

# Charge Carrier Dynamics in Protic Ionic Liquids

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Protic ionic liquids (PILs) are a promising class of materials for electrochemical applications due to their unique properties.<sup>1-3</sup> A fundamental understanding of the molecular level dynamics in PILs is crucial on the way to their application-oriented rational design. Although several studies have attempted to elucidate the underlying molecular level dynamics, the distribution of protons and their transport in PILs is not yet fully understood.<sup>4,5</sup>

To gain insights in the molecular level distribution and dynamics of protons in PILs we use dielectric relaxation and nuclear magnetic resonance spectroscopy. DRS is a powerful experimental technique to gain insights to the molecular dynamics over a broad frequency range. NMR spectroscopy provides different one- and two-dimensional techniques that reveal information not only about structure but also on dynamics of the investigated PIL. Additionally we use pump-probe spectroscopy to specifically address the proton contribution to the overall charge carrier dynamics.

We investigate 1-methylimidazolium acetate [Im][Ac], which has been suggested to be dominated by neutral species, given the low  $pK_a$  value of acetic acid.<sup>4,6,7</sup> Here, we explore the effect of the acidity by gradually shifting the degree of protonation in the PIL via adding 1-Methylimidazolium trifluoroacetate [Im][TFA] and also explore the effect of the molecular environment by investigating binary mixtures with organic solvents. Our results confirm the findings of previous studies that neutral hydrogen bonded species dominate [Im][Ac]. Increasing concentrations of [Im][TFA] lead to a higher number of free ions and higher dc conductivity. Our findings show that addition of dipolar solvents critically affect speciation and transport in the binary mixtures: While protic methanol leads to stabilization of free ions, aprotic dimethylformamide enhances ion pairing. Our results thus demonstrate that both, acidity of the Brønsted acids and the chemical environment, are crucial for the species formed in PILs, pertinent to an application-based design of PILs.

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