

Studying the solvation of the proton in imidazolium ionic liquids using Raman Spectroscopy

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Understanding fundamental levels of acidity accessible in non-aqueous solvents is critical for developing new chemical syntheses and applications in non-aqueous media[1]. Often the level of accessible acidity is expressed as the proton transfer activity coefficient, which is related to the free energy of transfer when the proton is transferred from one solvent to another, experiencing difference in solvation[2]. For the proton, values for the transfer activity coefficient can only be experimentally estimated from extra-thermodynamic models applied to electrode potentials, solubility or spectroscopic measurements[3,4]. Experimental values for the transfer activity coefficient of proton are essential to confront the computed values, as determining free energies of proton solvation, either experimentally or theoretically, in non-aqueous solvents is one of the most discussed questions in physical chemistry[5]. Proton solvation are particularly interesting to study in stable room temperature ionic liquids (RTILs), which emerged as alternative to volatile organic solvents for inorganic and organic syntheses, catalysis, electrolytes and microextraction[6–10]. The presence of small fractions of molecular impurities in RTILs has major impacts on their physico-chemical properties, especially the acidity levels accessible in these solvents, which need to be addressed to develop more robust applications. Here we report on the estimation of the free energy of solvation for proton in stable N,N'-substituted imidazolium ionic liquids using far-field classical Raman spectroscopy and the acidity function proposed by Hammett[11] in different RTILs, built from four different cations (C₂, C₄, C₆ and C₈ N-alkyl, N'-methyl imidazolium) and 4 different anions (OTf⁻, NTf₂⁻, BF₄⁻ and PF₆⁻).

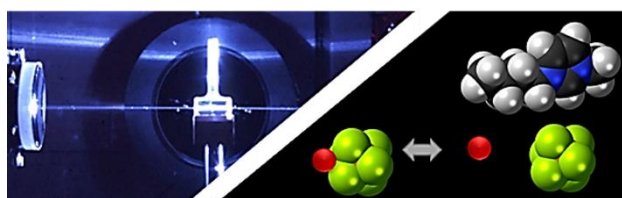


Fig. 1 Raman spectroscopy to evaluate the solvation energy of proton in RTILs.

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