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Towards accurate modelling of ^{1}H NMR spectra of ionic liquids: The case of [C4mim][BF4] and its aqueous mixtures

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Room-temperature ionic liquids (ILs) are organic salts that remain liquid near ambient conditions and are widely studied for their unique physicochemical properties. However, their locally anisotropic structure and nanoscale segregation complicate structural analysis using ^{1}H NMR spectroscopy. Earlier attempts to model proton chemical shifts of imidazolium-based ILs using single ion-pair models reproduced only qualitative spectral features.

In this work, an integrated approach combining molecular dynamics (MD) simulations and QM/MM calculations is applied to accurately predict ^{1}H NMR spectra of 1-butyl-3-methylimidazolium tetrafluoroborate (C4mim][BF_4]) and its aqueous mixtures (IL molar fraction 0.17–1). Classical MD simulations with an IL-specific force field were used to characterize local structure, followed by QM/MM calculations of isotropic ^{1}H shielding constants.

MD results show that BF_4^- anions preferentially localize near the C2–H2 site of the imidazolium ring rather than above the ring, contradicting earlier experimental assumptions. Even at low IL concentrations, water molecules rarely displace anions from the first solvation shell around C2–H2, leading to a relatively stable local environment. Nanosegregation is observed: butyl chains form nonpolar domains, while water accumulates in anion-rich regions.

The calculated ^{1}H chemical shifts agree closely with experiment, with deviations of only ~0.2 ppm across all systems. The notoriously difficult-to-predict H2 proton shift is reproduced with high accuracy. Overall, the ^{1}H NMR spectra of the [C4mim]$^+$ cation remain nearly composition-independent despite structural changes in the mixtures.

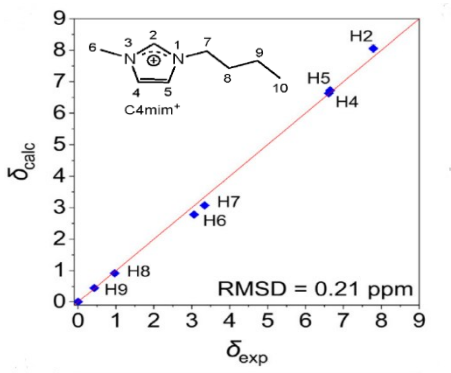

Fig. 1. Comparison between the calculated and measured relative ^{1}H NMR spectra of C4mim$^+$ cations in pure C4mim][BF_4]. The experimental and calculated ^{1}H NMR chemical shift values, denoted as δ_{exp} and δ_{calc}, are given in ppm [2].

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