COMPUTATIONAL NMR STUDY OF ION PAIRING OF 1-DECYL-3-METHYL-IMIDAZOLIUM CHLORIDE IN MOLECULAR SOLVENTS

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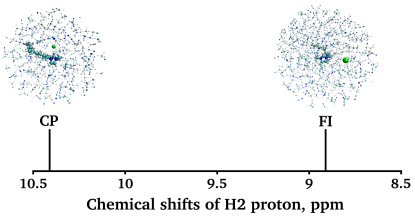
Ionic liquids (ILs) are salts with a melting point below 100 °C and are typically composed of asymmetric organic cations and organic or inorganic anions. The modulate effect of the molecular solvent on the properties of ionic liquid thorough understanding of intermolecular interactions between the constituent ionic and molecular species is crucial. One of these effects is ion pairing at low concentrations of the ionic in the molecular solvent. Ion pairing was detected in nonpolar solvents at rather low concentrations of ionic while polar solvents demonstrate the capability of breaking ionic aggregate into separate ions.



The ^{1}H NMR spectra of 10^{-5} mole fraction solutions of 1-decyl-3-methyl-imidazolium chloride ionic liquid in water, acetonitrile and dichloromethane have been measured. The chemical shift of the proton at position 2 in the imidazolium ring of 1-decyl-3-methyl-imidazolium is rather different for all three samples, reflecting the shifting equilibrium between the contact pairs and free fully solvated ions. Classical molecular dynamics simulations of the 1-decyl-3-methyl-imidazolium chloride contact ion pair as well as of free ions in three solvents have been conducted, and the quantum mechanics/molecular mechanics methods have been applied to predict NMR chemical shifts for the proton at position 2. By comparing experimental and computational results, we found that the ion pair breaks into free ions in an aqueous solution. Around 23% of the ion pairs were found to form contact pairs in acetonitrile. Ion-pairing breaking into free ions was predicted not to occur in dichloromethane.[a]

[a]D. Lengvinaite, V. Klimavicius, V. Balevicius, K. Aidas, J. Phys. Chem. B, 2020, 124, 47, 10776–10786.