

# Solvation of Carbohydrates in $N,N'$ -Dialkylimidazolium Ionic Liquids: A Multinuclear NMR Spectroscopy Study

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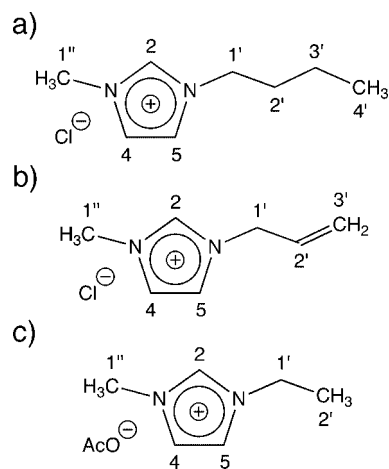
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The solvation of carbohydrates in  $N,N'$ -dialkylimidazolium ionic liquids (ILs) was investigated by means of  $^{13}\text{C}$  and  $^{35/37}\text{Cl}$  NMR relaxation and  $^1\text{H}$  pulsed field gradient stimulated echo (PFG-STE) diffusion measurements. Solutions of model sugars in 1- $n$ -butyl-3-methylimidazolium chloride ( $[\text{C}_4\text{mim}]\text{Cl}$ ), 1-allyl-3-methylimidazolium chloride ( $[\text{C}=\text{C}_2\text{mim}]\text{Cl}$ ), and 1-ethyl-3-methylimidazolium acetate ( $[\text{C}_2\text{mim}][\text{OAc}]$ ) were studied to evaluate the effects of cation and anion structure on the solvation mechanism. In all cases, the changes in the relaxation times of carbon nuclei of the IL cations as a function of carbohydrate concentration are small and consistent with the variation in solution viscosities. Conversely, the  $^{35/37}\text{Cl}$  and  $^{13}\text{C}$  relaxation rates of chloride ions and acetate ion carbons, respectively, have a strong dependency on sugar content. For  $[\text{C}_2\text{mim}][\text{OAc}]$ , the correlation times estimated from  $^{13}\text{C}$  relaxation data for both ions reveal that, as the carbohydrate concentration increases, the reorientation rate of the anion decreases faster than that of the cation. Although not as marked as the variations observed in the relaxation data, similar trends were obtained from the analysis of cation and, in the case of  $[\text{C}_2\text{mim}][\text{OAc}]$ , anion self-diffusion coefficients of the sugar/IL systems. Our results show that the interactions between the IL cation and the solutes are nonspecific, confirm that the process is governed by the interactions between the IL anion and the carbohydrate, and, more importantly, indicate no change in the solvation mechanism regardless of the structure of the anion.

## 1. Introduction

Ionic liquids (ILs) have been the subject of an important number of books and thousands of journal articles over the past decade.<sup>1</sup> While many of the myths originally driving the field of ILs have now been laid to rest, particularly those regarding nonvolatility and thermal stability,<sup>2,3</sup> these materials still hold enormous potential as “green” substitutes for volatile organic compounds (VOCs) currently employed in different industrial processes. However, the most appealing characteristic of ILs is arguably that their properties can be fine-tuned by modifying the chemical structure of their cation and anion moieties.<sup>1,4</sup> These low-melting salts can therefore be tailored to dissolve solutes of wide-ranging polarities and have varied miscibilities with other solvents.<sup>1,5,6</sup> Accordingly, ILs have found uses as alternative media for synthesis and liquid–liquid extractions, catalysts, battery electrolytes, gas storage and heat transport fluids, lubricants, and fuel desulfuration agents.<sup>1,7,8</sup>

Certain ILs have also been shown to readily dissolve carbohydrates from a variety of sources. Perhaps the most notable in this regard are salts belonging to the  $N,N'$ -dialkylimidazolium class such as 1- $n$ -butyl-3-methylimidazolium



**Figure 1.** Structure and numbering of  $[\text{C}_4\text{mim}]\text{Cl}$  (a),  $[\text{C}=\text{C}_2\text{mim}]\text{Cl}$  (b), and  $[\text{C}_2\text{mim}][\text{OAc}]$  (c).

chloride ( $[\text{C}_4\text{mim}]\text{Cl}$ , Figure 1a), an IL that can dissolve cellulose and other polysaccharides in high concentrations and with no prior derivatization.<sup>9,10</sup> In addition to improved methods for the chemical functionalization of these biopolymers,<sup>11,12</sup> this has led to the development of novel and otherwise unattainable polysaccharide-based composites with diverse chemical, physical, and biological properties.<sup>13,14</sup> Furthermore, we and others recently proved that  $[\text{C}_4\text{mim}]\text{Cl}$ -based solvent systems are well-suited to extract carbohydrates present in lignocellulosic materials and other natural matrixes.<sup>10,15,16</sup> Therefore, this and related ILs have the potential to improve currently available methods

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for the utilization of biorenewable resources in areas ranging from the development of advanced materials to the generation of alternative energy.

The common denominator to all the processes summarized above is the solvation of carbohydrates by *N,N'*-dialkylimidazolium ILs, and detailed knowledge of this mechanism is critical both to decipher basic aspects of these processes as well as to improve them and design new ones. We and others have used NMR spectroscopy and molecular dynamics (MD) simulations to investigate this phenomenon on a series of carbohydrate/IL model systems.<sup>17–21</sup> These studies reveal that solvation involves the formation of hydrogen bonds between the anions of the imidazolium salt and the hydroxyl group protons of the sugar in approximately stoichiometric ratios. Although they provide support for the dissolution mechanism postulated originally,<sup>9</sup> these results still fail to explain certain aspects of the process that are critical for future developments of IL-based carbohydrate solvents. To begin with, the specific function of the cation is not entirely understood. While NMR and MD studies of cellobiose/[C<sub>4</sub>mim]Cl and glucose/[C<sub>4</sub>mim]Cl solutions indicate that the cation plays only a peripheral role,<sup>18,19</sup> weak interactions between 1,3-dimethylimidazolium ions ([C<sub>1</sub>mim]<sup>+</sup>) and the carbohydrate hydroxyl group oxygens were reported in simulations of the glucose/[C<sub>1</sub>mim]Cl system.<sup>21</sup> In addition, and despite the fact that imidazolium ILs bearing anions such as acetate, dicyanamide, and phosphonate have been recognized as media for the dissolution of sugars,<sup>22–24</sup> the process has only been investigated in detail for chloride salts.

