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Probing cellulose–solvent interactions with self-diffusion NMR: Onium hydroxide concentration and co-solvent effects

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ABSTRACT

The molecular self-diffusion coefficients were accessed, for the first time, in solutions of microcrystalline cellulose, dissolved in 30 wt% and 55 wt% aqueous tetrabutylammonium hydroxide, TBAH (aq), and in mixtures of 40 wt% TBAH (aq) with an organic co-solvent, dimethylsulfoxide (DMSO), through pulsed field gradient stimulated echo NMR measurements. A two-state model was applied to estimate α (*i.e.*, average number of ions that "bind" to each anhydroglucose unit) and P_b (*i.e.*, fraction of "bound" molecules of DMSO, TBAH or H_2O to cellulose) parameters. The α values suggest that TBA^+ ions can bind to cellulose within 0.5 TBA^+ to 2.3 TBA^+/AGU. On the other hand, the P_b parameter increases when raising cellulose concentration for TBA^+, DMSO and water in all solvent systems. Data suggests that TBAH interacts with the ionized OH groups from cellulose forming a sheath of bulky TBA^+ counterions which consequently leads to steric hindrance between cellulose chains.

1. Introduction

Cellulose represents an astonishing annual natural production of *ca.* 1.5×10^{12} tons. It is one of the most used polymers worldwide, finding applications in many areas, ranging from paper and packaging to biofuels, textiles or biomedicine (Klemm, Heublein, Fink, & Bohn, 2005; Singh et al., 2015). However, its peculiar hierarchical organization and complex network of interactions makes its processing into novel advanced materials a non-straightforward task (Lindman et al., 2017; Lindman, Medronho, Alves, Norgren, & Nordenskiöld, 2021; Medronho & Lindman, 2014). As a recalcitrant and non-meltable polymer, cellulose manipulation may require initial solubilization, but the list of suitable solvents is rather restricted and the key mechanisms governing such process are still under debate (Glasser et al., 2012; Heinze & Koschella, 2005; Liebert, 2010; Lindman, Karlström, & Stigsson, 2010; Medronho & Lindman, 2015; Medronho, Romano, Miguel, Stigsson, & Lindman, 2012). Moreover, traditional solvent systems are typically not viable on a large scale due to economic and environmental issues. Therefore, generalized use of cellulose is still, somehow, hindered by the development of efficient "green" dissolution and processing methodologies. The cellulose solubility in aqueous media is governed by the free energy of mixing and thus dissolution is expected to spontaneously occur when the free energy change on mixing is negative. In the cellulose case, aqueous dissolution is unfavorable and this is mainly due to the unbalance between the energy penalty arising from the water–cellulose interactions and the entropy gains originated from the increased degrees of freedom (chain conformations) upon dissolution (Bao, Qian, Lu, & Cui, 2015; Bergenstråhle, Wohlert, Himmel, & Brady, 2010; Parthasarathi et al., 2011). In fact, despite being a hydrophilic molecule with plentiful OH groups, cellulose solubility in water is very low and therefore its behavior in solution is mainly achieved in unusual solvent systems (*i.e.*, salt solutions of high concentration, ionic liquids,

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mixtures of organic/salt compounds, *etc.*) (Heinze & Koschella, 2005; Liebert, 2010; Medronho & Lindman, 2014). Another relevant entropic argument relies on the significant contributions from hydrophobic interactions in its aqueous insolubility owing to the striking amphiphilic features of cellulose (Bao et al., 2015; Cousins & Brown, 1995; French, Dowd, Cousins, Brown, & Miller, 1996; French, Miller, & Aabloo, 1993; Isobe, Kimura, Wada, & Kuga, 2012; Lindman et al., 2010, 2017, 2021; Medronho et al., 2015, 2016, 2012; Nishiyama, Langan, & Chanzy, 2002). Extreme pHs seem to favor cellulose solubility in aqueous media. Such behavior has been rationalized regarding cellulose capacity to acquire net charges (deprotonation/protonation) behaving like a typical polyelectrolyte (Bialik et al., 2016; Isogai, 1997). In this respect, it has been suggested that cellulose solubility is boosted if the dissolution strategy considers both weakening of hydrophobic interactions and cellulose ionization. A successful example is, for instance, the use of strong hydroxides composed of bulky organic ions, such as tetrabutylammonium hydroxide (TBAH), whose dissolution capacity is superior to the related inorganic systems (*e.g.*, NaOH). The striking differences in dissolution performance have been attributed to the fact that organic cations are capable of weakening the hydrophobic interactions while the inorganic counterparts are not (Alves et al., 2015; Gubitosi, Duarte, Gentile, Olsson, & Medronho, 2016). Moreover, such superior dissolution capacity of TBAH in comparison to NaOH-based systems has been also rationalized based on the precipitation of the Na-cellulose salts (low solubility) at high NaOH concentrations, while the replacement of Na^+ with the bulky TBA^+ prevents the formation of salt crystals (Gubitosi et al., 2017; Martin-Bertelsen et al., 2020). TBAH belongs to a family of aqueous solvents based on alkylammonium hydroxide (also referred to as onium hydroxides) which display notable capacity of solubilizing large cellulose concentrations in reasonably mild conditions (Abe, Fukaya, & Ohno, 2012; Abe, Kuroda, et al., 2015; Ema, Komiyama, Sunami, & Sakai, 2014). Onium hydroxides are often stable during the dissolution procedure which favors solvent recovery and reusability. Furthermore, different types of biomass, like wood residues or wheat straw, have shown improved dissolution in onium hydroxides-based solvents when compared with alkali-based ones (Abe, Yamada, & Ohno, 2014; Abe, Yamanaka, et al., 2015; Hyväkkö, King, & Kilpeläinen, 2014; Zhong, Wang, Huang, Jia, & Wei, 2013). At low concentrations, molecularly dissolved cellulose is obtained in TBAH (aq), while at higher cellulose concentrations aggregation is observed (Gubitosi et al., 2016). It should be highlighted that molecularly dissolved cellulose is not obtained in most solvents even at low cellulose content. Some of us have demonstrated by diffusion NMR studies that, in 40 wt% TBAH (aq), TBA^+ ions bind to cellulose with *ca.* 1.2 TBA^+ ions/AGU (Gentile & Olsson, 2016) and this was further supported by detailed scattering assays. Moreover, the SAXS results are consistent with the formation of a sheath of bulky TBA^+ ions solvating the cellulose molecules (Behrens, Holdaway, Nosrati, & Olsson, 2016; Gubitosi et al., 2016). From a mechanistic point of view, the electrostatic interactions between the ionized cellulose molecules and the TBA^+ cations are suggested to be the main driving force (Gentile & Olsson, 2016). Due to TBA^+ amphiphilic features, it is reasonable to expect hydrophobic interactions to contribute for such favorable TBA^+-cellulose interactions.

