CPP 50: Charged Soft Matter, Polyelectrolytes and Ionic Liquids II

Time: Wednesday 15:00–17:15   Location: C 243

CPP 50.1   Wed 15:00   C 243
Polyelectrolyte Complexes with Oppositely Charged Microemulsion Droplets: Investigations of Structure and Dynamics — ●Michael Gradzielski[1], Miriam Simon[1], Laurence Noirez[2], and Ingo Hoffmann[3] — [1]Stranski-Laboratorium, Institut für Chemie, TU Berlin — [2]Laboratoire Leon-Brillouin (LLB), Saclay, France — [3]Institut Laue-Langevin (ILL), Grenoble, France

Mixing polyelectrolytes (PE) with oppositely charged colloids leads to modifications of structure and rheology of the systems. For the case of surfactants that leads to polyelectrolyte/surfactant complexes (PESCs). As loaded micelles are relevant for delivery we studied mixtures of positively charged O/W microemulsion (ME) droplets with negatively charged polyelectrolytes. Based on a thorough determination of the phase behavior, the combination of SLS, DLS, SANS yielded a detailed description of the formed complexes in terms of size, shape and composition. Dynamics were studied by PFGNMR, NSE, and FCS. This yielded a comprehensive picture of how the structure depends on ME size and the type and Mw of the PE.

CPP 50.2   Wed 15:15   C 243
Electronic Continuum Correction for Multivalent Ions in Water — ●Ellen Bruce and Nico van der Vegt — Technische Universität Darmstadt, Alarich-Weiss-Straße 10, 64287 Darmstadt, Germany

Short range interactions between hydrated ions and/or charged chemical groups on (bio)polymers lie at the basis of several physical phenomena in aqueous solvation science that remain ill-understood. These interactions are commonly studied with molecular simulation methods that use non-polarizable models, as these are computationally cheap. This approach is however problematic due to strong electronic polarization effects. One way of accounting for polarization effects in non-polarizable models is by using the electronic continuum correction (ECC).[1] ECC has been widely used for monovalent and some divalent salts. However, the performance for multivalent salts which have stronger polarization effects is largely unexamined. We show that the ECC model provides accurate description for multivalent ions solutions (K_3PO_4 and K_2HPO_4).[2] The osmotic coefficients are used as a measure to assess ECC models and are in good agreement with experiments. The results demonstrate accurate modeling of electrolyte structure as well as effective short-range ion-ion interactions. This approach opens routes for simulations of aqueous soft matter systems in which short-range electrostatic interactions drive interesting physical phenomena. [1] I. V. Leontyev et al., J. Chem. Phys. 119, 8024 (2003) [2] E. E. Bruce et al., J. Chem. Phys. (submitted 2017)

CPP 50.3   Wed 15:30   C 243
Solvate induced surface order in ionic liquids — ●Julian Mars[1,2], Henning Weiss[2], Sven Festersen[3], Bridget Murphy[3], Veijo Honkimäki[4], Markus Bier[5], and Markus Mezger[1,2] — [1]Max Planck Institute for Polymer Research, Mainz, Germany — [2]Institute of Physics and MAINZ Graduate School, Johannes Gutenberg University Mainz, Germany — [3]Institute of Experimental and Applied Physics, Kiel University, Germany — [4]ESRF The European Synchrotron, Grenoble, France — [5]Max Planck Institute for Intelligent Systems, Stuttgart, Germany

In supported ionic liquid (IL) phase catalysis, the chemical reaction takes place in a sub-micrometer IL film, wetting a solid support material with high surface area. To understand diffusion of reactants and products across the IL/vapor interface, knowledge of the interfacial structure is crucial. We employ X-ray scattering techniques to investigate the near surface structure on the molecular length scale. In microheterogeneous ILs, solvates aggregates site-specifically within high affinity domains. Non-polar molecules are preferentially situated in the aliphatic regions, affecting the near surface structure. For different classes of binary model systems, we observe the formation of adsorbate layers and solvate induced surface phase transitions.

CPP 50.4   Wed 15:45   C 243
Effect of Salt on the Surface Absorption and Structures of aqueous Polyelectrolyte/Surfactant Mixtures at the air/water Interface — ●Larissa Braun[1], Richard Campbell[2], and Regine von Klitzing[1] — [1]TU Darmstadt, Darmstadt, Germany — [2]Institut Laue-Langevin, Grenoble, France

The surface properties of mixtures of polyelectrolyte and oppositely charged surfactant play an important role in colloidal dispersions (foams, emulsions) e.g. for cosmetics, cleaning products and in food technology.

This work focuses on the effect of salt (LiBr) on the adsorption behavior of mixtures of the anionic polyelectrolyte sPSO2-S220 with the cationic C14TAB. Neutron reflectometry experiments including extensive contrast matching were performed to get insight into the exact composition and structure of the adsorbed polyelectrolyte/surfactant complexes at the air/water interface.

There is no linear relation between surface composition and bulk composition. The salt influences both the surface composition as well as the formed structures at the surface.

