

## Proton activity in ionic liquids: The ILPA index and its application in optimizing fuel cell efficiency, protein stability, and large molecule solubility.

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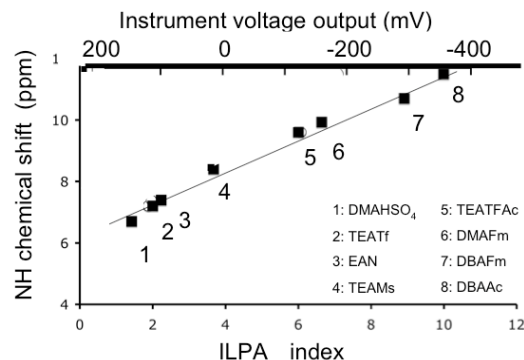
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[CH<sub>3</sub>CH<sub>2</sub>NH<sub>3</sub><sup>+</sup>][NO<sub>3</sub><sup>-</sup>], called EAN, [H<sub>3</sub>O<sup>+</sup>][CH<sub>3</sub>SO<sub>3</sub><sup>-</sup>], 1:1NH<sub>4</sub>NO<sub>3</sub>.NH<sub>4</sub>SCN, are all liquid below 100°C, and consist only of ions, hence are “ionic liquids”. They are of the protic class, organic and inorganic. Every positive ion is protonated and their concentration is of order V<sub>M</sub><sup>-1</sup>, (5-10M). Despite such similar concentrations, the differences in proton activities can be many orders of magnitude due to the different proton “energy gaps”, and thus proton bindings on the base[1].

We show that H<sup>+</sup> activities, which had not been quantified before our work reported at this meeting (see also Byrne, and Belieres, abstracts), can control the energy conversion efficiency of fuel cells in which they are the electrolytes, the stability of folded hydrated proteins in liquid storage systems, and presumably the kinetics of many chemical reactions and other processes. In the case of PILs with nitrogenic proton acceptor sites, an internal measure of the protonic state is available through the N-H proton magnetic resonance PMR chemical shift [2]. The more basic the PIL, the greater the downfield proton shift (opposite to the usual aqueous solution experience).

An “apparent pH” can be measured with a standard solution pH meter (after large calibration voltages are applied) but the correlation with the N-H PMR chemical shift is erratic and saturates at ~pH 7. Here we report our development of a device [3] that gives voltage output of ~zero for the “neutral” PILs (EAN and TEAMS), positive voltages for more acid, and negative voltages for more basic cases, and a

linear, non-saturating, relation to the N-H proton chemical shift [2], Fig. 1. We use these voltages to define an Ionic Liquid Proton Activity (ILPA) index. Since the device also measures standard solutions we assign ILPA values to correspond with aqueous buffer pH values. We relate the voltage output of the new device (an ILPA meter) to energy levels in the Gurney diagram for PILS [1] that were previously [1] based on pK<sub>a</sub> values from aqueous solutions for want of a better metric. Then we use the quantified H<sup>+</sup> energy levels to correlate/predict other IL applications.



**Figure 1:** Linear variation of the proton activity (ILPA index) with N-H proton chemical shift (NMR) for 8 protic ILs.

Since the ILPA changes rapidly near PIL stoichiometry, buffering is desirable. We demonstrate various buffers and the “tuning” of H<sup>+</sup> activity to desired values. Aprotic ILs (with trace H<sub>2</sub>O?) are base-shifted relative to PILs of like anions.

### References

- [1] Belieres Angell. J. Phys. Chm. 2007
- [2] Byrne, Belieres, Angell, (to be publ.)
- [3] Provisional Pat Appl. No.9138-0123.