

Hydrogen Bonds in Ionic Liquids Revisited: $^{35/37}\text{Cl}$ NMR Studies of Deuterium Isotope Effects in 1-*n*-Butyl-3-Methylimidazolium Chloride

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Received: July 18, 2007; In Final Form: September 4, 2007

Detailed knowledge of the structure, dynamics, and interionic interactions of ionic liquids (ILs) is critical to understand their physicochemical properties. In this letter, we show that deuterium isotope effects on the chloride ion $^{35/37}\text{Cl}$ NMR signal represent a useful tool in the study of interionic hydrogen bonds in imidazolium chloride ILs. Sizable $\Delta^{35/37}\text{Cl}(\text{H,D})$ values obtained for the model system 1-*n*-butyl-3-methylimidazolium chloride ($[\text{C}_4\text{mim}]\text{Cl}$) upon deuteration of the imidazolium C-2 and C-2,4,5 positions, of nearly 1 and 2 ppm, respectively, show that the approach can readily identify and differentiate $\text{Cl}\cdots\text{H}$ hydrogen bonds between the anion and cation. Our study is one of a few examples in which hydrogen-bonding in ILs has been investigated using deuterium isotope effects and, to our knowledge, the only one employing $^{35/37}\text{Cl}$ NMR to detect these interactions. The methodology described could be easily extended to the study of other systems bearing NMR-active nuclei.

1. Introduction

The interest in ionic liquids (ILs), compounds broadly defined as salts with melting points below 100 °C, has grown enormously over the past decade.¹ Owing to their generally low vapor pressures and high thermal stabilities, these neoteric solvents have potential as “green” alternatives to volatile organic compounds (VOCs).^{1,2} ILs have been used as media for synthesis and extractions, battery electrolytes, gas storage fluids, lubricants, and many other applications with industrial potential.^{1,2} Perhaps more importantly, the physicochemical characteristics of these materials can be controlled by judicious selection of the anion and cation components, allowing for the preparation of ILs with tailored properties and functions.^{1–3} Although this process can be oftentimes guided by simple trial and error, knowledge of the structure, dynamics, and interionic interactions of representative types of ILs could be of critical importance in the design of novel ones.

Some of the best-studied ILs in this regard are those bearing imidazolium cations. Indeed, their structural features and dynamic behavior have been explored through a myriad of experimental and theoretical methods, including X-ray crystallography,^{4–6} neutron diffraction,⁷ NMR and IR spectroscopy,^{8,9} and classical and ab initio molecular dynamics (MD) simulations,^{10–12} to mention just a few. These studies have revealed that the structure of imidazolium-based ILs is characterized by short- and long-range ordering that exists in both the solid and, more remarkably, liquid states.¹³ The majority of these investigations have also identified hydrogen bonds between the anion and the imidazolium cation protons as one of the most important interionic forces at play in this class of ILs.^{4–13} Gaining a

detailed understanding of these interactions is thus critical to the aforementioned rational design efforts.

Most of the experimental data on hydrogen-bonding in imidazolium ILs have been obtained from X-ray studies of frozen samples (i.e., in the solid state).^{4–6} On the other hand, the formation of interionic hydrogen bonds in the liquid phase has been examined mainly indirectly using NMR techniques, including relaxation, NOE, and diffusion measurements,^{8,14,15} or neutron diffraction experiments.⁷ Results from IR studies of protiated versus deuterated *N,N'*-dialkylimidazolium chloroaluminate melts are an exception. In these studies, Dieter et al. show that the imidazolium protons hydrogen-bond to chloride ions in the melts by analysis of deuterium isotope effects on the absorption frequency of aromatic C–H stretching bands.⁹ Prompted by these early findings and on the basis of our previous application of multinuclear NMR spectroscopy to the study of imidazolium chloride IL interactions,¹⁶ we decided to assess if isotope effects on nuclear shieldings could also be employed to directly explore hydrogen bonding in this type of ILs.

