Thermodynamics of Solvation of Small Solutes on Ionic Liquids

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Precise low pressure gas solubility data can be used to assess the solute-solvent interactions and provide valuable informations about the dissolution process. In this work, a double approach based on solubility experiments and in molecular simulation was used to provide insights about the structure of the solutions and the molecular mecanisms that explain the observed macroscopic behavior.

The solubility of several gases (carbon dioxide, ethane, methane, oxygen, nitrogen, hydrogen, argon and carbon monoxide) was determined experimentally as a function of temperature. Four ionic liquids based on the 1-butyl-3-methylimidazolium cation [bmim] were studied, as well as two liquids based on the 1-ethyl-3-methylimidazolium cation[emim], and six liquids sharing the bis(trifluoromethanesulfonyl)amide anion [$NTf2^-$].

The solubility of the gases studied vary from 10^{-4} to 10^{-2} in mole fraction and it was observed that carbon dioxide and ethane are the most soluble gases, while hydrogen exhibits in general the lowest mole fraction. The solutes studied are (up to two times) more soluble in ionic liquids based in the [$NTf2^-$] anion, independently of the imidazolium cation considered. The patterns found in the gas solubility in ILs with different cations sharing the same [$NTf2^-$] anion are subtler and depend on the molecular family of the cation.

When expressed in terms of Henry's law constants, gas solubility is directly related to the standard Gibbs energy of solvation and, from its variation with temperature, the enthalpy and entropy of solvation can be derived. These thermodynamic properties of solvation can serve to validate molecular simulation calculations that in turn provide information about the microscopic features (structural and energetic) controlling the dissolution process. Simulation tools will be used to interpret the different gas solubilities determined experimentally.