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Non-exchanging hydroxyl groups on the surface of cellulose fibrils: The role of interaction with water

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ABSTRACT

The interaction of water with cellulose stages many unresolved questions. Here ^{2}H MAS NMR and IR spectra recorded under carefully selected conditions in ^{1}H-^{2}H exchanged, and re-exchanged, cellulose samples are presented. It is shown here, by a quantitative and robust approach, that only two of the three available hydroxyl groups on the surface of cellulose fibrils are exchanging their hydrogen with the surrounding water molecules. This finding is additionally verified and explained by MD simulations which demonstrate that the ^{1}HO(2) and ^{1}HO(6) hydroxyl groups of the constituting glucose units act as hydrogen-bond donors to water, while the ^{1}HO(3) groups behave exclusively as hydrogen-bond acceptors from water and donate hydrogen to their intra-chain neighbors O(5). We conclude that such a behavior makes the latter hydroxyl group unreactive to hydrogen exchange with water.

1. Introduction

Cellulose is the most voluminous renewable raw material on Earth. It has many traditional and emerging applications, all of which would be promoted by a better molecular-scale understanding of its properties [1]. Yet, such an understanding remains incomplete with significant white spots. One such spot is centered on the interaction of cellulose with water [2] – water that wets and significantly changes the macroscopic properties, such as the tensile strength, of the cellulose fibrils but does not dissolve the cellulose.

The basic associative structural unit of a cellulose fiber is the partly crystalline fibril. The fibril diameter, in the order of several nanometers, together with the crystallinity both depend on the biological source and the subsequent processing [3]. Within fibrils of the dominant crystalline form in higher plants, namely cellulose Iβ, the chains are ordered in flat sheets with hydrogen bonds between neighboring chains. The sheets are in turn stacked on top of each other with no hydrogen bonds between adjacent layers. Hence, both hydrogen bonds and hydrophobic forces play a role in keeping the crystal intact in water [4]. There is a broad agreement concerning some basic features of the interaction of cellulose fibers with water: the water molecules seem to be able to (i) penetrate the fibers and (ii) interact with the surface of the constituting fibrils. Such interaction involves the hydroxyl groups residing on the non-crystalline surface of the fibrils [5]. The questions we investigate here, with the help of infrared (IR) and nuclear magnetic resonance (NMR) spectroscopies, as well as molecular dynamics (MD) simulations, are: (i) which hydroxyl groups interact with water and (ii) in which manner does this interaction occur? The hydrogen bond network within the fibrils has been accessed by neutron diffraction [6] and the relative stability of hydrogen bonds have been assessed [7–9]. Yet, even though various aspects of the water-cellulose interface have been comprehensively investigated by molecular simulations [10–12] the site-specific reactivity of hydroxyl groups on the surface of the fibrils remains, from a quantitative standpoint, incompletely characterized and, thus still poorly understood.

The glucose unit within the cellulose chain possesses three hydroxyl groups, indexed as ^{1}HO(2), ^{1}HO(3), and ^{1}HO(6) by their respective carbon position. The accessibility of those groups, to

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various reactive chemicals, has been investigated in connection to the chemical modification of cellulose [13,14]. It was found that molecules like diethylamine or acetic anhydride preferentially react with the ^{1}HO(2) and ^{1}HO(6) moieties. The insight offered by MD simulations is that the ^{1}HO(3)-O(5) hydrogen bond is rather strong at the surface of cellulose fibril, which may limit its accessibility [12,15]. Water molecules are smaller than, for instance, acetic anhydride and may interact in a different manner with the fibril surface. In addition, adsorbed water affects the structure of the cellulose-surface chains. Hence, the questions stated above are still persistent.

One way of investigating these issues is to study, in the presence of heavy water, the site-selectivity of the exchange of the hydrogen nuclei (protons, ^{1}H) in the different ^{1}HO groups of cellulose to the deuterium nuclei (deuterons, ^{2}H). Previously, IR features that appeared after proton-deuteron exchange have been explained by assuming particular exchanging ^{1}HO populations [16,17]. But, even though the ^{1}HO region of static FT-IR spectra have previously been successfully deconvoluted and compared to computed models of cellulose crystals [18,19], detailed decomposition of difference bands alone (or jointly with ^{2}HO bands) has not been performed. Previous NMR results are similarly inconclusive on this point: ^{13}C magic angle spinning (MAS) NMR with ^{2}H recouping could not reveal significant differences between different hydroxyl groups [20]; the single previous attempt by ^{2}H MAS NMR spectroscopy [21] did only consider the behavior of water, and the ^{2}H quadrupole-echo spectrum of dry cellulose lacks chemical selectivity [22]. In the present paper, we provide conclusive evidence that only two of the three available hydroxyl groups are subject to proton exchange in the presence of adsorbed water. Our conclusions are derived from joint interpretation of FT-IR and ^{2}H MAS NMR spectra, recorded in carefully prepared samples, together with state-of-the-art MD simulations.