Cellulose-solvent interactions are often accessed by computational studies, such as Molecular Dynamics simulations. Despite the vast number of assumptions to simply the systems and possible parameters to tune, these methods still provide relevant insight not available in typical experiments, particularly regarding the location and dynamics of the involved molecules or ions. In this regard, NMR appears as a quite powerful method to experimentally access such aspects, and, in this work, self-diffusion measurements were performed extending the concentration range of TBAH to lower (*i.e.*, 30 wt%) and higher (*i.e.*, 55 wt %) values. Moreover, the role of an organic co-solvent, DMSO, is also evaluated for different TBAH/DMSO ratios. DMSO is an aprotic, polar co-solvent with remarkable swelling properties for cellulose. Additionally, it can play the role of hard or soft base. From an application perspective, it should be added that the dissolution efficiency is not compromised, even when high concentrations of organic co-solvent (TBAH/DMSO 1:4) are present (Medronho et al., 2017). Compared with the standard TBAH (aq) solvent, the TBAH/DMSO is highly promising and valuable, since much less TBAH is used, thus turning the dissolution procedure affordable and eventually suitable for scale up. The TBAH/DMSO system has been reported to be suitable for the development of novel materials, such as regenerated cellulose films (Cao et al., 2018) or complex 3D structures (Hu et al., 2020) or even to study the effect of storage time and temperature on the solution state of cellulose (Li, Tan, Fan, Wei, & Zhou, 2021). However, the detailed role of each compound in the dissolution process remains unclear.

The effect of co-solvents, such as DMSO, has been explored in related onium-based systems. Many successful solvent systems including DMSO in its composition have been reported in the last decade (Casarano, Pires, Borin, & El Seoud, 2014; Heinze et al., 2000; Huang et al., 2016; Jiang, Miao, Yu, & Zhang, 2016; Kostag, Liebert, El Seoud, & Heinze, 2013; Medronho et al., 2017; Miao, Sun, Yu, Song, & Zhang, 2014; Ramos, Frollini, & Heinze, 2005; Ren et al., 2021; Rinaldi, 2011; Sun, Miao, Yu, & Zhang, 2015). DMSO is particularly efficient in decreasing the viscosity of different solvent systems which benefits mass transport and dissolution efficiency (Andanson et al., 2014). Of particular interest, is the work of Idström et al. in a related system, the tetrabutylammonium acetate/dimethyl sulfoxide, where the cellulose-DMSO contacts were found to be three times longer than the DMSO-DMSO interactions (Idström et al., 2017). Despite the similarities among systems and generally accepted role of hydrogen bonding and hydrophobic interactions in dissolution and regeneration phenomena, no clear dissolution mechanism has been suggested for the TBAH/DMSO system. Therefore, this work allows a more complete picture and understanding of critical cellulose-solvent interactions and consequently it sheds light on the dissolution mechanism.

2. Materials and methods

2.1. Materials

Microcrystaline cellulose, MCC (Avicell PH-101, ~50 μm particle size and degree of polymerization of 260) was acquired from Sigma-Aldrich and used as "model" cellulose. Dimethylsulfoxide, DMSO, was acquired from Fisher Scientific and chromatographic grade tetrabutylammonium hydroxide, TBAH (aq), was supplied as 40 wt% and 55 wt% aqueous solutions from Sigma-Aldrich. In-house purified water, MILLIPORE Milli-Q Gradient A10 (Millipore, Molsheim, France), was used when required in all samples.

