

CPP 62: Charged Soft Matter, Polyelectrolytes and Ionic Liquids III

Time: Thursday 9:30–13:00

Location: C 243

CPP 62.1 Thu 9:30 C 243

Hydrophobicity/hydrophilicity altered by light: A case study of photosensitive cationic azobenzene surfactants — MARIA MONTAGNA¹ and •OLGA GUSKOVA^{1,2} — ¹Institute Theory of Polymers, Leibniz Institute of Polymer Research Dresden, Hohe Straße 6, 01069, Dresden, Germany — ²Dresden Center for Computational Materials Science (DCMS), Technische Universität Dresden 01062, Dresden, Germany

In this work we present a computational study of the photosensitive cationic surfactants with a conventional trimethylammonium or pH-sensitive polyamine hydrophilic head and the azobenzene containing hydrophobic tail immersed in water. The azobenzene molecules are known to undergo a reversible *trans-cis-trans* isomerization upon the UV-visible light irradiation. Combining the density functional theory and the atomistic molecular dynamics simulations, the structural and the hydration properties of the *trans*- and the *cis*-isomers are investigated. We establish and quantify the correlations of the isomerization state of the surfactant tail and the molecular hydrophilicity/hydrophobicity altered by light. Furthermore, our findings are compared with the experimental data [1] and the predictions of the thermodynamic theory [2] on the self-assembly of photosensitive cationic azobenzene surfactants incorporated in soft nano-objects. This work was supported by DFG (Project GU 1510/3-1).

[1] S. Schimka et al. *Phys. Chem. Chem. Phys.* 2017, 19, 108.

[2] A.M. Rumyantsev et al. *Macromolecules* 2014, 47, 5388.

CPP 62.2 Thu 9:45 C 243

Interfaces in fluids of ionic liquid crystals — •HENDRIK BARTSCH^{1,2}, MARKUS BIER^{1,2}, and SIEGFRIED DIETRICH^{1,2} — ¹Max-Planck-Institut für Intelligente Systeme, Stuttgart, Deutschland — ²Universität Stuttgart, Stuttgart, Deutschland

Ionic liquid crystals are attracting increasing scientific, as well as technological attention, since they are expected to exhibit unique structural properties, which are directly linked to the interplay of the anisotropy of the molecules, on the one hand, and their charges, on the other hand. Recently, for such an ionic liquid crystal system a new type of smectic-A bulk structure could be observed, the smectic layer spacing of which is significantly larger than that of the ordinary smectic-A phase [HB et al, 2017, *J. Phys.: Condens. Matter* 29 464002]. Moreover, unlike the ordinary smectic-A phase it shows alternating layers of particles parallel to the layer normal and oriented perpendicular to it. This finding stresses that ionic liquid crystals exhibit distinct structural and orientational behavior. In particular in inhomogeneous systems, e.g., an electrolyte in the vicinity of an electrode or interfaces between bulk phases, these properties are very important and they are expected to affect the interfacial phenomena of these materials crucially.

In this talk, we report on new findings, obtained within classical density functional theory, concerning the fluid structure and molecular orientations at a free interface of coexisting bulk phases. We discuss and compare the density and orientational order parameter profiles for different kinds of the liquid-smectic phase coexistence occurring in ionic liquid crystals and ordinary (uncharged) liquid crystals.

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Salt and Polymer Dynamics in PPG based Polymer Electrolytes: A ¹H and ⁷Li NMR study — •MANUEL BECHER, SIMON BECKER, LUKAS HECHT, and MICHAEL VOGEL — TU Darmstadt Condensed Matter Physics, Darmstadt, Germany

Facing an increasing need for safe and mechanically stable devices for energy storage, solid-state (lithium)-ion conducting batteries are in the focus of current research. As one of the central components, the electrolyte determines desirable features like high energy density, light weight and high ion conductivity. Polymer electrolytes (salts dissolved in polymers) are already used in portable devices, but suffer from lower electric conductivity as compared to other alternatives. Hence, it is of great interest to enhance the ion diffusivity in the polymer matrix. For this purpose, a fundamental understanding of the transport mechanisms is necessary, but still not available. Here, we focus on amorphous polypropylene glycol (PPG) lithium-salt mixtures, comparing different salts and salt concentrations. We combine several nuclear magnetic resonance (NMR) experiments, namely diffusometry, relaxometry, spectroscopy and exchange studies to ascertain ion and poly-

mer dynamics over a wide range of length and time scales. Selectively investigating cation, anion and polymer host dynamics (⁷Li, ¹⁹F and ¹H measurements, respectively) yields a strong correlation between polymer reorientation and ion diffusion. Moreover, we show that the ion transport is strongly affected by a structural inhomogeneity of the mixtures which depends on the solubility of the salts. In this context, we discuss the differences in conductivity of LiClO₄ and LiTFSI salts.

