Supporting information for "On the dissolution of cellulose in tetrabutylammonium acetate/dimethyl sulfoxide: A frustrated solvent"

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1 NMR spectra

An example ^{1}H spectrum for cellulose-free solvent of 2:7 TBAAc:DMSO weight ratio is shown in Figure S1. In Figure S2, ^{13}C spectra for the same solvent with and wthout 10 wt% cellulose are shown.

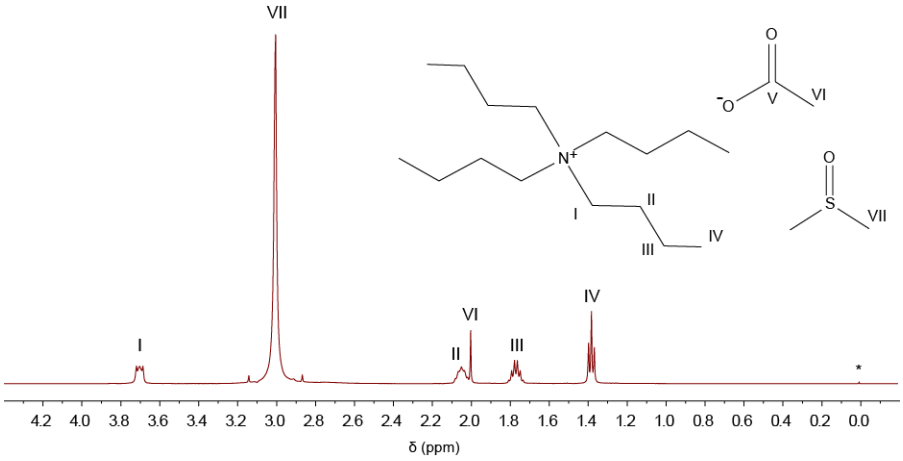

Fig. S1 Example ^{1}H spectrum and labeled molecular structures of all components of the solvent: TBA^{+} (I,II,III,IV), acetate (V, VI), and DMSO (VII). Hydrogen atoms are labeled according to the carbon atom to which they are bonded; hence the absence of peak V in the spectrum. Star (*) denotes the internal-external TMSP-d_4 reference.

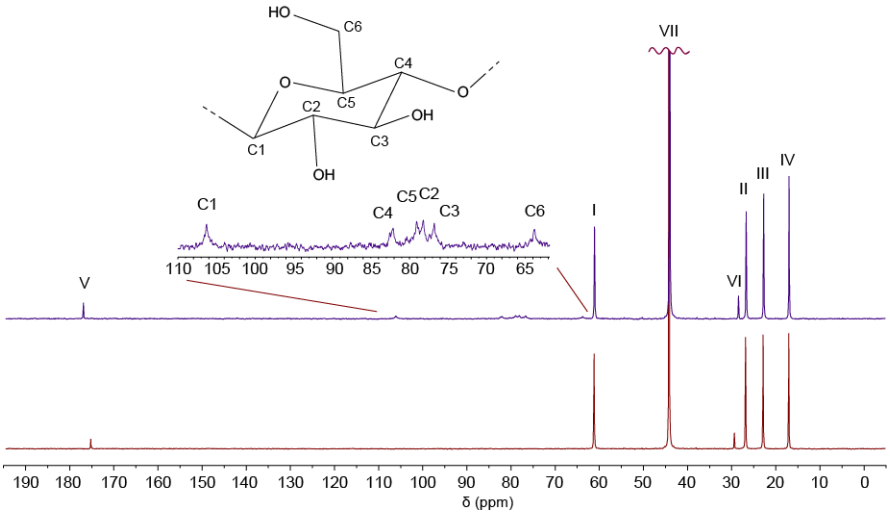

Fig. S2 Example ^{13}C spectra with (blue) and without (red) cellulose, labeled as in Fig S1 and according to the cellulose structure.

