

# 1 Cellulose-solvent interactions from self- 2 diffusion NMR

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8

## 9 Abstract

10 Molecular self-diffusion coefficients were measured in solutions of microcrystalline cellulose  
11 (MCC) and dissolving pulp, in 40 wt.% aqueous tetrabutylammonium hydroxide, TBAH, using  
12 pulsed field gradient stimulated echo NMR. From the cellulose diffusion coefficients, a weight  
13 averaged radius of hydration  $\langle R_h \rangle_w = 6.1$  nm for MCC and  $\langle R_h \rangle_w = 15$  nm for pulp were obtained.  
14 Water and TBA<sup>+</sup> ions show a significantly different dependence on the cellulose concentration,  
15 revealing different molecular interactions with the polymer. Water-cellulose are essentially excluded  
16 volume. TBA<sup>+</sup> ions, on the other hand, bind to cellulose with approximately 1.2 TBA<sup>+</sup> ions per  
17 glucose unit.  
18

19 *KEYWORDS: Cellulose, self-diffusion, NMR, polymer-solvent interaction, Tetrabutylammonium*  
20 *hydroxide.*  
21

## 22 Introduction

23 Cellulose has unique hierarchical structures, i.e. linear glucan chains, crystalline cellulose  
24 microfibrils, bundles of microfibrils, cell walls, plant tissue and plants (Zugenmaier 2001). Pulp is  
25 defined as a lignocellulosic fibrous material prepared by separating cellulose fibers from wood, fiber  
26 crops or waste paper; pulp has a relatively high molecular weight. Microcrystalline cellulose, MCC,  
27 has relatively low chemical reactivity and it has several industrial applications (Bolhuis et al. 1996;  
28 Wei et al. 2015). Cellulose is insoluble in many organic solvents and also in water, but can be  
29 dissolved in a number of solvents of intermediate properties (Lindman et al. 2010). The low aqueous  
30 solubility is quite difficult to understand since cellulose is a polar molecule and it has created a lot  
31 of interest. The most reliable explanation takes in account the amphiphilic properties of the cellulose  
32 and that the low aqueous solubility must have a marked contribution from hydrophobic interactions  
33 (Medronho et al. 2012; Alves et al. 2016; Lindman et al. 2015). However, it can be dissolved in  
34 water at high and low pHs (Isogai & Atalla 1998; Zhang et al. 2006). Nowadays the main challenge  
35 is to find eco-friendly solvents to dissolve and process cellulose. In fact, except for direct application

in its natural fiber form, cellulose cannot melt, it should be processed via dissolution or derivatization. Several solvents were studied to dissolve cellulose showing several cellulose-solvent interaction mechanisms (Sen & Martin 2013). Nuclear magnetic resonance (NMR) is one of the most suitable techniques to study cellulose dissolution and aggregation (Isogai 1997; Kamide et al. 1985; VanderHart & Atalla 1984). In particular polarization transfer solid-state NMR (PTssNMR) was shown to provide molecular level information on the dissolved and insoluble fractions of cellulose in an aqueous medium (Gustavsson et al. 2014). Self-diffusion NMR measurements were performed on several ionic liquids and mixture of ionic liquids with other solvents, like DMSO, mainly to demonstrate deviation from simple ideal mixing rules due to cellulose association with solvent ions (Youngs et al. 2011; Hall et al. 2012; Radhi et al. 2015). Thus self-diffusion measurements can be used to investigate solvent-solute interactions. Here self-diffusion measurement was used to investigate cellulose in 40 wt.% of aqueous tetrabutylammonium hydroxide, TBAH(aq). Self-diffusion coefficients of TBA<sup>+</sup>, water and cellulose were measured, using both microcrystalline cellulose and pulp.