2.2. Sample preparation

The cellulose solutions were prepared by firstly weighing pre-established amounts of MCC followed by its careful addition to the TBAH (aq) solvent. The solutions were vigorously stirred in an ARE stirrer (VELP Scientifica) to promote homogenization. Similar protocol was followed when DMSO was used as a co-solvent. The required amounts of cellulose were added to different TBAH/DMSO ratios previously prepared. Note that cellulose (mass fraction from 0.001 to 0.06 which corresponds to concentrations ranging from 0.1 wt% to 6 wt%) was dissolved in 30 wt% and 55 wt% TBAH (aq) solvents. It is important to notice that the 30 wt% TBAH (aq) solvent was prepared by diluting the 40 wt% TBAH (aq) commercial solution. The commercial 40 wt% TBAH (aq) solvent was also used to make the mixtures with different TBAH/DMSO weight fraction ratios (*i.e.*, 1:1, 1:2, 1:3 and 1:4). Samples were allowed to equilibrate at room temperature until reaching full dissolution. An optical microscope (polarized light mode) was used to periodically evaluate the dissolution state. When dissolution was considered completed, the solutions were loaded into nuclear magnetic resonance (NMR) tubes and placed in a NMR spectrometer (Bruker

Avance DMX200).

3. Method

The experimental parameters used in this work were adapted from Gentile et al. (Gentile & Olsson, 2016). In brief, pulsed gradient stimulated echo (PFSTE) experiments were carried out on a 200 MHz Bruker Avance DMX200 spectrometer using a DIF-255 mm diffusion probe with a gradient strength maximum of 960 g/cm. 3.2 ms were set as interval between the first two pulses while 26.8 ms was the time selected between the second and third pulses, with a repetition time of 5 s. Moreover, the spacing between gradient pulses $\Delta = 140$ ms, and the pulse duration $\delta = 2$ ms. The gradient strength g varied from 25.3 to 101.1 G/cm for TBA^+ and from 0 to 16 G/cm for H_2O in 16 gradient steps.

4. Results and discussion

As mentioned above, nuclear magnetic resonance is a very suitable technique to study cellulose behavior in solution (Alves et al., 2018; Alves et al., 2021; Alves, Medronho, Antunes, Topgaard, & Lindman, 2016a, 2016b). In particular, self-diffusion measurements are relevant to infer solvent–solute interactions, thus providing important insight on the dissolution and aggregation phenomena (Gentile & Olsson, 2016; Idström et al., 2017). Here, diffusion NMR spectroscopy was performed to evaluate the effect of cellulose concentration and different solvent compositions on the diffusion coefficients of DMSO, TBA^+ and H_2O.

Fig. 1 shows typical experiments performed on a cellulose solution where the decay of the TBAH and DMSO signals is plotted as a function of the gradient strength.

The resulting spin-echo decays were evaluated following the well-known Stejskal and Tanner equation (Stejskal & Tanner, 1965):

$$ln\left(\frac{I}{I_0}\right) = -D\left[(\gamma\tau g)^2\left(\Delta - \frac{\delta}{3}\right)\right] = -Db \tag{1}$$

In which I represents the echo amplitude, I_0 is the amplitude at $g = 0$, γ is the proton's gyro-magnetic ratio, g is the strength of the gradient pulse, δ is the duration of the pulse, Δ is the time between the two gradient pulses, D is the diffusion coefficient and b is the diffusion attenuation factor, which contains information regarding the gradient duration and strength used to produce diffusion-weighted images.

Fig. 2 shows the diffusion behaviors of H_2O and TBA^+ ion as a function of the MCC concentration for 30 wt% and 55 wt% TBAH (aq), relative to the diffusion values of the pure solvents D_0. As clearly noticed, the TBA^+ diffusion coefficients display an almost linear decrease with increasing cellulose mass fraction. It is well known that the presence of colloidal particles may reduce the diffusion coefficient of neat solvent. This is due to the hindrance of diffusion paths (Jönsson, Wennerström, Nilsson, & Linse, 1986). However, such effect does not account for the much stronger concentration dependence observed for D_{TBA^+} than for D_{H_2O} (Gentile & Olsson, 2016). The noticeable decrease of the TBA^+ self-diffusion coefficient with the increase of cellulose concentration fits into the picture of cellulose molecules being bound by a well-defined number of TBA^+ ions in fast exchange with the bulk. Therefore, just an average TBA^+ diffusion coefficient is seen on the experimental time.

Therefore, in fast exchange conditions, the accessed diffusion coefficient is a population weighted average (Björn Lindman, Puyal, Kamenka, Brun, & Gunnarsson, 1982)

$$D_i = (1 - P_i)D_i^0 + P_i D_{cell} \tag{2}$$

where P_i represents the fraction of bound molecules regarding species i (*i.e.*, TBA^+, DMSO, H_2O), D_i is the measured diffusion coefficient, D_i^0 is the 'free' molecule of species i diffusion coefficient (here considered the diffusion coefficient in a cellulose-free solution), and D_{cell} represents the diffusion coefficient of cellulose and any other molecules bound to it.

