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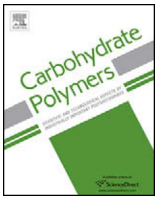

Dissolution state of cellulose in aqueous systems. 2. Acidic solvents

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ABSTRACT

Cellulose is insoluble in water but can be dissolved in strong acidic or alkaline conditions. How well dissolved cellulose is in solution and how it organizes are key questions often neglected in literature. The typical low pH required for dissolving cellulose in acidic solvents limits the use of typical characterization techniques. In this respect, Polarization Transfer Solid State NMR (PT ssNMR) emerges as a reliable alternative. In this work, combining PT ssNMR, microscopic techniques and X-ray diffraction, a set of different acidic systems (phosphoric acid/water, sulfuric acid/glycerol and zinc chloride/water) is investigated. The studied solvent systems are capable to efficiently dissolve cellulose, although degradation occurs to some extent. PT ssNMR is capable to identify the liquid and solid fractions of cellulose, the degradation products and it is also sensitive to gelation. The materials regenerated from the acidic dopes were found to be highly sensitive to the solvent system and to the presence of amphiphilic additives in solution.

1. Introduction

The effort to develop efficient, environmentally and human friendly solvents for cellulose is of major importance. However, cellulose dissolution is generally a challenging process and unfeasible in most common solvents. Nevertheless, it can be dissolved in some specific systems, such as strong alkaline or acidic media (Medronho & Lindman, 2014). The cohesion among cellulose chains and concomitant wide range of interactions involved (i.e. extended hydrogen-bonding network and hydrophobic interactions) (Lindman, Karlström, & Stigsson, 2010; Xiong, Zhao, Hu, Zhang, & Cheng, 2014) makes the accessibility of the solvent molecules to the inner core of the cellulose fibrils quite restricted compromising the solvent efficiency. On the other hand, higher cellulose chains accessibility is probably the most important factor influencing cellulose hydrolysis (Sathitsuksanoh, George, & Zhang, 2013; Zhang & Lynd, 2004).

Acidic solvents are recognized as highly competent systems to dissolve cellulose. Such good performance has been attributed to the efficient fast diffusion of the protons from the acid compounds; due to the very small size, the ion can easily penetrate and diffuse into the heterogeneous and rather compact regions of the cellulose matrix (Zhang, Cui, Lynd, & Kuang, 2006). However, one note that rather than a thermodynamic question, this is essentially a kinetic problem which apparently is favored in acid systems.

Cellulose dissolution in acidic media is typically accompanied by considerable chemical degradation, which takes place within a couple of hours after dissolution and may be reduced using low temperatures during the process. Such degradation might be useful in some cases, such as in fundamental chemical analysis of cellulose or for 2nd generation biofuel production, but it is definitely not desired or beneficial for other applications where higher molecular weights are required, such as in fibre spinning (Liebert, Heinze, & Edgar, 2010). Therefore, the solution state of the dissolved cellulose is an important parameter to consider not only to develop new efficient solvents but also to understand and prevent undesired side effects such as an extensive material degradation. In line with general features of polymer solubility it seems reasonable to attribute the solubility of cellulose at extreme pHs to the ionization of the hydroxyl groups which, apart from the counterion entropy effects, it is expected to generate electrostatic repulsions among the charge groups. This charging up effect has been extensively explored in the polymer field, in particular with cellulose derivatives (Sannino, Demitri, & Madaghiele, 2009). This work also intends to shed light on a hypothetical dissolution mechanism based on a protonation/deprotonation of cellulose. Moreover, it

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follows our previous studies on alkaline solvent systems where the high potential of PT ssNMR became patent in the characterization of the solution state of cellulose (Alves, Medronho, Antunes, Topgaard, & Lindman, 2015). Here, the selected systems comprise phosphoric acid (85%) (Boerstoel, Maatman, Westerink, & Koenders, 2001; Zhang et al., 2006), sulphuric acid based solutions (66%) (Camacho, González-Tello, Jurado, & Robles, 1996; Ioelovich, 2012) and aqueous zinc chloride salt (60%) hydrate melt (Fischer, Leipner, Thümmler, Brendler, & Peters, 2003).

Despite some experimental innovations, the novelty of this work lies not on the acidic solvents used which are reasonably well known to dissolve cellulose. Instead, the systems were selected to highlight some of the virtues and weakness of the PT ssNMR technique regarding the characterization of cellulose dopes. For example, the more common way to detect cellulose degradation is by measuring the degree of polymerization before and after dissolution and precipitation of cellulose. With the present approach focussed PT ssNMR (Nowacka, Mohr, Norrman, Martin, & Topgaard, 2010) we intend to be able to anticipate the degradation of cellulose already during the dissolution process. Thus, this approach might contribute to the development of new effective strategies to prevent cellulose degradation during dissolution in harsh acidic conditions.

It is worth mentioning that this technique combines features of both high resolution and solid-state NMR, and enables the study of all the constituent phases in complex materials. Apart from cellulose dissolution (Alves, Medronho, Antunes, Topgaard et al., 2015; Gustavsson, Alves, Lindman, & Topgaard, 2014), the method has been successfully applied to study phase behaviour of amphiphiles, e.g., lipids and surfactants (Hellstrand, Nowacka, Topgaard, Linse, & Sparr, 2013; Nowacka, Bongartz, Ollila, Nylander, & Topgaard, 2013; Nowacka, Douezan, Wadso, Topgaard, & Sparr, 2012; Nowacka et al., 2010) and intact stratum corneum (Björklund et al., 2013).

Combining the PT ssNMR with microscopic techniques and X-ray diffraction we expect to provide a clear picture on how cellulose organizes in acid media and how different chemical species influence its dissolution and stability of the dopes formed.

