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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^+ 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^+ ions, on the other hand, bind to cellulose with approximately 1.2 TBA^+ 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

36 in its natural fiber form, cellulose cannot melt, it should be processed via dissolution or
37 derivatization. Several solvents were studied to dissolve cellulose showing several cellulose-solvent
38 interaction mechanisms (Sen & Martin 2013). Nuclear magnetic resonance (NMR) is one of the
39 most suitable techniques to study cellulose dissolution and aggregation (Isogai 1997; Kamide et al.
40 1985; VanderHart & Atalla 1984). In particular polarization transfer solid-state NMR (PTssNMR)
41 was shown to provide molecular level information on the dissolved and insoluble fractions of
42 cellulose in an aqueous medium (Gustavsson et al. 2014). Self-diffusion NMR measurements were
43 performed on several ionic liquids and mixture of ionic liquids with other solvents, like DMSO,
44 mainly to demonstrate deviation from simple ideal mixing rules due to cellulose association with
45 solvent ions (Youngs et al. 2011; Hall et al. 2012; Radhi et al. 2015). Thus self-diffusion
46 measurements can be used to investigate solvent-solute interactions. Here self-diffusion
47 measurement was used to investigate cellulose in 40 wt.% of aqueous tetrabutylammonium
48 hydroxide, TBAH(aq). Self-diffusion coefficients of TBA^+ , water and cellulose were measured,
49 using both microcrystalline cellulose and pulp.
50

51 **Materials and methods**

52 *Materials*

53 The weight-average molecular weight of microcrystalline cellulose, MCC was $M_w = 29 \text{ kg/mol}$ and
54 for pulp was $M_w = 162 \text{ kg/mol}$ as reported by Löfgren, C. - Södra. MCC and TBAH(aq) were
55 obtained from Sigma, while the pulp was a kind gift from Södra. MCC and pulp concentrations in
56 the range 1-10 wt. % and 1-8 wt. %, respectively, were investigated at a fixed temperature of 30 °C.
57 The cellulose range was chosen as a function of solubility, pulp solubility limit was estimated to be
58 ~8wt.%. It has been reported that cellulose can be dissolved in TBAH at lower temperature than
59 30°C (Wei et al. 2015), this temperature was chosen to definitely avoid TBAH-water clathrate
60 formation (Kumagai et al. 2015). Solutions were prepared by weighing appropriate amounts of
61 cellulose directly into 40 wt.% TBAH(aq) and stirring the sample overnight.

62 *Methods*

63 Pulsed gradient stimulated echo (PGSTE) experiments were performed on a Bruker Avance
64 DMX200 spectrometer operating at 200 MHz on ^1H nuclei, and equipped with a commercial
65 diffusion probe (DIF-25 5mm) having a maximum gradient strength of 960 G/cm. In the PGSTE
66 sequence, a pair of trapezoidal narrow magnetic field gradient pulses, with amplitude g and duration
67 δ , encode for spin displacement over a controlled observation time Δ , corresponding to the gradient
68 pulse separation. In the PGSTE three $\pi/2$ radio frequency pulses are applied. The time between the
69 first and second pulse was 3.2 ms while the time between the second and third pulse was 26.8 ms.
70 The repetition time for all experiments was chosen of 5 seconds allowing sufficient time for
71 longitudinal (T_1) relaxation. However, the $\text{H}_2\text{O}-\text{OH}$ peak at 4.3 ppm and one of the TBA^+ peaks at
72 2.6 ppm covered cellulose signals between 2.4 and 4.5 ppm. Since cellulose self-diffusion here is
73 ca. two orders of magnitude slower than $\text{H}_2\text{O}-\text{OH}$ and TBA^+ , it is possible to distinguish

74 spectroscopically the species. Due to the fast hydrogen exchange between H₂O, OH⁻ and -OH
75 groups of cellulose the echo-decay of the 4.3 ppm peak take account of a weighted average diffusion
76 coefficient of these sites, although dominated by H₂O.