## Materials and methods

### *Materials*

The weight-average molecular weight of microcrystalline cellulose, MCC was  $M_w = 29$  kg/mol and for pulp was  $M_w = 162$  kg/mol as reported by Löfgren, C. - Södra. MCC and TBAH(aq) were obtained from Sigma, while the pulp was a kind gift from Södra. MCC and pulp concentrations in the range 1-10 wt. % and 1-8 wt. %, respectively, were investigated at a fixed temperature of 30 °C. The cellulose range was chosen as a function of solubility, pulp solubility limit was estimated to be ~8wt.%. It has been reported that cellulose can be dissolved in TBAH at lower temperature than 30°C (Wei et al. 2015), this temperature was chosen to definitely avoid TBAH-water clathrate formation (Kumagai et al. 2015). Solutions were prepared by weighing appropriate amounts of cellulose directly into 40 wt.% TBAH(aq) and stirring the sample overnight.

### *Methods*

Pulsed gradient stimulated echo (PFSTE) experiments were performed on a Bruker Avance DMX200 spectrometer operating at 200 MHz on <sup>1</sup>H nuclei, and equipped with a commercial diffusion probe (DIF-25 5mm) having a maximum gradient strength of 960 G/cm. In the PGSTE sequence, a pair of trapezoidal narrow magnetic field gradient pulses, with amplitude  $g$  and duration  $\delta$ , encode for spin displacement over a controlled observation time  $\Delta$ , corresponding to the gradient pulse separation. In the PGSTE three  $\pi/2$  radio frequency pulses are applied. The time between the first and second pulse was 3.2 ms while the time between the second and third pulse was 26.8 ms. The repetition time for all experiments was chosen of 5 seconds allowing sufficient time for longitudinal ( $T_1$ ) relaxation. However, the H<sub>2</sub>O-OH peak at 4.3 ppm and one of the TBA<sup>+</sup> peaks at 2.6 ppm covered cellulose signals between 2.4 and 4.5 ppm. Since cellulose self-diffusion here is ca. two orders of magnitude slower than H<sub>2</sub>O-OH and TBA<sup>+</sup>, it is possible to distinguish

spectroscopically the species. Due to the fast hydrogen exchange between H<sub>2</sub>O, OH<sup>-</sup> and -OH groups of cellulose the echo-decay of the 4.3 ppm peak take account of a weighted average diffusion coefficient of these sites, although dominated by H<sub>2</sub>O.

## Results and discussion

—insert **Fig. 1** here—

Self-diffusion NMR is able to resolve otherwise separate intractable spectra of mixtures and it can be used to determine the size of molecules and aggregates, determining the degree of polymerization or size of a solvation shell.

The experimental parameters to measure H<sub>2</sub>O-OH and TBA<sup>+</sup> self-diffusion coefficients have been  $\Delta = 140$  ms,  $\delta = 2$  ms and  $g$  was varied from 8 to 32 G·cm<sup>-1</sup> for H<sub>2</sub>O-OH and from 25.3 to 101.1 G·cm<sup>-1</sup> for TBA<sup>+</sup> in 16 gradient steps. **Fig. 1** reports the 3 experiments performed on one sample taken as example. The echo decays were analyzed according to (Stejskal & Tanner 1965),

$$\frac{I}{I_0} = e^{-bD} \quad (1)$$

where  $b = \gamma^2 g^2 \delta^2 (\Delta - \delta/3)$ .  $I$  is the echo amplitude,  $I_0$  being the amplitude at  $g=0$ .  $\gamma$  is the magnetogyric ratio. **Fig. 2** shows the diffusion behaviors of H<sub>2</sub>O-OH and TBA<sup>+</sup> as a function of the MCC and pulp concentration.  $D^0$  is the diffusion coefficient of H<sub>2</sub>O and TBA<sup>+</sup> in the pure solvent. The OH signal in the NMR spectrum is dominated by the most abundant site, water, but there is a non-negligible contribution coming from OH<sup>-</sup> ions and the -OH groups of cellulose. There is fast exchange between these proton sites on the experimental time scale ( $\Delta=140$  ms) and a weighted average diffusion coefficient,  $D_{OH}^{obs}$ , is obtained from the echo decay of this peak

