High-resolution ^{13}C NMR studies of cellulose and cellulose oligomers in ionic liquid solutions†

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High-resolution ^{13}C NMR studies of cellulose and cellulose oligomers dissolved in the ionic liquid (IL) 1-butyl-3-methylimidazolium chloride ([C$_4$mim]Cl) show that the β-(1→4)-linked glucose oligomers are disordered in this medium and have a conformational behavior which parallels the one observed in water, and thus, reveal that the polymer is disordered in IL solution as well.

While ionic liquids (ILs) have been known for decades, their enormous potential as environmentally affable solvents has come to light only recently.[1–3] Among their main advantages over conventional solvent systems are their negligible vapor pressure and thermal stability of many ILs over a wide range of temperatures.[2,3] Furthermore, the solvent properties of ILs can be fine tuned through modification of the chemical structure of their cation and anion moieties, allowing them to dissolve both polar and non-polar solutes.[2–4] Of particular interest in this regard are earlier results which showed that celluloses from a variety of sources could be readily dissolved in concentrations of up to 25 wt% in the IL 1-butyl-3-methylimidazolium chloride ([C$_4$mim]Cl, Fig. 1a).[5] The chloride ions present in [C$_4$mim]Cl solutions, which are non-hydrated and in a concentration of approximately 20 wt%, effectively break the extensive hydrogen bonding network of the polysaccharide by interacting with its hydroxyl groups, thereby promoting cellulose dissolution with no apparent degradation of the glycosidic bonds.[5]

In order to better understand how [C$_4$mim]Cl effects cellulose dissolution, the conformational behavior of the polysaccharide upon solvation by this IL needs to be investigated. Towards this goal, we carried out a high-resolution NMR study of cellulose and cellulose oligomers in [C$_4$mim]Cl solution (Fig. 1b). We and others have shown that the chemical shifts of glycosidic bond carbons hold a periodic dependence with the conformation of the glycosidic linkage.[6–9] This has made ^{13}C NMR spectroscopy a very useful tool in the study of the conformational preferences of repetitive polysaccharides both in the solid state as well as in aqueous solution.[7–11] As described in this report, the technique proved to be equally valuable for our purposes.

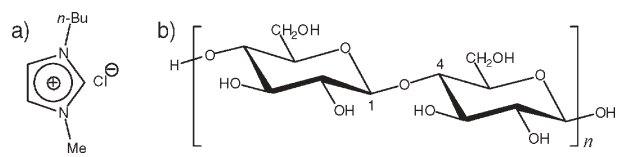

Fig. 1 Structures of [C$_4$mim]Cl (a), and cellobiose (n = 1), cellotetraose (n = 2), cellohexaose (n = 3), and cellulose (n = 400 to 1000) (b).

† Electronic supplementary information (ESI) available: detailed assignments of the ^{13}C spectra of cellulose and cellulose oligomers in [C$_4$mim]Cl/DMSO-d$_6$. See http://www.rsc.org/suppdata/cc/b4/b417745b/

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While [C$_4$mim]Cl displays no signals in the 55 to 120 ppm region of the ^{13}C NMR spectrum that could interfere with the carbohydrate resonances,[3] solutions of this IL are quite viscous and oftentimes solidify near room temperature making it a non-ideal NMR solvent.[3,5] As evidenced by the ^{13}C NMR spectra of 5 wt% cellobiose in neat [C$_4$mim]Cl recorded at 40 °C (Fig. 2a),‡ this high viscosity reduces molecular tumbling, resulting in lower resolution and sensitivity. Furthermore, the IL solutions become increasingly viscous as the length of the dissolved cellulose oligomer increases. However, this limitation can be overcome easily by raising the temperature of the samples. The resulting decrease in viscosity is evidenced by an improvement in resolution