As $D_{cell} \approx 0$, Eq. 2 simplifies to $D_i = (1 - P_i)D_i^0$. Considering the TBA^+ ion, the fraction of bound TBA^+ can be described as

$$P_b = \left(1 - \frac{D}{D^0}\right) \tag{3}$$

If TBA^+ "binds" stoichiometrically to cellulose, α, per AGU, then

$$P_b = \frac{\alpha}{\beta}\frac{M_{TBAH}}{M_{AGU}}\left(\frac{W_{AGU}}{1 - W_{AGU}}\right) \tag{4}$$

where $M_{TBAH} = 259$ g mol^{-1} and $M_{AGU} = 162$ g mol^{-1} represent the molecular weights of TBAH and AGU, respectively. W_{AGU} is the weight fraction of AGU and β represents the weight fraction of TBAH. A similar equation can be obtained concerning the DMSO "binding" to cellulose.

Previously, some of us have shown that the two state model provides a reasonably good description of TBA^+ biding to cellulose; a binding stoichiometry of 1.2 TBA^+/AGU in the 40 wt% TBAH (aq) was reported (Gentile & Olsson, 2016). Similar values were observed for the 30 wt% TBAH (aq) solvent (Fig. 3a) where α ranges from *ca.* 1 to 1.4. For the highest concentration, 55 wt% TBAH (aq), α ranges from *ca.* 2.1 to 3. In both cases, the higher the cellulose concentration, the lower the TBA^+ binding stoichiometry to AGU. This is somehow expected since at low cellulose concentrations, TBA^+ is in considerable large excess. Cellulose can be also seen as a weak acidic polyelectrolyte due to the hydroxyl groups and, as its concentration increases, more OH^- will be consumed to ionize it. Thus, the more cellulose we have in the medium, the higher is the need of OH^- to ionize cellulose to the same α. As expected, the fraction of bound TBA^+ and H_2O, increases with cellulose concentration and TBAH (aq) (Fig. 3b). P_b is considerably larger for TBA^+ than for H_2O, which supports the preferential binding between TBA^+ and AGU, due to both its electrostatic attraction towards the ionized hydroxyl groups on cellulose and the favorable hydrophobic interactions (Gentile & Olsson, 2016; Idström et al., 2017).

The effect of an organic co-solvent, DMSO, was also evaluated by diffusion NMR. Previously we have demonstrated that the TBAH/DMSO mixture is suitable to solubilize reasonably high concentrations of cellulose in rather mild conditions (*i.e.*, dissolution at room temperature and without extensive mixing). Moreover, it was observed that the superior dissolution performance is maintained even for high concentrations of DMSO (Medronho et al., 2017). In ionic liquids, it has been claimed that DMSO can substantially decrease the solvent viscosity, thus benefitting its diffusion and overall dissolution performance (Andanson et al., 2014). Other authors also suggest that the addition of DMSO may enhance cellulose solubility in the ionic liquids by weakening the electrostatic interactions among ions (Li et al., 2016). When compared to the neat solvent (TBAH (aq)), DMSO addition may benefit the dissolution capacity while turning the entire process economically viable.

In Fig. 4, the relative diffusion coefficients of TBA^+, DMSO and water are represented as a function of cellulose mass fraction for different TBAH/DMSO ratios. It should be noted that the TBAH used is not a pure solvent but rather a 40 wt% TBAH (aq).

The first striking observation is that when the cellulose concentration increases, an essentially linear decrease of the relative diffusion coefficients is noted for all TBAH/DMSO ratios. This observation agrees with our previous discussion on the TBAH systems without DMSO (see Fig. 2) but also with related NMR self-diffusion studies on systems containing DMSO, thus suggesting relevant interactions between the solvent components (in particular, TBA^+ ions) and AGU from cellulose. Moreover, one can observe that the TBAH/DMSO ratio affects the relative diffusion coefficients: for a constant cellulose concentration, the higher the DMSO concentration the lower the relative diffusion coefficients of all species (*i.e.*, TBA^+, water and DMSO). A similar trend has been observed by Idström et al. in a related solvent, tetrabutylammonium acetate/DMSO (Idström et al., 2017). As previously discussed, this observation might be due to the advantageous effect of DMSO in

