

## **Bridging the Gap between Ionic Liquids and Molten Salts. Vaporization Studies and the Nature of the Gas Phase**

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The idea that ionic liquids were essentially involatile was recently shown to be incorrect, when it was found that some of them could be distilled at low pressure without decomposition, and their vapor pressures and enthalpies of vaporization could be accessed by different experimental and simulation techniques.[1] This fact raised the fundamental question of elucidating the nature of the species present in the gaseous phase during the reduced pressure distillation of ionic liquids. In this presentation, we address this problem through the analysis of experimental data obtained by Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FTICR-MS).[2] The experiments demonstrated that aprotic ionic liquids, namely those based on the bistriflamide anion,  $[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$ , distil under reduced pressure exclusively as neutral anion-cation pairs. This conclusion is quite different from that characteristic of Group 1 metal halides. These compounds melt well above room temperature (742-1269 K) and the vapors originating from the liquids under low pressure show significant fractions of aggregates larger than ion-pairs (particularly dimers). To bridge the gap between the gas-phase behaviour of these two classes of compound, we have decided to study the distillation of  $\text{M}[\text{N}(\text{SO}_2\text{CF}_3)_2]$  ( $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ) salts. The FTICR-MS experiments have shown that distillations of  $\text{M}[\text{N}(\text{SO}_2\text{CF}_3)_2]$  molten salts yield (like in the case of aprotic ionic liquids) vapour phases that consist of neutral ion pairs. However, the observation of large charged aggregates generated through a sequence of ion-molecule reactions is closer to what might be expected for Group 1 metal halides.

[1] Rebelo et al. *Accounts Chem Res* 2007, 40, 1114-1121.

[2] J. P. Leal, et al. *J. Phys. Chem. A* 2007, 111, 6176-6182; *ibid*, *J. Phys. Chem. B* 2009 (in press).