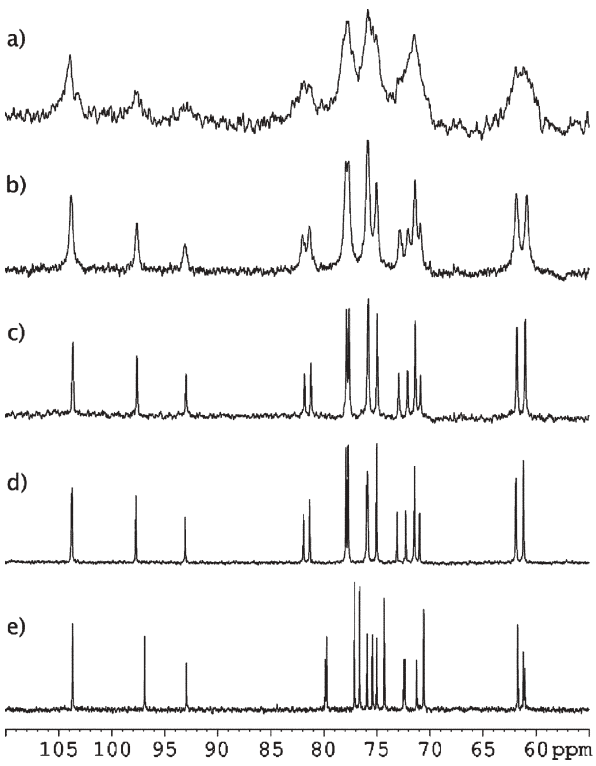

Fig. 2 ^{13}C NMR spectra of 5 wt% cellobiose solutions in [C$_4$mim]Cl at 40 (a), 65 (b), and 90 °C (c), in [C$_4$mim]Cl/DMSO-d$_6$ at 90 °C (d), and in D$_2$O at 25 °C (e).

roughly proportional to probe temperature (Fig. 2a–c), with the spectrum recorded at 90 °C showing baseline resolution for most signals. The addition of 15 wt% DMSO-d_6 to the [C_4mim]Cl solution further improves resolution (Fig. 2d). Indeed, spectra of cellobiose in [C_4mim]Cl/DMSO-d_6 at 90 °C and in D_2O at 25 °C (Fig. 2e) are comparably well resolved. It is important to note that the addition of DMSO-d_6 as a co-solvent has no impact on the chemical sifts observed in neat [C_4mim]Cl for any of the oligomers studied, with the largest variations being less than 0.1 ppm. Thus, it is valid to assume that the solvation dynamics and conformational preferences of these molecules in the presense or absence of this co-solvent are comparable.

Fig. 3 shows the ^{13}C NMR spectra obtained for the 5 wt% solutions of the β-(1→4)-linked glucose oligomers in [C_4mim]Cl/DMSO-d_6 at 90 °C.† Resonances for the internal C1 and C4 carbons in the di-, tetra-, and hexasaccharide are observed at 103.7 and 81.3 ppm, 103.3 and 80.7 ppm, and 103.1 and 80.1 ppm, respectively. These values are comparable with those recorded in aqueous solution (103.6 to 103.2 ppm for C1 and 79.9 to 79.0 for C4).[10] The chemical shifts for the C4 carbon of the non-reducing ends and for the C1α and C1β anomers of the reducing ends of the three oligomers in [C_4mim]Cl/DMSO-d_6 solution also compare well with those observed in water.[10,]† On the other hand, the signals for the internal C1 and C4 carbons in cellobiose, cellotetraose, and cellohexaose in the solid state occur at 104.6 and 85.0 ppm, 108.3 and 89.7 ppm, and 108.3 and 89.3 ppm, respectively.[10] Our results therefore show that despite the extreme differences in chemical and physical properties between the two solvent systems, there is a similar time-averaging of ^{13}C resonances in aqueous and IL solutions. Since these phenomena are governed by the internal mobility of the solutes, our data suggest that the oligomers have comparable conformational preferences and are disordered in the two media.

