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^{35}Cl Solid-State NMR of Halide Ionic Liquids at Ultrahigh Fields

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This Letter describes recent work investigating the solid-state NMR spectra of ^{35}Cl nuclei in an assortment of ionic liquids under static and MAS conditions at field strengths of 9.4 and 21.1 T. At high field it was possible to resolve and extract information from multiple unique crystallographic sites and to resolve otherwise complex spectra that were analyzed to extract information regarding the electric field gradient (EFG) and chemical shift tensors, including their relative orientation. The NMR parameters were found to be typical of organic salts in general.

Introduction

Ionic liquids (ILs) have been known for nearly a century[1] but are recently garnering increased interest due to their unique characteristics. The term room temperature ionic liquid (RTIL) is often used interchangeably with ionic liquid and is by convention defined as an organic salt with a melting point ca. 100 °C or less. We are careful to point out that in this contribution all spectra were acquired from solid samples.

A broad spectrum of tunable properties arises from the customizability of the organic cation and the variety of cation−anion pairings. Common properties that are of central interest include negligible volatility, wide liquidus range and ease of recycling. ILs are finding uses as solvents and reaction media in a large number of diverse applications such as carbon dioxide sensors,[2] catalysis,[3,4] energy storage,[5] nanostructure synthesis,[6,7] and many others.

A great deal of recent effort has gone into the characterization of ILs in order to determine if they have properties that are uniquely different from other liquids.[8−14] The NMR spectra of quadrupolar nuclei offer sensitive ways to learn about the structure of both the liquid and solid phases. To give us some baseline values for the various chemical shift and quadrupolar coupling parameters, we have determined a number of these in the solid state. RTIL anion moieties include but are not limited to tetrafluoroborate, nitrate, perchlorate, and the halides. Here, we have examined chloride salts, demonstrating that spectra can indeed be obtained with sufficient resolution for analysis. Resolving the field-dependent spectral features at lower fields remains a challenge and so high field spectra, both MAS and static, were used to determine both quadrupolar and chemical shift parameters (Table 1).

NMR Tensor Conventions

In this work the Herzfeld−Berger convention for the chemical shift tensor is followed. The span, Ω, describes the maximum width of the pattern and the skew, κ, is a measure of the asymmetry of the tensor. The nuclear electric quadrupolar interaction is the interaction of the electric quadrupole moment of the nucleus (Q) with the surrounding electric field gradient (EFG), which depends on the symmetry of the site. The interaction can be represented by a second-rank tensor: its strength is represented by the nuclear quadrupolar coupling constant, C_Q, and its symmetry is described by the asymmetry parameter, η_Q. Euler angles α, β, and γ describe the relative orientations of the chemical shift and quadrupolar tensors. Here we use the same convention as Mehring.[15,16]

The spectra reported in this work show only the central (−1/2 to +1/2) transition, which carries all of the significant information of interest. It is affected by the second-order quadrupolar coupling as well as the chemical shift interaction and is sensitive to the angles between the two tensors.[19] Because the chemical shift and second-order quadrupolar couplings have opposite magnetic field dependencies, spectra obtained at different fields offer a good confirmation of the parameters determined via simulation.

Experimental Section

[BMMIM]$^+$Cl$^-$, [EMIM]$^+$Cl$^-$ and [MBPyri]$^+$Cl$^-$ were supplied by EMD Chemicals and [BMIM]$^+$Cl$^-$ was supplied by Strem Chemicals. All samples were provided sealed under argon.

