

The fate of the proton in protic and aprotic ionic liquids: acidity and ion transfer studied by Raman spectroscopy

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Ionic liquids (ILs), interesting for their tunable solvation behavior and ability to reach high acidities, are commonly classified as protic (PILs) and aprotic (AILs). PILs result from proton transfer between a Brønsted acid and a Brønsted base, yielding a protonated cation. However, acidity is not restricted to PILs, as both PILs and AILs can be acidic depending on whether the proton is associated with the cation or with an acidic anion, respectively.¹ Moreover, high acidity can also be achieved by dissolving Brønsted acids in ILs, owing to the weakly coordinating nature of their anions, leading to high proton activity.

Acidity in ILs is commonly evaluated using Hammett acidity functions, based on the protonation of weakly basic indicators. Protonation is traditionally monitored by UV-Visible spectroscopy, but Raman spectroscopy has been recently implemented in AILs, which allowed us to reveal the influence of the indicator concentration on acidity determination, an effect previously unexplored.^{2,3} These results also highlighted the presence of ion pairing in ILs, and its possible distinct impact on UV and Raman spectra, leading to differences in the measured acidity.

Raman spectroscopy is also a valuable tool for probing proton transfer in PILs. Studies were performed on a sulfonic acid-functionalised ammonium IL paired with a methanesulfonate anion in the presence of different amounts of methanesulfonic acid. The analysis of Raman specific bands of the IL, coupled with computational modeling using SMD-GIL solvation model, enabled discussing the evolution of the proton chemical environment, hydrogen bonding and cation-anion interactions in the IL upon increasing acid concentration.

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