ROESY NMR of Basic Ambient-Temperature Chloroaluminate Ionic Liquids

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The ambient-temperature chloroaluminate ionic liquids employed in this study comprise mixtures of 1-ethyl-3-methylimidazolium chloride (ImCl, Figure 1) and aluminum chloride ($AlCl_3$). ImCl itself is an organic salt composed of the Im^+ cation and the chloride anion; however, its melting point is well above room temperature. ImCl and $AlCl_3$ react over a wide range of stoichiometries to yield room-temperature molten salts.[1]

$$\text{ImCl} + \text{AlCl}_3 \rightarrow \text{Im}^+ + \text{AlCl}_4^- \tag{1}$$

The melts are defined as acidic, basic, or neutral if the mole ratio of $AlCl_3$ to ImCl is greater than, less than, or equal to unity. Basic melts contain the chloride and tetrachloroaluminate anions while neutral melts only contain tetrachloroaluminate anions and acidic melts contain tetrachloroaluminate and heptachlorodialuminate anions. Basic melts exhibit a much greater viscosity than their neutral and acidic counterparts. The viscosity at 25 °C of a 1.5:1 ($AlCl_3$:ImCl) acidic melt is 15.3 cP and that of a 1:1 neutral melt is 17.8 cP while that for a 0.4:1 melt is 412 cP.[2] This viscosity increase suggests a structure-making interaction is present in basic melts that is absent in neutral and acidic melts.

The presence of local structure in basic chloroaluminate ionic liquids has been suggested previously.[3−5] Infrared measurements in our laboratory showed strong cation−anion interactions in the basic melts. Data from the C−H stretching region of the infrared spectrum indicated possible hydrogen bonding between Cl^- and H-2 of the imidazole ring.[3] Dymek and coworkers investigated the local structure present in the basic $AlCl_3$−ImCl melts by combining crystallographic and infrared data with theoretical calculations. They found that the crystal structure of ImCl(s) consists of stacks of imidazolium cations with chloride anions interspersed between the stacks such that they are hydrogen bonded to a ring hydrogen on three different imidazolium cations. They also found that the C−H stretching region in the infrared spectrum of ImCl remained essentially unchanged in going from a solid to a chloroaluminate ionic liquid and concluded that the same bonding and structure present in ImCl(s) are present in basic $AlCl_3$−ImCl melts.[5] Furthermore, they were able to accurately predict the C−H stretches in the infrared spectrum of the melts by employing a model based on the ImCl crystal structure.[6]

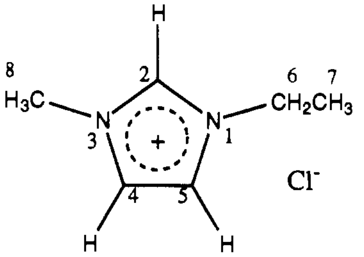

Figure 1. Structure and numbering of 1-ethyl-3-methylimidazolium chloride (ImCl).

Internuclear distances can be determined using the nuclear Overhauser effect (NOE). Simply described, NOE is the dipole−dipole interaction through space between two nuclei. This manifests itself when a single resonance in a spectrum is irradiated and the intensities of other resonances are changed. The dependence of the NOE for a two-spin system on the internuclear distance (r_{AB}) is given by[7]

$$1/\eta_A(B) = K(r_{AB})^6 \tag{2}$$

$\eta_A(B)$ is the NOE enhancement at nucleus A due to the saturation of spin B. K is a constant which includes the effects of molecular tumbling and alternative relaxation pathways; normally, the value of K is difficult to determine. The ratio between two NOE's is proportional to the ratios of the distances. Therefore, if an internuclear distance is known, the NOE enhancements can be compared to determine the unknown internuclear distance.