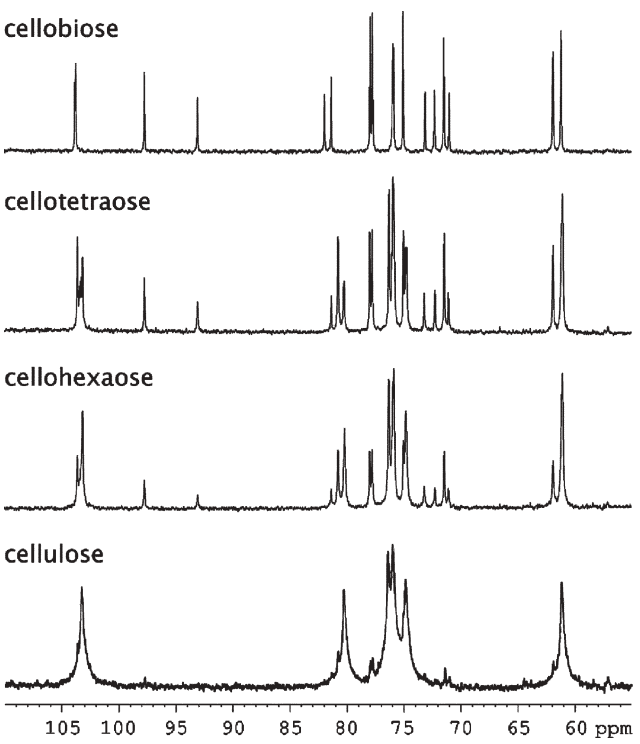

Fig. 3 ^{13}C NMR spectra of cellulose oligomers and cellulose in [C_4mim]Cl/DMSO-d_6 solutions at 90 °C. The carbohydrate concentration was 5 wt% in all cases.

The ^{13}C NMR spectrum of 5% cellulose in [C_4mim]Cl/DMSO-d_6 at 90 °C shows signals at 103.2 and 80.2 ppm corresponding to the C1 and C4 carbons, respectively (Fig. 3). These chemical shifts are virtually identical to those observed for the cellulose oligomers, indicating that the resonances of the polymer and the oligomers are affected by a similar time-averaging regime. Hence, the conformational behavior of cellulose in [C_4mim]Cl solution resembles the one observed for the smaller β-(1→4)-linked glucose fragments, and this polysaccharide appears to be disordered in this medium as well. Equally convincing is the fact that the chemical shifts for the C1 and C4 carbons for the cellulose II ordered polymorph measured in the solid state are 4.7 and 8.7 ppm downfield,[10] respectively, from those reported here in IL solution.

The spectrum of cellulose also shows minor impurities whose chemical shifts correspond with those of the β-(1→4) glucose oligomers. This could be interpreted as an indication of polymer degradation in [C_4mim]Cl. However, the intensity of these signals did not change even after the samples were subjected to repeated cycles of heating and cooling or kept for prolonged periods of time at 90 °C. Therefore, we believe that these impurities were present in the commercial sample of microcrystalline cellulose used for the studies (Sigma-Aldrich).

In summary, our results indicate that cellulose oligomers are disordered in IL solutions as in aqueous solution despite the considerable differences of the two media, and they also demonstrate that, at least qualitatively, this conformational behavior is conserved for cellulose. The ^{13}C NMR data presented in this preliminary report will be used in combination with our recently developed chemical shift surface method to validate molecular dynamics simulations of cellulose oligomers in [C_4mim]Cl solution.[6,7] These studies will ultimately explain the process of cellulose solvation by ILs at the atomic level.

Finally, this is one of a few ^{13}C NMR studies of cellulose solutions,[12] and perhaps the only one in which a truly nonderivatizing/nondegrading solvent was employed. Moreover, the techniques outlined here further showcase the versatility of ILs and could be easily extended to the analysis of cellulosic materials such as those produced by the wood and cellulose processing industries.

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Notes and references

‡ 5 wt% solutions of cellobiose, cellotetraose, and cellohexaose in [C_4mim]Cl were prepared by heating a mixture of the respective oligosaccharide and the IL to 100 °C with constant stirring.[5] Upon dissolution, the samples were transferred to 5 mm NMR tubes subsequently fitted with capillary inserts containing D_2O required for field-frequency lock. Barring the use of capillary inserts, an analogous approach was followed to prepare 5 wt% solutions and cellulose and its oligomers in [C_4mim]Cl/DMSO-d_6. Proton-decoupled ^{13}C spectra were collected at temperatures between 40–90 °C on a Bruker AVANCE 400 NMR spectrometer operating at a ^{13}C frequency of 100.61 MHz. With the exception of the cellobiose sample in [C_4mim]Cl/DMSO-d_6, which required the accumulation of only 5000 scans, a total of 20 000 scans were collected in all cases. Line broadenings of 10.0, 5.0, and 2.5 Hz were employed to process data recorded in [C_4mim]Cl at 40 °C, [C_4mim]Cl at 65 and 90 °C, and [C_4mim]Cl/DMSO-d_6 at 90 °C, respectively. All spectra were referenced indirectly to the temperature-corrected ^{13}C resonance of dioxane in D_2O.[13]

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