The Fluorination Effect on the Volatility of Ionic Liquids

Ana Rodrigues [C, S]
Chemistry and Biochemistry, University of Porto, Porto, Portugal
anasofiaconde@gmail.com

Ana Fernandes
Chemistry, University of Aveiro, Aveiro, Portugal

Margarida Costa Gomes
Institut de Chimie de Clermont-Ferrand, Université Blaise Pascal, Clermont-Ferrand, France

Luis Santos
Chemistry and Biochemistry, University of Porto, Porto, Portugal

Task-specific ionic liquids (TSILs) incorporate functional groups chosen to confer particular properties and to render them useful for particular applications. Fluorinated aprotic ILs are examples of task-specific ILs. The fluorination of the alkyl side-chain of imidazolium based ILs affects significantly their thermophysical properties such as density, viscosity and gas-solubility. These ILs present a high thermal stability and resistance towards oxidation and are promising due to the expected unique and specific characteristics properties associated with the fluorination. In this project, we explore the effect of cation and anion fluorination on the volatility, enthalpies and entropies of vaporization of imidazolium ILs. Electrospray ionisation mass spectrometry (ESI-MS) was used to study in detail the association of these ionic liquids to form aggregates. The vapour pressures of pure ILs were measured at different temperatures using Knudsen effusion apparatus integrated with a quartz crystal microbalance. The results showed that the fluorination of the cation and the anion increase significantly the volatility of the imidazolium ILs in comparison to their hydrogenated alkyl chain counterparts. The volatility and the thermodynamic properties of vaporization of the fluorinated ILs were analysed on the basis of the molecular interactions and structure. The ESI-MS analysis of the aggregate ion stability is in agreement with the standard enthalpy of vaporization derived from the vapour pressure measurements. It was found that the volatility increase of the fluorinated ILs is entropically driven, arising from the decrease of the molecular conformational entropy in the liquid. A parallel is established between the behaviour of these ILs and similar trends were previously observed in perfluorinated hydrocarbons.

Acknowledgements

This work was supported by Fundação para a Ciência e a Tecnologia. Ana S. M. C. Rodrigues acknowledge the financial support from Fundação para a Ciência e a Tecnologia for the award of research grant with reference SFRH/BD/81261/2011.