

Hydrophobic Type Interactions between Ionic Liquids and Inorganic Salt Ions in Aqueous Environments

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The effect of common salts on the aqueous solubility of charged molecules has long been well described.¹ The qualitative order of the ions' effects according to their salting-in or salting-out inducing ability is known as the Hofmeister series.¹ Although this effect is phenomenologically well-established, the molecular level mechanisms by which ions operate is still elusive and not well understood. Common knowledge usually classifies the salting-out inducing ions as "kosmotropes" while the salting-in inducing ions are typically referred as "chaotropes" based on their supposed ability to, respectively, "create" or "destroy" the water bulk structure, as this was believed to be the central mechanism behind the Hofmeister series.¹ Recent experimental data and simulation results have cast doubts on this paradigm of the change of the bulk water structure as the main phenomenon behind the effect of salts on the molecules' aqueous solubility.²⁻³ Experimental data on the ionic liquids' (ILs) solubility in aqueous salt solutions, proved that two effects - regarding the interaction between salt ions and the IL solute - are predominant in the salting-in/salting-out phenomena:⁴ (i) an entropic effect associated with the molecules' salting-out that results from the tendency of high charge density ions to form hydration complexes away from the solute; and (ii) a direct interaction of the low charge density ions to the solute. The entropic effects leading to salting-out are well supported by thermophysical experimental solubility data and the Langmuir isotherm-based model employed⁴, while evidence for the direct binding of the ions to the solute were established from NMR spectroscopic studies. The solvation of the hydrophobic IL 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide in aqueous (D₂O) salt solutions of sodium- and chloride-based inorganic salts, as well as function of their concentration, was systematically investigated. It was found that there are favorable interactions between the salting-in inducing ions and the terminal protons at the hydrophobic alkyl chain of the IL, while an opposite effect was observed for the salting-out inducing salts. The results obtained clearly indicated that the interaction between the salt ions and the hydrophobic moiety of the IL cation is the controlling factor that explains the whole solubility scenario.

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