In this manuscript, we present results from <sup>13</sup>C and <sup>35/37</sup>Cl NMR relaxation experiments and <sup>1</sup>H pulsed field gradient stimulated echo (PFG-STE) diffusion measurements on several model systems which further explain how ILs solvate carbohydrates. Cellobiose and glucose solutions in imidazolium salts known to dissolve cellulose efficiently, including [C<sub>4</sub>mim]Cl, 1-allyl-3-methylimidazolium chloride ([C=C<sub>2</sub>mim]Cl, Figure 1b),<sup>25</sup> and 1-ethyl-3-methylimidazolium acetate ([C<sub>2</sub>mim][OAc], Figure 1c),<sup>22</sup> were considered to evaluate differences in the solvation mechanism as a function of cation and anion structure. In agreement with earlier findings, our results show that there are no specific interactions between the IL cation and the solutes. The data also confirm that the process is governed by the interactions between the IL anion and the carbohydrate, and, more importantly, indicate no change in the solvation mechanism regardless of the structure of the anion.

## 2. Materials and Methods

**2.1. General.** [C<sub>4</sub>mim]Cl and [C=C<sub>2</sub>mim]Cl were prepared following reported procedures,<sup>25,26</sup> and [C<sub>2</sub>mim][OAc] was a gift from the BASF Corporation. D-Cellobiose (98%) and D-glucose (99%) were purchased from Sigma-Aldrich (Milwaukee, WI). The ILs were dried *in vacuo* (1 × 10<sup>-4</sup> Torr) under vigorous stirring at 110 °C for at least 16 h, and all materials were kept under a vacuum until used.

**2.2. NMR Studies.** Solutions of cellobiose and glucose in [C<sub>4</sub>mim]Cl, [C=C<sub>2</sub>mim]Cl, and [C<sub>2</sub>mim][OAc] were prepared by heating a mixture of the appropriate carbohydrate and the IL to 80 °C with constant stirring. Upon complete dissolution, the samples were transferred to 5 mm NMR tubes that were subsequently fitted with 60 μL coaxial inserts containing DMSO-*d*<sub>6</sub> required for field-frequency lock. Samples of the neat ILs were prepared analogously.

Longitudinal (*T*<sub>1</sub>) and transverse (*T*<sub>2</sub>) <sup>13</sup>C relaxation data for the [C<sub>4</sub>mim]<sup>+</sup>, [C=C<sub>2</sub>mim]<sup>+</sup>, [C<sub>2</sub>mim]<sup>+</sup>, and [OAc]<sup>-</sup> ions were obtained with standard <sup>13</sup>C-<sup>1</sup>H inversion recovery (180° –

*t*<sub>d</sub> – 90° – Acq) and Hahn spin-echo (90° – *t*<sub>d</sub>/2 – 180° – *t*<sub>d</sub>/2 – Acq) pulse sequences, respectively, using eight *t*<sub>d</sub> increments in both cases. The *T*<sub>1</sub> and *T*<sub>2</sub> relaxation times were computed by fitting the raw data to exponentials of the form

$$I(t_d) = I_0 \cdot (1 - 2 \cdot e^{-t_d/T_1}) \quad (1)$$

$$I(t_d) = I_0 \cdot e^{-t_d/T_2} \quad (2)$$

where *I*<sub>0</sub>, *T*<sub>1</sub>, and *T*<sub>2</sub> are the fit variables. <sup>35/37</sup>Cl longitudinal relaxation measurements for the Cl<sup>-</sup> anion were performed using 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.<sup>18</sup> Twelve *t*<sub>d</sub> increments were employed in this case, and the values of *T*<sub>1</sub> were estimated using eq 1. Since the natural line width of the <sup>35/37</sup>Cl resonances in the [C<sub>4</sub>mim]Cl and [C=C<sub>2</sub>mim]Cl solutions were several orders of magnitude larger than the line broadening due to magnetic field inhomogeneities, <sup>35/37</sup>Cl *T*<sub>2</sub> relaxation times were estimated directly from the linewidths (*λ*) of the chloride ion signals (*T*<sub>2</sub> ≈ *T*<sub>2</sub>\* = 1/π*λ*).<sup>27</sup> When necessary, NOE enhancement factors for <sup>13</sup>C nuclei of the IL ions were computed from the ratio of the <sup>13</sup>C-<sup>1</sup>H signal area recorded with continuous decoupling relative to that obtained using inverse-gated decoupling. Experiments for the neat ILs were performed in 10 °C increments at temperatures ranging from 40 to 90 °C for [C<sub>4</sub>mim]Cl, 30 to 90 °C for [C=C<sub>2</sub>mim]Cl, and 30 to 80 °C for [C<sub>2</sub>mim][OAc]. Measurements for [C<sub>4</sub>mim]Cl and [C=C<sub>2</sub>mim]Cl carbohydrate solutions were carried out at 90 °C and at 80 °C in the case of [C<sub>2</sub>mim][OAc] solutions.

Diffusion coefficients for ions in the neat ILs and carbohydrate/IL solutions were obtained using the <sup>1</sup>H-detected PFG-STE sequence 90° – *G* – 90° – Δ – 90° – *G* – Acq,<sup>29</sup> where Δ is the diffusion time and *G* represents a bipolar *z*-gradient block of the form *G*<sub>+z</sub> – 180° – *G*<sub>-z</sub> with overall duration δ and strength *g*.<sup>30</sup> For each measurement, a total of 16 data points were recorded by varying the gradient strength linearly while keeping the Δ and δ diffusion parameters constant. Self-diffusion coefficients (*D*) were estimated by fitting the variations in the intensities of the <sup>1</sup>H signals versus gradient strength to mono-Gaussian curves of the form<sup>31</sup>

$$I(g) = I_0 \cdot e^{-\gamma^2 g^2 \delta^2 D \cdot (\Delta - \delta/3)} \quad (3)$$

where *I*<sub>0</sub> and *D* are the fit variables, γ represents the <sup>1</sup>H gyromagnetic ratio, and the remaining parameters were previously defined. The self-diffusion coefficient for any given ion was computed as the average of the *D* values obtained for all its protons. Diffusion measurements were carried out in 10 °C increments at temperatures ranging from 40 to 100 °C for [C<sub>4</sub>mim]Cl and [C=C<sub>2</sub>mim]Cl solutions and from 30 to 90 °C for [C<sub>2</sub>mim][OAc] solutions.

