

Hydrogen bonding and local structure of imidazolium-based ionic liquids in the water-rich domain

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Abstract

Since water has a high impact on the chemical-physical characteristics of Ionic Liquids (IL), both as a contaminant or as cosolvent, the detailed knowledge of the intermolecular interactions in IL/water solutions is a crucial step for understanding and predicting the range of properties of these non-conventional solvents for applications in many fields including electrochemistry, biochemistry, and synthesis [1-4]. In this work, aqueous solutions of a prototypical set of imidazolium (MIM)-based IL are investigated by UV Raman spectroscopy in the water-rich domain. Analysis of selected Raman signals in different wavenumber ranges provides insights into the local organization of cation-anion pairs as a function of the increasing amount of water in a wide range of concentrations. In particular, the high-frequency range of Raman spectra is analyzed by a differential method to extract from the OH stretching profile of water the solute-correlate (SC) spectra [5], which emphasize the molecular structuring of the interfacial water present in the hydration shells around the selected anions. Peculiar solvation behavior is observed for the different MIM-based systems in connection with the hydrogen bonding features of the hydrating water molecules. Related insights on the solvation properties of the ILs are obtained by analyzing specific signals of the MIM cation when different anions are considered. Interestingly, the ionic liquid [MIM]Cl seems most sensitive to hydration than [MIM]TfO even in an extremely hydrated regime.

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