

How Many Neighbors? Alkali cation solvation in [BMIm][NTf₂] revealed by Raman spectroscopy

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Room-temperature ionic liquids (RTILs) have emerged over the last decades as attractive alternatives to conventional molecular solvents due to their negligible vapor pressure, wide electrochemical windows and tuneable physico-chemical properties¹. Among them, imidazolium-based ionic liquids built from weakly coordinating anions such as bis(trifluoromethane)sulfonimide (NTf₂⁻) are of particular interest for applications involving strong acidity and highly reactive ionic species. In such media, the nature and extent of ionic solvation play a key role in controlling reactivity, yet remain difficult to quantify². In contrast to molecular solvents like water, where small ions are strongly solvated by extended hydrogen-bond networks, ionic liquids provide a highly structured but weakly coordinating environment. As a result, the solvation of small cations, including protons and alkali metal ions, is expected to differ markedly from aqueous behaviour, with important consequences for acidity, ion pairing and transport properties^{3,4}. For the proton, we demonstrated that a unitary solvation number is obtained in the ionic liquid [BMIm][NTf₂], indicating coordination to a single NTf₂⁻ anion⁵. This weak solvation contrasts sharply with aqueous systems and provides a direct spectroscopic explanation for the super-acidity commonly experienced in NTf₂⁻-based imidazolium ionic liquids. In this communication, we report a systematic investigation of the solvation numbers of monovalent cations (H⁺, Li⁺, Na⁺, K⁺, Rb⁺ and Cs⁺) in [BMIm][NTf₂] derived from *in situ* far-field Raman spectroscopy. Extension of our experimental approach to alkali cations beyond proton reveals systematic trends in coordination numbers across the series, reflecting the balance between ion size, charge density and anion affinity in low-solvating medium, providing direct, non-invasive and fundamental insight into ion-solvent interactions in [BMIm][NTf₂].

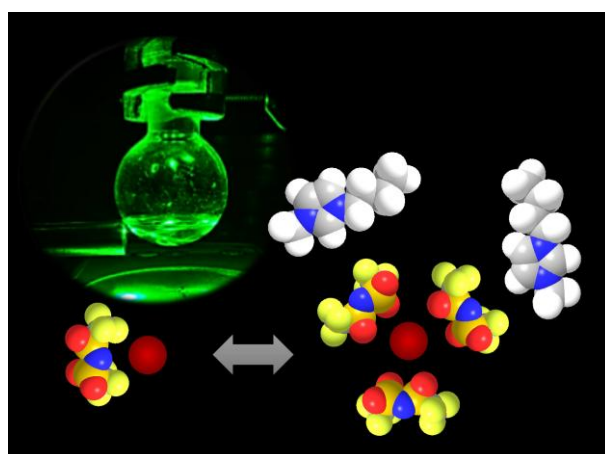


Fig. 1 Raman spectroscopy to evaluate the solvation number of alkali cations in RTILs.

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