All experiments were carried out on a Bruker AVANCE 400 NMR spectrometer equipped with a 5 mm BBO shielded *z*-gradient probe, operating at <sup>1</sup>H, <sup>13</sup>C, <sup>35</sup>Cl, and <sup>37</sup>Cl frequencies of 400.13, 100.61, 39.21, and 32.64 MHz, respectively.

**2.3. Viscosity Measurements.** Absolute viscosities for all of the systems were determined under the same conditions employed in the NMR experiments described above, using a ViscoLab 3000 temperature-controlled piston-type viscometer (Cambridge Applied Systems, Inc., Medford, MA).

## 3. Results and Discussion

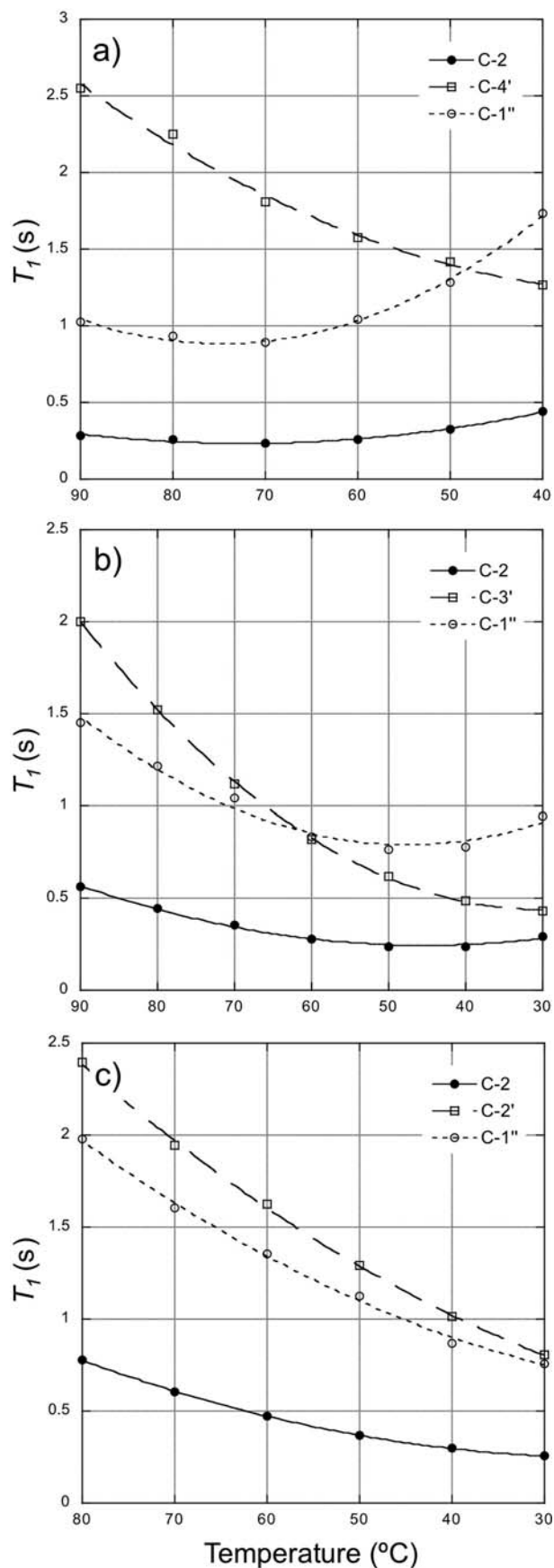
**3.1. <sup>13</sup>C and <sup>35/37</sup>Cl Relaxation Studies.** As we and others have reported, the analysis of longitudinal and transverse relaxation times of the NMR-active nuclei of ILs can yield

valuable information pertaining to the dynamics of both ions and their interactions with solutes. In particular, the marked variation of  $^{35/37}\text{Cl}$  relaxation parameters with changes in the environment of the chloride ion makes these quadrupolar nuclei ideal to investigate sugar/[C<sub>4</sub>mim]Cl solutions.<sup>27,32–34</sup> Indeed, the dependency of  $^{35/37}\text{Cl}$   $T_2$  times with carbohydrate concentration allowed us to establish that the solvation of sugars in this IL occurs through the formation of hydrogen bonds between the chloride ion and the solute hydroxyl group protons.<sup>18</sup> A similar approach was therefore followed to investigate [C=C<sub>2</sub>mim]Cl and [C<sub>2</sub>mim][OAc] carbohydrate solutions. For the latter IL, the concentration dependency of the relaxation times of the acetate carbons is not expected to be as marked as that of the anions in imidazolium chloride salts. However, the relaxation rates of protonated carbons of the cation and anion in [C<sub>2</sub>mim][OAc] solutions can be used to compute changes in their rotational correlation times ( $\tau_c$ ) as a function of carbohydrate concentration. As detailed below, the variations in  $\tau_c$  values of the two ions provide valuable information regarding the solvation mechanism under investigation.