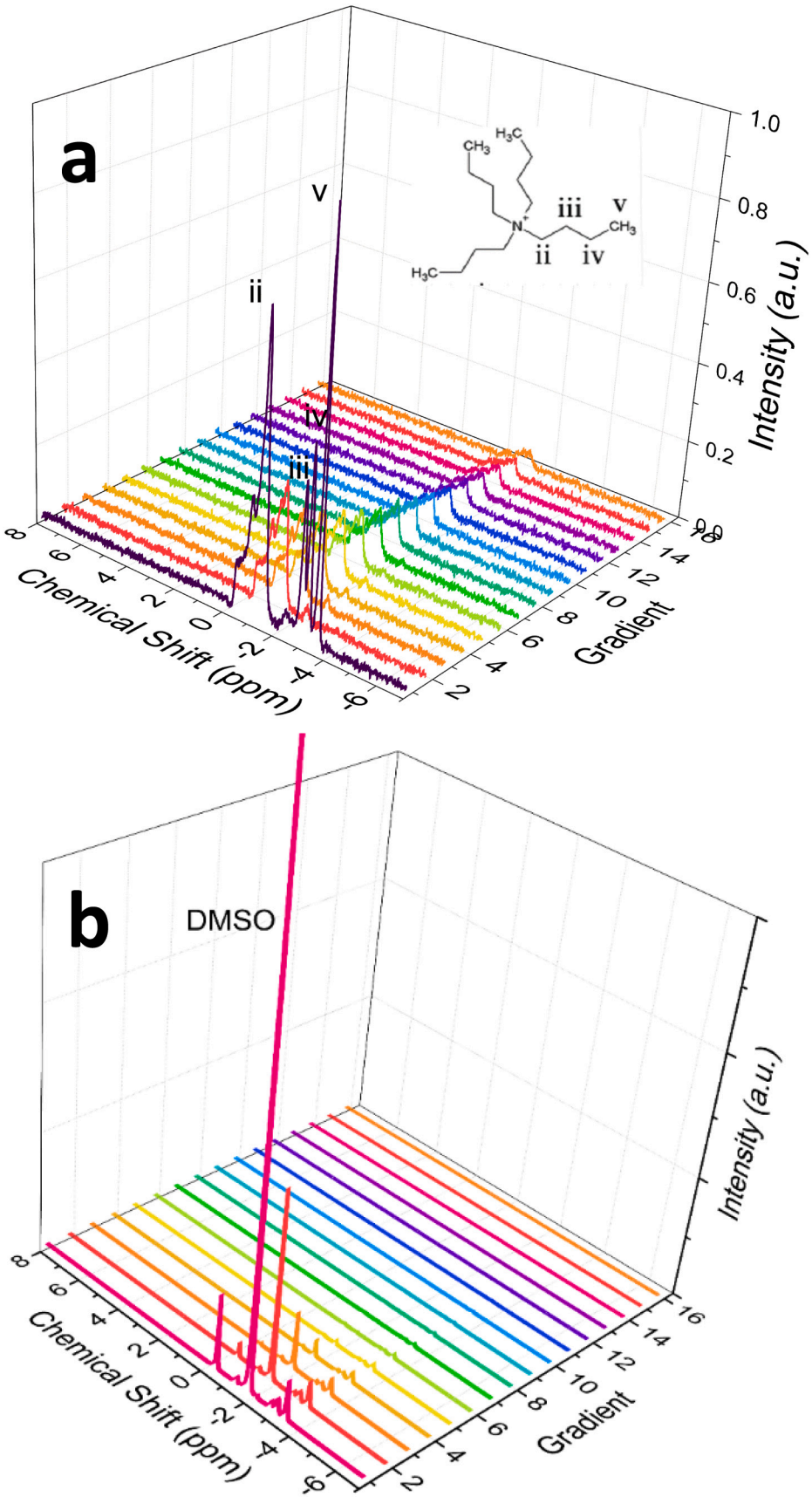

Fig. 1. Schematic representation of typical data from self-diffusion assays. Waterfall plots of TBAH (a) and DMSO (b) signals dependence on gradient strength. The sample consists of a 4 wt% MCC in a TBAH/DMSO (1:1) mixture at 25 °C. The experimental parameters used are described in the method section.

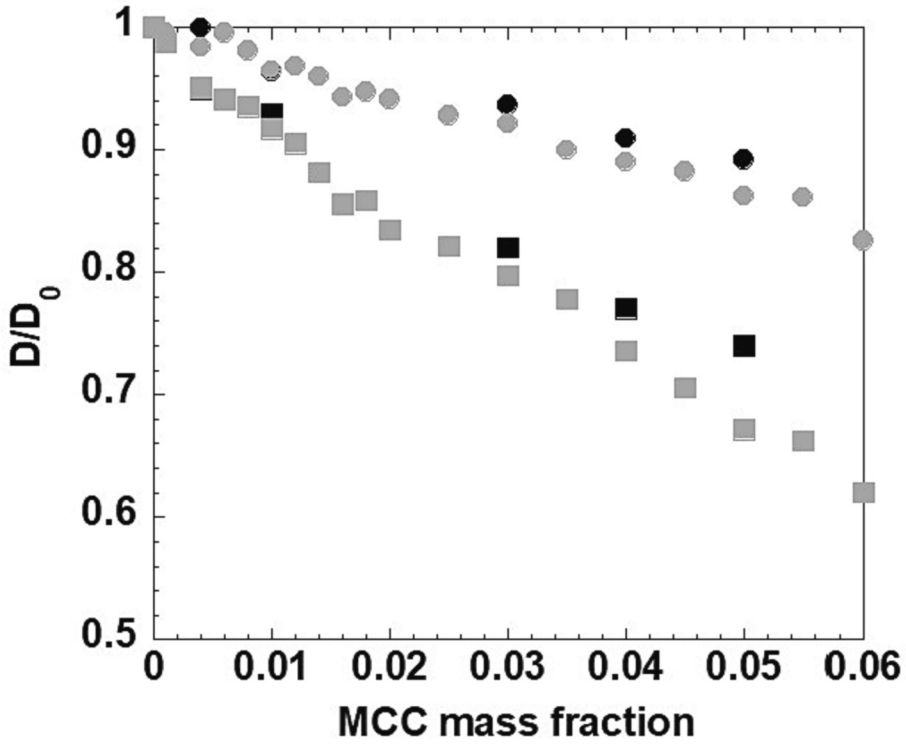

Fig. 2. Relative diffusion coefficients of water (circles) and TBA^+ ions (squares) as a function cellulose for 30 wt% (black symbols) and 55 wt% (grey symbols) TBAH (aq) at 25 °C.

