

## CPP 39: Charged Soft Matter, Polyelectrolytes and Ionic Liquids

Time: Tuesday 9:30–12:15

Location: ZEU 114

CPP 39.1 Tue 9:30 ZEU 114

**Ion Correlations in Polymer Electrolyte-Ionic Liquid Mixtures** — ●DIDDO DIDDENS<sup>1</sup> and ANDREAS HEUER<sup>1,2</sup> — <sup>1</sup>Helmholtz-Institut Münster (IEK-12), Forschungszentrum Jülich GmbH, Corrensstraße 46, 48149 Münster — <sup>2</sup>Institut für physikalische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstraße 28/30, 48149 Münster

Polymer electrolytes consist of a salt dissolved in a polymer matrix such as poly(ethylene oxide) (PEO). Even though they are safer than conventional liquid battery electrolytes due to their reduced flammability and mechanical stability, their conductivity is still too low for an efficient technological use. To overcome this issue, the use of small molecular shuttles has been proposed [1], in which the cation of an ionic liquid (IL) is functionalized by a small oligoether side chain that can detach the lithium ions from the slow PEO chains. Additionally, dynamically coupling the lithium ions to the IL cations in this way, it is expected that IL and lithium cations move cooperatively in an electric field, giving rise to enhanced transference numbers. In this contribution, we explicitly check this assumption by focusing on dynamical ion correlations within the electrolyte, and on their impact on the lithium transference number as well as the overall conductivity.

[1] D. Diddens *et al.*, *J. Electrochem. Soc.* **2017**, 164, E3225

CPP 39.2 Tue 9:45 ZEU 114

**Hydrogen Bonding and Charge Transport in a Protic Polymerized Ionic Liquid** — ●ARTHUR MARKUS ANTON<sup>1,2</sup>, FALK FRENZEL<sup>2</sup>, JIAYIN YUAN<sup>3</sup>, MARTIN TRESS<sup>2,4</sup>, and FRIEDRICH KREMER<sup>2</sup> — <sup>1</sup>The University of Sheffield, Department for Physics & Astronomy, Sheffield, UK — <sup>2</sup>Leipzig University, Peter Debye Institute for Soft Matter Physics, Leipzig, Germany — <sup>3</sup>Stockholm University, Department of Materials and Environmental Chemistry, Stockholm, Sweden — <sup>4</sup>University of Tennessee Knoxville, Department of Chemistry, Knoxville, USA

Fourier transform infrared and broadband dielectric spectroscopy are combined in order to study hydrogen bonding and charge transport in the protic polymerized ionic liquid PAAPS in a wide temperature range from 170 to 300K. While the former allows to follow the formation of hydrogen bonds, the latter enables to record the complex conductivity in the spectral range from  $10^{-2}$  to  $10^{+9}$  Hz. On the one hand, the formation of the H-bond network exhibits a pronounced thermal hysteresis, whereas, on the other hand, the effective conductivity is reversibly affected by temperature. In combination with the fact that the conductivity changes with temperature by orders of magnitude, whereas the integrated absorbance of the N-H stretching vibration (being proportional to the number density of protons in the hydrogen bond network) changes only by a factor of 4, it is concluded that charge transport takes place predominantly due to dynamic glass transition assisted hopping conduction mechanism and is not significantly affected by the establishment of H-bonds.

CPP 39.3 Tue 10:00 ZEU 114

**Transport properties of two water-in-salt electrolytes: LiTFSI and LiOTF** — ●MAEDEH ZAHEDIFAR and AXEL GROSS — Institut für Theoretische Chemie, Universität Ulm, 89069 Ulm, Germany

Over the past two decades, “solvent-in-salt” electrolytes have gained attention as a promising electrolyte concept for safer energy storage applications. Water is in principle an ideal solvent, but it has only a small range of electrochemical stability, which does not allow it to be used in high-voltage batteries. However, this limitation can be overcome by using highly concentrated aqueous electrolytes together with LiTFSI and LiOTF [1], so-called water-in-salt electrolytes. In order to better understand the properties of solvent-in-salt electrolyte, we have performed molecular dynamics simulations [2] of mixtures of water molecules with either LiTFSI or LiOTF salts. SPC/E and Lennard-Jones parameters are used for the description of water molecules and anions, respectively [3]. Values of the viscosity for both LiTFSI and LiOTF salts in water have been derived from the time integral of the stress tensor auto-correlation function. Besides the viscosity, we will discuss further properties of the electrolytes such as radial distribution functions and mean-square displacements, and we will also present results of first-principles electronic structure calculations addressing

these electrolytes.

[1] L. Suo *et al.*, *Angew. Chem. Int. Ed.* **55**, 7136-7141 (2016).

[2] S. Plimpton, *J. Comp. Phys.* **117**, 1 (1995).

[3] J. Chandrasekhar *et al.*, *J. Am. Chem. Soc.* **106**, 903 (1984).

