

Theoretical Investigations of the Role of Ion-Ion Correlations and Ion-Specific Interactions in Electric Double Layers

Erik Wernersson

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE FIELD OF PHYSICAL CHEMISTRY

This thesis is to be defended in English on the 2:nd of October 2009
at 10:15 in room 10:an, kemivägen 10, Göteborg.

Faculty opponent is Dr. Luc Belloni,
LIONS, CEA/SACLAY, France.



UNIVERSITY OF GOTHENBURG
DEPARTMENT OF CHEMISTRY
2009

ISBN 978-91-628-7869-6

Abstract

Electric double layers are ubiquitous, arising in some form in almost every situation involving an interface with an aqueous electrolyte solution. In order to gain insight into the behavior of electrolytes and electric double layers, simple models of bulk and inhomogeneous electrolyte solutions are considered in this thesis. As the main focus is on situations where mean field theory is not applicable, due to high concentration, strong electrostatic interactions, polarization of the interface or a combination of these, the spatial correlation between ions is explicitly considered.

This is done within the framework of integral equation theory. The hypernetted chain (HNC) approximation is employed, which may be regarded as an approximate expression for the relation between the correlation functions and the potential of mean force. The excess contribution to the chemical potential is readily obtainable in the HNC approximation. By exploiting the fact that the ideal contribution to the chemical potential only depends on the local concentration and that thermodynamic equilibrium requires that the total chemical potential is equal everywhere, the concentration profile for each species of ion can be determined. Thus, the HNC approximation gives rise to a theory for electric double layers as well as for bulk electrolytes.

The model of ions and interfaces is based on the assumption that the ions are hard, charged spheres that are embedded in a dielectric continuum that represents the solvent. This type of model obviously ignores any effect of the atomic granularity of the solvent, but takes into account both electrostatic and excluded volume effects that together give rise to several interesting and counter-intuitive phenomena. These have implications for both single interface properties and interface-interface interactions.

Any contrast in dielectric properties on each side of the interface gives rise to forces on the ions in the vicinity, which may also be of importance for the behavior of the system. Dispersion interactions between ions and interfaces are present whenever the ions have a non-zero polarizability. Each ionic charge in the vicinity of an interface also causes polarization, creating a charge distribution that gives rise to forces on all ions in the vicinity. Thus, such polarization modifies the forces amongst ions as well as those between ions and interfaces. Both dispersion forces and the polarization of interfaces are explicitly considered in this thesis.