Deuterium isotope effects on chemical shifts have long been used to investigate hydrogen bonds.¹⁷ Although most examples involve variations of ^1H and ^{13}C resonances upon H/D substitution (i.e., $\Delta^1\text{H}(\text{H,D})$ and $\Delta^{13}\text{C}(\text{H,D})$),¹⁷ some of the largest deuterium isotope effects due to hydrogen bonding have been observed for halides in aqueous solution.^{17,18} In the case of the chloride ion, for example, the observed $\Delta^{35}\text{Cl}(\text{H,D})$ when going from H_2O to D_2O solution is nearly 5 ppm.¹⁸ Deuterium isotope effects on $^{35/37}\text{Cl}$ NMR resonances could therefore be used as probes in the study of $\text{Cl}\cdots\text{H}$ interactions, particularly in systems such as imidazolium chloride ILs. To test this hypothesis, we chose 1-*n*-butyl-3-methylimidazolium chloride ($[\text{C}_4\text{mim}]\text{Cl}$, Figure 1) and its deuterated isotopologues as models. Apart from

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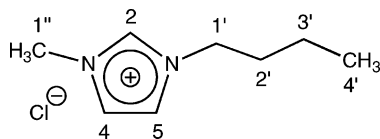


Figure 1. Structure and numbering of [C₄mim]Cl.

being well-characterized and simple to prepare and purify,¹⁹ the ^{35/37}Cl NMR spectral properties of this IL have been extensively studied in our laboratory,¹⁶ making it ideal for our purposes.

2. Materials and Methods

The [C₄mim]Cl used in the studies was prepared following reported procedures,¹⁹ and its deuteration was carried out according to the methods of Dieter et al. with minor modifications.⁹ In the case of [C₄mim]Cl-2-*d*₁, [C₄mim]Cl was dissolved in D₂O in a 1:20 weight ratio, and the resulting solution was heated to reflux under N₂ for 24 h. Excess D₂O was removed by rotary evaporation, and the process was repeated to ensure maximal deuterium incorporation. [C₄mim]Cl-2,4,5-*d*₃ was prepared analogously, except that K₂CO₃ was used to catalyze the H/D substitution of the less-acidic C-4 and C-5 protons. After the two exchange passes and removal of excess D₂O, the crude [C₄mim]Cl-2,4,5-*d*₃ was dissolved in a minimal volume of CH₂Cl₂, the resulting slurry was filtered to remove solid K₂CO₃, and the solvent was removed by rotary evaporation. Both isotopologue samples were then dried in vacuo (1 × 10⁻⁴ Torr) under vigorous stirring at 110 °C for 16 h. Following these protocols, average deuterium incorporation levels of 91% for [C₄mim]Cl-2-*d*₁ and 93% for [C₄mim]Cl-2,4,5-*d*₃ were achieved. All H/D exchange reactions were done in triplicate and alongside reference experiments carried out under identical conditions but using H₂O instead of D₂O.

The dried samples were transferred to 5 mm NMR tubes, and these were subsequently fitted with 60 μL coaxial inserts containing a solution of 0.5 M sodium 3-(trimethylsilyl)propionate-2,2,3,3-*d*₄ (TSP) and 0.5 M NaCl, used respectively as ¹H and ^{35/37}Cl references, in D₂O, which was required for field-frequency lock. Spectra were collected with standard 1D acquisition sequences, using a 30° read pulse for ¹H and a 90°–90°–90° ARING pulse train to reduce acoustic ringing artifacts in ^{35/37}Cl measurements.¹⁶ Data sizes and processing parameters were selected so as to yield a resolution of 0.1 Hz per point or better in the final spectra. Automatic peak-picking, manual pick-picking, and more complex peak-fitting to Lorentzian curves yielded statistically identical ¹H and ^{35/37}Cl chemical shift estimations, and thus, the former method was employed throughout the study. As detailed in earlier reports,¹⁶ experiments were carried out at 90 °C to reduce the effects of viscosity on ^{35/37}Cl linewidths. All spectra were recorded on a Bruker Avance 400 NMR spectrometer equipped with a 5 mm BBO probe, operating at ¹H, ³⁵Cl, and ³⁷Cl frequencies of 400.13, 39.21, and 32.64 MHz, respectively.

