

On the state of the proton in protic ionic liquids.

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Protic ionic liquids have been recently found of particular interest for applications such as fuel cell electrolytes, bio-preservation media and pharmaceutical materials [1,2], to name only a few.

Made by neutralizing a Brønsted acid with a Brønsted base of suitable pK_a value, these protic ILs (PILs) may have either inorganic [3] or organic [4] cations, and may be neutral, acid or basic in their behavior depending mainly on the anion. The proton activity is highly variable, depending on free energy of proton transfer. For aqueous solutions these are easily obtained from the difference in pK_a values for which many data exist. For PILs, these energies of proton transfer have been used, as the best available, to construct Gurney-type proton energy level diagrams to assist in predicting PIL properties. However, being derived from aqueous solutions measurements, these are obviously not reliable for systems from which the water has been removed.

Clearly, a direct measurement of the proton activity is needed. Direct electrochemical measurements of the energy of proton transfer, under development in our lab, are not simple because of the liquid junction potentials that are different for every PIL. Fortunately there are a number of possible spectroscopic probes of the state of the proton in the PIL, for instance, the N-H vibration frequency and, more directly, the NMR proton chemical shift.

The proton chemical shift reflects the electron density around the proton. The electron density will be higher the closer the proton approaches the nitrogen of the Brønsted base, hence will be a direct reflection of the acid strength. The stronger the acid the more covalent the nature of the N-H bond will be and so the less downfield from the common reference TMS (tetramethyl silane) the resonance will be found. Thus the chemical shift is a useful tool to indicate the proton activity of a PIL as a relative quantity

In this work we measure the N-H chemical shift for a variety of very dry PILs and use the relative values to discuss such controversial acidity assignments as those for nitric acid, methane sulfonic acid, and particularly triflic acid for which pK_a has been previously assigned values ranging from -14 to about -3.8.

Fig.1: ¹H NMR spectrum of neat ethylammonium nitrate (EAN) with DMSO-d₆ as external lock and referenced to TMS. (¹H NMR, 500 MHz, DMSO-d₆, δ): 7.334ppm (s, -NH₃, 3H), 2.916ppm (m, CH₃CH₂-, 2H), 1.062ppm (t,

J=7.5 Hz, CH₃CH₂-, 3H).

References

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- However to estimate the energy of proton transfer is not trivial because the binding of the proton to the conjugate base of the Brønsted acid, which is broadly considered as a measure of the acid strength, is not properly known.