Cation dependence of cellulose solution structure in alkaline solvent

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Cellulose is a readily available and renewable biopolymer. It is fascinatingly insoluble in most common solvents, but may be dissolved in strong alkali, such as 8 wt.% NaOH(aq) and 40 wt. % tetra butyl ammonium hydroxide, TBAH(aq).[1-3] In this study, the dissolution state of microcrystalline cellulose (MCC) has been studied in mixtures of these two solvents to understand if such a mixture could behave as a better or a worse solvent than the precursor. We used 8 wt.% NaOH(aq) and 40 wt. % TBAH(aq) stock solutions and mixed them in different proportions. The mixed solvent composition is expressed as the parameter X_{NaOH} being the fraction of the NaOH solvent in the mixture. The mixtures have been analyzed by scattering, light microscopy, and turbidity experiments. Furthermore the formation of a structured film appears in certain condition and it has been studied by optical and confocal microscopy. When mixing NaOH and TBAH, the cellulose solubility decreases. This is seen in Figure 1 which shows the turbidity of 2 wt.% MCC solutions/dispersions as a function of X_{NaOH}. For X_{NaOH}< 0.04 and X_{NaOH}> 0.9 transparent solutions are formed. For 0.04< X_{NaOH}<0.9, 2 wt.% MCC can not be fully solubilized. X-ray diffraction indicates that it is Cellulose II that precipitates, possibly as partial sodium salt. MCC in the mixed solvent x_{NaOH}= 0.5, shows precipitation and a pattern formation under confinement between microscope slides. The patterns were characterized using conventional light and confocal microscopy (Fig. 2).

Fig 1. Turbidity curve versus X_{NaOH} in weight %. Black symbols represent the turbidity shortly (minutes) after mixing. Red symbols show the turbidity after 60 minutes.

Fig 2. A) Images of the sample X_{NaOH}=0.5. B) Image of sample X_{NaOH}= 0.5 doped with rhodamine recorded with the confocal microscope. C) 3D image of sample X_{NaOH}=0.5 doped with rhodamine, obtained by combining images of different confocal planes. The colour of the picture was adjusted in order to highlight different regions.

References