Mechanism of cellulose dissolution in the ionic liquid 1-*n*-butyl-3-methylimidazolium chloride: a ^{13}C and $^{35/37}Cl$ NMR relaxation study on model systems†

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Received (in Columbia, MO, USA) 27th December 2005, Accepted 23rd January 2006
First published as an Advance Article on the web 9th February 2006
DOI: 10.1039/b600586c

^{13}C and $^{35/37}Cl$ NMR relaxation measurements on several model systems demonstrate that the solvation of cellulose by the ionic liquid (IL) 1-*n*-butyl-3-methylimidazolium chloride ([C_4mim]Cl) involves hydrogen-bonding between the carbohydrate hydroxyl protons and the IL chloride ions in a 1 : 1 stoichiometry.

In addition to their potential as environmentally affable solvents with a myriad of synthetic and industrial applications,[1] ionic liquids (ILs) are capable of dissolving complex macromolecules and polymeric materials with high efficiency.[2–6] Of particular interest in this regard have been results obtained with 1-*n*-butyl-3-methylimidazolium chloride ([C_4mim]Cl, Fig. 1). This IL can effect dissolution of celluloses from a variety of sources, silk fibroin, and wool keratin with no degradation of the solutes.[3,4,6] Since most solvent systems currently employed to process these materials have undesirable environmental and chemical characteristics, these findings could have a tremendous impact on industries that depend on natural polymers. More importantly, a variety of chemically and biologically active compounds can be co-dissolved with polymeric solutes in [C_4mim]Cl. In combination with methods for polymer reconstitution from the IL solutions,[3,7] this has enabled us to create an array of novel biopolymer-based functionalized composites unattainable through the use of traditional molecular solvents.[8]

Detailed knowledge of the mechanism governing the dissolution of proteins and polysaccharides in [C_4mim]Cl is critical if this and related ILs are to be used rationally in the processing of biopolymers or for the development of novel synthetic polymer blends and polymer-based composites. In the case of cellulose, the solvation mechanism is proposed to involve the interaction of the IL chloride ions, which are non-hydrated and in a concentration of approximately 20 wt%, with the hydroxyl protons of the carbohydrate.[3] This has the effect of breaking the extensive hydrogen bonding network of the polysaccharide and promotes its dissolution. While indirect, several experimental observations provide evidence in support of this qualitative solvation model. First, [C_4mim]Cl displays the highest hydrogen bonding basicity among commonly used ILs.[9] In addition, 1-*n*-butyl-3-methylimidazolium salts bearing weaker hydrogen bond acceptors or non-coordinating groups as anions are poor cellulose solvents.[3] Finally, ^{13}C NMR studies of cellulose in [C_4mim]Cl solution show that the polymer is disordered in this medium, indicating that its hydrogen bonding network is indeed disrupted.[10]

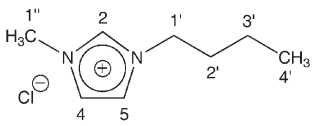

Fig. 1 Structure and numbering of [C_4mim]Cl.

To better understand the mechanism of solvation of cellulose and other polysaccharides by [C_4mim]Cl at the microscopic level, we resorted to NMR relaxation measurements of the IL ^{13}C and $^{35/37}Cl$ nuclei at varying temperatures and concentrations of dissolved carbohydrate. Variations in relaxation times can yield information on the dynamics of both moieties making up the solvent, providing quantitative data regarding their interaction with the solutes. These changes can be particularly pronounced for the chloride ion, as both ^{35}Cl and ^{37}Cl have spin numbers, I, of $^3/_2$, and thus their relaxation rates are not only proportional to their correlation time, τ_c, but also to their asymmetry parameter, η, and nuclear quadrupole moment, Q.[11] Therefore, when the spherical symmetry of an isolated chloride ion is disturbed, marked variations in its relaxation rates are observed as a result of the interaction between the nuclear quadrupole and the non-zero electric field gradient at the nucleus.[11] This has made the study of $^{35/37}Cl$ relaxation parameters ideal to investigate hydrogen bonding, binding, and diffusion of chloride ions in a variety of systems.[12–15]

