The Molarities of Ionic Liquid Species- Densities are Not Boring

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In the course of studying ionic liquids, it is customary to obtain density data, either for simple practical needs or for use with other physical measurements such as the determination of solute concentrations. Interest in molar volumes and their inverse, molar concentrations, has been minimal.

We have assembled density data for a wide range of ionic liquids, including molten single and mixed alkali metal salts and ambient temperature chloroaluminate liquids. It is simple to calculate the molarities of the ions present in most cases. We observe a range from ~35 M for Li^+ and Cl^- in liquid LiCl to ~1.5 M for the ions of a particular phosphonium salt with values of 3 — 6 M for a selection of chloroaluminate liquids. Within chloroaluminate systems, the anion concentrations are determined (a) by the $AlCl_3$ mole fraction but also (b) by the density which varies with the cation. Thus if the anion is a reactant, its reactivity should depend on the complete constitution of the liquid.

Liquid water has a molarity of ~55 but aqueous solutions can be prepared containing concentrations of ions within the 1.5 to 35 M span. In the ionic liquids, have we simply substituted space for water compared to the aqueous solutions?

Molecular orbital calculations were performed for constituent ions of liquids to estimate close-packed volumes. For simple salts these values can be compared to the lattice parameters from X-ray studies of solids. In all cases, ionic liquids appear to contain substantial (~40%) free volume.

This approach offers the possibility of designing an ionic liquid of appropriate density and species concentrations, although non-ionic interactions such as H-bonding need to be accounted for in certain systems.