The Hofmeister Series and the Mutual Solubilities of Water and Ionic Liquids

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Ionic liquids (ILs) are salts composed of large cations and anions that cannot easily form an ordered crystal, and thus remain liquids at or near room temperature. Their intrinsic properties, such high thermal stability, large liquidus range, high ionic conductivity, the fact that they are non-volatile and non-flammable, and their highly solvating capacity, for both polar and nonpolar compounds, make them interesting as solvents in conventional organic liquid-phase reactions and in separations, especially of organic compounds produced in biological fermentations. Their physical properties can be modified over a wide range by changes in the detailed structure of the cation or the identity of the anion. The more common ILs are based on imidazolium and pyridinium composed cation salts.

For ILs to be used effectively as solvents in liquid-liquid extractions, it is important to know the mutual solubilities between the IL and the second liquid phase. In this work, we address the mutual solubilities between pure water or aqueous salt solutions and ILs.

This study focuses on hydrophobic imidazolium based ILs with low water solubilities. The IL content in the water-rich phase was analyzed using UV-vis spectroscopy. The water content in the IL-rich phase was analyzed by Karl Fischer titration. The temperature range of the experimental analysis was between 288 and 318 K at atmospheric pressure.

The influence of various anions and cations on the mutual solubilities of the water and several ionic liquids was verified and explained based on the Gibbs-Duhem equation. It was found that the Hofmeister series can adequately predict the influence of salts on the mutual solubilities studied.

The COSMO-RS, a quantum chemical based method, was applied to predict the mutual solubilities of the water and several ILs studied.