3. Results and Discussion

The preparation of deuterated imidazolium chloride IL isotopologues has been previously described,⁹ and we followed these reported methods with slight modifications to obtain [C₄mim]Cl-2-*d*₁ and [C₄mim]Cl-2,4,5-*d*₃ (Figure 2). As stated in the previous section, the H/D exchange reactions involve treating the protiated IL with an excess D₂O, followed by removal of any catalyst employed in the process and thorough drying of the deuterated samples by heating under high vacuum prior to the NMR studies. However, it is well-known that the

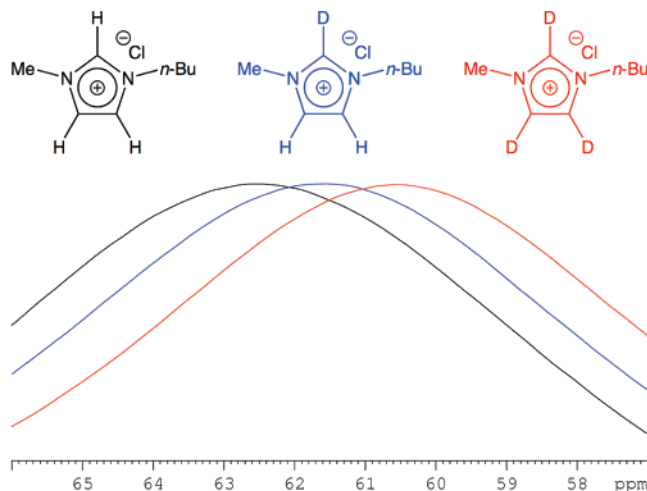
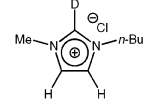
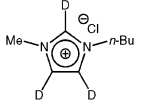


Figure 2. Structure and ³⁵Cl NMR spectra of [C₄mim]Cl (black), [C₄mim]Cl-2-*d*₁ (blue), and [C₄mim]Cl-2,4,5-*d*₃ (red).

TABLE 1: Isotope Effects for the ^{35/37}Cl and ¹H Signals of [C₄mim]Cl Deuterated Isotopologues Relative to the Fully Protiated IL^a

Isotope effect	Isotopologue	
		
Δ ³⁵ Cl(H,D)	1.093 ± 0.068	1.898 ± 0.036
Δ ³⁷ Cl(H,D)	1.194 ± 0.112	1.880 ± 0.109
Δ ¹ H(H,D) ^b	0.002 ± 0.002	0.004 ± 0.003

^a Δ(H,D) values are in ppm and represent the mean of three independent repeats. ^b Isotope effects for all signals in the ¹H spectra of the repeats were averaged prior to computing the Δ¹H(H,D) values reported above.

NMR signals of imidazolium ILs are extremely sensitive to the presence of traces of water and other contaminants.^{8,15} Variations in the concentration of these impurities from sample to sample could thus lead to significant inaccuracies in the Δ(H,D) estimations, particularly if a unique protiated [C₄mim]Cl sample is used as the reference for all measurements. To minimize this potential source of error, all H/D exchange reactions were carried out simultaneously with reference experiments done under identical conditions but using H₂O instead of D₂O. ^{35/37}Cl and ¹H Δ(H,D) values were then computed using spectral data of the deuterated sample against its corresponding protiated pair. As a further precaution, we assessed the effect of known amounts of H₂O on the ¹H and ^{35/37}Cl spectra of [C₄mim]Cl. Spiking one of the protiated IL samples with up to 0.5 wt % H₂O, a concentration easily detectable by ¹H NMR, leads to no appreciable change in its ¹H and ^{35/37}Cl chemical shifts, indicating that the methodology has tolerance for vestigial amounts of moisture that may remain even after high-vacuum drying.

The ³⁵Cl NMR spectrum of a representative [C₄mim]Cl-2-*d*₁ sample, presented in Figure 2, shows an upfield shift for the chloride ion signal of ~1.1 ppm with respect to the fully protiated isotopologue (Table 1). This large, positive Δ³⁵Cl(H,D) indicates a substantial shielding of the ³⁵Cl nuclei upon H/D substitution that is consistent with the stronger Cl···D vis-à-vis Cl···H interactions,¹⁷ and reveals clearly that the anion hydrogen-

bonds to the imidazolium proton at position C-2. In agreement with theory, and barring the larger error in the estimations due to its lower receptivity, identical results were obtained when ^{37}Cl NMR data were used in the analyses (Table 1). As we had originally envisioned, these findings confirm that deuterium isotope effects on the chloride ion $^{35/37}\text{Cl}$ NMR resonance can be used in the study of $\text{Cl}\cdots\text{H}$ hydrogen bonds in imidazolium chloride ILs.