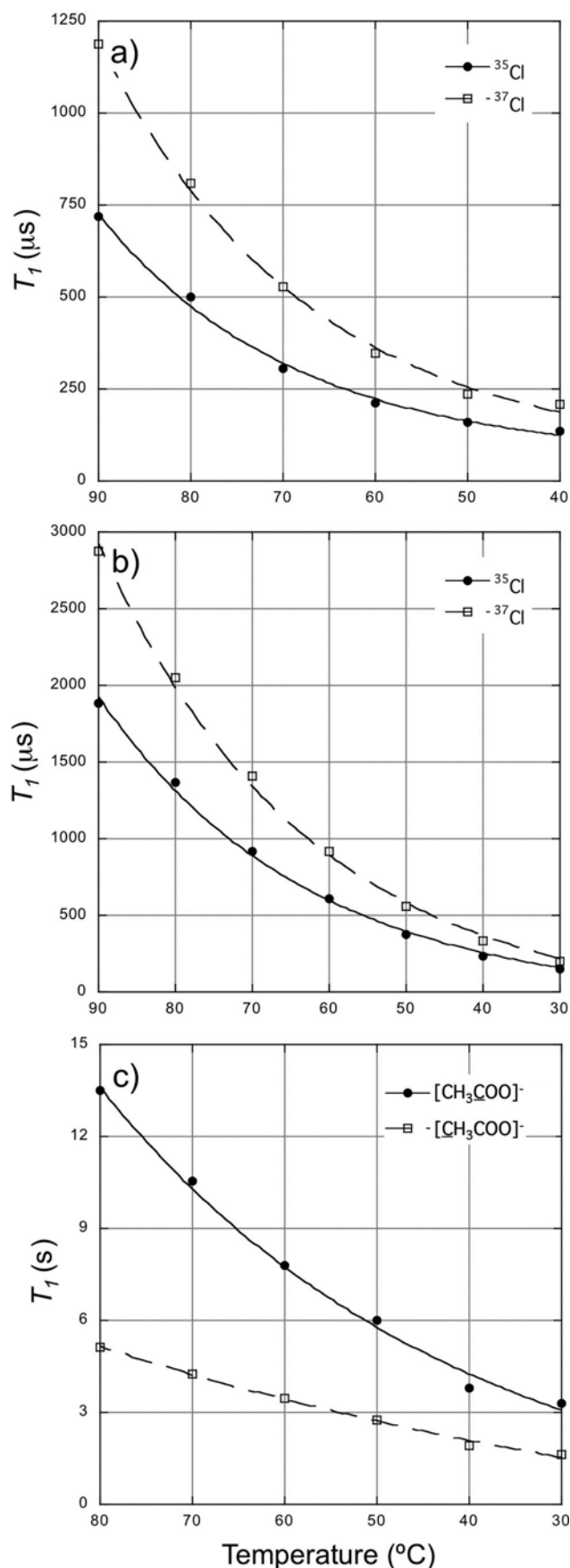
In order to better understand the dynamics of the systems in the absence of solutes, the temperature dependency of the relaxation rates of  $^{13}\text{C}$  and  $^{35/37}\text{Cl}$  nuclei in the neat ILs was studied. Longitudinal relaxation times for selected carbons of the [C<sub>4</sub>mim]<sup>+</sup>, [C=C<sub>2</sub>mim]<sup>+</sup>, and [C<sub>2</sub>mim]<sup>+</sup> ions are presented in Figure 2. The remaining  $T_1$  and  $T_2$  data for all  $^{13}\text{C}$  nuclei are available as Supporting Information. For [C<sub>4</sub>mim]<sup>+</sup>, the  $T_1$  minima observed for the imidazolium ring carbons, C-1', and C-1'' indicate that these nuclei transition from the extreme narrowing ( $\omega_0\tau_c < 1$ ) to the diffusion limit ( $\omega_0\tau_c > 1$ ) relaxation regime at  $\sim 70$  °C (Figure 2a). Due to their higher mobility, the remaining *n*-butyl chain carbons fail to undergo this transition in the range of temperatures studied. Although  $T_1$  minima are also observed for the imidazolium ring carbons, C-1', and C-1'' of the [C=C<sub>2</sub>mim]<sup>+</sup> ion, the transitions occur in the 40–50 °C range (Figure 2b). Consistent with the restriction in mobility imposed by the allyl group, the C2' carbon features a  $T_1$  minimum in the same temperature range. In the case of [C<sub>2</sub>mim]<sup>+</sup>, all carbons remain in the extreme narrowing relaxation regime in the range of temperatures studied (Figure 2c). Due to the smaller size of the ethyl side chain, the C-2' and C-1'' carbons of this cation have similar mobilities. Overall, and in agreement with previous NMR and molecular dynamics simulation studies on analogous systems,<sup>18,19,35–41</sup> the temperature dependency of the  $^{13}\text{C}$  relaxation rates for the three imidazolium cations reflects the variations observed in the viscosities of the neat ILs.

Longitudinal relaxation data as a function of temperature for the anions of the three ILs are presented in Figure 3. The pronounced increase in the  $T_1$  times with rising temperature correlates with the observed changes in viscosity and is consistent with a weakening of interionic interactions.<sup>18</sup> It is also worth noting that, in the range of temperatures considered, the anions of the three ILs remain in the extreme narrowing relaxation regime. This is evidenced by the fact that the anions of both imidazolium chlorides have virtually indistinguishable  $T_1$  and  $T_2$  values,<sup>28</sup> and that no  $T_1$  minima are observed for the carbons of the acetate ion.

On the basis of the results discussed above, the studies of carbohydrate dissolution in both imidazolium chlorides and [C<sub>2</sub>mim][OAc] were carried out at 90 and 80 °C, respectively. All nuclei in the neat ILs are in the extreme narrowing region at these temperatures, and thus, pronounced changes in their relaxation behavior as a function of concentration are indicative



**Figure 2.**  $^{13}\text{C}$   $T_1$  relaxation times as a function of temperature for the C-2, C-4', and C-1'' carbons of [C<sub>4</sub>mim]<sup>+</sup> (a), the C-2, C-3', and C-1'' carbons of [C=C<sub>2</sub>mim]<sup>+</sup> (b), and the C-2, C-2', and C-1'' carbons of [C<sub>2</sub>mim]<sup>+</sup> (c).



**Figure 3.** Temperature dependence of the  $^{35/37}\text{Cl}$   $T_1$  relaxation times for the chloride ion of [C<sub>4</sub>mim]Cl (a) and [C=C<sub>2</sub>mim]Cl (b) and  $^{13}\text{C}$   $T_1$  for the carbonyl and methyl carbons of the [OAc]<sup>-</sup> ion (c).

of IL–solute interactions. As shown in Figure 4, there are only slight variations in the relaxation rates of the carbons in the cations of the three ILs as a function of cellobiose content. In all cases, the changes in  $T_1$  and  $T_2$  times over the whole concentration range are comparable with those observed upon varying the temperature of the neat ILs by 10 °C, and can be rationalized satisfactorily on the basis of changes in solution viscosity.