Sample Preparation. Samples were lightly ground, packed and sealed into sample tubes under argon since very low concentrations of water can significantly alter RTIL properties.[17,18] Sample tube sizes ranged from 4 mm ceramic MAS tubes on the 900 MHz spectrometer to 5 mm glass tubes for static spectra on the 400 MHz spectrometer. The IUPAC-recommended chemical shift reference was employed (0.1 M solution of NaCl in D_2O) with resonance set to 0 ppm.[21]

Experiments and Data Processing. Solid-state NMR experiments were carried out with the following: a Bruker AVANCE-II 900 MHz NMR spectrometer operating at a magnetic field of 21.1 T (Larmor frequency for ^{35}Cl: 88.19 MHz) using a

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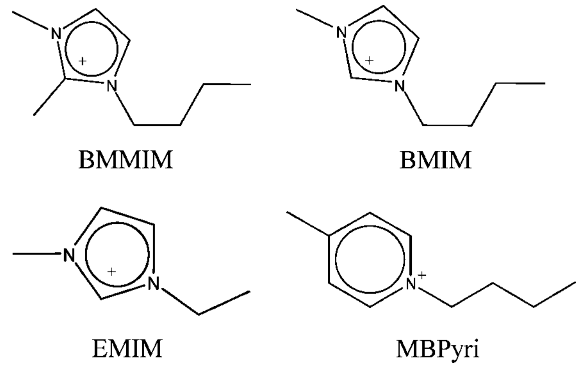
TABLE 1: ^{35}Cl spectrum simulation fit parameters.

cation[a]		C_Q/MHz	η_Q	δ_{iso}/ppm	Ω/ppm	κ	α/deg[b]	β/deg	γ/deg
MBPyri	1	0.857 ± 0.008	0.525 ± 0.005	83.15 ± 0.07					
	2	0.889 ± 0.008	0.08 ± 0.08	70.56 ± 0.04					
BMMIM		0.978 ± 0.004	0.10 ± 0.02	71.60 ± 0.02	77.7 ± 0.2	0.66 ± 0.01	16 ± 1	82.5 ± 0.5	−34 ± 4
EMIM	1	0.808 ± 0.004	0.95 ± 0.01	91.72 ± 0.03					
	2	0.805 ± 0.005	0.20 ± 0.02	74.98 ± 0.04					
	3	0.884 ± 0.004	0.86 ± 0.01	71.36 ± 0.04					
	4	0.972 ± 0.005	0.80 ± 0.01	60.60 ± 0.03					
BMIM		1.500 ± 0.002	0.390 ± 0.005	71.65 ± 0.05	43.5 ± 0.5	−0.45 ± 0.04	78 ± 2	76 ± 1	12 ± 2

[a] See Chart 1 for a list of abbreviations. [b] Euler angles use the ZYZ convention. Quadrupolar parameter errors estimated using MAS 21.15 T spectra, CSA parameter errors estimated using static 21.15 T spectra. Labeled parameters correspond to their respective peaks in Figure 1. Isotropic chemical shifts are reported relative to 0.1 M NaCl in D_2O.

CHART 1: Cations in This Work and Their Abbreviations



standard-bore double-resonance 4 mm MAS NMR probe and a Bruker AVANCE 400 MHz NMR spectrometer operating at a magnetic field of 9.39 T (Larmor frequency for ^{35}Cl: 39.19 MHz) using a Morris Instruments wide-bore double-resonance 7 mm static NMR probe.

The FIDs of the signals acquired in this work were often quite short leading to a loss of information from the initial part of the fid during the ring-down time; to ensure that the experimental lineshapes would be relatively free of distortions, the spectra were acquired with Hahn Echo pulse sequences. Left shifts were applied to ensure processing began at the top of the echo. Proton decoupling was used to improve the resolution of line shape features. A saturated KCl solution was employed to determine $\pi/2$ pulse lengths: On the 9.4 T instrument, the radio frequency pulse length was 2.1 μs at a power of 4 dB; on the 21.1 T it was 6.2 μs at 0 dB.

Simulations and fitting were carried out using the dmfit[19] and TopSpin programs. In dmfit simulations the “Q mas 1/2” model was used for MAS spectra and the Quasar[20] model was used for static spectra.

Results and Discussion

The spectra, experimental and simulated, for the chloride salts are shown in Figure 1. Experimentally determined quadrupolar and CS tensor parameters obtained by simulation of the acquired spectra are listed in Table 1. Spectra acquired under magic angle spinning (MAS) were analyzed first to provide a CT center band line shape; this allowed for the unambiguous determination of C_Q, η_Q and the isotropic chemical shift. The static spectrum of the sample was then analyzed with these parameters held fixed to determine the CS tensor parameters. To further refine the simulations, analysis of spectra acquired at different field strengths was performed. Reported errors on the parameters were obtained by visual inspection of the deviation of the simulation from best fit.

