

CPP 42: Charged Soft Matter, Ionic Liquids and Polyions I

Time: Wednesday 15:00–18:00

Location: ZEU 114

CPP 42.1 Wed 15:00 ZEU 114

Reactivity and structure of NaOH solutions from neural-network-based simulations — ●MATTI HELLSTRÖM and JÖRG BEHLER — Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, Germany

Sodium hydroxide (NaOH) is soluble in water up to very high concentrations and has many applications in chemical industry. Using a high-dimensional neural network potential for NaOH(aq) based on dispersion-corrected DFT calculations, we have performed large-scale molecular dynamics simulations with close to ab initio quality. The simulations reveal an unexpected multitude of concentration-dependent presolvation mechanisms governing the proton-transfer rate from H₂O to OH⁻ [1], and a large variety of coordination environments around the Na⁺ ions [2].

[1] M. Hellström, J. Behler. *J. Phys. Chem. Lett.* **7** (2016) 3302

[2] M. Hellström, J. Behler. *Phys. Chem. Chem. Phys.* DOI: 10.1039/C6CP06547C

CPP 42.2 Wed 15:15 ZEU 114

Preferential solvation and ion association properties in aqueous dimethyl sulfoxide solutions — ●ANAND NARAYANAN KRISHNAMOORTHY, JOHANNES ZEMAN, CHRISTIAN HOLM, and JENS SMIA TEK — Institute for Computational Physics - University of Stuttgart

We study the solvation and the association properties of ion pairs in aqueous dimethyl sulfoxide (DMSO) solution by atomistic molecular dynamics (MD) simulations. The ion pair is composed of two lithium and a single sulfonated diphenyl sulfone ion whose properties are studied under the influence of different DMSO concentrations. For increasing mole fractions of DMSO, we observe a non-ideal behavior of the solution as indicated by the derivatives of the chemical activity. Our findings are complemented by dielectric spectra, which also verify a complex DMSO-water mixing behavior. In agreement with these results, further simulation outcomes reveal an aqueous homoselective solvation of the ion species which fosters the occurrence of pronounced ion association constants at higher DMSO mole fractions. The consequences of this finding are demonstrated by lower ionic conductivities for increasing concentrations of DMSO.

CPP 42.3 Wed 15:30 ZEU 114

Image-charge effects on the dissociation of acids at dielectric discontinuities — ●PHILIP LOCHE, ALEXANDER SCHLAICH, CIHAN AYAZ, SENTA VOLKENANDTS, and ROLAND NETZ — Department of Physics, Free University Berlin, Arnimallee 14, 14195 Berlin, Germany

In colloid and interface sciences image-charge effects are considered to play a key role for ion transport and double layer attraction. Image-charge effects are also an important component for the self-energy of ions or functional groups and thus contribute to the dissociation constant of acids.

We use molecular dynamics simulations in combination with the local dielectric permittivity tensor and the solution of the tensorial Green's functions to investigate electrostatic effects at interfaces. The potential of mean force and free energy calculations are deployed for simple ions and functional groups. The analytical self-energy obtained from the tensorial Green's function is compared to simulation results.

CPP 42.4 Wed 15:45 ZEU 114

Cation-induced hydration effects cause lower critical solution temperature behavior in protein solutions — ●OLGA MATSARSKAIA¹, MICHAL K. BRAUN¹, FELIX ROSEN-RUNGE², MARCELL WOLF¹, FAJUN ZHANG¹, ROLAND ROTH³, and FRANK SCHREIBER¹ — ¹Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen — ²Institut Laue-Langevin, Grenoble, France — ³Institut für Theoretische Physik, Universität Tübingen

Systems consisting of negatively charged proteins and trivalent salts feature strong short-range attractive forces and exhibit a rich phase behaviour including reentrant condensation, clustering and crystallisation [1]. Here, we report a *lower critical solution temperature* liquid-liquid phase separation (LCST-LLPS) behaviour in a system of bovine serum albumin (BSA) and the trivalent salt YCl₃. Combining isothermal titration calorimetry (ITC) and ζ potential data into a comprehensive model, we show that cation-protein binding is an endothermic and thus entropy-driven process. We attribute the entropic contribution to

a partial release of hydration water molecules around Y³⁺ cations and protein carboxyl groups. Our findings have implications for the general understanding of hydration-mediated interactions of soft matter.

[1] Zhang *et al.* *Pure & Appl. Chem.* 2014, 86, 191-202; [2] Matsarskaia *et al.* *JPCB* 2016, 120, 7731-7736.