$$D_{OH}^{obs} = \frac{1}{n_{OH}^{tot}} (2n_w D_w + n_{OH^-} D_{OH^-} + 3n_{AGU} D_c) \quad (2)$$

where  $n_w$ ,  $n_{OH^-}$  and  $n_{AGU}$  are the number of water molecules, hydroxide ions and (anhydrous) glucose units, respectively, in the sample, and  $n_{OH}^{tot} = 2n_w + n_{OH^-} + 3n_{AGU}$  is the total number of hydroxyl (OH) proton sites.  $D_w$ ,  $D_{OH^-}$  and  $D_c$  are the self-diffusion coefficients of water, hydroxide ions and cellulose, respectively. As  $n_{OH^-} \ll n_w$  and  $D_c \ll D_w$  eq. (2) can be approximated by

$$D_{OH}^{obs} \simeq \frac{2n_w}{n_{OH}^{tot}} D_w \quad (3)$$

Eq. 3 was used to evaluate  $D_w$ .

**Fig. 2** shows the diffusion coefficients of water ( $D_w$ ) and TBA<sup>+</sup> ions ( $D_{TBA^+}$ ) as a function of the cellulose concentration, relative to the diffusion values,  $D_w^0$  and  $D_{TBA^+}^0$ , respectively, in the absence of cellulose. As can be seen, the TBA<sup>+</sup> diffusion coefficients decrease essentially linearly with the cellulose concentration,  $c$ . The addition of colloidal particles generally reduce the solvent

diffusion coefficient, because of obstruction of diffusion paths, an excluded volume effect (Jönsson et al. 1986). For polymer chains this effect is small, only a few percent within the present concentration range, but essentially accounts for the concentration dependence of  $D_w$  where no decrease is observed in the error bar.  $D_{TBA^+}$ , on the other hand, has a much stronger concentration dependence than what can be explained by obstruction effects.

—insert **Fig. 2** here—

The essentially linear decrease of the  $TBA^+$  self-diffusion coefficient with the cellulose concentration is consistent with a saturated fixed number of bound  $TBA^+$  ions per cellulose molecule, but with fast exchange with the bulk on the experimental time scale so that only an average  $TBA^+$  diffusion coefficient is observed. In this case, the observed diffusion coefficient is a population weighted average (Lindman et al. 1982)

$$D_{TBA^+} = (1-P)D_{TBA^+}^0 + P\langle D_c \rangle \approx (1-P)D_{TBA^+}^0 \quad (4)$$

where  $D_{TBA^+}^0 = 1.1 \cdot 10^{-10} \text{ m}^2/\text{s}$  is the bulk  $TBA^+$  diffusion coefficient and  $P$  is the fraction of “bound”  $TBA^+$  ions. If  $TBA^+$  binds stoichiometrically to cellulose, with a fixed number,  $N$ , of  $TBA^+$  ions per anhydrous glucose unit (AGU), then

$$P = N \frac{M_{TBAH}}{M_{AGU}} \left[ \frac{c}{0.4(1-c)} \right] \quad (5)$$

In Eq. 5 we have also taken into account that the density of 40 wt.% TBAH(aq) equals  $1.0 \text{ g/cm}^3$ .  $M_{TBAH}=259 \text{ g}$  and  $M_{AGU}=162 \text{ g}$  are the molecular weights of TBAH and AGU, respectively. This model, Eq 5, was fitted to  $TBA^+$  diffusion data (both MCC and pulp), and the best fit, corresponding to  $N \approx 1.2$  is shown in **Fig 2** as a solid line. At higher cellulose concentration we see a deviation from the linear dependence. This is not surprising, as Eq. (5) is expected to hold only at lower cellulose concentrations, where  $P$  is small, and the specific solvation does not significantly affect (lower) the bulk concentration of  $TBA^+$  ions. At the highest concentration of cellulose studied,  $c=10 \text{ g/cm}^3$ , the overall molar ratio  $[TBA^+]/[AGU] \approx 2$  and a decrease in  $N$  is expected compared to lower  $c$  where  $TBA^+$  ions is in large excess. In principle the same type of analysis could be done on the water/ $OH^-$  diffusion. However, because the water on a molar basis is in so large excess, the effect of possible binding on the water diffusion is small, and can not be quantified accurately. The strong association of  $TBA^+$  ions to cellulose was also proposed from SAXS experiments (Behrens et al. 2014).