Inspection of the ^{35}Cl NMR spectrum of $[\text{C}_4\text{mim}]\text{Cl}-2,4,5-d_3$, also shown in Figure 2, indicates that the chloride ion signal shifts further upfield following H/D exchange of both the C-2 and C-4/5 positions. This larger $\Delta^{35/37}\text{Cl}(\text{H,D})$, of nearly 1.9 ppm with respect to the protiated salt (Table 1), is consistent with the fact that anions are known to hydrogen-bond to all three imidazolium ring protons in this class of ILs.^{4–13} However, deuterium isotope effects are largely additive,¹⁷ and on the basis of the results obtained for $[\text{C}_4\text{mim}]\text{Cl}-2-d_1$, a $\Delta^{35/37}\text{Cl}(\text{H,D})$ greater than 3.0 ppm should be expected if all three imidazolium protons interacted equally with the anion. In agreement with several crystallographic studies and recent ab initio calculations,^{4–6,20} these results indicate that the hydrogen bonds formed by the protons at positions C-4/5 are weaker than the one involving the C-2 proton. Therefore, deuterium isotope effects on the $^{35/37}\text{Cl}$ signal of the anion are well-suited not only to detect the presence of hydrogen bonds in these ILs but also to differentiate, albeit qualitatively, their relative intensities.

Finally, it is worth noting that in agreement with the fact that deuterium isotope effects on ^1H resonances are either small or undetectable,¹⁷ the $\Delta^1\text{H}(\text{H,D})$ values observed for both deuterated isotopologues of $[\text{C}_4\text{mim}]\text{Cl}$ are statistically negligible (Table 1). As stated above, large perturbations of ^1H resonances would most likely indicate the presence of impurities and moisture in the samples,⁸ and thus, these data further confirm the absence of contaminants in the ILs employed in our studies.

In summary, the results presented here for $[\text{C}_4\text{mim}]\text{Cl}$ demonstrate that deuterium isotope effects on the chloride ion $^{35/37}\text{Cl}$ NMR signal can be employed to study $\text{Cl}\cdots\text{H}$ hydrogen bonds in imidazolium chloride ILs in the liquid state. Our data shows that these effects are sufficiently sensitive to readily identify these interactions as well as to qualitatively differentiate them according to their relative strength. Although $\text{Cl}\cdots\text{H}$ hydrogen bonds in ILs and other classes of compounds are well-known and have been extensively scrutinized,²¹ this is one of the first times in which these interactions have been studied using deuterium isotope effects on $^{35/37}\text{Cl}$ resonances. Indeed, our work is one of a few examples in which these effects are used as structural probes since they were first observed for chloride ions in aqueous solutions by Loewenstein and co-workers nearly 40 years ago.¹⁸ In addition to imidazolium chloride salts, we believe that a similar method could be employed to investigate hydrogen bonds between anions and cations in other ILs. In particular, anions bearing NMR-active nuclei for which sizable deuterium isotope effects are known, including $^{10/11}\text{B}$, ^{13}C , ^{15}N , ^{19}F , and ^{31}P ,^{17,22} should in principle

be amenable to this methodology. Furthermore, the approach outlined in this letter could be extended to the study of hydrogen bonding between ILs and a variety of solutes. In these cases, either the IL or the solute could be deuterated, allowing for different interactions to be scrutinized independently. Our work in these areas is underway, and relevant findings will be reported shortly.

Acknowledgment. The authors thank Mr. Diego A. Fort for insightful discussions during the early stages of the work. Financial support from the NSF CCLI-A&I Program (Grant DUE-9952264) and the Camille and Henry Dreyfus Foundation (Award TH-04-008) is also recognized.

Supporting Information Available: Complete ^1H and $^{35/37}\text{Cl}$ spectral data for all $[\text{C}_4\text{mim}]\text{Cl}$ isotopologue samples considered in the study. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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