THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Ion Solvation in Critical Binary Aqueous Solvents Probed by Advanced Synchrotron-Based Techniques

Monika Witala

Institutionen för kemi och molekylärbiologi
Naturvetenskapliga fakulteten

GÖTEBORGS UNIVERSITET

Institutionen för kemi och molekylärbiologi

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Abstract

The Poisson-Boltzmann equation is the standard tool for studying the electrostatic interactions in electrolyte solutions, although it neglects e.g. the ion size and ion-ion correlations. Even experimentally observed specific ion effects cannot be explained in a view of this approximation. Some recent investigations suggest the ion-solvent coupling as an important factor.

This ion-solvent coupling plays particularly a role in systems composed of two different liquid components. The binary liquid mixtures containing salts have been found to exhibit a range of intriguing phenomena. First, a hydrophilic salt added to the binary solvent with suspended colloidal particles may cause emergence of anomalous interactions between those colloidal particles. A possible explanation is given by unequal partitioning of hydrophilic ions, driven by different preferences of cations and anions for one of the solvent's component. Second, if an antagonistic salt is added to the binary mixture, the solvent's mesoscale structuring has been found. Here, the responsible mechanism remains under debate, whether this occurs due to preferential ion solvation or ion size asymmetry.

In order to address these underlaying mechanisms, I studied hydrophilic ion distributions and cation-to-anion size effects in binary solvent. For this purpose, I used advanced synchrotron-based techniques: grazing-incidence x-ray fluorescence (GIXF) and small-angle x-ray scattering (SAXS). The binary solvent was composed of water and 2,6-dimethylpyridine containing different salts: potassium chloride and symmetrical quaternary ammonium bromides.

The obtained results are as follows. First, I show direct experimental evidence of microscopic segregation of hydrophilic ions at the binary liquid-vapor interface. Second, by proposing a method for determining the relative ion surface excess in binary solvents, I further quantify the observed interfacial excess of cations. Third, by choosing salts with systematic increase of cation-to-anion size ratio, I provide the first data on gradual build-up of the solvent's mesoscale order. Additionally, I demonstrate use of binary solvents for characterizing the x-ray beam-induced temperature increase in sample. This thesis work will contribute to the clarification of the salt-induced effects in aqueous binary solvents.

Keywords: Preferential ion solvation, microscopic segregation of hydrophilic ions, ion size asymmetry, critical binary liquid mixtures, 2,6-dimethylpyridine, potassium chloride (KCl), quaternary ammonium bromides, grazing-incidence x-ray fluorescence (GIXF), small-angle x-ray scattering (SAXS), x-ray beam-induced local heating