2. Results and discussion

2.1. NMR measurements

The cellulose investigated here is nominally “microcrystalline” cellulose (MCC) and was derived from cotton linters. Available X-ray or NMR-based methods for estimating the crystalline content in cellulose are not fully conclusive [23]. Yet, cotton-linter cellulose is typically indicated to be highly crystalline with fibril diameters in the order of 7–9 nm [24]. The presented sample-preparation procedure provided sufficiently long time for allowing hydrogen-deuterium exchange to reach dynamic equilibrium in a controlled heavy-water atmosphere (approximately 93–95% relative humidity) after which the sample was vacuum dried. After this, the detected ^{2}HO-band reports exclusively about the exchanged hydroxyl-groups. The NMR experiments were then performed on such dry samples, with the ^{2}H signal (see Fig. 1, left inset) arising from exchanged deuterons in the hydroxyl groups. Such ^{2}H MAS NMR spectrum is a collection of spinning side bands (SSBs) whose intensity roughly follows the spectral intensity of the corresponding non-spinning spectrum (data not shown here). Within each SSB, the narrowed peaks appear at their respective isotropic chemical shifts [25].

The chemical shift differences in carbohydrates are small [26] and therefore the individual spectral components within the SSB manifold of the ^{2}H NMR spectrum in Fig. 1 could be resolved only by recording a spectral series with increasing evolution time in an inversion recovery experiment (see SI) [27]. Hence, the component intensities within the SSBs are modulated by their respective site-specific longitudinal relaxation times (T_1). A simultaneous fit of all SSBs permits one to separate the spectral components [27] and to obtain their respective chemical shift and T_1 value (see Table 1).

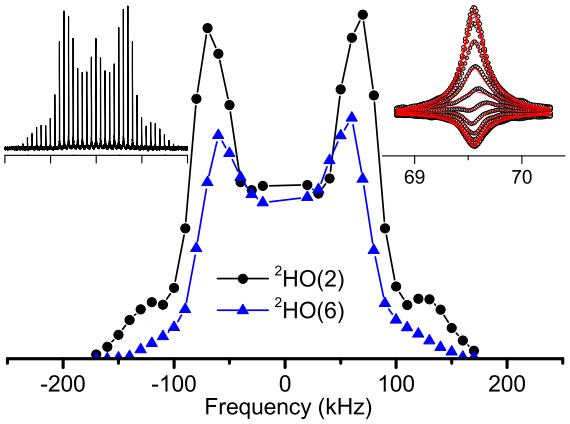

Fig. 1. ^{2}H MAS NMR spectra of MCC, first deuterated in heavy-water atmosphere and then vacuum dried. The ^{2}H NMR signal arises from deuterons located in exchanged hydroxyl groups. Main plot: deconvoluted individual contributions to the SSB intensities of the inversion-recovery ^{2}H MAS NMR experiment, assigned to ^{2}HO(2) (black filled circles) and to ^{2}HO(6) (blue filled triangles). Left inset: the measured ^{2}H MAS spectrum plotted between −200 and 200 kHz. Right inset: evolution of one SSB in an inversion-recovery ^{2}H MAS NMR experiment, with x-axis values in kHz (black dots: experimental data, red lines: global spectral fit). All intensities are in arbitrary units. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The spectral fits illustrated in Fig. 1 were assumed to consist of two distinct hydroxyl groups that participate in the hydrogen-deuterium exchange. With this assumption we obtain a plausible and consistent outcome: the band shapes of the deconvoluted spectral contributions are, as expected for quadrupole-broadened spectra, symmetric around the central frequency. In addition, the obtained chemical shifts for the two deuteroxyl groups are consistent with the existing literature data about ^{1}H chemical shifts of glucose oligomers dissolved in a water/acetone solution: the peak at 5.9 ppm is then assigned to the ^{2}HO(2) group and the peak at 5.4 ppm is assigned to the ^{2}HO(6) group [26]. Small discrepancies between liquid ^{1}H and solid ^{2}H chemical-shift values are expected because of two effects: (i) differences in the local molecular environments between the solid and the liquid states [28,29], and (ii) second-order quadrupolar-shift effects for the ^{2}H nuclei [30]. This latter effect is expected to be very similar for all the three hydroxyl groups and, therefore, does not change the relative chemical shift of those.

Moreover, ^{13}C CP-MAS longitudinal relaxation measurements of cellulose [31,32] have previously indicated that molecular motions for the C-^{1}HO(2) groups are more restricted and, thus, slower than those for the C-^{1}HO(6) groups. This is also reflected here by the smaller second moment (M_2) and by the shorter T_1 for the assigned ^{2}HO(6) population. If we allow for a third component, i.e. the ^{2}HO(3) sites, to contribute to our ^{2}H MAS NMR spectra, the band shapes for the different sites become unphysically asymmetric (see

Table 1
Spectral parameters extracted from the inversion-recovery ^{2}H MAS NMR experiment, the presented values are averages over measurements of three different samples (the corresponding standard deviation is shown within brackets).

	Site A: ^{2}HO(2)	Site B: ^{2}HO(6)
Population fraction (%)	60 (3)	40 (3)
Chemical shift (ppm)	5.9 (0.1)	5.4 (0.2)
T_1 (ms)[a]	640 (150)	50 (10)
M_2 (10^9 s^{-2})[b]	3.9 (0.1)	3.3 (0.1)

[a] Longitudinal relaxation-time (T_1).
[b] Second moment (M_2).