77

78 Results and discussion

79 —insert Fig. 1 here—

80

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

84 The experimental parameters to measure H₂O-OH and TBA⁺ self-diffusion coefficients have been
85 $\Delta = 140$ ms, $\delta = 2$ ms and g was varied from 8 to 32 G·cm⁻¹ for H₂O-OH and from 25.3 to 101.1
86 G·cm⁻¹ for TBA⁺ in 16 gradient steps. **Fig. 1** reports the 3 experiments performed on one sample
87 taken as example. The echo decays were analyzed according to (Stejskal & Tanner 1965),

$$88 \quad \frac{I}{I_0} = e^{-bD} \quad (1)$$

89 where $b = \gamma^2 g^2 \delta^2 (\Delta - \delta/3)$. I is the echo amplitude, I_0 being the amplitude at $g=0$. γ is the
90 magnetogyric ratio. **Fig. 2** shows the diffusion behaviors of H₂O-OH and TBA⁺ as a function of the
91 MCC and pulp concentration. D^0 is the diffusion coefficient of H₂O and TBA⁺ in the pure solvent.
92 The OH signal in the NMR spectrum is dominated by the most abundant site, water, but there is a
93 non-negligible contribution coming from OH⁻ ions and the -OH groups of cellulose. There is fast
94 exchange between these proton sites on the experimental time scale ($\Delta=140$ ms) and a weighted
95 average diffusion coefficient, D_{OH}^{obs} , is obtained from the echo decay of this peak

$$96 \quad D_{OH}^{obs} = \frac{1}{n_{OH}^{tot}} (2n_w D_w + n_{OH^-} D_{OH^-} + 3n_{AGU} D_c) \quad (2)$$

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

$$101 \quad D_{OH}^{obs} \simeq \frac{2n_w}{n_{OH}^{tot}} D_w \quad (3)$$

102 Eq. 3 was used to evaluate D_w .

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

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

112

113 —insert Fig. 2 here—

114

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

120
$$D_{TBA^+} = (1 - P) D_{TBA^+}^0 + P \langle D_c \rangle \approx (1 - P) D_{TBA^+}^0 \quad (4)$$

121 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”
122 TBA^+ ions. If TBA^+ binds stoichiometrically to cellulose, with a fixed number, N , of TBA^+ ions per
123 anhydrous glucose unit (AGU), then

124
$$P = N \frac{M_{TBAH}}{M_{AGU}} \left[\frac{c}{0.4(1 - c)} \right] \quad (5)$$

125 In Eq. 5 we have also taken into account that the density of 40 wt.% TBAH(aq) equals 1.0
126 g/cm^3 . $M_{TBAH} = 259 \text{ g}$ and $M_{AGU} = 162 \text{ g}$ are the molecular weights of TBAH and AGU, respectively.
127 This model, Eq 5, was fitted to TBA^+ diffusion data (both MCC and pulp), and the best fit,
128 corresponding to $N \approx 1.2$ is shown in **Fig 2** as a solid line. At higher cellulose concentration we see a
129 deviation from the linear dependence. This is not surprising, as Eq. (5) is expected to hold only at
130 lower cellulose concentrations, where P is small, and the specific solvation does not significantly
131 affect (lower) the bulk concentration of TBA^+ ions. At the highest concentration of cellulose studied,
132 $c = 10 \text{ g}/\text{cm}^3$, the overall molar ratio $[TBA^+]/[\text{AGU}] \approx 2$ and a decrease in N is expected compared to
133 lower c where TBA^+ ions are in large excess. In principle the same type of analysis could be done on
134 the water/ OH^- diffusion. However, because the water on a molar basis is in so large excess, the effect
135 of possible binding on the water diffusion is small, and can not be quantified accurately. The strong
136 association of TBA^+ ions to cellulose was also proposed from SAXS experiments (Behrens et al.
137 2014).

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

143 The TBA⁺ cation is directly involved in the dissolution of the carbohydrates, with these interactions
 144 preferably slowing down the motion of the TBA⁺ relative to the water. The TBA⁺ 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⁺ molecules will interact
 148 with OH⁻ (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)

$$164 \quad \langle D_c \rangle = D_0^i \cdot e^{-\alpha c^\nu} \quad (8)$$

165 where c is the polymer concentration and α and ν 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 (Zettl 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 Phillips 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): ν was equal to 0.7 and 0.8, while α 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 $\langle D_0^{MCC} \rangle \approx 5.2 \cdot 10^{-12} \text{ m}^2/\text{s}$ and $\langle D_0^{pulp} \rangle \approx 2.2 \cdot 10^{-12} \text{ m}^2/\text{s}$. The hydrodynamic radius, R_h , can be
179 calculate applying the Stokes-Einstein relation

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

181 where η 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).

186

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.

195

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199

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- 289
- 290

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^+ ions as a function of $c/(1-c)$, where c is
297 the cellulose concentration in g/cm³ 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 $D_w^0 = 7.5 \cdot 10^{-10} m^2 / s$. $D_{TBA^+}^0 = 1.1 \cdot 10^{-10} m^2 / s$.

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 Phillips model
304 by using D_0 obtained from the intercept of a linear fit of data below 0.03 g/cm³.