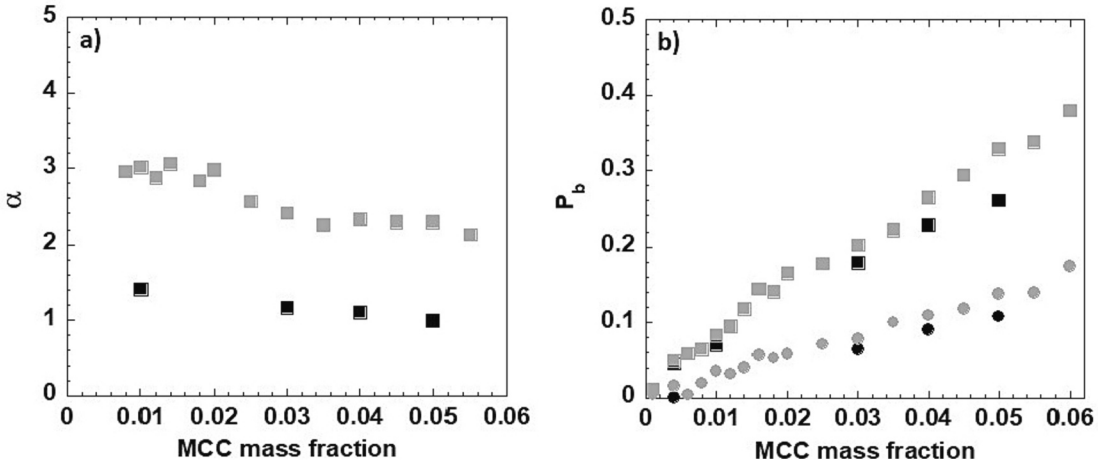

Fig. 3. Representation of the α (a) and P_b (b) parameters as a function of cellulose mass fraction for the solvent systems 30 wt% TBAH (aq) (black symbols) and 55 wt % TBAH (aq) (grey symbols), at 25 °C. The TBA^+ ions and H_2O are represented by squares and circles, respectively.

cellulose swelling and dissolution. Consequently, more individual cellulose molecules disaggregate from microfibrils and become available for solvation. DMSO boosts the solvation capacity of the TBA^+ ions, facilitating the mass transport without compromising the specific cellulose-TBA^+ interactions (Andanson et al., 2014). Consequently, the number of cellulose molecules per unit volume raises, as well as the interactions between all the other species in solution and cellulose.

The relative diffusion coefficients for water and DMSO are rather similar. Nevertheless, DMSO is more influenced by the cellulose content than water, for the different TBAH/DMSO ratios. The differences in the relative diffusion values are much superior for the TBA^+ ion. This is so because, as its concentration decreases with the addition of more DMSO, less TBA^+ cations are present in the bulk and more susceptible to interact with cellulose backbone, slowing down its overall diffusion. The α and P_b parameters for the TBAH/DMSO systems are reported in Fig. 5. For simplicity, only the TBAH/DMSO ratios of 1:1 and 1:4 are represented.

The α parameter is larger for TBAH/DMSO (1:1), which supports the idea that α increases with TBAH concentration in solution. A similar trend was found for the systems without DMSO (see Fig. 3), but with larger α values, which might be due to the higher OH^- concentration and consequent enhanced ionization of cellulose, favoring its binding to TBA^+ ions. Overall, data supports the picture of a gradual titration of the OH groups with increasing pH and thus the α parameter can be regarded as a measure of cellulose's deprotonation state.

Generally, the P_b parameters of TBA^+, water and DMSO increase with increasing cellulose concentration. However, and focusing only on TBA^+, P_b progressively decreases as the TBAH concentration raises. This behavior may be ascribed to stereochemical effects: since TBA^+ ions are

