



On the role of hydrophobic interactions in cellulose dissolution and regeneration: Colloidal aggregates and molecular solutions



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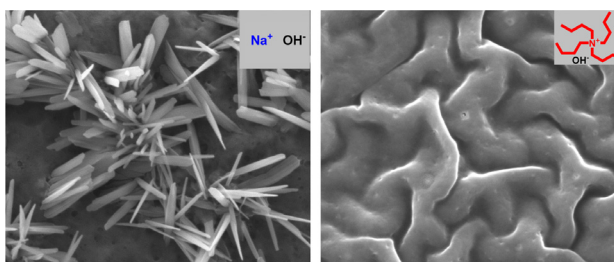
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HIGHLIGHTS

- Cellulose presents amphiphilic properties.
- Amphiphilic cation promotes cellulose dissolution to the molecular level.
- Inorganic cation makes dissolution less efficient.
- Crystallinity of the regenerated material depends on the cation used in dissolution.
- Morphology of regenerated materials is dependent on the solvent composition.

GRAPHICAL ABSTRACT



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ABSTRACT

The development of strategies for dissolution and regeneration of cellulose constitutes an increasingly active research field due to the direct relevance for many production processes and applications. A wide variety of suitable solvents for cellulose are already available. However, cellulose solvents are of highly different nature reflecting the great challenges in the understanding of the subtle balance between the different interactions. Here, we report on the effect of two different solvents on the dissolution of cellulose on multiple length scales and its consequences for the characteristics of the regenerated material. While an aqueous tetrabutylammonium hydroxide solution gives rise to what appears to be dissolution down to the molecular level, a sodium hydroxide solution does not dissolve cellulose molecularly but rather leaves aggregates of high crystallinity stable in the cellulose dope. The dramatic difference between a small inorganic cation and an amphiphilic cation indicates a critical role of hydrophobic interactions between cellulose molecules and provides support for the picture that cellulose molecules have pronounced amphiphilic properties.

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1. Introduction

Cellulose is a widely used biopolymer finding applications in several different areas. Since cellulose is not meltable it typically has to be first dissolved in a solvent. However, most of the common solvents found in the laboratory usually fail in this respect.

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Through the years, several suitable solvents for cellulose dissolution have been developed and the list provides a wide variety of quite unusual options: from simple or multicomponent mixtures, aqueous and organic media, inorganic and organic salts, with peculiar experimental conditions (e.g. high and low temperatures, high and low pH), etc. [1,2]. Similarly, regeneration procedures cover a broad range of systems depending on the dissolution medium. From a mechanistical point of view, the generally accepted mechanism for cellulose regeneration from common alkali-based systems suggests that the inclusion complex (responsible for dissolution) associated with cellulose is broken down by adding a non-solvent such as water, leading to the self-association of cellulose [3–7]. In the case of ionic liquids, ILs, the suggested regeneration mechanism proposes that the ordered cation–anion polar interaction network is disrupted by water that forms a network of interactions with the anion and with the cation [8]. Recent visions highlight the predominant role of hydrophobic interactions both in dissolution and regeneration [9–16].

In theory, a successful polymer dissolution completely eliminates the supramolecular structure resulting in a clear solution where the polymer is molecularly dispersed. Experience with synthetic polymers reveals that these solutions are typically mostly fully dispersed down to the molecular level. This has led to the simplified conclusion that either a polymer is dissolved or it is not dissolved. However, this two-option rule does not always hold; intermediate stages between swelling and complete solubility exist and cellulose and its derivatives are clear examples of this [17,18]. In the majority of the cases, cellulose and its derivatives only rarely form molecularly dispersed solutions; cellulose is not dissolved down to a molecular level but rather forms stable colloidal dispersions where ordered cellulose aggregates are present (aggregation numbers between 10 to 800 have been estimated) [19]. These supramolecular structures are preserved even when solutions are highly diluted and the structure in solution has been proposed to consist of aggregates of star-branched macromolecules or fringed “micelles” characterized by a highly ordered cylindrical core of aligned chains (most likely, reminiscent of crystalline fractions of the native cellulose fibers), which is insoluble in the solvent, and two soluble spherical coronas surrounding the core ends [19]. These metastable clusters of cellulose chains have been suggested to behave like covalently bound macromolecules, comparable to worm-like chains. Different techniques (mainly scattering, i.e. small angle X-ray scattering (SAXS), static light scattering (SLS), dynamic light scattering (DLS) and depolarized dynamic light scattering (DDLS)) have been used to infer about cellulose structure (e.g. estimation of aggregation number, shape of the aggregate) in different solvents [17,20].