The dependencies of the cation and anion relaxation times *versus* temperature for neat [C_4mim]Cl are shown in Fig. 2.‡ The imidazolium ring, C-4′, and C-1″ carbons show a transition from the diffusion limit ($\omega_o\tau_c > 1$) to the extreme narrowing ($\omega_o\tau_c < 1$) regions at approximately 70 °C and are less mobile than the remaining *n*-butyl chain carbons, all of which fail to reach a T_1 minimum in the range of temperatures investigated. Analysis of the $^{35/37}Cl$ data for the chloride ions reveals a marked drop in relaxation rates as temperature increases. These findings agree with results from similar studies of [C_2mim]BF_4 and [C_4mim]PF_6,[16,17] and, together with the observed changes in the viscosity of the neat IL, are consistent with the weakening of ion-pairing interactions expected at higher temperatures.[16]

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† Electronic supplementary information (ESI) available: Complete ^{13}C and $^{35/37}Cl$ relaxation and spectral data and derivation of interaction stoichiometry equations. See DOI: 10.1039/b600586c

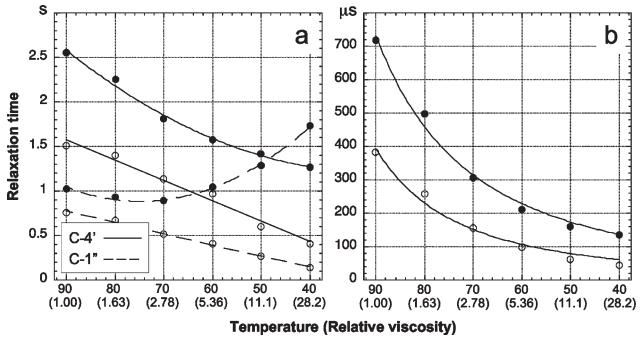

Fig. 2 ^{13}C and ^{35}Cl T_1 (●) and T_2 (○) relaxation times *versus* temperature (°C) for the C-4′ and C-1″ carbons (a) and chloride ions (b) in neat [C_4mim]Cl.†

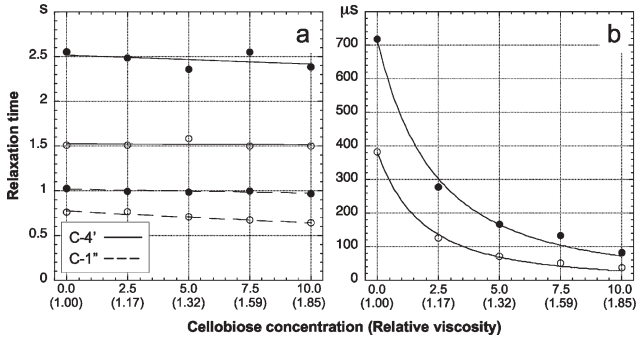

Fig. 3 ^{13}C and ^{35}Cl T_1 (●) and T_2 (○) relaxation times as a function of cellobiose concentration (wt%) for the C-4′ and C-1″ carbons (a) and chloride ions (b) in [C_4mim]Cl measured at 90 °C.†

Variations of the [C_4mim]Cl ^{13}C and $^{35/37}Cl$ relaxation rates as a function of carbohydrate concentration were studied at 90 °C using cellobiose as a model system.‡ There is only a slight variation in the cation relaxation times with solute concentration, consistent with the moderate increase in solution viscosity (Fig. 3a). Indeed, the changes in ^{13}C T_1 and T_2 when going from 0.0 to 10.0 wt% cellobiose correspond roughly with the variations observed between 80 and 90 °C in neat [C_4mim]Cl, indicating that all carbons are in an extreme narrowing relaxation regime ($\omega_o\tau_c < 1$), and suggesting that there are no specific interactions between the IL cation and the sugar solute. On the other hand, there is a dramatic dependency of the $^{35/37}Cl$ relaxation rates for the IL anion on cellobiose concentration (Fig. 3b and 4a). In fact, the T_1 and T_2 for the chloride ions at 10 wt% cellobiose concentration and 90 °C are smaller than those measured for neat [C_4mim]Cl at 40 °C. In contrast to the imidazolium moiety, these data indicate that the anion interacts strongly with the dissolved carbohydrate.