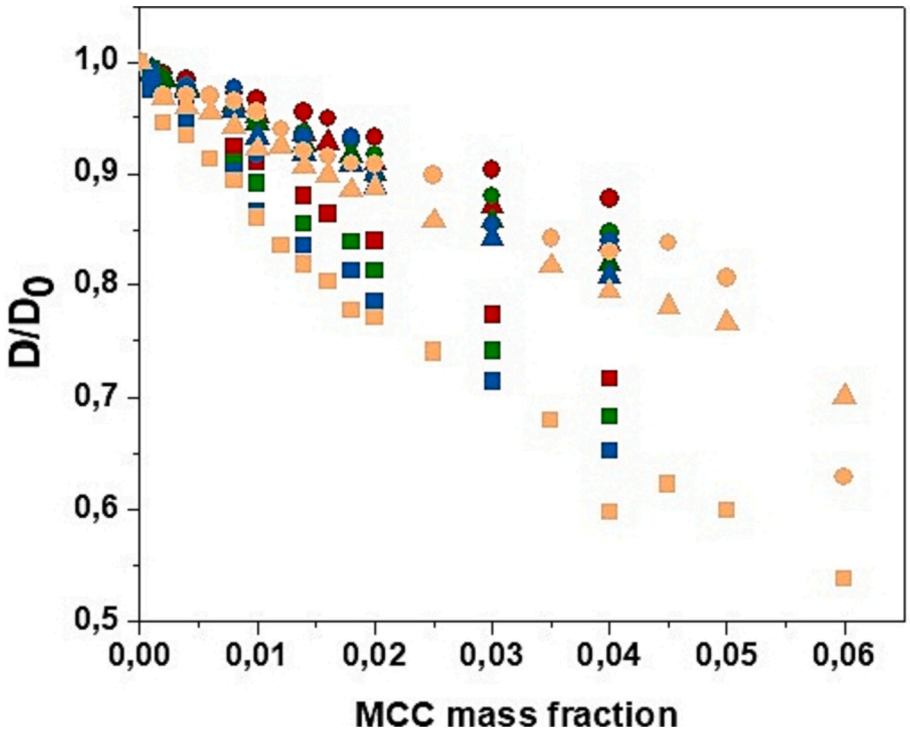

Fig. 4. Relative diffusion coefficients of TBA^+ (squares), water (circles) and DMSO (triangles) as a function of cellulose concentration in the solvent systems composed of 40 wt% TBAH (aq) and DMSO at 1:1 (red symbols); 1:2 (green symbols); 1:3 (blue symbols) and 1:4 (orange symbols) TBAH/DMSO ratios, at 25 °C.

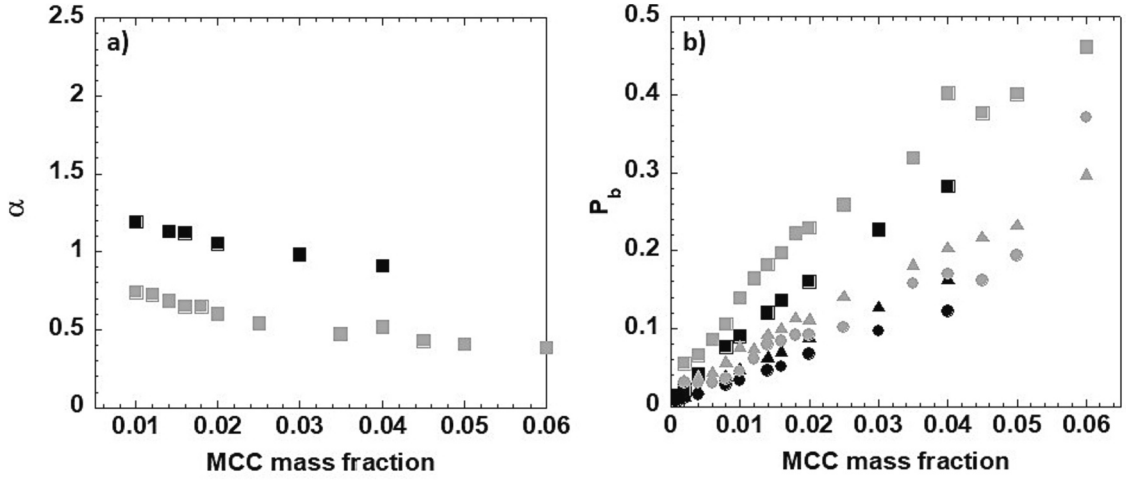

Fig. 5. Representation of the α (a) and P_b (b) parameters as a function of cellulose concentration for the solvent systems TBAH/DMSO (1:1) (black symbols) and TBAH/DMSO (1:4) (grey symbols) at 25 °C. The TBA^+ ions, water and DMSO are represented by squares, circles and triangles, respectively.

bulky, their approach and interaction with the ionized OH groups of cellulose, as well as with its more hydrophobic regions, will be facilitated in lower concentrations. With the raise of TBAH and decline of DMSO in solution, the steric effects are expected to be more noticeable; thus, TBA^+ ions are prevented to interact with cellulose due to the spatial competition with other TBA^+ ions. On the other hand, since DMSO improves cellulose dissolution, this may also contribute to have more molecularly dissolved cellulose molecules at higher DMSO contents, thus also contributing for the enhancement of P_b of TBA^+ ions.

In Fig. 6, the P_b and α parameters are plotted as a function of TBAH concentration for a fixed cellulose concentration (*i.e.*, 4 wt%). The increase of the TBAH concentration decreases its P_b (minimum value of *ca.* 25 %), most likely due to steric effects (see discussion above). In the systems containing the organic co-solvent, the P_b of DMSO is also observed to decrease as the TBAH increases. This is expected, since less DMSO is available as the DMSO/TBAH ratio decreases. The estimated P_b of DMSO is *ca.* 2 times lower than the P_b of TBA^+, which demonstrates the preferential interaction of TBA^+ with cellulose. In fact, the highly polar character of the S—O bond in DMSO places a negative charge density in the oxygen atom. As for the sulfur atom, despite having a positive charge density, it bears a pair of non-bonding electrons (Wen, Kuo, & Jia, 2016). Therefore, both atoms are nucleophilic and not prone to interact with the negatively charged oxygen atoms of ionized cellulose. Moreover, the hydrophobic character of the methyl groups in DMSO is expected to be lower than that of the butyl groups in TBA^+, which further justifies the preference of cellulose for the latter. The fact that the P_b values change less for DMSO than for TBA^+ suggests a weaker adsorption of the former.