$$(r_{CD})^6\left(\frac{\eta_C(D)}{\eta_A(B)}\right) = (r_{AB})^6 \tag{3}$$

This equation assumes the values of K are the same for both NOE enhancements. This assumption is valid when similar molecules are being compared under identical conditions and the extreme narrowing limit condition is met.[8] However, in basic melts, the extreme narrowing limit condition is not met due to the high viscosity. To overcome this, rotating frame nuclear Overhauser enhancement spectroscopy (ROESY) can be used.[9,10] The ROESY experiment is conducted in such a way that the nuclei are always in the extreme narrowing condition. ROESY measures the transient instead of equilibrium NOE. The buildup of intensity (I) of NOE cross-peaks (dI/dt) is proportional to the internuclear distance and can be substituted into eq 2 for NOE enhancement (η) to yield

$$(r_{CD})^6\left(\frac{dI/dt_{CD}}{dI/dt_{AB}}\right) = (r_{AB})^6 \tag{4}$$

The rate of NOE buildup is determined by varying the mixing time and determining the resulting change in volume of the two-

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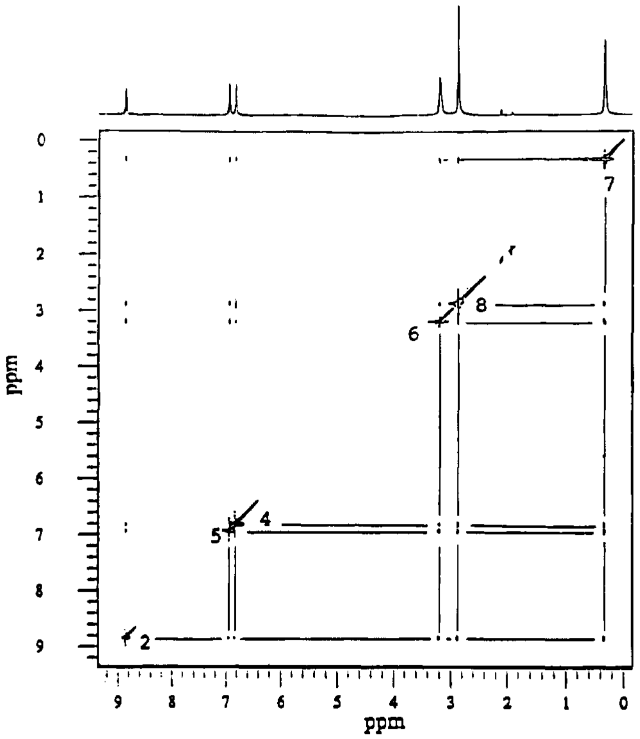

Figure 2. 500 MHz ^1H NMR ROESY (spin locking time 250 ms) spectrum of a 0.5:1.0 melt. The spectrum was obtained using GE Omega NMR spectrometer at 25 °C and a between-scan delay of 7 s. (Individuals unfamiliar with the interpretation of two-dimensional NMR spectra should refer to ref 8. The numbers along the diagonal refer to the positions on the 1-ethyl-3-methylimidazolium chloride. Lines have been added to the spectrum for each cross-peak to aid in interpretation.)

dimensional cross-peak. The volume of the cross-peaks is inversely proportional to the internuclear distance to the sixth power.

Proton NMR of basic chloroaluminate molten salts yields well-resolved one-dimensional spectra corresponding to the protons of the 1-ethyl-3-methylimidazolium chloride. In Figure 2, the ROESY spectrum shows cross-peaks due to NOE transfer. To interpret the ROESY spectra, trace horizontally from a peak on the diagonal until you reach another peak (cross-peak) and then trace vertically back to the diagonal. This cross-peak represents NOE transfer between the two positions indicated by the peaks on the diagonal. Lines have been added to the spectra for each cross-peak to aid in interpretation. The numbers along the diagonal correspond to the positions on the imidazolium cation. Projection of the two-dimensional spectrum onto either the *X* or the *Y* axis simply results in the one-dimensional ^1H spectrum. NOE cross-peaks are not normally observed for internuclear distances beyond 4 Å because of the r^{-6} dependence.[11] The ROESY spectrum (Figure 2) shows cross-peaks which are clearly due to intramolecular NOE transfer (i.e. between H-6 and H-7). It should be noted that these peaks can contain intermolecular contributions as well. In addition, there are cross-peaks which are most likely due to intermolecular NOE transfer. For example, H-2, which is separated across the imidazole ring from H-4 and H-5 by 4.3 Å, still shows cross-peaks to both H-4 and H-5, thus indicating some type of structure making intermolecular interaction. In addition, although H-4 and H-7 are separated by a minimum of 5.2 Å and H-5 and H-8 are separated by 4.7 Å, they both still show significant NOE interactions. If correct, this further demonstrates the existence of hydrogen bonding that leads to structure in basic $AlCl_3$–ImCl melts.