Similar results were obtained when [C_4mim]Cl solutions of glucose were studied under the same conditions (Fig. 4b).†‡ Further inspection of the $^{35/37}Cl$ data obtained for solutions of both carbohydrates reveals that the chloride relaxation rates depend on the molar concentration of free hydroxyl groups (*vide infra*), and suggests that the IL anions interact specifically with the hydroxyl protons of the solutes. In order to corroborate this, analogous relaxation measurements were carried out on solutions of glucose pentaacetate [Glcp(Ac)$_5$],‡ a molecule lacking hydrogen bond donors with a molecular weight comparable to that of cellobiose. Consistent with the conclusion stated above, there is only a minor variation in the ^{13}C as well as the $^{35/37}Cl$ relaxation rates as the concentration of this solute increases (Fig. 4c).† The fact that solutions of Glcp(Ac)$_5$ in [C_4mim]Cl become saturated at concentrations slightly above 5 wt% is also in agreement with the proposed dissolution mechanism.

The $^{35/37}Cl$ linewidth data as a function of solute concentration were then employed to study the interaction stoichiometry between the chloride ion and non-derivatized carbohydrates. For a rapid exchange process, the linewidth of the observed chloride signal is the weighted sum of the linewidths for signals corresponding to free chloride ions and those interacting with the sugar (*i.e.*, bound). Following the approach of Falke and co-workers, the following relationship can be derived:[14,15]

$$\lambda_{obs} = \lambda_{free} + (\lambda_{bound} - \lambda_{free}) N \frac{[\text{carb}]_{\%} \text{MW}_{\text{IL}}}{\text{MW}_{\text{carb}}(100 - [\text{carb}]_{\%})}$$

where λ_{obs}, λ_{free}, and λ_{bound} are the linewidths of the observed, free, and bound $^{35/37}Cl$ signals, respectively, $[\text{carb}]_{\%}$ is the carbohydrate wt% concentration, MW_{IL} and MW_{carb} are the molecular weights of the IL and the sugar, and N is the interaction stoichiometry. The detailed derivation of this relationship and a discussion of its validity are presented as supporting information.† Fits of ^{35}Cl linewidth data to the above equation yield interaction stoichiometries, N, of 7.8 for cellobiose and 4.9 for glucose, and similar estimations are obtained if ^{37}Cl data are used in the calculations.† If the number of free hydroxyl groups in the two sugars is taken