Conversely, the relaxation parameters of the IL anions are strongly influenced by the presence of sugars. For [C<sub>4</sub>mim]Cl and [C=C<sub>2</sub>mim]Cl solutions, the changes in the longitudinal and transverse relaxation rates of the chloride ion as a function of carbohydrate concentration are vastly larger than those expected on the basis of the variation of the solution viscosity alone (Figure 5a and b). For example, the  $T_1$  and  $T_2$  times for the anion in 10 wt % solutions of cellobiose and glucose in [C<sub>4</sub>mim]Cl at 90 °C, whose viscosities are, respectively, 112.3 and 82.2 cP, are considerably lower than those in the neat IL at 40 °C, which has a viscosity of 1716.0 cP. These large changes in the  $^{35/37}\text{Cl}$  relaxation parameters point to the disruption of the spherical symmetry around the quadrupolar nuclei, and are consistent with the formation of hydrogen bonds between the chloride ions and the carbohydrate hydroxyl group protons.<sup>18</sup> Although less pronounced, the dependency of the  $T_1$  and  $T_2$  times of the acetate carbons with sugar concentration in [C<sub>2</sub>mim][OAc] solutions is also clear (Figure 5c).

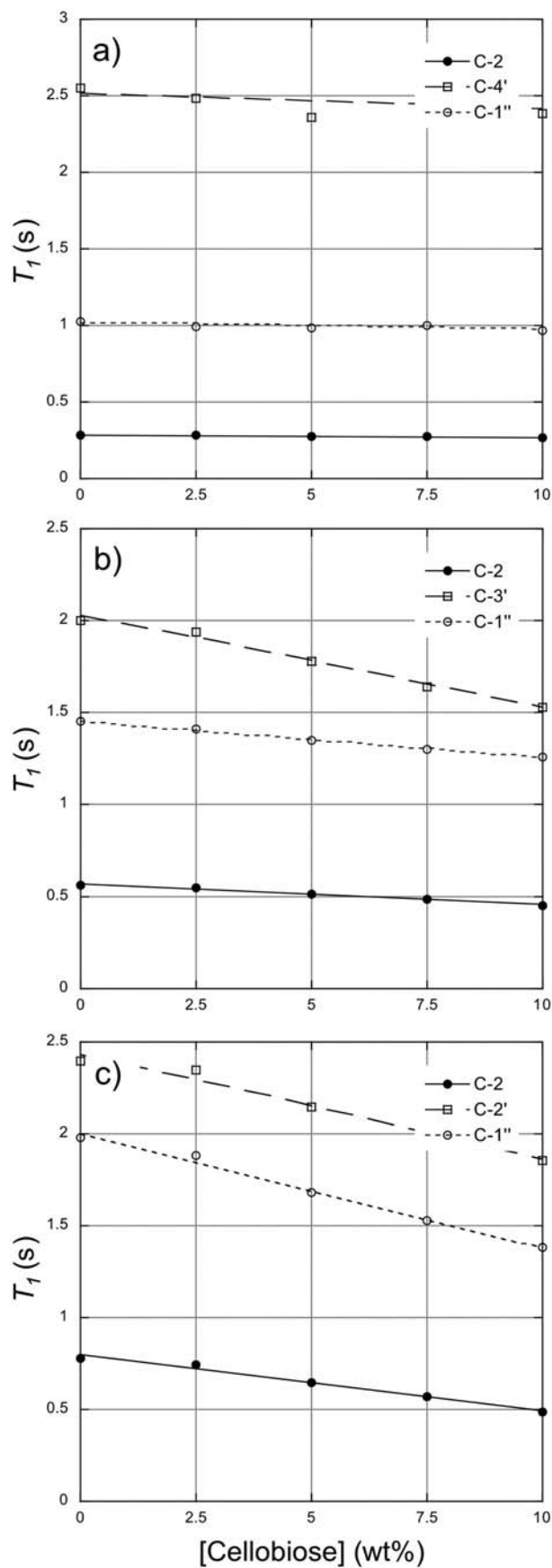
As stated earlier, the relaxation parameters of proton-bearing carbons of [C<sub>2</sub>mim][OAc] can also be used to compute the rotational correlation times of these nuclei, and thus to estimate relative changes in the mobility of both ions as a function of carbohydrate concentration. The longitudinal relaxation of protonated carbons in these systems is due primarily to dipolar interactions with directly bonded protons ( $R_1^D$ ) and chemical shift anisotropy ( $R_1^{\text{CSA}}$ ), both of which are related to their  $\tau_c$ :<sup>28,35–38</sup>