Invited Talk

CPP 42.5 Wed 16:00 ZEU 114

Aqueous Ionic Liquids and Their Influence on Peptide Conformation: Denaturation and Dehydration Mechanisms — ●JENS SMIA TEK — Institut für Coputerphysik, Universität Stuttgart, D-70569 Stuttgart, Germany

The influence of low concentrated aqueous ionic liquid (ILs) solutions on protein structures has attracted a lot of interest in the last years. This can be mostly attributed to the distinct roles of the aqueous ILs as protein protectants or protein denaturants. I will review the results of atomistic molecular dynamics (MD) simulations to study the influence of different ILs on the conformational properties of a short hairpin peptide. The results reveal distinct binding and denaturation effects for 1-ethyl-3-methylimidazolium (EMIM) in combination with the different anions chloride (CL), tetrafluoroborate (BF₄) and acetate (ACE). The simulation outcomes indicate that ILs with larger anions induce a stronger dehydration effect which is accomplished by a more pronounced accumulation behavior of the individual ion species around the peptide. All findings can be related to the implications of the Kirkwood-Buff theory, which provides a thermodynamic explanation for the denaturation strength in terms of the IL accumulation behavior. The outcomes of this analysis are in good agreement with the results of metadynamics simulations to determine the energetically most favorable conformations of the peptide in presence of the individual aqueous ILs. All findings indicate that the denaturation strength decreases in the order EMIM/ACE, EMIM/BF₄ and EMIM/CL, which coincides with the size of the anion species.

15 min break

CPP 42.6 Wed 16:45 ZEU 114

Dynamics of Room Temperature Ionic Liquids: A ¹H and ¹⁹F NMR Relaxometry and Diffusometry study — ●MANUEL BECHER and MICHAEL VOGEL — TU Darmstadt Solid State Physics, Darmstadt, Germany

Room Temperature Ionic Liquids (RTIL) are salts with a low melting point and vapour pressure, caused by a rather big and asymmetric cation. They are usually glass forming systems with complex and heterogeneous molecular dynamics. The combination of different cations and anions opens wide ranges of chemical and physical applications, e.g. as solvents or fluid electrolytes, and their optimization. Hence, a fundamental understanding of molecular dynamics is of crucial importance. Here, imidazolium based RTILs with an [Tf₂N]⁻ anion are in the experimental focus, with a variation of alkyl chain lengths at the cation so as to vary structural and dynamical heterogeneity. Nuclear Magnetic Resonance (NMR) provides access to glassy dynamics in wide range of temperature and length scales. Due to its isotope sensitivity the dynamical behaviour of different molecules/molecular groups can be separated. In a static field gradient, we measure the self-diffusion coefficient of the cation (¹H) and anion (¹⁹F), revealing hints to clustering. Field-Cycling relaxometry provides frequency-dependent relaxation times T₁(ω) and yields translational and rotational correlation times as well as insight into local dynamics. Comparing long-range self-diffusion with short-range structural relaxation, we analyze cation-anion couplings against the background of alkyl-chain length dependent structural heterogeneities.

CPP 42.7 Wed 17:00 ZEU 114

A Coarse-Grained Model for Polyionic Liquids — ●ALEXANDER WEYMAN¹, JENS SMIA TEK¹, MARKUS BIER², and CHRISTIAN HOLM¹ — ¹Institut für Computational Physics, University of Stuttgart — ²Max Planck Institute for Intelligent Systems

Polyionic liquids or polymerized ionic liquids (PILs) are a relatively new class of polyelectrolytes that combine both the advantages of polymeric materials and the unique properties of ionic liquids and therefore have become the focus of scientific interest in recent years.

We show results from molecular dynamics (MD) simulation using a

coarse-grained model for polyionic liquids in order to analyze structural features and transport properties. The polymer chains are described by a bead-spring model where the single PIL monomers are represented by single beads that are interconnected via bond potentials.

Following the observation of microphase separation in dense bulk systems of ionic liquids, dense systems of polyionic liquids are simulated, and partial structure factors are calculated for the quantitative analysis of the likewise occurring microphases.

Using a classical density functional theory framework, a selection of partial structure factors is calculated and compared with MD simulations.

Furthermore, we also find an enhancement of the conductivity, if the PILs are confined between two plane-parallel interfaces, due to the occurrence of a larger conductivity near the interfaces which is in agreement with experimental findings that have speculated about the occurrence of conductivity channels.