2 Contact life times

We take two atoms to be in contact if they are within a given distance, here 0.72 nm, from each other. We analyze the lifetimes of contact states in terms of what we call the *survival function* $s(t)$. We start by defining the ion pair *existence matrix*, the elements of which are

$$e_{ij} = 1 \tag{1}$$

if anion i and cation j form an ion pair and

$$e_{ij} = 0 \tag{2}$$

otherwise. The time correlation function of each element in the existence matrix is

$$c_{ij}(t) = \langle e_{ij}(t) e_{ij}(0) \rangle - \langle e_{ij} \rangle^2, \tag{3}$$

where $\langle \cdots \rangle$ denoted ensemble average. The first term of the RHS is to be interpreted as shorthand for *the ensemble average of the product of the value at a given time and the value at a time t later*. The survival function is given by

$$s(t) = \frac{1}{N} \sum_i \sum_j c_{ij}(t), \tag{4}$$

where N is the number of ions of each species. Optionally, the survival function can be normalized such that $s(0) = 1$. Otherwise, $s(0)$ can be identified with the average proportion of ion pairs.

To estimate an average lifetime, we fitted a stretched exponential,

$$f(t) = \alpha \exp(-(t/\tau)^{\beta}), \tag{5}$$

to the survival functions. The stretched exponential form can be interpreted as representing a distribution of exponential decays with different half-lives, with the average half-life given by

$$\langle \tau \rangle = \frac{\tau}{\beta}\Gamma(1/\beta), \tag{6}$$

which we take to be the ion-pair lifetime. We identify α, an approximant to $s(0)$, as the population of ion pairs, rather than the actual, directly computed $s(0)$. Effectively, this introduces a time cut-off of 10 ps, the time between frames, in the survival time for the contact to be counted.

3 Modelling of SAXS data

The scattering intensity in the Pedersen-Schurtenberger model (PSM) (Pedersen and Schurtenberger (1996)) was calculated as

$$I(q) = cKM_wP(q) \tag{7}$$

where K is the optical constant given by

$$K = \frac{\Delta\rho^2}{d_c^2 N_A}. \tag{8}$$

Here, $\Delta\rho$ =3.5$\times 10^{10}$ cm^{-2} is the scattering length density (SLD) difference between cellulose and solvent and $d_c = 1.5$ g/cm^3 is the cellulose density. The model parameters used in these calculations were a contour length of 90 nm and a persistence length of 2.5 nm (Behrens et al (2016)), the latter corresponding to ca. 5 glucose units. The contour length corresponds to an assumed average degree of polymerization of 180 (Löfgren (2015)).

The aggregates were modeled as fractal clusters, using the corrected Beaucage model (Hammouda (2010)), where the the fractal cluster is described in terms of the radius of gyration of the cluster $R_{g,c}$ and the fractal dimension d. The cluster form factor $P_c(q)$ can be written as (Hammouda (2010))

$$P_c(q) = \exp\left(-\frac{q^2R_{g.c}^2}{3}\right) + \frac{C}{q^d}\left(\mathrm{erf}\left(\frac{qR_{g,c}}{\sqrt{6}}\right)\right)^{3d} \tag{9}$$

with

$$C = \frac{d}{R_{g,c}^d}\left(\frac{6d^2}{(2+d)(2+2d)}\right)^{d/2}\Gamma(d/2). \tag{10}$$

However, this describes the scattering only at lower $q-$values where we are not sensitive to the structural details of individual chains. Assuming that the clusters dominate the scattering at lower $q-$values, we write $I_c(q) = c_cK_{SAXS}M_{w,c}P_c(q)$, where c_c and $M_{w,c}$ refer to the total cellulose concentration in the clusters and the effective cluster molecular weight, respectively. $c_c = \beta c$, where $\beta \leq 1$ is the fraction of cellulose

molecules participating in clusters. $M_{w,c}$ can be written as $M_{w,c} = n_{agg} M_w$, where n_{agg} is the aggregation number, i.e. the average number of cellulose chains in the clusters. In Figure 8a of the main text we show a calculated scattering curve, $I_c(q)$, as a green solid line, that is in good agreement with the experimental. In the calculated curve we have used $\beta n_{agg} = 70$, $R_{g,c} = 140$ Å and $d = 2.4$.

References

Behrens MA, Holdaway JA, Nosrati P, Olsson U (2016) On the dissolution state of cellulose in aqueous tetrabutylammonium hydroxide solutions. RSC Adv 6:30,199–30,204

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