Not Just Gas Solubilities Anymore:
Simple Solutes as Probes to Explore the Molecular Structure of Ionic Liquids

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It is now common knowledge among the scientific community that ionic liquids form a novel class of solvents with potential industrial applications in environmentally acceptable processes. They can act as sophisticated solvation or reaction media as they can dissolve a wide range of polar or nonpolar, organic or inorganic molecules, providing new paths to carry out chemical reactions or industrial separations. In addition to the numerous possible applications of ionic liquids, they offer an interesting research subject on how the macroscopic properties of fluids can be related to their molecular structures. At a microscopic level, ionic liquids exhibit medium range ordering with the existence of persistent domains in the liquid phase [1]: one formed by aggregates of the non-polar side chains, and the other by a network composed by the charged head groups and dominated by electrostatic interactions. This segregation of polar and nonpolar domains changes the way in which solvation can be understood in these liquids[2] . Solutions of simple molecular compounds, for example gases at ambient conditions, can be used to probe the molecular structure of the ionic solvents. When expressed in terms of Henry's law constants, precise gas solubility data are directly related to the standard Gibbs energy of solvation and, from its variation with temperature, the enthalpy and entropy of solvation can be derived [3]. These thermodynamic properties of solvation provide information about the microscopic features (both structural and energetic) controlling the dissolution process. We present several examples for which the behavior of different ionic liquids as solvents can be understood by considering their nanoscale segregation. We also show how the insights obtained can be used in the development of new ionic liquids capable of selectively dissolving different molecular solutes.

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