CPP 42.8 Wed 17:15 ZEU 114

Dielectric study on mixtures of ionic liquids — ●PIT SIPPEL¹, ERIK THOMS¹, DANIEL REUTER¹, ALOIS LOIDL^{1,2}, and STEPHAN KROHNS^{1,2} — ¹Experimental Physics V, Center for Electronic Correlations and Magnetism, University of Augsburg, 86135 Augsburg, Germany — ²Institute for Materials Resource Management, University of Augsburg, 86152 Augsburg, Germany

Ionic liquids are salts that are liquid below 100 °C and offer outstanding properties (e.g., low volatility and high electrochemical stability). These make them promising candidates for solvent-free electrolytes to improve energy storage systems [1]. However, most ionic liquids exhibit low conductivity, hampering their applicability in supercapacitors and battery systems. We demonstrate the tuning of the conductivity via mixing various ionic liquids. An increased conductivity has been reported for particular mixing series. Nonetheless, these are exceptions and most mixing series behave close to linear mixing-laws. To gain more insight into the molecular dynamics we performed detailed investigations by dielectric spectroscopy and differential scanning calorimetry on two mixing series of ionic liquids. The analysis of the glass temperatures and the thorough evaluations of the measured dielectric spectra reveal that the dynamics in these mixtures are well defined by the fractions of their parent compounds. Moreover the room-temperature conductivity in these mixtures is still directly related to their glass properties, as in pure ionic liquids [2].

[1] D. R. MacFarlane, *et al.*, *Energy Environ. Sci.* **7**, 232 (2014).

[2] P. Sippel *et al.*, *Sci. Rep.* **5**, 13922 (2015).

CPP 42.9 Wed 17:30 ZEU 114

Insights on the diversity of smectic phases in ionic liquid crystals — ●HENDRIK BARTSCH^{1,2}, MARKUS BIER^{1,2}, and SIEGFRIED DIETRICH^{1,2} — ¹Max Planck Institute for Intelligent Systems, 70569

Stuttgart, Germany — ²Institute of Theoretical Physics IV, University of Stuttgart, 70569 Stuttgart, Germany

Ionic liquid crystals (ILCs) can be described as anisotropic molecules, which carry charges and therefore combine properties of liquid crystals, e.g. mesophases, and ionic fluids, e.g. low melting temperatures and tiny triple-point pressures. However, the combination of both, orientational degrees of freedom and electrostatics renders a particular challenge for theoretical studies.

Recently a promising model of ILCs has been proposed and studied within the framework of density functional theory [1]. It turns out, that the phase diagram is strongly affected by the molecules' properties, i.e. the length-to-breath ratio, the position of charges and the interaction strengths. Here, we report on very recent findings on the phase behavior of ILCs obtained by means of density functional theory and Monte Carlo simulations. The most striking is the occurrence of a novel, second smectic A phase at low temperature, whose layer spacing is larger than that of the ordinary high-temperature smectic A phase and increasing upon decreasing temperature at constant packing fraction or pressure.

[1] S. Kondrat, M. Bier, and L. Harnau, *J. Chem. Phys.* **132**, 184901 (2010)

CPP 42.10 Wed 17:45 ZEU 114

Determination of the optical constants of ionic liquids by ellipsometry — ●XIA WU¹, MAREN MUNTZECK², TERESA DE LOS ARCOS³, IGNACIO GINER³, GUIDO GRUNDMEIER³, RENÉ WILHELM², and THORSTEN WAGNER¹ — ¹Inorganic and analytical chemistry, Department of Chemistry, University of Paderborn, Warburger Straße 100, D-33098, Paderborn, Germany — ²Organic chemistry, Department of Chemistry, University of Paderborn, Warburger Straße 100, D-33098, Paderborn, Germany — ³Technical chemistry, Department of Chemistry, University of Paderborn, Warburger Straße 100, D-33098, Paderborn, Germany

We determined the optical constants (complex refractive index, dispersion and temperature coefficient) of ionic liquids by ellipsometry method mainly in visible range (360 nm - 1000 nm). We focus on the ionic liquids with high refractive indices ($n > 1.7$) since it is not possible to measure this high index by normal refractometer. We synthesized ionic liquids with such high indices. These high index ionic liquids can be used as index matching liquids in determination of refractive indices of metal oxides inside photonic crystals or porous materials in general. These ionic liquids are particularly suitable for index matching, because they are stable (low vapor pressure) and less toxic than commercial available index matching liquids with equally high indices [1].

Reference: [1] M. Deetlefs, K. R. Seddon, M. Shara, *New Journal of Chemistry* **30**, 317-326 (2006); doi: 10.1039/b513451j