$$\frac{1}{T_1} \equiv R_1 = R_1^D + R_1^{\text{CSA}} \quad (4)$$

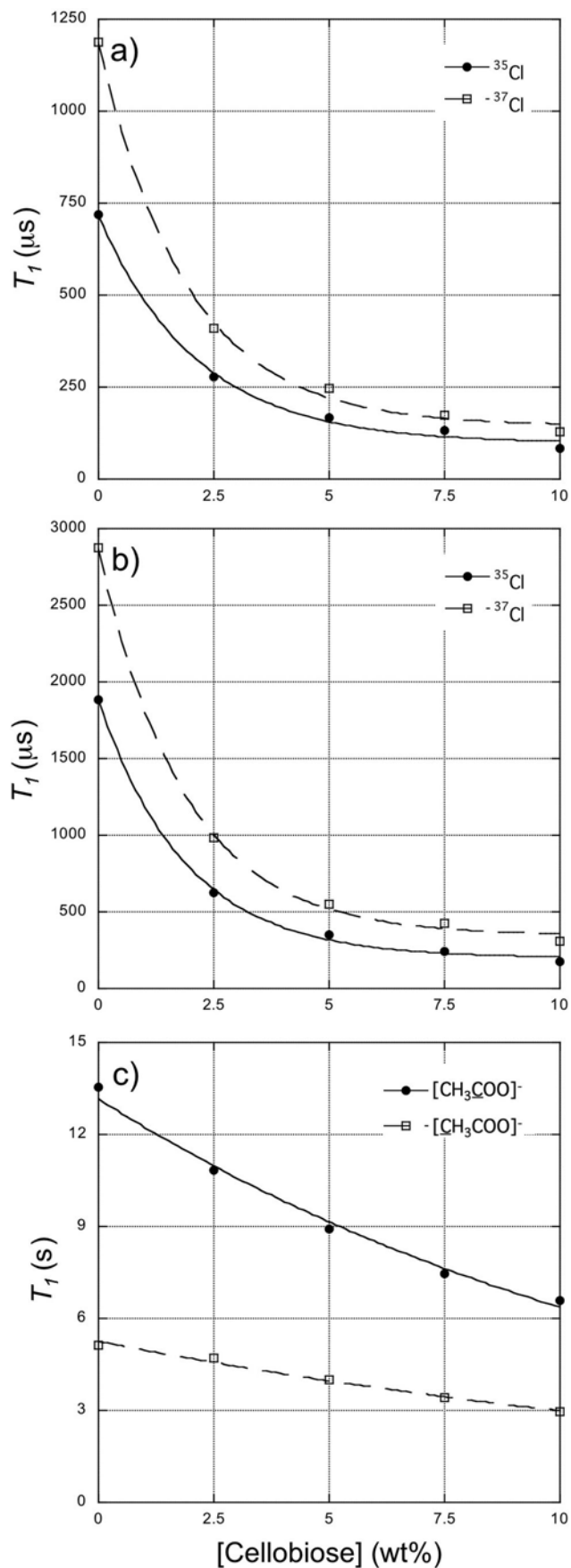
$$R_1^D = \frac{N_H}{40} \cdot \frac{\gamma_C^2 \gamma_H^2 \mu_0^2 \hbar^2}{r_{\text{CH}}^6} \cdot \left( \frac{\tau_c}{1 + (\omega_C - \omega_H)^2 \tau_c^2} + \frac{3\tau_c}{1 + \omega_C^2 \tau_c^2} + \frac{6\tau_c}{1 + (\omega_C + \omega_H)^2 \tau_c^2} \right) \quad (5)$$

$$R_1^{\text{CSA}} = \frac{1}{15} \cdot \gamma_C^2 B_0^2 (\Delta\sigma)^2 \cdot \left( \frac{2\tau_c}{1 + \omega_C^2 \tau_c^2} \right) \quad (6)$$

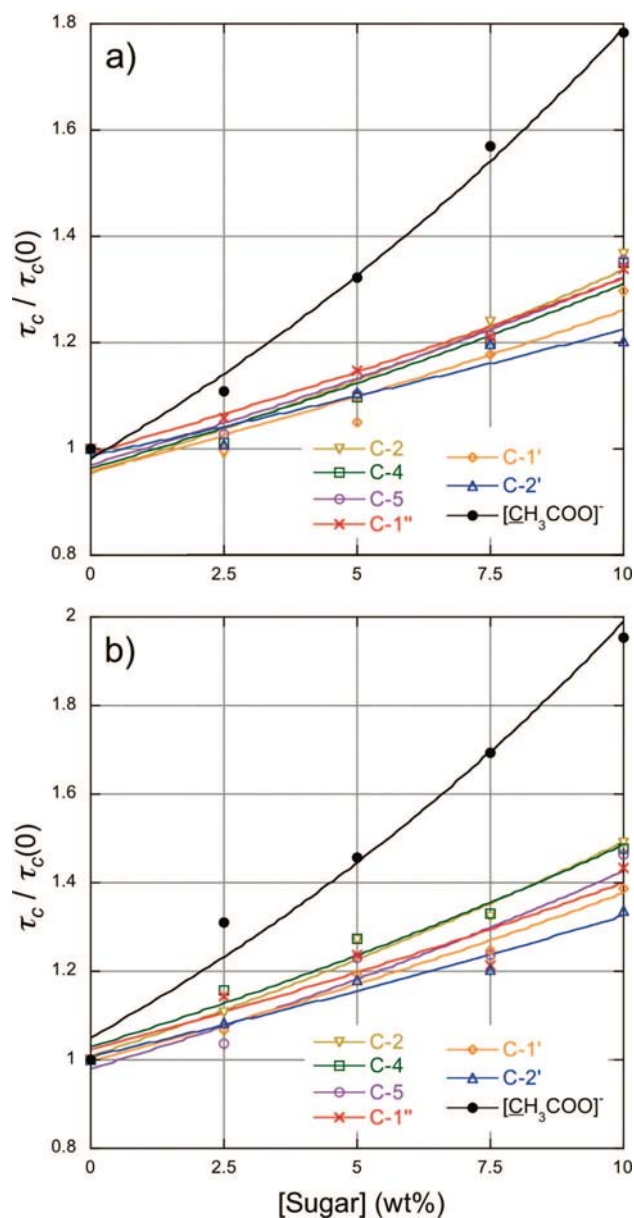
$N_H$  represents the number of attached protons and  $r_{\text{CH}}$  the C–H bond distance,  $\mu_0$  is the permeability of vacuum,  $\gamma_C$  and  $\gamma_H$  are the gyromagnetic ratios of  $^{13}\text{C}$  and  $^1\text{H}$  and  $\omega_C$  and  $\omega_H$  their Larmor frequencies, respectively,  $\hbar$  is the reduced Planck constant,  $B_0$  is the spectrometer magnetic field, and  $\Delta\sigma$  is the chemical shift anisotropy of the nucleus under consideration. The estimation of  $\tau_c$  values using  $T_1$  times and eqs 4–6 is complicated by the fact that  $R_1^{\text{CSA}}$  cannot be obtained without a priori knowledge of  $\Delta\sigma$ . However, Carper and co-workers have recently proposed an iterative approach for the calculation of molecular reorientation rates from experimental  $T_1$  data and NOE enhancement factors for proton-bearing carbons which circumvents the need to compute the contributions of  $R_1^{\text{CSA}}$  to longitudinal relaxation. The method was developed and tested on a number of imidazolium ILs, and is therefore ideal for the systems under scrutiny in the present study.<sup>35–38</sup> Following this approach, the  $\tau_c$  values for protonated carbons of the [C<sub>2</sub>mim]<sup>+</sup> and acetate ions were computed for all sugar/[C<sub>2</sub>mim][OAc]



**Figure 4.**  $^{13}C$   $T_1$  relaxation times as a function of cellobiose concentration for the C-2, C-4', and C-1'' carbons of  $[C_4mim]^+$  (a), the C-2, C-3', and C-1'' carbons of  $[C=C_2mim]^+$  (b), and the C-2, C-2', and C-1'' carbons of  $[C_2mim]^+$  (c).



