

Manifestation of ion-specificity: from methane solubility to volume transition of smart polymers

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Abstract:

Materials with controllable properties have great potential for future applications in various disciplines. The subgroup of these, smart, materials are thermoresponsive polymers, which undergo volume phase transition when crossing their critical solution temperature. Their use as drug carriers, nanoreactors, antifouling materials, or soft biomimetic model systems for cells is already established. The real understanding of thermodynamic and kinetic properties of such polymers in aqueous solutions is essential for future design of new materials with desired properties. Apart of the behavior in neat water, understanding of the effect of ubiquitous buffers and salts is ultimately needed.

Since 1888 a lot of knowledge was gained about the repeatedly appearing Hofmeister series, which orders ions with respect to their power to salt out proteins, but are encountered frequently in soft matter biophysics. From the viewpoint of computer simulations the most flexible framework towards quantitative description of salt-specific effects on solutes is based on fluctuation theory of solutions, also called Kirkwood-Buff theory. From the known solution structure the preferential binding coefficient (excess adsorption) of salt over water near the solute's interface can be calculated and the change of solute's chemical potential determined.

We will illustrate the salt-specific effects and the preferential binding concept on few simple examples such as surface tension or methane solubility. Here the qualitative (salt-order) and quantitative (magnitude of the effect) analyses of experimental and computer simulation data are straightforward.

After this motivation and introduction, in the central part of the talk, we present our recently developed thermodynamic theory, which connects changes in solution structure to the salt-specific changes with transition thermodynamic properties of a biomolecule. On an example of a thermoresponsive polymer PNIPAM, we demonstrate, how can our theory be used to bridge the microscopic information gained in atomistic and coarse-grained simulations with the macroscopic thermodynamic properties of polymer collapse-transition obtained experimentally.

References:

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