



Hammett acidity functions via Raman spectroscopy as a tool to probe the acidity levels of ionic liquids

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Ionic liquids (ILs) have attracted significant interest over the last few decades due to their unique acidity-related properties. For many applications, the level of acidity achievable in ILs (often much higher than in water) is crucial for reactivity. For instance, Brønsted acidic ILs are used in acid-catalyzed reactions, battery and fuel cells applications, and biomass valorization. [1,2]

A common method for evaluating the acidity of ILs is the Hammett acidity functions, which rely on measuring the protonation ratio of colored weak bases (usually nitroanilines) in acidic media via UV-Visible spectroscopy. [3] Originally proposed to assess the acidity of aqueous solutions, this method was later extended and has become the reference method for probing the acidity in non-aqueous solvents, including ILs. However, the Hammett acidity functions suffer from a few limitations, especially when applied to ILs, mainly due to the choice of colored nitroanilines as acidity indicators. These molecules possess a conjugated π -system, which might induce specific interactions with aromatic cations of ILs, thereby invalidating the Hammett extra-thermodynamic hypothesis (i.e., that the ratio of the activity coefficients of the basic and acidic forms of the indicator is equal for a series of related nitroanilines). Moreover, in a given medium, different nitroanilines should theoretically yield the same acidity levels. However, studies have shown that this is not the case for non-dissociating solvents, including ILs, leading to apparent acidity functions, shifted according to the strength of the ion pairs between the nitroaniline and the partially dissociated acid. [4,5] This is why the method was recently implemented in Raman spectroscopy, which has multiple advantages over UV-Visible spectroscopy. First, this technique offers greater flexibility in selecting the base acting as the acidity indicator, as non-colored bases can be used. New, non-aromatic, more spherical indicators can be developed, for which specific solvation effects are likely to be decreased.

In this work, we examined the issues associated with the Hammett acidity functions. First, the effect of the nitroaniline concentration was studied, as Raman spectroscopy requires higher base concentrations than UV-Visible spectroscopy, which influences the acidity of the medium. Second, different cations were selected to study the influence of specific interactions (such as π -stacking or steric hindrance, for instance) between the IL and the indicator on acidity. Additionally, the role of ion pairing in the acidity levels of ILs was assessed using a series of structurally related nitroanilines, which enables access to the ion pair formation constant involved in the apparent acidity functions and determine the absolute acidity levels of the medium. Finally, a new nitrile-functionalised nitroaniline was used as an acidity indicator, which exhibits Raman signals in the silent region of the Raman spectrum (between 1800 and 2100 cm^{-1}). This approach enables the use of low indicator concentrations (i.e., μM range), as the accumulation of the Raman signal over an extended period can be performed without interference from IL signals.

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