The obtained result can be compared with previous work on glucose, cellobiose and MCC dissolved in 1-ethyl-3-methyl-Imidazolium acetate, where the diffusion of both the cation and the anion species were monitored (Ries et al. 2014). Ries et al. demonstrated that the cations were preferentially solvating the glucose units/molecule and a value of 3 associated ions per AGU was estimated for the cellulose.

143 The TBA<sup>+</sup> cation is directly involved in the dissolution of the carbohydrates, with these interactions  
 144 preferably slowing down the motion of the TBA<sup>+</sup> relative to the water. The TBA<sup>+</sup> self-diffusion  
 145 behaviors as a function of cellulose concentration is due to the interactions with their environment,  
 146 i.e. cellulose. This is true independently from the cellulose molecular weight, since from **Fig 2** the  
 147 same cation/glucose unit ratio in MCC and pulp can be found. The TBA<sup>+</sup> molecules will interact  
 148 with OH<sup>-</sup> (alkaline environment) that in turn interact with cellulose. On the other hand the water  
 149 molecules mobility is essentially not affected, except for the increasing viscosity of the system.  
 150 The self-diffusion measurement for cellulose were performed using  $\Delta = 30$  ms,  $\delta = 3$  ms and  $g$  were  
 151 varied from 10 to 610 G/cm in 16 steps. MCC and pulp are polydisperse, and as a consequence the  
 152 echo decay is a weighted sum of exponentials,

$$153 \quad \frac{I}{I_0} = \frac{\sum_i n_i M_i e^{-bD_i}}{\sum_i n_i M_i} \quad (6)$$

154 where  $n_i$  are the number of molecules of molar mass  $M_i$  in the solution. The weight averaged  
 155 diffusion coefficient  $\langle D_c \rangle$  is obtained from the initial slope of  $I/I_0$  versus  $b$  (Nilsson et al. 2007).

$$156 \quad \langle D_c \rangle = \left. \frac{d}{db} \frac{I}{I_0} \right|_{b=0} \quad (7)$$

157 —insert **Fig 3** here—

158

159 In **Fig 3**  $\langle D_c \rangle$  was plotted as a function of the cellulose concentration for MCC and pulp,  
 160 respectively.

161 With increasing cellulose concentration the mobility of the chains decreases. The behavior of the  
 162 cellulose self-diffusion observed in **Fig 3** can be described by a stretched exponential as proposed  
 163 by Phillies (Phillies 2011)

$$164 \quad \langle D_c \rangle = D_0^i \cdot e^{-ac^v} \quad (8)$$

165 where  $c$  is the polymer concentration and  $\alpha$  and  $v$  are scaling parameters, while  $i = \text{MCC or pulp}$ .  
 166 Phillies provided physical interpretations of the scaling parameters (Phillies 1987; Phillies 1988).  
 167 However, there still remains a debate concerning their precise physical meanings (Zetttl et al. 2009;  
 168 Furukawa et al. 1991). This model was proposed to describe the self-diffusion of one macromolecule  
 169 in another over a wide range of concentrations (Phillies 2011). The polymer chains are considered  
 170 mobile and can be described by spheres joined by rods that can rotate as defined by Kirkwood &  
 171 Riseman (Kirkwood & Riseman 1948). The cellulose-concentration behaviors is qualitatively well  
 172 described by Phillies model, on the other hand quantitative evaluation from the fitting parameter are  
 173 not taken in account due to the polydispersity of cellulose. On the qualitative point of view the  
 174 resulting fitting parameters from eq. 6 are reasonable in agreement with what it is expected (Nydén  
 175 1999):  $v$  was equal to 0.7 and 0.8, while  $\alpha$  was found to be equal to 8 and 9 for pulp and MCC,  
 176 respectively.