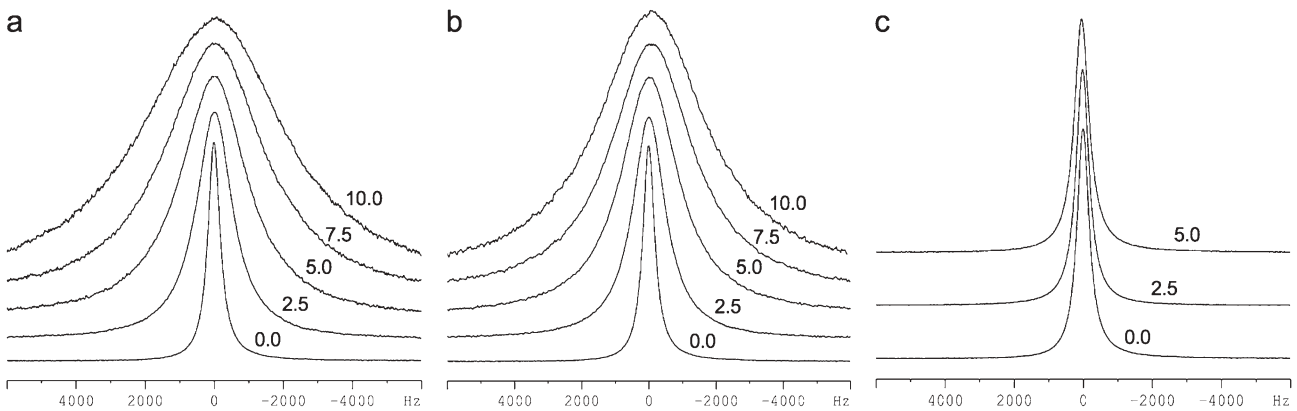

Fig. 4 ^{35}Cl NMR spectra of [C_4mim]Cl *versus* wt% concentration of cellobiose (a), glucose (b), and Glcp(Ac)$_5$ (c) recorded at 90 °C.

into account, these results indicate clearly that, in the range of concentrations considered, the chloride ions interact in a 1:1 ratio with the carbohydrate hydroxyl protons.

Our findings demonstrate conclusively that the solvation of carbohydrates by [C_4mim]Cl involves stoichiometric hydrogen-bonding between the hydroxyl protons of the solutes and the chloride ions of the IL, and therefore provide direct evidence in support of the cellulose dissolution model previously postulated by us. While additional experimental and theoretical studies are needed to fully elucidate this process at the atomic level, the information presented here should be of value in the rational development of new IL-based methods for the processing of polymeric materials with industrial applications.

RCR and GM acknowledge funding from the Camille and Henry Dreyfus Foundation and the NSF CCLI-A&I program (Grant DUE-9952264). RPS and RDR recognize the assistance of the US-EPA STAR program (Grant R83143201-0), the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Research, US-DoE (Grant DE-FG02-96ER14673), and Merck KGaA and their subsidiary EMD Chemicals.

Notes and references

‡ The [C_4mim]Cl used for all the studies was prepared following reported procedures.[18] D-Cellobiose (98%), D-glucose (99%), and β-D-glucose pentaacetate (98%) were purchased from Sigma-Aldrich (Milwaukee, WI) and used as received. Solutions of cellobiose (2.5, 5.0, 7.5, and 10.0 wt%), glucose (2.5, 5.0, 7.5, and 10.0 wt%), and glucose pentaacetate (2.5 and 5.0 wt%) in [C_4mim]Cl were prepared by heating a mixture of the appropriate carbohydrate and the IL to 100 °C with constant stirring. Upon complete dissolution, the samples were transferred to 5 mm NMR tubes that were subsequently fitted with 60 μL co-axial inserts containing DMSO-d_6 required for field-frequency lock. A sample of neat IL was prepared analogously. ^{13}C T_1 and T_2 relaxation times for the IL cation were computed from data obtained with standard ^{13}C–{^{1}H} inversion recovery (180°–t_d–90°–Acq) and Hahn spin-echo (90°–t_d–180°–t_d–Acq) pulse sequences, respectively, using eight t_d increments in both cases. $^{35/37}$Cl T_1 relaxation time measurements for the IL anion were done with an inversion recovery sequence in which the 90° read pulse was substituted by a 90°–90°–90° ARING pulse train to reduce acoustic ringing effects, using twelve t_d increments. Since the natural linewidth (λ) of the $^{35/37}$Cl resonances in the [C_4mim]Cl solutions ranged from several hundred to several thousand Hz, $^{35/37}$Cl T_2 relaxation times were estimated directly from the λ values of the chloride ion signal ($T_2 \approx T_2^* = \frac{1}{2}\pi\lambda$),[13] which were in turn obtained as the average of three independent measurements. Experiments for neat [C_4mim]Cl were performed at temperatures ranging from 40 to 90 °C in 10 °C increments, while for IL solutions at different carbohydrate concentrations measurements were done at 90 °C. All experiments were carried out on a Bruker AVANCE 400 NMR spectrometer equipped with a 5 mm BBO probe, operating at ^{13}C, ^{35}Cl, and ^{37}Cl frequencies of 100.61, 39.21, and 32.64 MHz, respectively. Viscosities for all the solutions were determined under the same conditions employed in the NMR experiments described above, using a ViscoLab 3000 temperature-controlled laboratory viscometer (Cambridge Applied Systems, Inc., Medford, MA).