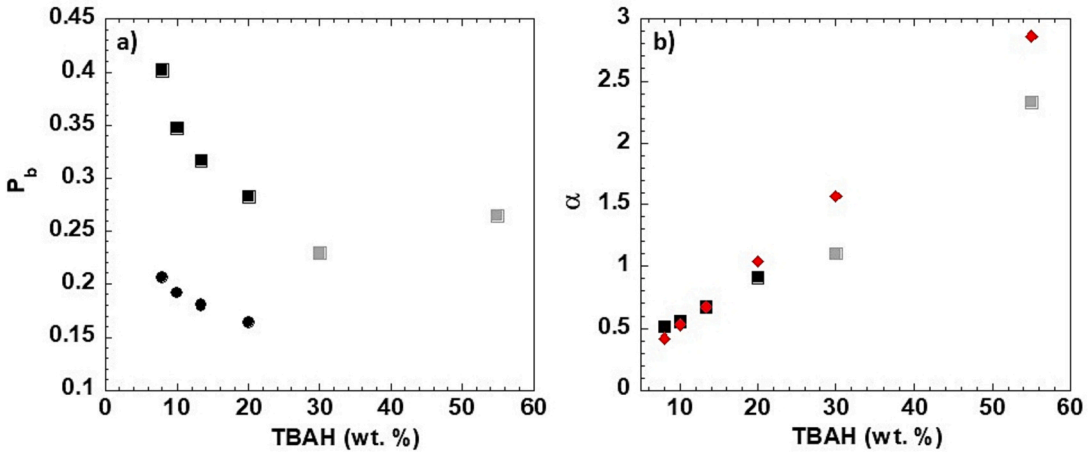

Fig. 6. Representation of the P_b (a) and α (b) parameters as a function of TBAH (aq) concentration for 4 wt% cellulose at 25 °C. The TBA^+ (squares) and DMSO (circles) behavior are represented for systems with (black symbols) and without (grey symbols) organic co-solvent. The n_{TBAH}/n_{AGU} ratio is represented as red diamonds.

The α values of TBA^+ increase with the TBAH concentration. The ionization degree of cellulose is expected to increase with the TBAH concentration, which benefits its interaction with the TBA^+ ions. A good agreement is obtained between α values derived from the diffusion measurements (see Eq. 4) and the n_{TBAH}/n_{AGU} ratio (*i.e.* ratio between the number of moles of OH^- from the different TBAH (aq) solutions and the number of moles of OH groups in cellulose (keeping in mind that each AGU has three OH groups). For larger TBAH concentrations, the n_{TBAH}/n_{AGU} ratio over-estimates the effective binding stoichiometry, α, obtained from diffusion measurements. The reason relies on the fact that the simple n_{TBAH}/n_{AGU} ratio does not account for steric effects, which are expected to be particularly relevant for higher TBAH concentrations. Nevertheless, the simple n_{TBAH}/n_{AGU} ratio captures the α tendency with great accuracy, reinforcing the idea that the TBA^+ binding to cellulose is preferentially driven by its electrostatic attraction with the ionized OH groups in cellulose.

5. Conclusions

The molecular self-diffusion coefficients were accessed in cellulose solutions, in 30 wt% and 55 wt% TBAH (aq) and in TBAH (aq)/DMSO at different weight fraction ratios. The binding stoichiometry, α, is observed to be strongly dependent on the TBAH (aq) concentration, which suggests that TBA^+ ions bind to cellulose preferentially *via* electrostatic attraction towards the deprotonated hydroxyl groups in cellulose. The amphiphilic features of the TBA^+ may also contribute. Data supports the picture of a progressive titration of the OH groups with increasing pH and thus α is here suggested as a measure of the deprotonation state of cellulose.

The fraction of bound molecules, P_b, increases with the cellulose content but decreases with TBAH (aq) concentration, most likely due to steric effects associated to the bulkiness of the TBA^+ ions. The steric and electrostatic repulsions among bound TBA^+ cations are likely to hinder cellulose association, thus favoring a molecularly-like dissolved state. DMSO facilitates cellulose dissolution, not only by tuning the solvent viscosity (enhancing mass transport), but also by solvating cellulose (here the binding is not in the same sense as with the TBA^+ ions), which facilitates further interaction between the TBA^+ ions and cellulose.

This study represents a significant step forward in the understanding the critical aspects in cellulose dissolution in onium-based systems and sheds light on the dissolution mechanism, particularly contributing to unravel critical cellulose-solvent interactions and role of co-solvents. We do expect such knowledge to be beneficial for the development of novel cellulose-based materials with improved properties.

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CRediT authorship contribution statement

Bruno Medronho: Conceptualization, Writing- Original draft preparation, Writing- Reviewing and Editing, Supervision, Project administration, Funding acquisition Ana Pereira: Conceptualization, Validation, Formal Analysis, Investigation, Writing- Original draft preparation Hugo Duarte: Investigation, Writing - Review & Editing Luigi Gentile: Conceptualization, Methodology, Validation, Formal Analysis, Investigation, Writing - Review & Editing, Supervision Ana Rosa da Costa: Writing - Review & Editing, Formal Analysis Anabela Romano: Writing - Review & Editing, Supervision Ulf Olsson: Conceptualization, Methodology, Validation, Formal Analysis, Resources, Writing - Review & Editing, Supervision, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.carbpol.2022.120440.

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