CPP 62.4 Thu 10:15 C 243

Force fields for monovalent and divalent metal cations in TIP3P water based on thermodynamic and kinetic properties — •NADINE SCHWIERZ¹ and SHAVKAT MAMATKULOV² — ¹Max Planck Institut für Biophysik, Frankfurt, Germany — ²The Centre of Higher Technologies, Tashkent, Uzbekistan

Metal cations are essential in many vital processes. In order to capture the role of different cations in all-atom molecular dynamics simulations of biological processes, an accurate parametrization is crucial. Here, we develop force field parameters for the metal cations Li⁺, Na⁺, K⁺, Cs⁺, Mg²⁺, Ca²⁺, Sr²⁺, and Ba²⁺ in combination with the TIP3P water model that is frequently used in biomolecular simulations. In progressing toward improved force fields, the approach presented here is an extension of previous efforts and allows us simultaneously reproduce thermodynamic and kinetic properties of aqueous solutions. We systematically derive the parameters of the 12-6 Lennard-Jones potential which accurately reproduce the experimental solvation free energy, the activity derivative, and the characteristics of water exchange from the first hydration shell of the metal cations. In order to reproduce all experimental properties, a modification of the Lorentz-Berthelot combination rule is required for Mg²⁺. Using a balanced set of solution properties, the optimized force field parameters aim to capture the fine differences between distinct metal cations including specific ion binding affinities and the kinetics of cation binding to biologically important anionic groups.

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structural and transport properties of Li/S battery electrolytes using molecular dynamics simulations — •CHANBUM PARK^{1,2}, MATEJ KANDUČ¹, RICHARD CHUDOBA^{1,2}, ARNE RONNEBURG^{1,2}, SEBASTIAN RISSE¹, MATTHIAS BALLAUFF^{1,2}, and JOACHIM DZUBIELLA^{1,2} — ¹Institut für Weiche Materie und Funktionale Materialien, Helmholtz-Zentrum Berlin für Materialien und Energie, Hahn-Meitner-Platz 1, 14109 Berlin, Germany — ²Institut für Physik, Humboldt-Universität zu Berlin, Newtonstr. 15, 12489 Berlin, Germany

Lithium-Sulfur (Li/S) batteries are a promising energy storage device as post lithium-ion battery candidates. Despite the vast experimental and theoretical research on Li/S batteries, practical performance is not yet achieved. Fundamental molecular insights of transport and structure properties of lithium polysulfides in solvents are necessary. We constructed a classical molecular dynamics (MD) computer simulation model of lithium polysulfides (Li₂S₄, Li₂S₆ and Li₂S₈), lithium-bis(trifluoromethane)sulfonimide (LiTFSI), lithium nitrate (LiNO₃) and the organic solvents, 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL). We benchmarked and validated our simulations by comparing structural and dynamic features with various available experimental reference systems. We discuss the detailed transport and structural properties of Li/S electrolytes. In particular, our study shows how the ionic conductivity which is affected by ion pairing of Li⁺ with counter ions and clustering of polysulfides in Li/S battery electrolytes.

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Ionic liquid post-treatment of PEDOT:PSS thin films for improvement of thermoelectric properties — •NITIN SAXENA, BENJAMIN PRETZL, XAVER LAMPRECHT, LUCAS KREUZER, and PETER MÜLLER-BUSCHBAUM — TU München, Physik-Department, LS Funktionelle Materialien, 85748 Garching

Thermoelectric devices based on conducting polymers, especially PEDOT:PSS, have attracted great research attention in recent years, mainly focusing on improving electrical conductivities and Seebeck coefficients of thin films. We perform post-treatments of PEDOT:PSS thin films using solutions of different ionic liquids dissolved in THF

based on a rational choice of ionic liquids, i.e. keeping the same cation, while varying the anion. This leads to strong implications regarding the thermoelectric properties, especially since Seebeck coefficient and electrical conductivity are increased simultaneously, leading to high power factors of thin films. Spectroscopic methods are used to identify changes in the electronic structure, while x-ray scattering techniques are used to determine changes in the morphology. In addition, temperature-dependent resistivity measurements allow for investigation of changes in the charge transport mechanism upon treatment with ionic liquids.

