



The role of cyclodextrin-tetrabutylammonium complexation on the cellulose dissolution



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ABSTRACT

Cellulose dissolution is a challenging process which is typically very sensitive to the solvent characteristics such as pH, temperature or presence of additives. Regarding the later aspect, it is here reported the interaction between α -cyclodextrin (α -CD) and β -cyclodextrin (β -CD) with the tetrabutylammonium cation (TBA^+) by 1H NMR titration experiments. The analysis by the continuous variation method suggests the formation of 1:1 CD: TBA^+ complexes. However, the computed apparent association constants reveal that the interaction of TBA^+ with the β -CD ($K=1580 M^{-1}$) is unexpectedly stronger than with α -CD ($K=106 M^{-1}$). In both CD cases, the formation of CD: TBA^+ complexes decrease the dissolution efficiency of the solvent and this has been rationalized as an effective decrease in the concentration of the amphiphilic cation and concomitant weakening of the hydrophobic interactions in solution influencing the overall performance of the solvent. Additionally, the data also supports the fact that amphiphilic species in solution are beneficial for the enhancement of cellulose solubility.

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1. Introduction

Cellulose is structurally an anisotropic molecule displaying amphiphilic properties (Biermann, Hadicke, Koltzenburg, & Muller-Plathe, 2001; Diddens, Murphy, Krisch, & Müller, 2008; Medronho et al., 2015; Medronho & Lindman, 2014b; Miyamoto et al., 2009; Yamane et al., 2006). Such amphiphilicity has not always been recognized and its role in cellulose solubility is often neglected in detriment to the more conceptual view which attributes to hydrogen bonding the leading responsibility in the cellulose solubility pattern (Glasser et al., 2012; Lindman, Karlström, & Stigsson, 2010; Medronho & Lindman, 2014a; Medronho, Romano, Miguel, Stigsson, & Lindman, 2012). Cellulose solvents are of vast nature regarding the composition, pH, operating temperature, etc. However, the majority are limited to lab scale applications and share similar problems and concerns such as the costs of production, safeness, recyclability, environmental impact and capacity of dissolution (Heinze & Koschella, 2005; Medronho & Lindman, 2014b). Among them the alkaline systems based on NaOH have claimed more attention in a hypothetical replacement of more hazardous

routes used nowadays worldwide such as the viscose process (Cai & Zhang, 2005; Isogai & Atalla, 1998). The NaOH aqueous system draws attention mainly due to its simplicity and inexpensive chemical composition, low environmental impact and an apparent easy implementation in the existing large scale facilities. The use of different additives has further improved the dissolution efficiently on NaOH aqueous solutions (i.e. increasing the kinetics of dissolution and stability of the dopes formed) (Cai et al., 2007; Liu, Budtova, & Navard, 2011a; Wan & Li, 2015; Yan & Gao, 2008; Zhang, Ruan, & Gao, 2002). However, some important limitations still persist in these systems such as the sub-zero temperatures needed to efficiently dissolved cellulose and the rather low molecular weights (i.e. DP < 400) and cellulose contents (i.e. <10 wt%) that the solvents are capable to handle. An interesting alternative alkaline system is the aqueous tetrabutylammonium hydroxide solvent (TBAH) (Abe, Fukaya, & Ohno, 2012). This system is capable to dissolve high amounts of cellulose with high molecular weight at room temperature reasonably fast. Additionally, while cellulose in the TBAH appears to be dissolved down to the molecular level, the dissolution in the analogous NaOH aqueous system is far of being complete where fairly large and crystalline colloidal aggregates are found to be stable in solution. This difference in the dissolution performance was suggested to arise from the amphiphilicity of the tetrabutylammonium (TBA^+) cation which supposedly facilitates

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the dissolution of cellulose via the weakening of the hydrophobic interactions (Alves et al., 2015).

In this work the effect of two different natural (α - and β -) cyclodextrins (CDs) on the aqueous TBAH performance is studied. The question of how CDs interact and affect the availability of the TBA⁺ specie and how that influences the cellulose dissolution will be addressed by means of NMR methodologies. Further X-ray, infrared and microscopy studies elucidate the effect of CDs in the dissolution performance of the solvent and some thermodynamic parameters will be discussed.

2. Materials and methods

2.1. Chemicals and solution preparation

Dissolving pulp was supplied from Buckeye Tech. Inc., USA with an averaged degree of polymerization (estimated by intrinsic viscosity measurements) of ca. 630. Tetrabutylammonium hydroxide (TBAH) of chromatographic grade (40 wt% solution in water), α -cyclodextrin (>98%), β -cyclodextrin (>98%), 3-(trimethylsilyl)propionic-2,2,3,3-d₄ acid sodium salt and urea were purchased from Sigma-Aldrich. All chemical were used as received. The NMR samples were prepared using D₂O (99.8%) supplied by EURISO-TOP (France). NaOD was also supplied by EURISO-TOP (France). The cellulose pulp solutions were prepared by simply mixing a known amount of cellulose with a 40 wt% TBAH/H₂O solution at room temperature for 30 min (Abe et al., 2012).