2. Materials and methods

2.1. Materials

Microcrystalline cellulose (MCC) Avicel PH-101, with an average particle size of 50 μm and degree of polymerization of ca. 260, alkyl-polyglucoside (APG) 50% aqueous solution, glycerol (purity > 99.5%), zinc chloride (reagent grade, purity > 98%) and sulfuric acid (98% purity ACS reagent) were acquired from Sigma Aldrich. Ortho-phosphoric acid (purity 99%) and NaOH pellets (>98% purity) were obtained from Fluka. All chemicals were used as received.

2.2. Methods

2.2.1. Sample preparation

Cellulose dissolution was obtained following the adapted standard procedures in literature (Hao et al., 2015; Ioelovich, 2012; Lu & Shen, 2011). Briefly, a known amount of cellulose was dispersed in a 85 wt% phosphoric acid pre-cooled at 5 °C, and the solution was stirred for 12 h until complete dissolution of cellulose (Hao et al., 2015). The dissolution of cellulose in H_2SO_4/glycerol was obtained by the addition of a known amount of MCC into a solution of 66 wt% of sulfuric acid and 33 wt% glycerol (Karlsson, 2013). The solution was heated to 60 °C for 15 min to achieve complete dissolution of cellulose. Dissolution in the highly concentrated salt system was achieved by dissolving the desired amount of MCC in a 60 wt% $ZnCl_2/H_2O$ solution at 80 °C for 15 min (Lu & Shen, 2011).

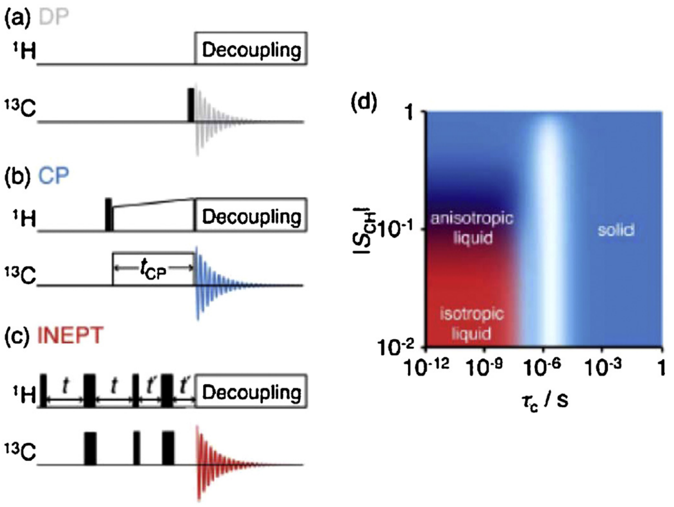

Fig. 1. NMR pulse sequences using magic-angle spinning (MAS) with detection of the ^{13}C signal under ^1H decoupling (a–c). Thermal equilibrium polarization of ^{13}C is used in DP (direct polarization), while CP (cross polarization) and INEPT (insensitive nuclei enhanced by polarization transfer) depend on polarization transfer from ^1H to ^{13}C. Vertical lines (narrow and broad) indicate 90° and 180° radiofrequency pulses, respectively. (d) Theoretical ^1H–^{13}C polarization transfer efficiency as a function of correlation time τ_c and order parameter $|S_{CH}|$. The enhancement factor was calculated as described in Nowacka et al. (Nowacka et al., 2013) for a tertiary carbon atom, calculated with input parameters equal to the present experimental settings, able to discriminate between isotropic liquids (only INEPT), anisotropic liquids (both INEPT and CP), and solids (only CP). Total absence of signal for both INEPT and CP is represented by the white area. (Reproduced from Gustavsson et al. (Gustavsson et al., 2014) with permission from the Royal Society of Chemistry.).

The regenerated materials were obtained by simple precipitation of the cellulose dopes in distilled water at room temperature. The samples were then allowed to dry at 50 °C, in a kiln, during 12 h.

2.2.2. PT ssNMR

NMR experiments were performed on a Bruker AVII-500 spectrometer with a 4 mm$^{13}C/^{31}P/^1H$ E-free probe (Bruker, Germany), running at the ^1H and ^{13}C Larmor frequencies of 500 and 125 MHz, respectively. The spectra were recorded at 25 °C and at 60 °C, using a 4 mm HR-MAS rotors (Bruker, Germany) specifically designed for retaining liquids during magic angle spinning (MAS) at a spinning frequency of 5 kHz. The temperature was varied using a BVT-2000 temperature control and the spectra were acquired under 88 kHz two-phase pulse modulation (TPPM) decoupling, using 20 ms acquisition time with 300 ppm spectral width, and a 80 kHz nutation frequency for the 90° and 180° pulses. CP was performed with $\tau_{CP} = 1$ ms, 80 kHz ^{13}C nutation frequency, linearly ramped from 72 to 88 kHz ^1H nutation frequency. The time delays of $\tau = 1.8$ ms and $\tau' = 1.2$ ms were used for refocused INEPT. The ^{13}C spectra were externally referenced to alpha-glycine at 43.67 ppm (α carbon). The pulse sequences schemes that together constitute PT ssNMR are showed in Fig. 1a–c. In Fig. 1d the theoretical CP and INEPT efficiencies as a function of the rate and anisotropy of C—H bond reorientation are represented. This approach demonstrates potential for the detailed characterization of both the liquid and the solid phases in cellulose dissolution media. Through the ^{13}C chemical shifts, the PT ssNMR method gives information about chain packing, molecular structure and conformation. Also provides information about molecular dynamics by means of the signal intensities obtained with the polarization transfer schemes CP (cross polarization) and INEPT (insensitive nuclei enhanced by polarization transfer) (Gustavsson et al., 2014).