

Hofmeister Effect from First Principles: How Ions modify H-Bonds of Water

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27. Oktober 2011

In 1887, Franz Hofmeister recorded the concentration of ionic aqueous solutions at which precipitation of egg protein was observed. Ions were then first classified as either *kosmotropes*, which enhance the structure of water, or *chaotropes* which favor disorder in the hydrogen bond network. Since then, there have been many attempts to answer the *how* and *why* of water H-bond network modification that leads to the *Hofmeister Effect* in salt solutions.

Solvation shell water molecules form hydrogen bonds with the ions and electrostatically screen the Coulomb charge of the ion. On the other hand, the impact of the ion on water molecules beyond the solvation shell, the bulk water, is subject to an ongoing discussion. It is often stated that in the presence of ions, bulk water H-bond network is modified, while others claim no effect on bulk water. *The main target of our project is to shed light on the ion impact beyond the solvation shell.*

If it is not the direct action of the ion on the solute, then it is the effect of the ion on the H-bond network that makes it easier for the macromolecule to dissolve. This effect depends on the electrostatic attraction between ion and water molecules. The *NMR shifts* of water in different salt solutions will be calculated in order to study the strength of this attraction, based on our numerous studies of computational NMR shift calculations. Then we will compare results with experimental values from our collaborators at the MPIP. Our purpose is to determine a realistic structure for solvation and bulk water.

Besides the structural modification to the water H-bond network, the intermolecular and intramolecular dynamics are also affected by solvated ions. The impact of dissolved ions on the dynamics in the water molecule has been measured with spectroscopic techniques and they confirm our preliminary results: The configuration of water molecules in a radius of about 50 nm around the ion, is more stable when the charge density of the ion is higher. Our calculated trajectories will enable us to compare the level of “stiffness” of the solvation shell for different ions.

The future goals of this project point towards deeper understanding of structural arrangements and effects on dynamics of, at least, four ions in water.