Addressing the mechanism of ion specific effects

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The classical treatment of ions at a charged interface is based on the framework of the Poisson-Boltzmann theory and captures mainly the electrostatics. The striking deficiency of the treatment on the pure electrostatic level is the prediction that ions of the same valence produce the same results, independent of their chemical nature. In contrast, experiments reveal striking differences depending on the nature of the ions. Specific ion effects can be found everywhere in chemistry and biology and there are many reports of pronounced differences in the properties of charged monolayers, micelles, vesicles, protein solubility, enzyme reaction rate, dispersions or polyelectrolyte multilayers using different identically charged counter-ions. The effect of ions on a particular set of experiments can be put in a typical ordering. The most prominent set classifies ions according to their ability to precipitates proteins and date back to the work of Franz Hofmeister in the 19th century. The term Hofmeister series has been adopted for all kinds of ion specific effects and the existence of a Hofmeister series of ions suggests an underlying common principle.

Kim Collins introduces the law of matching water affinities that interprets the majority of ion specific effects as the formation of contact ion pairs. Here the driving force is not a specific chemical interaction between the oppositely charged ions; instead it is the consequence of the attractive force which is put in relation to the strength of the prevailing ion-water interaction. Small (hard) ions possess a tightly bound hydration shell, but the force between the ions is sufficiently strong to squeeze out the hydration shell. Big (soft) ions possess a loosely bound hydration shell, the electrostatic interaction is much weaker but still sufficiently strong to expel the hydration shell. The combination of hard and soft ions leads to a mismatch and both ions remain separated by a hydration layer. This simple concept possesses predictive power.

In this talk we assess the truth of this concept by using sum frequency generation spectroscopy on selected model compounds. IR-VIS SFG is a highly surface specific vibrational spectroscopy that probes only oriented molecules. The oscillator strength of the SFG band is analytically linked to the number of oriented water dipoles. Water is a dipole and sensitive to the local electric field produced by the ions. The energy of a dipole within an electric field is given by the scalar product of its dipole moment and the local electric field leading to a Langevin type function for the dependence between orientation and electric field. This approach can be used in a first approximation for the analysis of the strength of the SFG band. The formation of a contact ion pair leads from an electrostatic point of view to the formation of a dipole with a much weaker field than isolated ions. These elements outline the experiments discussed in this contribution.