Phase-separation of cellulose from ionic liquid upon cooling: preparation of microsized particles. Cellulose 28, 10921–10938 (2021).

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