NMR Relaxation Studies and Molecular Modeling of 1-butyl-3-methyl Imidazolium PF6 [BMIM][PF6] and Related Ionic Liquids

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The molecular reorientational dynamics of [BMIM][PF6] has been studied by ^{13}C NMR spectroscopy. The ^{13}C relaxation times and nuclear overhauser enhancement (NOE) measurements are used to determine reorientational correlation times. The continuous distribution of correlation times defined by Cole and Davidson that has been used to interpret the relaxation data of viscous liquids and glassy solids is used to model the [BMIM][PF6] and related systems.

The Cole Davidson model is combined with the model-free approach of Lipari and Szabo. The combination of the Cole-Davidson and Lipari-Szabo models successfully represents both the imidazolium ring and its more flexible side chains in the [BMIM][PF6] and related ionic liquids.

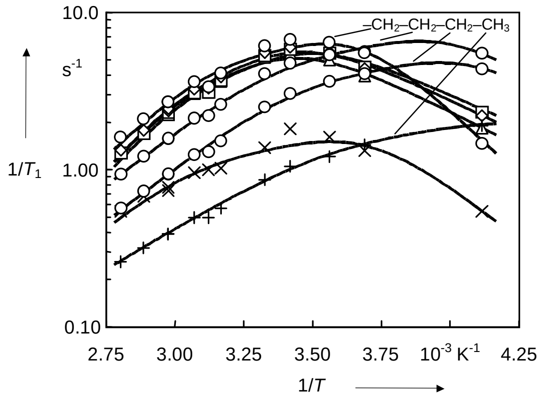

Fig. 1. ^{13}C relaxation rates $1/T_1$ of [BMIM][PF$_6$] in neat liquid as a function of reciprocal temperature T (Δ: C2, □ and ◊: C4 and C5, X: CH$_3$(ring), +: CH$_3$(butyl group), ○: CH$_2$, lines: functions calculated with the fitted parameters).

The relationship between ^{13}C correlation times and equivalent conductivity of the [BMIM][PF6] is also reported. As is the case with certain chloroaluminate ionic liquids, one observes a biphasic relationship that suggests a change in solution structure at a specific temperature.

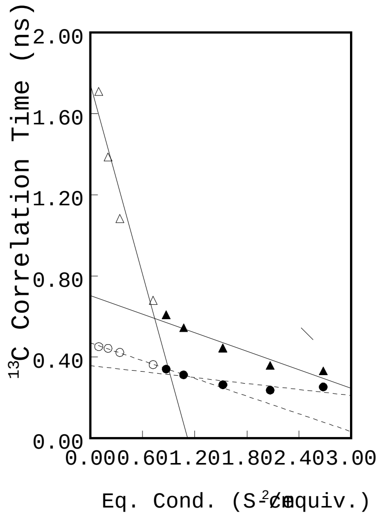

Fig. 2. ^{13}C Correlation Times vs Equiv. Conductivity For [BMIM][PF6].

The results of semi-empirical (AM1 and PM3) and *ab initio* (Hartree-Fock and Density Functional Theory) calculations are compared for the [BMIM][PF6] ionic liquid. The *ab initio* calculations include fully optimized structures at the RHF/3-21G(*), RHF/6-31G*, RHF/6-31G**, MP2/6-31G*, B3LYP/6-31G* and B3LYP/6-31G** levels.

In addition to the gas phase calculations of these ion pairs, semi-empirical modeling of the formation of multiple ion pair dimers also provides insight into their possible aggregation in the liquid state.

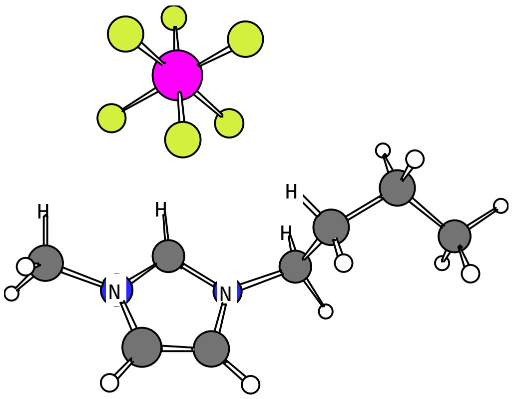

Fig. 3 Molecular Structure of [BMIM][PF6] (B3LYP/6-31G**)