CPP 39.4 Tue 10:15 ZEU 114

**Identifying Mg<sup>2+</sup> binding sites on RNA using MD simulations with accelerating force field parameters** — ●KARA K. GROTZ, SERGIO CRUZ-LEÓN, and NADINE SCHWIERZ — Department of Theoretical Biophysics, Max Planck Institute of Biophysics, Frankfurt am Main, Germany

Mg<sup>2+</sup> is one of the most abundant cations in living cells. The interaction between Mg<sup>2+</sup> and RNA is essential for folding and function of the diverse macromolecule. Mg<sup>2+</sup> binds specifically and often directly (inner-sphere configuration) to individual functional groups on the RNA. Localizing Mg<sup>2+</sup> binding sites, however, is challenging as Mg<sup>2+</sup> is silent in most experimental approaches. Computational studies can contribute molecular insight but often struggle with insufficiently accurate atomistic models (force fields) and time scale limitations due to the slow binding kinetics of Mg<sup>2+</sup> (millisecond time scale). Herein, we use a recently developed Mg<sup>2+</sup> force field that is based on ion-water and ion-ion properties of Mg<sup>2+</sup>. In addition, the parameters are chosen such that they accelerate the water exchange kinetics (nanosecond time scale). Moreover, by incorporating experimental binding affinities towards specific RNA binding positions, we are able to find Mg<sup>2+</sup> binding sites on RNA using unbiased simulations and observe outer-to-inner sphere transitions directly.

CPP 39.5 Tue 10:30 ZEU 114

**Helical twist of dsDNA depends on cation type and concentration** — ●SERGIO CRUZ-LEON<sup>1</sup>, WILLEM VANDERLINDEN<sup>2</sup>, JAN LIPPERT<sup>2</sup>, and NADINE SCHWIERZ<sup>1</sup> — <sup>1</sup>Department of Theoretical Biophysics, Max Planck Institute of Biophysics, Max-von-Laue-Str. 3 60438 Frankfurt am Main, Germany — <sup>2</sup>Department of Physics, Nanosystem Initiative Munich and Center for Nanoscience, LMU Munich, Amalienstr. 54, 80799 Munich, Germany

The structural properties of double-stranded (ds)DNA determine many of its biological functions and are central for the development of precise artificial structures in nanotechnological applications. One of the most fundamental and iconic properties of DNA is its helicity, which depends on environmental factors such as temperature and salt concentration. While it has been known that DNA twist changes in a salt-dependent manner, the molecular origin of the effect remains unexplained. Here, we quantify the changes of dsDNA helical properties with ion type and concentration for a set of mono- and divalent cations. We combine single-molecule magnetic tweezers, molecular dynamics simulations, and theoretical modeling, and find that dsDNA changes its helical twist in a unique form depending on both ion type and concentration. Furthermore, we propose a mechanical model that captures the dependence on salt conditions for the changes in the dsDNA structure. Our structural insights and the mechanistic model facilitate the use of ion type and concentration as a tool to delicately manipulate DNA structures, for example, in the growing field of DNA origami technology.

CPP 39.6 Tue 10:45 ZEU 114

**The effects of ethanol and salt on the phase behavior and interactions of aqueous protein solutions** — RAJEEVANN UTHAYAKUMAR, ●FLORIAN PLATTEN, and STEFAN U. EGELHAAF — Condensed Matter Physics Laboratory, Heinrich Heine University, Düsseldorf, Germany

The addition of salts or organic solvents to aqueous protein solutions alters their optical and dielectric properties and the interactions between protein molecules in these mixtures change accordingly. Here, the effects of NaCl and ethanol on the phase behavior and interactions of protein solutions are studied in terms of the metastable liquid-liquid phase separation and second virial coefficient  $B_2$  of lysozyme solutions. The cloud-point temperatures are reduced and raised by the addition of ethanol and salt, respectively. The extended law of corresponding states allows to interpret these trends as changes of  $B_2$ . Remarkably, the dependence of  $B_2$  on both salt and ethanol content is quantitatively modelled by the DLVO theory.

CPP 39.7 Tue 11:00 ZEU 114

**The Kinetic Pathway for Polyelectrolyte Coacervate Formation revealed by Time-resolved Synchrotron SAXS** — MATTHIAS AMANN<sup>1</sup>, JAKOB DIGET<sup>1</sup>, JAN-SKOV PEDERSEN<sup>2</sup>, THEYENCHERI NARAYANAN<sup>3</sup>, and •REIDAR LUND<sup>1</sup> — <sup>1</sup>Department of Chemistry, University of Oslo, Norway — <sup>2</sup>Aarhus University, Denmark — <sup>3</sup>ESRF, France

The kinetic pathways for coacervation and micelle formation are still not fully understood. Driven by electrostatic interactions and entropically driven counter-ion release, complexation of oppositely charged macromolecules lead to the formation of micellar nanostructures. Here we study the coacervation process, from initial formation and growth of stable micelles, on a nanometric length scale using time-resolved small-angle X-ray scattering (TR-SAXS). The micellar coacervates are formed through the complexation of anionic polyelectrolyte (PSS) and cationic block copolymer (PEO-b-PVBTA). The results reveal that the formation polyelectrolyte coacervates follows a two-step process; i) first, metastable large-scale aggregates are formed upon a barrier-free complexation immediately after mixing; ii) Subsequently the clusters undergo charge equilibration upon chain rearrangement and exchange processes yielding micellar-like aggregates with net neutral charge that are pinched off to yield the final stable micelle-like coacervates. Interestingly, the overall kinetic process was essentially concentration independent, indicating that the rearrangement process is mainly accomplished via noncooperative chain rearrangement and chain exchange processes.