15 min. break

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Molecular Mobility and Ionic Conductivity of Ionic Liquid Crystals Forming a Hexagonal Columnar Mesophase — ●ARDA YILDIRIM¹, PAULINA SZYMONIAK¹, KATHRIN SENTKER², MARTIN BUTSCHIES³, ANDREA BÜHLMAYER³, SABINE LASCHAT³, PATRICK HUBER², and ANDREAS SCHÖNHALS¹ — ¹Bundesanstalt für Materialforschung und -prüfung (BAM), Unter den Eichen 87, 12205 Berlin, Germany — ²Institut für Materialphysik und -technologie, Technische Universität Hamburg, Eißendorfer Str. 42, 21073 Hamburg, Germany — ³Institut für Organische Chemie, Universität Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany

For the first time, the molecular mobility of two linear-shaped tetramethylated guanidinium triflates ionic liquid crystals (ILCs) having different length of alkyl chains was investigated by a combination of broadband dielectric spectroscopy (BDS) and specific heat spectroscopy (SHS). SHS was carried out by differential AC-chip calorimetry at higher frequencies and temperature modulated DSC at lower frequencies. These ILCs can form a hexagonal ordered columnar mesophase. Two relaxation processes were found by BDS for both samples. At low temperatures, a γ -processes is observed which is assigned to specific localized fluctuations. At higher temperatures, α 1-processes take place. α 2-processes were also detected by SHS but with a completely different temperature dependence of the relaxation times. Different molecular assignments of α 1- and α 2-processes are suggested. At even higher temperatures, conductivity was detected by BDS.

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Nonlinear Conduction in Ionic Liquids – Insights from Molecular Dynamics Simulations — ●DIDDO DIDDENS¹ and ANDREAS HEUER^{1,2} — ¹Helmholtz-Institut Münster, Ionics in Energy Storage (IEK-12), Forschungszentrum Jülich GmbH, Corrensstraße 46, 48149 Münster, Germany — ²Institut für physikalische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstraße 28/30, 48149 Münster, Germany

Ionic liquids (ILs) are promising electrolyte materials for batteries or supercapacitors due to their intrinsically high density of charge carriers and their wide electrochemical stability window. With respect to electrolyte optimization, the ionic conductivity is another important key parameter. In experiments, this quantity is typically measured at rather weak electric fields, at which the conductivity itself is independent of the strength of the applied field. However, nonlinear conduction effects – typically leading to an increase of the ionic conductivity – may come into play at high electric fields [1], which in battery cells usually emerge near electrodes.

In this contribution, we employ nonequilibrium molecular dynamics simulations of ILs in order to characterize the nonlinear conduction mechanism at the molecular level. Special emphasis is put on the interplay of field-induced structural rearrangements and the emergence of nonlinear effects in the conductivity.

[1] L. N. Patro, O. Burghaus, B. Roling, *Phys. Rev. Lett.*, **2016**, 116(18), 185901

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Charge Transport and Glassy Dynamics in Polymeric Ionic Liquids as studied in its in Inter- and Intramolecular Interactions — ●FALK FRENZEL¹, PIA BORCHERT², ARTHUR MARKUS ANTON¹, VERONICA STREHMEL², and FRIEDRICH KREMER¹ — ¹Universität Leipzig, Leipzig, Germany — ²Hochschule Niederrhein, Krefeld, Germany

Polymeric Ionic Liquids (PILs) are a novel class of materials in which the properties of Ionic Liquids (ILs) are combined with them of polymeric systems. In the present study Broadband Dielectric Spectroscopy (BDS), Fourier Transform Infrared Spectroscopy (FTIR), AC-

Chip Calorimetry (ACC) and Differential Scanning Calorimetry (DSC) are employed to analyze the impact of inter- and intramolecular interactions on charge transport and glassy dynamics. By comparing PILs with their low molecular weight counterparts as well as by systematically varying the anion or cation enables one to unravel the mechanism of charge transport and its interplay with glassy dynamics. The detailed findings are in accordance with the model of a dynamic glass transition assisted hopping conduction.

Ref.:

[1] Frenzel, F.; Kremer, F. et al. Springer: Dielectric Properties of Ionic Liquids 2016

[2] Frenzel, F.; Kremer, F. *Macromolecules* 2017

CPP 62.10 Thu 12:00 C 243

Ionic Liquids in Nano-Confinement: Tuning and Suppressing Their Conduction in Nanoporous Metal-Organic Frameworks — ANEMAR BRUNO KANJ, RUPAL VERMA, MODAN LIU, JULIAN HELFERICH, WOLFGANG WENZEL, and ●LARS HEINKE — Karlsruhe Institute of Technology (KIT), Karlsruhe

Room-temperature ionic liquids (IL) are molten salts of organic molecules and possess outstanding physical and chemical properties. In addition to uses as unique solvents and in catalysis, it may find applications in electronics, sensors and batteries, where the properties under confinement are important. Metal-organic frameworks (MOFs) are nanoporous, crystalline hybrid materials composed of metal ions connected by organic linker molecules.