The number of sites observed in each sample agree with the crystal structures available for $[EMIM]^+$, $[BMIM]^+$ and $[BMMIM]^+Cl^-$ [21−24] and the one obtained for $[MnBPyri]^+Cl^-$.[25] A complete set of CS tensor parameters and angles between tensors were found for the single-site samples; multiple-site samples proved more difficult to fully characterize. Please see Chart 1 for structures corresponding to the abbreviations used above.

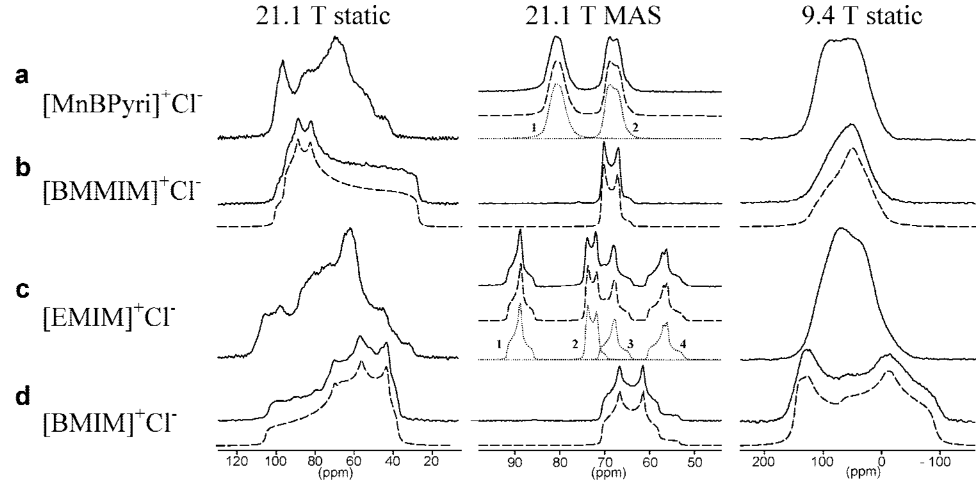


Figure 1. Chloride IL ^{35}Cl spectra of powdered samples: (a) ethylmethylpyridinium; (b) butyldimethylimidazolium; (c) ethylmethylimidazolium; (d) butylmethylimidazolium. Static spectra at 21.15 T (left), MAS spectra at 21.15 T (center) and static spectra at 9.39 T (right). Dashed lines are best-fit calculated spectra with parameters listed in Table 1. Labeled peaks denote corresponding table values. MAS rate = 10kHz.

The observed quadrupolar coupling constants ranged from 0.8 to 1.5 MHz and quadrupolar asymmetry parameters ranged from 0 to 0.95. Typical C_Q values for chloride ions in organic and inorganic salts range from zero to greater than 9.0 MHz.[25−28] The CS tensor values (Table 1) are consistent with those found in other organic−chloride systems; Wasylishen reported values for δ_{iso} of 10−53 ppm for a series of five organic hydrochlorides[29] and Bryce reported 37−120 ppm for another series of ten organic hydrochlorides.[26] Here we observe a relatively narrow range of 61−92 ppm. The same studies by Wasylishen and Bryce reported spans within a range of 45−150 ppm; spans of 44 and 78 ppm are found here. Wasylishen and Bryce investigated hydrogen-bonded chlorides, and hydrogen bonding is generally regarded as an important interaction governing the structure and behavior of imidazolium ILs.[21,22,24] It should be mentioned, however, that at least one ab initio study has been performed in which the authors conclude that the bonding is "considerably different from that of conventional hydrogen bonds".[30,31]

We note that some research has been reported that suggests that the solid state and liquid structures are "similar", although there is considerable controversy.[31−37] We can conclude that for the IL salts studied here the various NMR parameters are completely consistent with values found for organic chloride salts which do not have IL properties. Work on the halogen NMR of the ILs themselves is in progress.

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