CPP 50.5   Wed 16:00   C 243
Counterions in aqueous planar nano-confinement: Atomistic simulations and continuum modeling — ●Alexander Schlaich[1,2] and Roland R. Netz[1] — [1]Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany — [2]Laboratoire Interdisciplinaire de Physique (LIPhy), CNRS and Université Grenoble Alpes, F-38000 Grenoble, France

Continuum models for the electrostatic interaction between charged surfaces have been employed successfully to model the interaction between charged surfactants and lipid membranes, yet in nano-confinement additional effects such as the hydration force and dielectric effects need to be taken into account. Here, we perform water-explicit atomistic simulations of monovalent counter-ions confined between planar, charged decanol surfaces at prescribed water chemical potential, allowing to access the interaction pressures and charge distributions in sub-nanometer confinement. At low surface charge density we find additive contributions to the repulsion due to the exponential hydration interaction and counterion entropic effects. The modified Poisson-Boltzmann equation, including the dielectric profile, the fluctuating external charge distribution of the surface and ion-surface interactions, quantitatively describes the ion distribution from several nanometer separations down to strongest confinement, corresponding to kilobar interaction pressures.

CPP 50.6   Wed 16:15   C 243
Effects of counterions on conformation and counterion condensation on polyelectrolytes — ●Ulrich Scheler — Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Str 6, 01069 Dresden, Germany

Counterion condensation reduces the effective charge in polyelectrolytes. This in turn affects the conformation of the polyelectrolytes, because the repelling force between repeat units is reduced. The hydrodynamic size of the polyelectrolytes in solution is determined from the selfdiffusion coefficient measured by PFG NMR. In combination with electrophoresis NMR the effective charge is determined and compared with the nominal charge from the number of repeat units. Poly(styrenesulfonate) has been titrated with various hydroxides to generate the respective salts. There are the expected differences between mono and bivalent counterions, with the latter resulting in an effective charge reduced by about a factor of two and a hydrodynamic radius reduced by 30%. However the effective charge of the acid with H+ as counterion is 10% larger than for others monovalent counterions. Significant differences in the hydrodynamic radius are observed, which are not simply explained by the counterion condensation. Ion-specific effects are observed as well.

15 min. break

CPP 50.7   Wed 16:45   C 243
Temperature dependence and thermal response of electric double layer capacitors — ●Mathijs Janssen — Max Planck Institute for Intelligent Systems, Stuttgart, Germany

Where surfaces of charged electrodes meet fluids that contain mobile ions, so-called electric double layers (EDLs) form to screen the electric surface charge by a diffuse cloud of counterionic charge.

In this talk, we discuss the intricate interplay between temperature and EDL characteristics. First, we show that varying the electrolyte temperature gives rise to a temperature-induced surface charge varia-

tion [1]. Vice versa, variation of the electrode potential of a thermally insulated EDL capacitor gives rise to a charge-induced temperature variation [2]. Besides irreversible (bulk) Joule heating, this temperature variation is sourced by the reversible ion rearrangements that occur during EDL formation: heating upon charging, and cooling upon discharging. We derive a thermodynamic identity for this isentropic-heating-by-charging effect, and compare to the slow-charging thermal behavior of a Nernst-Planck model [2]. We finally argue that the thermal response to charging in fact contains valuable information on the EDL; we deduce the entropic part of the grand potential from the tiny temperature variations that can be measured during charging and discharging an EDL capacitor [3].

[1] M. Janssen et al., Phys. Rev. Lett. 113, 268501 (2014)
[2] M. Janssen and R. van Roij, Phys. Rev. Lett. 118, 096001 (2017)
[3] M. Janssen et al., Phys. Rev. Lett. 119, 166002 (2017)

CPP 50.8   Wed 17:00   C 243

A computational study on the properties of residual water in ionic liquids using the Kirkwood-Buff theory — ●Takeshi Kobayashi[1], Joshua E. S. J. Reid[2,3], Seishi Shimizu[2], Maria Fyta[1], and Jens Smiatek[1] — [1]Institute for Computational Physics, Universität Stuttgart, Germany — [2]York Structural Biology Laboratory, Department of Chemistry, University of York, UK — [3]TWI Ltd., UK

The properties of residual water in two different dialkylimidazolium based ionic liquids (ILs), namely 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM/BF4) and 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM/BF4), are studied at different water mole fractions by means of classical atomistic molecular dynamics simulations[1]. In order to provide a robust validation of the simulation results, the Kirkwood-Buff (KB) integrals for the ion-ion and ion-water pair correlations are calculated from the corresponding radial distribution functions and compared with the inverse KB results based on experimental data. It is shown that there is a quantitative agreement between these two approaches. Further analysis shows a negligible influence of residual water on the structures of ILs even at intermediate mole fractions. The majority of the water molecules are found as monomers, while a non-linear increase in the higher order water clusters is observed for higher mole fractions. According to these results, our work provides a detailed explanation of the properties of the binary mixtures of water and dialkylimidazolium based ILs. [1] T. Kobayashi et al., Phys. Chem. Chem. Phys. 19, 18924 (2017)