1 *Ionic Liquids IIIA/B: Fundamentals, Progress, Challenges, and Opportunities*, ed. R. D. Rogers and K. R. Seddon, *ACS Symp. Ser. 901/902*, American Chemical Society, Washington, DC, 2005.
2 D. W. Armstrong, L. He and Y.-S. Liu, *Anal. Chem.*, 1999, **71**, 3873–3876.
3 R. P. Swatloski, S. K. Spear, J. D. Holbrey and R. D. Rogers, *J. Am. Chem. Soc.*, 2002, **124**, 4974–4975.
4 D. M. Phillips, L. F. Drummy, D. G. Conrady, D. M. Fox, R. R. Naik, M. O. Stone, P. C. Trulove, H. C. De Long and R. A. Mantz, *J. Am. Chem. Soc.*, 2004, **126**, 14350–14351.
5 Q. Liu, M. H. A. Janssen, F. van Rantwijk and R. A. Sheldon, *Green Chem.*, 2005, **7**, 39–42.
6 H. Xie, S. Li and S. Zhang, *Green Chem.*, 2005, **7**, 606–608.
7 R. P. Swatloski, R. D. Rogers and J. D. Holbrey, *US Pat.* 6 824 599, 2004.
8 (*a*) J. D. Holbrey, S. K. Spear, M. B. Turner, R. P. Swatloski and R. D. Rogers, *US Pat.* 6 808 557, 2004; (*b*) M. B. Turner, S. K. Spear, J. D. Holbrey and R. D. Rogers, *Biomacromolecules*, 2004, **5**, 1379–1384; (*c*) M. B. Turner, S. K. Spear, J. D. Holbrey, D. T. Daly and R. D. Rogers, *Biomacromolecules*, 2005, **6**, 2497–2502.
9 J. L. Anderson, J. Ding, T. Welton and D. W. Armstrong, *J. Am. Chem. Soc.*, 2002, **124**, 14247–14254.
10 J. S. Moulthrop, R. P. Swatloski, G. Moyna and R. D. Rogers, *Chem. Commun.*, 2005, 1557–1559.
11 T. C. Farrar and E. D. Becker, *Pulse and Fourier Transform NMR. Introduction to Theory and Methods*, Academic Press, New York, 1971, ch. 4, pp. 58–59.
12 D. L. Bryce, M. Gee and R. E. Wasylishen, *J. Phys. Chem. A*, 2001, **105**, 10413–10421.
13 N. Hedin, I. Furó and P. O. Eriksson, *J. Phys. Chem. B*, 2000, **104**, 8544–8547.
14 J. J. Falke, R. J. Pace and S. I. Chan, *J. Biol. Chem.*, 1984, **259**, 6472–6480.
15 J. J. Falke, K. J. Kanes and S. I. Chan, *J. Biol. Chem.*, 1985, **260**, 9545–9551.
16 J.-F. Huang, P.-O. Chen, I-W. Sun and S. P. Wang, *Inorg. Chim. Acta*, 2001, **320**, 7–11.
17 W. R. Carper, P. G. Wahlbeck and A. Dölle, *J. Phys. Chem. A*, 2004, **108**, 6096–6099.
18 J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker and R. D. Rogers, *Green Chem.*, 2001, **3**, 156–164.