

Evaluating the solvation energy of the proton in super-acidic imidazolium ionic liquids using Raman Spectroscopy

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Understanding the levels of acidity accessible in non-aqueous solvents is paramount for developing new chemical syntheses and applications in non-aqueous media [1]. The highest level of acidity (lowest pH) accessible in a media is often 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]. Proton solvation is particularly interesting to study in stable room temperature ionic liquids (RTILs), resulting from the combination of organic cations (often derivatives of N,N'-substituted imidazolium, N-substituted pyridinium, quaternary ammonium or phosphonium) and inorganic or organic anions (e.g. carboxylates, sulphates, halogens), that were recognised as an alternative to volatile organic solvents (VOCs) for inorganic and organic syntheses, catalysis, electrolytes and microextraction, , especially for their capacity to dissolve sugar-based biopolymers such as lignin [3-6]. 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. 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 [7]. 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 [8,9]. Here we report on the novel approach estimating 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 [10] in different RTILs. Results obtained for 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⁻) will be discussed.

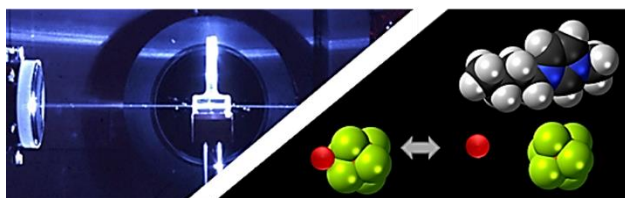


Figure 1: Raman spectroscopy to evaluate the solvation energy of proton in RTILs.

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