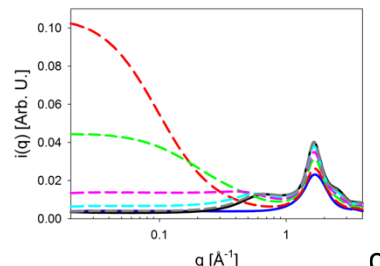
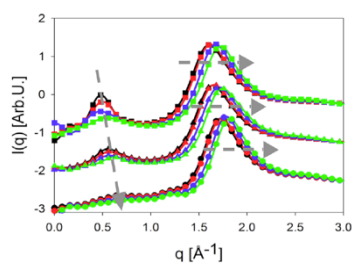


Pressure and Co-Solvent dependency of Ionic Liquid Structural Heterogeneity probed by experimental and computational methods

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Ionic Liquids (ILs) are likely one of the hottest topics in modern chemistry. Albeit it is possible to find some literature dealing with them in the XIX century, the paternity of ILs is commonly attributed to Peter Walden that in 1914 reported Ethylammonium Nitrate (EAN) as a “water-free salt [...] which melts at relatively low temperature”. Amongst their several interesting properties, in some of them emerge a peculiar intermolecular arrangement, often called “Sponge-like”. It consists of mesoscopic heterogeneity, arising from polar/apolar domain segregation. At this feature is attributed the *low q peak* in the Small Angle X-ray Scattering pattern of some IL [1]. In the first part of my presentation I will talk about the effect of pressure on such arrangement. It has been shown [2] that high pressures could induce the long alkyl chain folding, leading to the destruction of the polar/apolar segregation. I will explore the effect of pressure on three Protic Ionic Liquids, with short alkyl tail (stiffer), by means of classical molecular dynamics simulations. I observed [3] that high pressures affect their mesoscopic structure inducing chain folding and forcing progressive homogenization. The obvious question at this point is “What happens to a solute accommodated in the (a)polar domain when such a domain is stressed by pressure?” To answer, I chose an IL capable of dissolve both small amounts of water and large quantities of hexane. The simulations highlighted how the IL mesostructure is deeply changed when compressing the system up to 10 kbar, and how the domain segregation is less pronounced. In this scenario, there were two different possible behaviors for water and hexane: phase separation or aggregation. My results [4] clearly show association between water and induced by pressure rising. The second part of the presentation, will deal with some unusual binary mixtures containing EAN and a molecular co-solvent. These systems are macroscopically homogeneous mixtures that exhibit a nanoscopic segregation where an IL-rich region is percolating an IL-poor one. This nano-heterogeneity is witnessed by an intense feature in the extreme low q region of the SAXS pattern of such systems. This condition was observed only for mixtures with n -alcohols, and self-assembles structures were thought responsible of the diffracted intensity [5]. My experimental results on binary mixtures of EAN with some non-amphiphilic compounds [6] or with acetonitrile, shed a different light on this observation. Only recently the idea that the phenomenon is due to strong density fluctuations is being explored [7]. I will talk about the nature of the fluctuations and the consequences of this behavior.



(a): Schematic representation of the “Sponge-like” structure. In red the polar domain of the IL, in green the apolar one. (b) SWAXS patterns of three ILs as a function of pressure. The arrows follow the pressure rising. (c) SWAXS patterns of EAN-acetonitrile mixtures as a function of composition.

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