

## Probing the local structure of ionic liquid salts with $^{35}\text{Cl}$ , $^{79}\text{Br}$ and $^{127}\text{I}$ solid- and liquid-state NMR

Peter G. Gordon,<sup>a,b</sup> Darren H. Brouwer<sup>b</sup> and John A. Ripmeester<sup>a,b</sup>

(a) Carleton University, Ottawa, Ontario

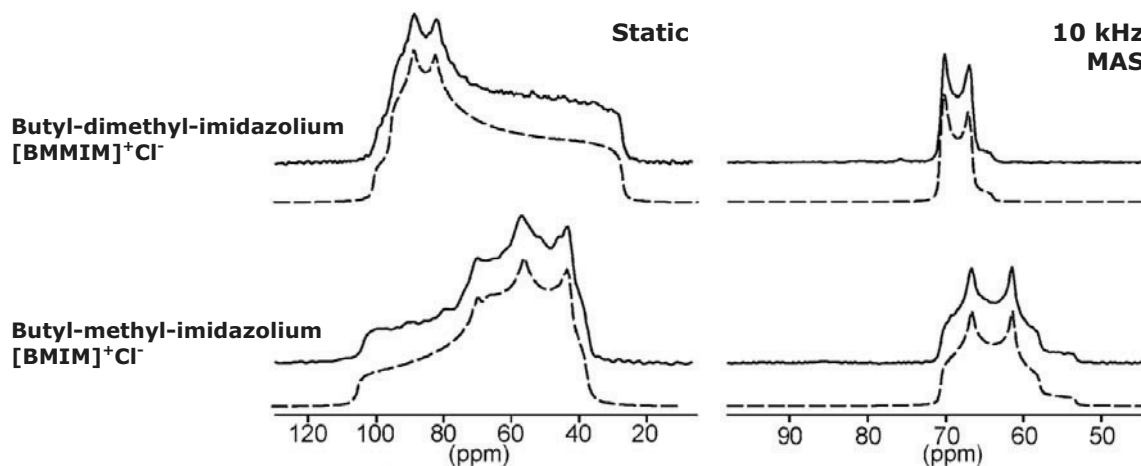
(b) Steacie Institute for Molecular Sciences, NRC, Ottawa, Ontario

[John.Ripmeester@nrc-cnrc.gc.ca](mailto:John.Ripmeester@nrc-cnrc.gc.ca)

Ionic liquids (IL) have been known for nearly a century 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. RTILs are considered part of the *green chemistry* paradigm due to their negligible vapour pressure and ease of recycling. A broad spectrum of tunable properties arises from the customizability of the organic cation and the variety of cation-anion pairings. A great deal of recent effort has gone into the characterization of ionic liquids in order to determine if they have properties that are uniquely different from other liquids. Evidence of liquid state order, observed by IR and Raman spectroscopy, diffraction studies, and simulated by *ab initio* methods, has been reported in the literature.

In this project we investigate the environment of IL halide counterions in the solid and liquid states by multinuclear quadrupolar nuclear magnetic resonance (NMR) spectroscopy [1, 2]. Resolving the field-dependent spectral features of the solid-state samples at lower fields remains a challenge and so high-field spectra at 21.1 T, both MAS and static, were used to determine both quadrupolar and chemical shift parameters.

Solid-state NMR spectra of quadrupolar nuclei involve a number of spin interactions and one of the tools we use to help tease out information from the nuclei is Magic Angle Spinning. For example, MAS



**Figure 1:** 21.1T  $^{35}\text{Cl}$  NMR static and MAS spectra of powdered solid ionic liquids containing chlorine, Butyl-dimethyl-imidazolium (top) and Butyl-methyl-imidazolium (bottom). Dashed lines are best-fit calculated spectra illustrating significant CSA effects in static spectra, which can easily be detected at higher magnetic field strengths.

eliminates anisotropic chemical shielding interactions. By examining spectra under static and MAS conditions, it is possible to determine both quadrupolar and CSA parameters, which provide information as to the local electronic environment of the nuclei. Also, the strength of the magnetic field will affect the lineshape; increasing magnet strength decreases the quadrupolar contribution to the line width, and increases the effect of chemical shift anisotropy (Fig.1). Gathering spectra at different field strengths is an effective way to refine the parameters used in simulating and verifying parameters. For halogen nuclei having large quadrupolar moments the 21.1 T instrument is an essential asset.

It was discovered that for chloride, bromide and iodide ILs in the solid state, the quadrupolar and chemical shift interactions of the halide nucleus are consistent with those found in other solid organic chloride, bromide and iodide salts. Theoretical simulation of the NMR interaction tensors showed reasonable agreement with experimental findings [2]. In addition, our relaxation time measurements demonstrate a lack of significant order on a timescale of  $\sim 10^{-8}$  sec. The results suggest that reports in the literature of observed "structure" must exist on a shorter timescale.

#### References

- [1] P.G. Gordon, D.H. Brouwer, J.A. Ripmeester, "<sup>35</sup>Cl Solid-State NMR of Halide Ionic Liquids at Ultrahigh Fields," *Journal of Physical Chemistry A* **112** (2008) 12527–12529.
- [2] P.G. Gordon, D.H. Brouwer, J.A. Ripmeester, "Probing the Local Structure of Pure Ionic Liquid Salts with <sup>35</sup>Cl, <sup>79</sup>Br and <sup>127</sup>I Solid- and Liquid-State NMR," *ChemPhysChem* (2009) accepted.