Here, we investigate the conduction properties of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide, referred to as [BMIM][NTf₂], ionic liquid under nano-confinement in nanoporous MOFs of type HKUST-1. We use MOFs in form of well-defined, dense films prepared in a layer-by-layer manner, also referred to as SUR-MOFs.

It was experimentally found that the percentage of pore filling of [BMIM][NTf₂] in HKUST-1 has a tremendous impact on the IL conduction properties. The conductivity and ion mobility decreases by three orders of magnitude when the pores of the MOFs are filled. Details of the conduction of IL in the nanopores are unveiled by detailed molecular dynamic (MD) simulations. Mutual pore blockage and transient jamming was found to be responsible for the conductivity drop.

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Dielectric Spectroscopy on Choline-Chloride Based Deep Eutectic Solvents — ●DANIEL REUTER, PETER LUNKENHEIMER, and ALOIS LOIDL — Experimental Physics V, University of Augsburg, Germany

Deep eutectic solvents (DES) are a promising new class of ionic liquid analogues [1]. Via mixing of two solid materials in eutectic composition, a DES liquid phase is obtained that is characterized by its low melting point compared to its individual constituents. Prominent examples are the mixtures of Choline Chloride (ChCl) with various hydrogen bond donors like, e.g., glycerol [2]. In this talk, we present dielectric spectroscopy data of three ChCl based DES in a broad frequency and temperature range. Especially, we investigate the so far widely neglected molecular reorientational dynamics and its correlation to the ionic conductivity. Here, our findings provide valuable information on molecular and ion diffusion in DES.

[1] E. Smith, A. Abbott, and K. Ryder, *Chem. Rev.* **114**, 11060 (2014). [2] D. Wagle, H. Zhao, and G. Baker, *Acc. Chem. Res.* **47**, 2299 (2014).

CPP 62.12 Thu 12:30 C 243

Interfacial Water Structure and Properties of Non-Equilibrium CTAB/Polyelectrolyte Mixtures with different Molecular Weights — ●FELIX SCHULZE-ZACHAU and BJÖRN BRAUNSCHWEIG — Institute of Physical Chemistry, Westfälische Wilhelms-Universität Münster, 48149 Münster, Germany

Mixtures of CTAB and 0.1 mM poly(sodium 4-styrenesulfonate) (NaPSS) with different molecular weights (MWs) from 10 kDa to 1 MDa were studied in the bulk with turbidity and ζ -potential measurements, while vibrational SFG spectroscopy and tensiometry provided information on the molecular structure of air/water interfaces. We also relate the molecular structure and the charging state of the interface to the stability and the structure of macroscopic foam. We propose that mostly negatively charged and well-solvated complexes are formed in the bulk at CTAB concentrations below 75 μ M. This is corroborated by the negligible turbidity and the ζ -potential of the mixtures. Increasing the CTAB concentration to stoichiometric bulk mixing ratio

yields complexes with negligible net charges. These complexes tend to aggregate and adsorb at the interface. The turbidity maximum is indicative to bulk aggregation and shifts with increasing MW to higher CTAB concentrations. The non-equilibrium nature of these mixtures is obvious from the surface tension kinetics which show two adsorption processes of free CTAB and aggregates. Above a threshold concentration, interfaces are dominated by free CTAB while positively charged complexes are well solvated in the bulk. This yields wet foams and is confirmed by measurements with deuterated CTAB.

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How to tune the surface forces of PDADMA terminated polyelectrolyte multilayers — •HEBA SOKER MOHAMAD, SVEN NEUBER, and CHRISTIANE A. HELM — Institut für Physik, Uni. Greif-

swald, Felix-Hausdorff-Str. 6 17489 Greifswald

Films built from the Poly (styrenesulfonate) (PSS) and poly (diallyl-methylammonium) (PDADMA) in 0.1 Mol/L NaCl are investigated. Colloid probe measurements show that PDADMA-terminated surfaces are always positively charged. They are flat if the film consists of few layers. By increasing the number of layers, steric forces due to chains protruding into solution are observed. The PDADMA chains scale as polyelectrolyte brushes and collapse at 1 M NaCl. If the top layers contain an excess of PDADMA monomers neutralized by Cl⁻ ions, at salt concentrations larger than 1 M NaCl again brushes form. Also NaCl penetrates into the film, breaks up ionic monomer-monomer bonds and causes irreversible changes. Concluding, surface forces of polyelectrolyte multilayer can be controlled by preparation and post-preparation treatment.