

NMR SPECTRA OF WATER-IONIC LIQUID MIXTURES: LARGE-SCALE MOLECULAR DYNAMICS AND QUANTUM MECHANICS/MOLECULAR MECHANICS MODELING

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Ionic liquids are salts that have a melting point below 100 °C. Many ionic liquids remain liquid at or near room temperature and are called room-temperature ionic liquids. Ionic liquids are typically composed of organic cations and mostly inorganic anions, and these liquids have many potential applications in separations, organic synthesis, catalysis and electrochemical devices. These liquids are considered as environmentally friendly solvents because they are nonvolatile, thermally stable and recyclable [1]. Besides many useful features of RTIL, they are known to be highly hygroscopic. RTIL will absorb water from the atmosphere as soon as they are exposed to it, and this is virtually unavoidable for any real-life application of these liquids. On one hand, even small amounts of water can change the properties of the RTIL considerably, on the other hand, the mixtures of water and IL can exhibit new unexpected properties [2].

The imidazolium based IL are in fact among the most widely studied RTIL. Imidazolium cations are composed of polar imidazolium ring with the apolar alkyl chain attached to it. Polar domains are composed of imidazolium rings and anions whereas alkyl chains assemble into nonpolar domains. Classical MD simulations predict that if water is dissolved in an IL, heterogeneous structure of the IL is maintained and water molecules tend to form the so-called water pockets [3]. Interestingly, the existence of water pockets has been recently confirmed experimentally using small-angle X-ray scattering and neutron scattering [4].

Very interesting NMR measurements of water mixtures with some imidazolium based IL have been very recently carried out by the NMR spectroscopy group of Vilnius University. RTIL of 1-butyl-3-methyl-imidazolium, C4Mim, and anions such as halides, Cl⁻/Br⁻/I⁻, tetrafluoroborate, BF₄⁻, and nitrate, NO₃⁻, were considered. Interestingly, the H-1 NMR chemical shift of water was found to evolve non-monotonically with the changing concentration of the binary solution IL and water. When molar fraction of IL is increased, the H-1 NMR chemical shift of water first goes down. However, this chemical shift starts to increase starting from certain concentration of the ionic liquid, thus exhibiting a pronounced minimum. This kind of behavior is observed for all IL composed of C4Mim and cosmotropic anions, - that is, nitrate and halides. On the other hand, the H-1 NMR chemical shift of water was always found to decrease with the rising concentration of the [C4Mim][BF₄] IL. Similarly, the chemical shift of the H2 proton in the imidazolium ring was found increase considerably with increasing concentration of [C4Mim][Cl⁻]/[Br⁻]/[I⁻]/[NO₃⁻], but it was seen to be insensitive to the concentration of [C4Mim][BF₄]. Clearly, these experimental findings reflect the structural changes of the samples with changing concentration of IL and water.

The aim of project is to model the H-1 NMR spectra of [C4Mim][Cl⁻] and [C4Mim][BF₄⁻] RTIL mixtures with water of various concentrations (see Fig. 1). Large-scale classical molecular dynamics (MD) simulations of the IL/water systems have been carried out in order to sample the phase space and record the trajectories. These have been used in the subsequent calculations of NMR shielding constants using linear response quantum mechanics/molecular mechanics approaches. The theoretical results would certainly shed light on the early stages of water pocket formation within the IL and give valuable theoretical interpretation for the experimental findings just discussed.

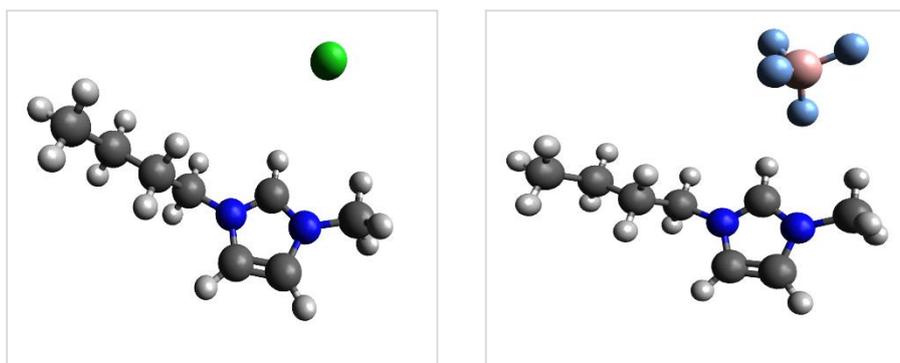


Fig. 1. 1-Butyl-3-methylimidazolium chloride (on the left side) and 1-Butyl-3-methylimidazolium tetrafluoroborate (on the right side).

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[3] Moreno et al., J. Phys. Chem. B, **112**, 7826 (2008).

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