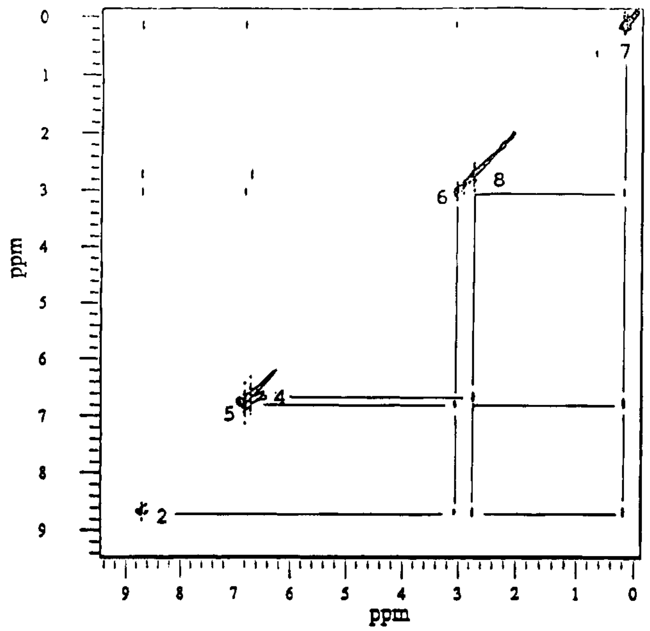

Figure 3. 500 MHz ^1H NMR ROESY (spin locking time 250 ms) spectrum of a 95% perdeuterated ImCl 0.5:1.0 melt. The spectrum was obtained using a GE Omega NMR spectrometer at 25 °C and a between-scan delay of 7 s.

To clearly distinguish between intramolecular and intermolecular NOE transfer, an additional sample was prepared. This sample contained a 0.5:1 melt in which 95% of the Im^+ cations were fully deuterated. In this sample, an ImCl molecule containing ^1H would be surrounded by perdeuterated molecules. The lack of ^1H on adjacent molecules prevents intermolecular NOE transfer. The resulting spectrum (Figure 3) shows the absence of the peaks between H-2 and H-4 as well as between H-2 and H-5, H-4 and H-6, H-4 and H-7, H-5 and H-8, H-6 and H8, and H-7 and H8. These have been assigned to intermolecular NOE transfer. The cross-peaks between H-2 and H6, H-2 and H-7, H-2 and H-8, H-4 and H-8, H-5 and H-6, H-5 and H-7, and H-6 and H-7 are still present. These cross-peaks have been assigned to intramolecular NOE transfer.

Evidence of intermolecular NOE transfer for basic ambient-temperature chloroaluminate melts has been presented. The intermolecular NOE transfer is possible due to the existence of structure caused by hydrogen bonding in the basic melts. The presence of the cross-peaks indicates the intermolecular distances between ImCl molecules is less than 4 Å. These results agree with those from infrared spectroscopy and with theoretical calculations which showed the presence of structure caused by hydrogen bonding with the chloride anion in the basic melts.[3-5] Further research is underway to quantify the average intermolecular distances between 1-ethyl-3-methylimidazolium chloride rings in melts of varying composition, at varying temperatures, and with several solutes.[12]

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