177 The extrapolated weight averaged diffusion coefficients at infinite dilution, are estimated  
 178 to be  $\langle D_0^{MCC} \rangle \simeq 5.2 \cdot 10^{-12} \text{ m}^2/\text{s}$  and  $\langle D_0^{pulp} \rangle \simeq 2.2 \cdot 10^{-12} \text{ m}^2/\text{s}$ . The hydrodynamic radius,  $R_h$ , can be  
 179 calculate applying the Stokes-Einstein relation

$$180 \quad \langle R_h^0 \rangle = \frac{k_B T}{6\pi\eta \langle D_0^i \rangle} \quad (9)$$

181 where  $\eta$  is the solvent viscosity, here  $\eta = 7 \text{ mPas}$ ,  $k_B$  is Boltzmann's constant and  $T$  is the absolute  
 182 temperature.  $\langle R_h \rangle$  is equal to 6 nm and 15 nm, for MCC and pulp, respectively. The difference is  
 183 consistent with the expected scaling  $R_h \sim M^\mu$ , where  $\mu \approx 0.55$  for polymer chains in good solvents  
 184 (De Gennes 1979, Sung and Chang 1993). Moreover these values are in agreement with other  
 185 reported in literature for other solvents (Saalwächter et al. 2000; Yuan and Cheng 2015).

## 187 Conclusions

188 The molecular self-diffusion coefficients were measured in solutions of cellulose, MCC and pulp,  
 189 in 40 wt.% TBAH(aq). These results highlighted that TBAH binds to cellulose with approximately  
 190 1.2 ions per glucose unit. The reason for this binding may be electrostatic attraction to deprotonated  
 191 hydroxyl groups on the cellulose or hydrophobic interactions, or a combination of both. Moreover,  
 192 the number of ions involved in the solvation process is independent from the cellulose molecular  
 193 weight. Finally the hydrodynamic radius of MCC and pulp was estimated to be 6 and 15 nm,  
 194 respectively.

## 196 ACKNOWLEDGMENT

197 Pegah Nosrati Hefzabad for MCC/TBAH solutions preparation. We thank Caroline Löfgren,  
 198 Södra, for providing the cellulose size distributions using SEC-MALS.

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291 **Figure legend**

292 **Fig. 1** Schematic illustration of the self-diffusion experiments.  $D_w$  was evaluated at small  $g$ -values  
293 (top),  $D_{TBA^+}$  at intermediate  $g$ -values and  $D_c$  from large  $g$ -values. The sample consists of 5 wt. %  
294 of pulp in 40 wt. % TBAH(aq) at 30°C. Parameter values are presented in the graphs.

295

296 **Fig. 2** Relative diffusion coefficients of water and TBA<sup>+</sup> ions as a function of  $c/(1-c)$ , where  $c$  is  
297 the cellulose concentration in g/cm<sup>3</sup> at 30 °C. Data from both MCC and pulp solutions are shown.  
298 The diffusion coefficients are normalized by the respective values in the pure solvent mixture.

299  $D_w^0 = 7.5 \cdot 10^{-10} \text{ m}^2 / \text{s}$  .  $D_{TBA^+}^0 = 1.1 \cdot 10^{-10} \text{ m}^2 / \text{s}$  .

300

301 **Fig. 3** Average cellulose self-diffusion as a function of their concentration at 30 °C. The average  
302 diffusion coefficient were obtained from the initial slope of the echo decay (Eq. 6). The error bars  
303 represent the standard deviation of 3 experiments. The dashed lines are fitting of the Phillies model  
304 by using  $D_0$  obtained from the intercept of a linear fit of data below 0.03 g/cm<sup>3</sup>.





