Investigation of Molecular Rotational Activation Energies in Ionic Liquids Using ^{14}N NMR Spectroscopy

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Introduction

The molecular rotational dynamics for a select series of room temperature ionic liquids (RTIL) were measured using ^{14}N NMR spectroscopy. While ^{1}H, ^{13}C and ^{19}F NMR has been used for monitoring molecular dynamics in RTIL, utilization of ^{14}N NMR has been limited due to the large nitrogen quadrupolar coupling and the correspondingly severe line broadening. Here we demonstrate that for RTIL containing quaternary ammonium cations, the symmetry around the nitrogen produces a nominal quadrupolar coupling constant allowing changes in the molecular reorientation correlation times with temperature to be determined from the ^{14}N NMR line width and spin-spin relaxation. These reorientations have Arrhenius type behavior with energies of activation ranging between 28 and 41 kJ mol^{-1}, and are a function of cation structure and identity of the coordinating anion.

Relaxation Theory

NMR spin-lattice (R_1) and spin-spin (R_2) relaxation rates for the ^{14}N nuclei (I=1) is dominated by the quadrupolar relaxation mechanism. This involves the coupling between the nucleus quadrupole moment (eQ) and the electrical field gradient (EFG) tensor. The rotational correlation time (τ) relationships for the R_1 and R_2 relaxation rates are defined by:

$$R_1 = K\left[2J(\omega_0)+8J(2\omega_0)\right]$$
$$R_2 = K\left[3J(0)+5J(\omega_0)+2J(2\omega_0)\right] \quad (1)$$

where

$$K = \frac{3\pi^2 P_Q^2}{40}, \qquad P_Q = \frac{e^2qQ}{h}\sqrt{1+\frac{\eta_Q^2}{3}} \quad (2)$$

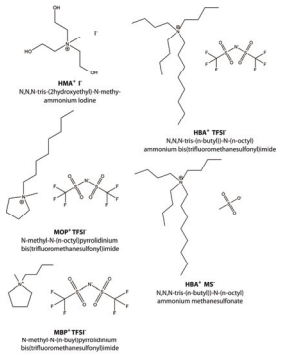
With the spectral densities $J(\omega_0)$ defined by

$$J(\omega_0) = \frac{2\tau}{1+(\omega_0\tau)^2} \quad (3)$$

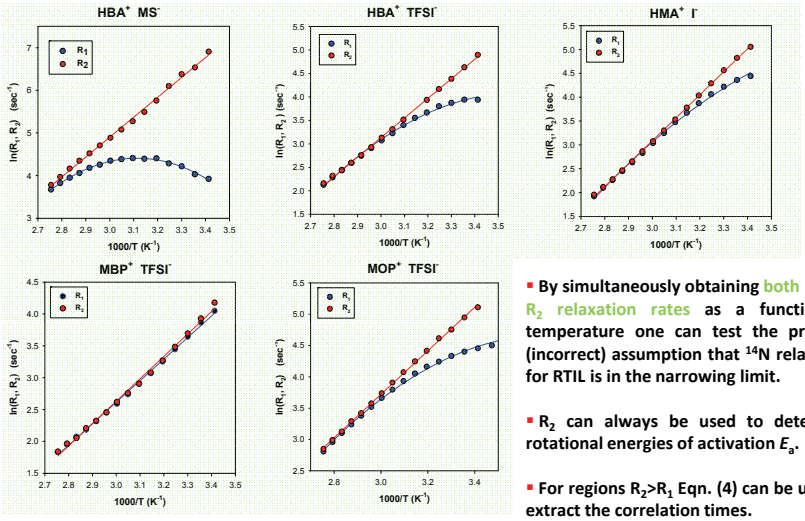
In the extreme narrowing limit R_1=R_2, and the correlation times (τ) and P_Q are intertwined. Outside this narrowing limit a unique solution for τ can be realized from the relaxation rate ratio R_2/R_1:

$$S^2 + \left[3.0833 - 0.6667(2R_2/R_1)\right]S$$
$$-\left[0.4167(2R_2/R_1) - 0.8333\right] = 0 \quad (4)$$
$$S = \omega_0^2\tau^2$$

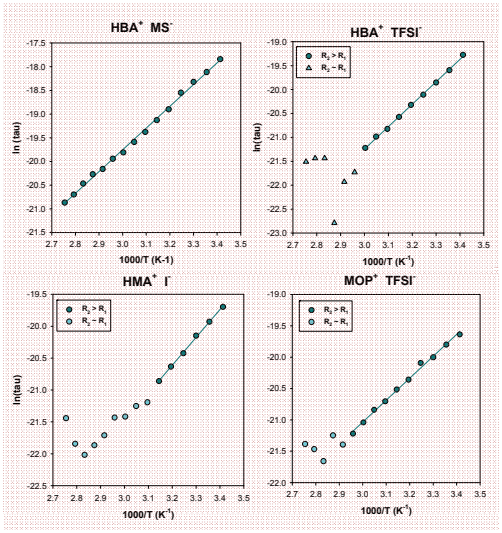
Ionic Liquids Studied

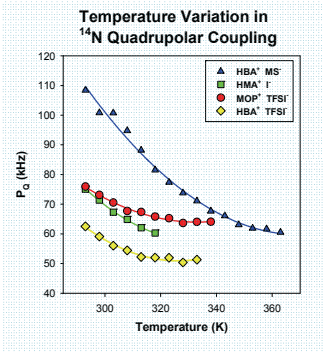


Results



- By simultaneously obtaining both R_1 and R_2 relaxation rates as a function of temperature one can test the previous (incorrect) assumption that ^{14}N relaxation for RTIL is in the narrowing limit.
- R_2 can always be used to determine rotational energies of activation E_a.
- For regions R_2>R_1 Eqn. (4) can be used to extract the correlation times.
- These correlation times can then be used to calculate the quadrupolar coupling constants via Eqn. (1) and (2).





Sample	E_a (kJ mol^{-1})[a]	E_a (kJ mol^{-1})[b]	τ (ns)[c]	P_Q (kHz)[c]
HMA$^+$ I$^-$	40.0 ± 0.4	36 ±3[d]	2.2	71.4
MOP$^+$ TFSI$^-$	28.9 ± 0.3	29.0 ± 0.3	2.5	73.1
MBP$^+$ TFSI$^-$	29.2 ± 0.3	--[e]	--[e]	--[e]
HBA$^+$ TFSI$^-$	34.6 ± 0.3	39 ±4[d]	3.1	59.0
HBA$^+$ MS$^-$	38.8 ± 0.4	38.2 ± 0.4	13.6	100.8

[a] Determined from R_2. [b] Determined from extracted correlation times. [c] At 298 K. [d] Increased error due to limit range of correlation times. [e] Not in R_2>R_1 limit.

Conclusions

- ^{14}N NMR provides a powerful tool to determine rotational correlation times in RTIL for quantenary ammonium cations .
- The quadrupolar coupling is temperature dependent!
- Rotational activation energies, both a function of structure and counter anions.

Research supported by the U. S. Department of energy, office of basic Sciences, Division of Materials Science and Engineering under Award DE-SC001951. Sandia is a multi=program laboratory operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin company, for the U. S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

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