**Figure 5.**  $^{35/37}Cl$   $T_1$  relaxation times for the chloride ion of  $[C_4mim]Cl$  (a) and  $[C=C_2mim]Cl$  (b) and  $^{13}C$   $T_1$  relaxation times for the carbonyl and methyl carbons of the  $[OAc]^-$  ion (c) as a function of cellobiose concentration.



**Figure 6.** Relative variation in the  $\tau_c$  values of protonated carbons of the  $[\text{C}_2\text{mim}]^+$  and  $[\text{OAc}]^-$  ions as a function of cellobiose (a) and glucose (b) concentration.

solutions, and their relative variation as a function of carbohydrate concentration is presented in Figure 6. The changes in  $\tau_c$  are modest and comparable for all carbons of the  $[\text{C}_2\text{mim}]^+$  ion. This indicates that the rotational mobilities of different regions of the imidazolium moiety are affected similarly by the solute, and is consistent with a lack of strong interactions between the cation and the carbohydrate. On the other hand, the variation of the acetate ion methyl carbon  $\tau_c$  values reveals that the reorientation rate of the anion decreases twice as much as that of the cation with increasing sugar concentration. These results agree with the preliminary conclusions derived from raw longitudinal relaxation data presented earlier, and provide further evidence regarding the presence of specific interactions between the acetate ion and the sugar solute.

**3.2. Diffusion Measurements.** Variations in translational mobility have also been used extensively to investigate ion dynamics in ILs and IL-based systems.<sup>42–47</sup> We therefore determined self-diffusion coefficients for the  $[\text{C}_4\text{mim}]^+$ ,  $[\text{C}=\text{C}_2\text{mim}]^+$ ,  $[\text{C}_2\text{mim}]^+$ , and  $[\text{OAc}]^-$  ions as a function of

temperature in the neat ILs, as well as in 5 and 10 wt % cellobiose and glucose IL solutions (Figure 7). Since the relatively high viscosities of these systems lead to short  $^1\text{H}$   $T_2$  times, PFG-STE techniques were employed to carry out all measurements, as suggested by Annat and co-workers.<sup>47</sup> As expected, there is an inversely proportional relationship between the self-diffusivity of the cations and the viscosity of the neat ILs, with  $D_{[\text{C}_2\text{mim}]^+} > D_{[\text{C}=\text{C}_2\text{mim}]^+} \gg D_{[\text{C}_4\text{mim}]^+}$ . In the case of  $[\text{C}_2\text{mim}][\text{OAc}]$ , it is worth noting that the smaller acetate ion diffuses slower than the imidazolium cation. This behavior has been observed for the  $\text{BF}_4^-$  and  $\text{TFSI}^-$  ions in  $[\text{C}_2\text{mim}]\text{BF}_4$  and  $[\text{C}_2\text{mim}]\text{TFSI}$ , to mention a few examples, and suggests that the anions do not diffuse as isolated species but as part of larger ion aggregates.<sup>44,46</sup>

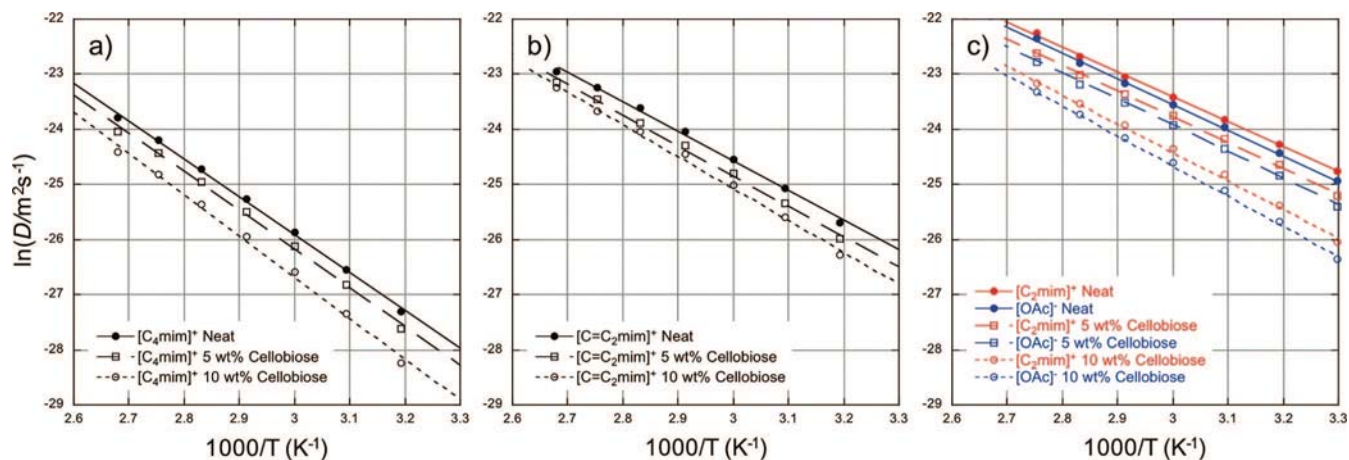
Concomitant with the rise in the viscosity of the systems, there is a substantial decrease in the diffusion coefficients of all species as sugars are dissolved in the ILs. The fast transverse relaxation rates of  $^{35/37}\text{Cl}$  nuclei preclude the determination of the anion self-diffusivity in imidazolium chloride solutions, and as a result, it is impossible to compare the changes in the mobilities of the anions and cations caused by the presence of solutes. On the other hand, both ions in  $[\text{C}_2\text{mim}][\text{OAc}]$  bear protons and the  $D$  of the anion and cation in solutions of this IL can be readily measured (Figure 7c). Although the diffusion of the acetate ion is affected more than that of the imidazolium cation by the dissolved carbohydrates, the differences are minimal and considerably smaller than those observed through analysis of  $^{13}\text{C}$  relaxation data. This is further evidenced if the self-diffusivity data are combined with viscosity measurements and evaluated in terms of the Stokes–Einstein approximation (eq 7):

