Modelling specific ion effects in solutions using integral equation theories

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Introduction

Ions play an important role in many natural, biological, and technological processes. As a consequence, various experimental techniques are used to assess properties of ionic solutions. A theoretical description of these solutions can provide complementary information, and can be also used for predictions of their properties without the need to perform experiments.
We use the integral equation theory (namely the Ornstein-Zernike equation with the Hypernetted Chain closure relation) for obtaining such models of ionic solutions.
Our study requires very close collaboration with specialists from other fields of (not only) physical chemistry. The development of reliable interaction potentials would not be possible without the methods of computational chemistry, namely molecular dynamics simulations and quantum mechanical calculations. The Poisson–Boltzmann equation can be used for modeling of the interfaces of ionic solutions and, therefore, provides interesting insights into the physics of the interfacial behavior of ions. It is also an important source of material for comparison with the integral equation theory. Finally, experiments (when available) provide essential data that can be used for benchmarking and validating theoretical findings.

Methodology

Quantum Mechanics

Schrödinger equation $\mathcal{H}\Psi = E\Psi$

unbiased (*ab–initio*) results

outputs

- interaction potentials
- ionic properties
- structural information

Molecular Dynamics Simulations

Newtonian equations of motion $\frac{d^2\vec{r}_i}{dt^2} = \frac{\vec{F}_i(\vec{r}_1,\vec{r}_2,\ldots\vec{r}_N)}{m_i}$

$\vec{F}_i = -\nabla_i U(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$

inputs

- interaction potentials

outputs

- potentials of mean force
- pair correlation functions $g(r)$

Experiments

bulk and interfacial properties of ionic solutions

- osmotic and activity coefficients
- surface tensions
- distribution functions
- and many more...

Statistical Mechanics of Liquids

Ornstein-Zernike Equation $h(r_{12}) = c(r_{12}) + \rho \int dr_3 c(r_{13})h(r_{23})$

Hypernetted Chain Approximation $c(r_{12}) = h(r_{12}) - \ln(h(r_{12}) + 1) - \frac{-U(r_{12})}{kT}$

theory is using the formalism of correlation functions ($h(r)$, $c(r)$, and $g(r)$)

inputs

- potentials of mean force
- interaction potentials

outputs

- pair correlation functions $g(r)$
- thermodynamic properties – osmotic and activity coefficients, surface tension, ...

Outcomes

description of bulk and interfacial properties of ionic solutions

generally usable set of physically meaningful parameters

theory with predictive capabilities

Goals of the work

We are aiming at obtaining precise and predictive description of properties of ionic solutions. The most important steps of this project will be:

- development of new **physically sound** solvent averaged interaction potentials
- definition of suitable fitting parameters, if needed
- description of both **bulk and surface properties of ionic solutions**
- description of **dissociation phenomena** - pK of weak electrolytes in mixtures and buffers
- application of the results in biology, biochemistry, engineering, ...

Collaborations

- **Roland Netz, Dominik Horinek** (TU München)
  - molecular dynamics and quantum mechanical calculations
- **Matthias Boström** (Linköping University)
  - description of solution interfaces using the Poisson–Boltzmann equation