It is to be expected that the way cellulose is dissolved and how it organizes in solution has a strong influence on the properties and characteristics of the regenerated material [21]. A couple of examples can be recalled. For instance, while in the viscose process (NaOH based solvent), cellulose chains apparently build up a loose network with gel particles, in the lyocell process (N-Methylmorpholine N-oxide (NMMO) based solvent) an entanglement network with highly swollen aggregates is observed [17]. Another study of the solution state of cellulose in NMMO shows the presence of a bimodal distribution of aggregates with up to 1000 chains [22,23]. On the other hand, it seems that a molecular dispersed solution is obtained in the LiCl/DMAc system. However, in this latter case, a high LiCl content leads to the formation of cellulose aggregates which disintegrate upon dilution with the DMAc cosolvent [24]. Curiously, the addition of small amounts of water induces the re-formation of the cellulose aggregates with characteristics comparable to the ones found in solutions based on the NMMO solvent. In all these cases, it is obvious that the regenerated material (in the form of films, fibers or other) behaves completely different,

from a structural level up to mechanical properties, depending on the process used.

The differences in mechanical properties of regenerated materials, such as lyocell and viscose fibers, is mainly due to the differences in the applied regeneration process (i.e. air gap vs. wet spinning) and the associated differences in the draw ratios. However, parameters such as the polymer concentration and the dissolved state are also speculated to markedly influence the properties of the regenerated materials and therefore this is an important motivation for a deeper characterization of the cellulose solutions. Another is that an investigation of the correlation between the state of cellulose in solution and the solvent properties may add a better understanding of the interactions involved. In our group we are, therefore, carefully investigating the solution state and the regenerated state for an extended range of solvents. In this report we focus on aqueous solutions with a high hydroxide concentration. Cellulose dissolution at extreme pHs can basically be related to the fact that cellulose molecules acquire net charges either by protonation (low pH) or deprotonation (high pH). This observation is based on the general finding that polyelectrolytes are more soluble in water than nonionic polymers, the driving force being the dissociation of counterions and the concomitant large counterion entropy. Whereas the fact that a high concentration of hydroxide ions facilitates dissolution is rather trivial, the observation that the nature of the cation dramatically affects dissolution needs further considerations. In particular we were interested in the question whether there are differences between hydroxides with different cations, particularly between inorganic and organic cations. Here, by means of scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), polarized light microscopy (PLM), X-ray powder diffraction (XRD) and DLS we report on the effect of two distinct solvents, i.e. cold NaOH solutions and aqueous solution of tetrabutylammonium hydroxide on the degree of dissolution and regeneration of cellulose. Additionally, the crystallinity index is estimated from XRD and FTIR.

2. Materials and methods

2.1. Materials

Microcrystalline cellulose (MCC) was obtained from Sigma (Avicel PH-101, average particles size of 50 μm and DP of ca. 260). Tetrabutylammonium hydroxide (TBAH) of chromatographic grade was acquired from Sigma Aldrich as a 40 wt% solution in water while the NaOH pellets were obtained from Fluka. Cellulose dissolution was obtained following the adapted standard procedures in literature [25,26]. Briefly, a known amount of cellulose was dispersed in a 8% NaOH/H₂O solution and then allowed to freeze at -20°C for 24 h. This was followed by thawing the solid frozen mass at room temperature with simultaneous vigorous mixing. On the other hand, for the TBAH based solvent, the dissolution procedure was simply the mixture of a known amount of cellulose with a 40 wt% TBAH aqueous solution at room temperature for 30 min. Regarding the regeneration protocol, the cellulose dope was simply coagulated in diluted H₂SO₄ solutions. Then the regenerated material was removed from the coagulation media and extensively washed with distilled water in order to eliminate any residuals of acidic media and dried at room temperature.

2.2. Methods

2.2.1. Dynamic light scattering

The mean particle size of the cellulose samples was estimated from dynamic light scattering (DLS) measurements using a Zetasizer NanoZS (ZN 3500, Malvern Instruments, UK), with a 532 nm

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