$$D = \frac{k_B}{c\pi r_s} \cdot \frac{T}{\eta} \quad (7)$$

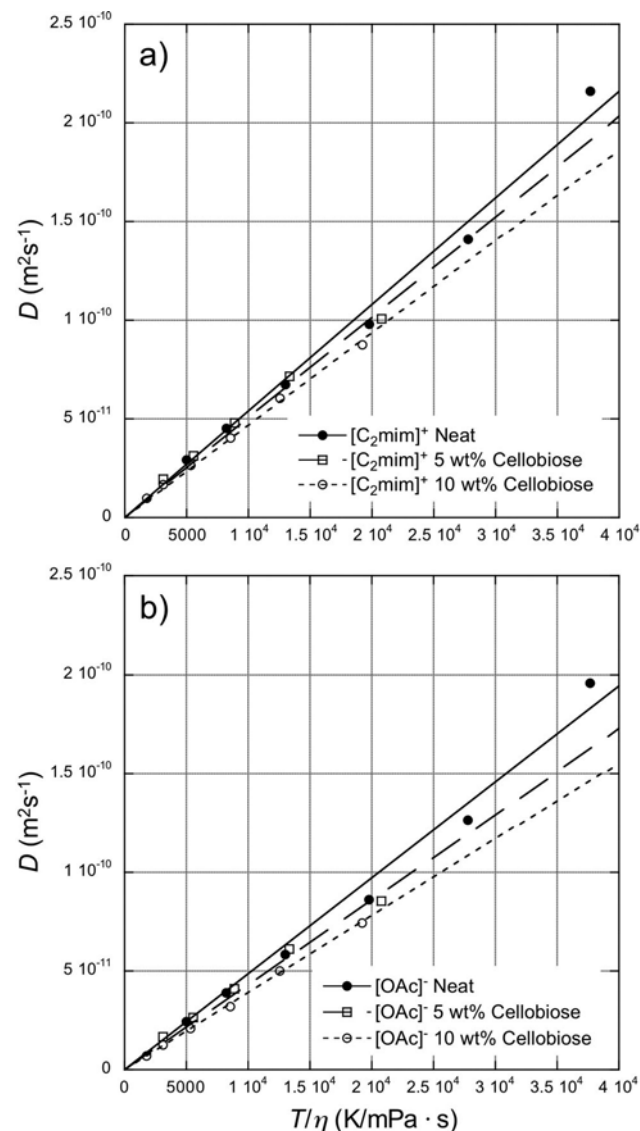
In this equation,  $k_B$  is the Boltzmann constant,  $c$  is a parameter that depends on the approximate shape of the diffusing particle,  $r_s$  is its hydrodynamic or Stokes radius, and  $T$  and  $\eta$  are the temperature and solution viscosity, respectively. Plots of  $D$  versus  $T/\eta$  for the  $[\text{C}_2\text{mim}]^+$  and acetate ions reveal a slight increase in the Stokes radii of both species with increasing carbohydrate concentration (Figure 8). However, the changes in the slope of the curves for both ions are comparable and indicate that the translation of the two is influenced similarly by the solute. This is not surprising considering that even when their local mobility may be affected differently by their interactions with carbohydrates (*vide supra*), comigration of the anion and cation is required to maintain the charge balance of the systems.

#### 4. Conclusions

The results presented in this manuscript provide valuable new information regarding the solvation of carbohydrates by imidazolium ILs. Analysis of  $^{35/37}\text{Cl}$  and  $^{13}\text{C}$  relaxation data for sugar solutions in both imidazolium chlorides and  $[\text{C}_2\text{mim}][\text{OAc}]$  clearly shows that the anions in these ILs are involved in specific interactions with the solutes, and thus govern the solvation process. On the other hand, the  $^{13}\text{C}$  relaxation rates of the imidazolium carbons show no strong correlation with sugar concentration, regardless of the structure of either the cation or the carbohydrate. Despite the fact that these findings alone cannot rule out the presence of weak interactions between the imidazolium ion and the solute recently suggested,<sup>21</sup> they do indicate that their role is not central to the solvation process. For the most part, changes in the diffusion rates of all ions as



**Figure 7.** Arrhenius plots for the  $[C_4mim]^+$  (a),  $[C=C_2mim]^+$  (b),  $[C_2mim]^+$  (c, blue), and  $[OAc]^-$  (c, red) ions in the neat ILs, as well as their 5 and 10 wt % cellobiose solutions.



**Figure 8.** Stokes–Einstein plots for the  $[C_2mim]^+$  (a) and  $[OAc]^-$  (b) ions in the neat IL, as well as its 5 and 10 wt % cellobiose solutions.

a function of carbohydrate concentration parallel changes in solution viscosity. Comparison of these variations with changes in correlation times derived from  $^{13}C$  relaxation data reveals that while the presence of solutes affects the translational

mobility of cations and anions similarly, it has a larger effect on the reorientation rates, and thus local mobilities, of the anions. Although preliminary, these data could be used for the rational development of novel IL-based carbohydrate solvents. For example, since the role of the imidazolium cation in the dissolution mechanism appears to be secondary and related mainly to its size and hydrophobicity,<sup>9</sup> this moiety could be modified to improve the physical properties of the IL without compromising its ability to dissolve polysaccharides.

Additional experimental and theoretical investigations are currently underway to corroborate our conclusions. In particular, the study of systems based on imidazolium phosphonates, some of which have been shown to be efficient cellulose solvents,<sup>24</sup> is of special interest. These ILs bear NMR-active nuclei in both the anion and cation, including  $^{31}P$ ,  $^{13}C$ , and  $^1H$ , and would allow us to confirm the results obtained with  $[C_2mim][OAc]$ . Results from our ongoing studies will be reported in due course.

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**Supporting Information Available:** Complete  $^{13}C$  and  $^{35/37}Cl$  relaxation and  $^1H$  diffusion data and absolute viscosities for all carbohydrate/IL systems investigated. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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