Ionic Liquids: What Have We Learned? A Personal, Thermodynamic Scenario

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We are currently witnessing an impressive explosion in the field of ionic liquids which impacts a wealth of distinct areas, from chemistry to physics, from environmental sciences to the life sciences. In fact, the recent years have seen the growing importance of ionic liquids – excellent solvents, which are liquid salts at or close to room temperature, and frequently studied, as part of the important field of green chemistry. However, many interesting features of their peculiar, surprising phase behaviour have just very recently been found (and many others are certainly still to be discovered).

Two examples:

(i) **Liquid - Vapour Transfer of Commonly Used Ionic Liquids**

Much of the potential of ionic liquids is underpinned by their involatility. This presumed lack of vapour pressure is responsible for their "green" status. We, in collaboration with the QUILL Centre, Belfast, and the NIST, Boulder, have just demonstrated [1] that many ionic liquids do evaporate (without decomposition) and can thus be distilled. This demonstration could have undermined their environmental friendly credentials. However, this is not the case because this phenomenon merely occurs under relatively extreme conditions [2] of moderately high-temperature and vacuum. These liquid salts are now easier to recycle and purify. Moreover, gas-phase processes involving ionic liquids are now reachable. An additional challenge will be the identification of the gas phase species, *i.e.*, the studies aimed at revealing the ionic liquids' gas-phase structure.

(ii) **Phase Behaviour and Elements of Structure of $[C_n\text{mim}][NTf_2]$ + CH_xCl_{4-x} or + Arenes**

In a very recent study [3] we found the first evidence for the existence of closed-loops in liquid phase diagrams of imidazolium plus bistrisflamide-type of ionic liquid solutions as well as critical demixing phenomena upon temperature increase – lower critical solution temperature (LCST). We concluded that, depending on the working temperature range considered, two distinct mechanisms for phase splitting upon temperature rise exist. Additionally, it was anticipated that benzene and benzene derivatives (*e.g.* toluene, or α-methylstyrene) would interact with $[C_n\text{mim}][NTf_2]$ in such a fashion that there would also be chances of finding unusual high-temperature demixing. This was in fact the case and we found [4] that as the imidazolium alkyl chain length of the ionic liquid increases, the mixtures containing an arene evolve from a rarely found high-temperature demixing behaviour, to "hour-glass", to the common phase splitting as temperature diminishes (UCST, whenever a critical point is found). Furthermore, the determination of the solid-liquid part of the phase diagram of the ($[C_2\text{mim}][NTf_2]$ + benzene) system revealed and allowed us to identify and characterize an equimolar inclusion compound, $[C_2\text{mim}][NTf_2]\cdot C_6H_6$, with a congruent melting temperature. This type of behaviour, original for ionic liquid-containing materials, together with the X-ray structure of the inclusion compound lay emphasis upon the interactions that are responsible for the existence of liquid clathrates at higher arene concentrations.

[1] Earle, M.J. *et al.*, The Distllation and Volatility of Ionic Liquids. *Nature*, **439**, 831-834 (2006).
[2] Rebelo, L.P.N. *et al.*, On the Critical Temperature, Normal Boiling Point and Vapor Pressure of Ionic Liquids. *J. Phys. Chem.* **B109**, 6040-6043 (2005).
[3] Lachwa, J. *et al.*, Evidence for Lower Critical Solution Behaviour in Ionic Liquid Solutions. *J. Am. Chem. Soc.*, **127**, 6542-6543 (2005).
[4] Lachwa, J. *et al.*, Changing from an Unusual High-Temperature Demixing to a UCST-type in Mixtures of 1-Alkyl-3-Methylimidazolium Bis{(Trifluoromethyl)Sulfonyl} Amide and Arenes. *Green Chem.* **8**, 262- 267 (2006).