2.2. Characterization

2.2.1. X-ray diffraction (XRD)

The X-Ray diffraction experiments were performed on a Siemens D5000 X-ray diffractometer, capable of identifying crystalline phases down to 3% of the bulk. This equipment consists of a $\theta/2\theta$ diffraction instrument operating in the reflection geometry. CuK α_1 is used as radiation source with $\lambda = 1.54056 \text{ \AA}$, focused by a primary Ge crystal monochromator. The detector is a standard scintillation counter. The Cu tube runs at 40 mA and 40 kV. The cooling is supplied by an internal water-filled recirculation chilling system, running at approximately 16 °C with a flow rate of 4–4.5 L/min. The slit arrangement is a 2 mm pre-sample slit, 2 mm post-sample slit and a 0.2 mm detector slit.

2.2.2. Fourier transform infrared spectroscopy (FTIR)

The infrared spectra were recorded at 25 °C with a ATR-FTIR spectrophotometer Thermo Nicolet, IR300 (USA), using a universal ATR sampling accessory. FTIR spectral analysis was performed within the wave number range of 400–4000 cm⁻¹. A total of 256 scans were run to collect each spectrum at a resolution of 1 cm⁻¹ in the transmission mode. The CrI (also referred to as “lateral order index”—LOI) was estimated from the ratio between the absorption band at 1430 cm⁻¹ and the absorption band at 890 cm⁻¹ (Hurtubise & Krasig, 1960; O’Connor, DuPreí, & Mitcham, 1958).

2.2.3. Turbidimetry

AT70 UV–vis spectrophotometer (PG Instruments Ltd) was used for the optical transmittance measurements. Essentially, the cellulose solutions were placed in a proper cell and the transmittance was measured at a wavelength of 600 nm.

2.2.4. Polarized light microscopy

A Linkam LTS 120 microscope equipped with a Q imaging (Qicam) Fast 1394 camera was used to observe the cellulose dissolution in the solvent systems used. Samples were kept between

cover slips and illuminated with linearly polarized light and analysed with a linear polarizer under crossed position. Images were captured and analyzed using Qcapture software.

2.2.5. ¹H NMR measurements

¹H NMR spectra were recorded at 25.0 (± 0.1) °C on a Varian 500 MHz spectrometer using a 5 mm NMR probe. Spectra were obtained with residual solvent (HOD) presaturation and the acquired parameters included 24k data points covering a spectral width of 8 kHz, a radiofrequency excitation pulse of 45° and a scan repetition time of 15 s to allow for full magnetic relaxation of proton nuclei. The resonance at 0 ppm due to Si-(CH₃)₃ signal, from 3-(trimethylsilyl)propionic-2,2,3,3-d₄ acid sodium salt (TSP) at tracer concentration (below 3 μ M), was used as internal reference. The method of continuous variation has been used to determine the stoichiometry of the CD:TBAH interaction; for that, samples were prepared by dissolving an amount of the solid in D₂O to achieve a concentration of CD and TBAH of 1.01 and 1.02 mM, respectively. The TBAH was previously lyophilized overnight just before using and the pH* of D₂O was adjusted to 12.08 with the addition of NaOD, in order to keep the pH of CD:TBAH solutions constant. The binding constant were computed by using experimental ¹H NMR chemical shifts of TBA⁺ nuclei for mixed solutions with different [α -CD]/[TBAH] and [β -CD]/[TBAH] molar ratios, and keeping the [TBAH] constant and equal to 1.13 and 1.20 mM, respectively.

3. Results and discussion

3.1. Characterization of the dissolved and regenerated cellulose pulp: Microscopy, turbidimetry, XRD and FTIR analysis

Cellulose dissolution is an intriguing process but essential in numerous applications due to the fact that this biopolymer does not melt. The addition of different additives (typically with amphiphilic like properties) has been observed to enhance cellulose dissolution (Medronho & Lindman, 2014b). On the other hand, simple salts tend to compromise the dissolution performance (Medronho et al., 2015). For instance, in the TBAH system it has been observed that alkali metal ions (e.g. LiCl, NaCl and KBr) when added to the solvent decrease its dissolution performance (Ema, Komiyama, Sunami, & Sakai, 2014). Ema et al. suggest an interpretation based on the salt effect on the disruption of the hydrogen bonding network. On the other hand, we believe that at such extreme high pH cellulose is, if not fully, at least, partially protonated. Therefore, the addition of simple salts is expected to screen the electrostatic repulsion between the charged cellulose chains. As cellulose molecules become less hydrophilic with the salt addition, the hydrophobic interactions start to dominate triggering the chain aggregation. In Fig. 1, polarizing optical micrographs are shown for 2 wt% cellulose dissolved in TBAH with different additives. Regardless the concentration of urea added, no visible effect on the dissolution is observed (Fig. 1b and c) when compared with cellulose dissolved in the pure solvent (Fig. 1a). Some substances, such as surfactants and urea, have intermediate polarity and, as recently reviewed, are known to eliminate hydrophobic association in aqueous media (Medronho & Lindman, 2014b). It is here noted that urea increases the kinetics of cellulose dissolution and slightly decreases the viscosity of the dopes. On the other hand, the addition of low concentrations of α -CD (Fig. 1d) and β -CD (Fig. 1g) does not change considerably the dissolution efficiency although a residual fraction of undissolved fibers are observed. The typical initial swelling step preceding dissolution, the formation of “balloons” (Cuissinat, Navard, & Heinze, 2008), is also clearly visible for the lower concentrations of CD. On the other hand, if the CD concentration is further increased no balloons are observed and the fraction of undissolved

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