15 min. break

CPP 39.8 Tue 11:30 ZEU 114

**Thermodynamics of Liquid-Liquid Phase Separation: Isothermal Titration Calorimetry of Hyaluronic Acid-Chitosan Coacervates** — •FATMA AKCAY OGUR and A. BASAK KAYITMAZER — Department of Chemistry, Bogazici University Istanbul, Turkey

Complex coacervation occurs between two oppositely charged macromolecules which undergo into macroscopic phase separation and form two liquid phases: polyelectrolyte-rich (coacervate) and polyelectrolyte-poor (dilute) liquid phases. Coacervation has several application areas including processed food, cosmetics, paper, textiles, pharmaceutical and food industries. For these industrial applications, coacervation is utilized as a microencapsulation platform for drugs, aromas, odors, and flavors. Recently, liquid-liquid phase separation has been shown to be the driving force for membraneless organelles such as P granules and nucleoli. In our study, we have studied a model coacervate system composed of two oppositely charged polysaccharides, i.e. namely, hyaluronic acid (HA) and chitosan (CH). Isothermal titration calorimetry (ITC) was employed to understand the thermodynamic characteristics of complex coacervation between these semiflexible biopolymers. Parameters (molecular weight of polyelectrolytes, pH and ionic strength of the medium, and temperature) that affect coacervation were studied to determine enthalpy change and binding

constant of soluble complexes, stoichiometry of soluble complexes and coacervation, and molar heat capacity.

CPP 39.9 Tue 11:45 ZEU 114

**Surface morphology of polyelectrolyte multilayer films with short PSS chains in water and air. Determining the surface elasticity of nanofilms** — •AMIR AZINFAR<sup>1</sup>, SVEN NEUBER<sup>1</sup>, JIRÍ VANĚČEK<sup>2</sup>, MARIE VANCOVÁ<sup>2,3</sup>, JAN STERBA<sup>2,3</sup>, VÍTEZSLAV STRAÑÁK<sup>3</sup>, and CHRISTIANE A. HELM<sup>1</sup> — <sup>1</sup>Institute of Physics - Angewandte Physik, University of Greifswald, Felix-Hausdorff-Str. 6, 17489 Greifswald, Germany — <sup>2</sup>Institute of Parasitology, Biology Centre, Czech Academy of Sciences, Branisovska 31, 37005 Ceske Budejovice, Czech Republic — <sup>3</sup>Faculty of Science, University of South Bohemia, Branisovska 1760, 37005 Ceske Budejovice, Czech Republic

We investigate the surface topology of polyelectrolyte multilayers made by sequential adsorption of polycations (PDADMA) and polyanions (low molecular weight PSS). We observed a buckling pattern of the film surface in air. The surface roughness  $\sigma$ (AFM) in air was always twice as high as in water. For PSS-terminated films, the periodicity of buckling patterns increased with the number of deposited layers from 185 nm to 225 nm. If the multilayer film was terminated with a PDADMA layer, the surface roughness  $\sigma$ (AFM) and the surface periodicity of buckling patterns were always bigger than for films terminated by a PSS layer. This is attributed to the larger surface coverage of PDADMA caused by its small linear charge density. We determined the surface elasticity of the film in non-linear and linear growth regimes by considering the surface strain and surface periodicity, and thus provide a model to explain the increase of periodicity with film thickness.

CPP 39.10 Tue 12:00 ZEU 114

**Environmental controlled Molecular Plasmon Resonance of Anthracene** — •WOLDEMAR NIEDENTHAL<sup>1,2</sup>, DENNIS PIETRUSCHKA<sup>2,3</sup>, DOREEN MOLLENHAUER<sup>2,3</sup>, and SANGAM CHATTERJEE<sup>1,2</sup> — <sup>1</sup>Institute of Experimental Physics I, Justus-Liebig-University, Giessen, Germany. — <sup>2</sup>Center for Materials Research, Justus-Liebig-University, Giessen, Germany. — <sup>3</sup>Physikalisch-Chemisches Institut, Justus-Liebig-Universität, Gießen, Germany.

Within the last years polycyclic hydrocarbons (PHCs) were investigated as materials for electrochromic applications. It was proposed that the underlying processes of the color change are based on purely electronic excitation processes, i.e. photon absorption and the formation of molecular plasmons. This mechanisms predict an ultrafast switching speed between the charged and the neutral state. We studied the absorption behavior of charged and neutral anthracene by changing the liquid electrolyte and in devices with polymer-gel-electrolytes by cyclo-voltametric measurements. The experiments show a clear dependence of the color changing process on the electrolyte and polymer surrounding. The results show that the color changing processes of the electrochromic devices are more complex than considered so far. Further investigations are needed to uncover the full effect of the surrounding medium on the colorization processes.