

## CPP 33: Poster: Charged Soft Matter

Time: Wednesday 16:30–18:30

Location: Poster C

CPP 33.1 Wed 16:30 Poster C

**Why is the partition coefficient of some ionic liquids concentration-dependent?** — ●AXEL ARNOLD<sup>1,3</sup>, DIRK REITH<sup>2,3</sup>, and THORSTEN KÖDDERMANN<sup>3</sup> — <sup>1</sup>Institute for Computational Physics, University of Stuttgart, Stuttgart, Germany — <sup>2</sup>Bonn-Rhein-Sieg University of Applied Studies, Sankt Augustin, Germany — <sup>3</sup>Fraunhofer-Institute for Algorithms and Scientific Computing (SCAI), Sankt Augustin, Germany

The partition coefficient of a substance measures its solubility in octanol compared to water, and is frequently used as a rough estimate of toxicity. If a substance is hardly soluble in octanol, it is practically impossible for it to enter (human) cells, and therefore is less likely to be toxic. While for simple substances, the partition coefficient is concentration-independent, this is not true for a few important classes of complex molecules, such as ionic liquids or tensides.

We present a simple model for the partition coefficient of ionic liquids based on the association and dissociation of ion pairs. Using solvation free energies in water and octanol from computer simulations, this model can reproduce the partition coefficient of the commonly used ionic liquid 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C<sub>4</sub>MIM][NTf<sub>2</sub>] for a wide range of concentrations. Our findings show that the concentration dependence of the partition coefficient is mostly an entropic effect due to the strong tendency of the ionic liquid to associate in water, but dissociate in octanol.

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**Coupling of surface charge and pH effects: charge inversion and reentrant condensation in protein solutions with multivalent cations** — ●FELIX ROOSEN-RUNGE<sup>1</sup>, BENJAMIN HECK<sup>1</sup>, FAJUN ZHANG<sup>1</sup>, OLIVER KOHLBACHER<sup>2</sup>, and FRANK SCHREIBER<sup>1</sup> — <sup>1</sup>Institut für Angewandte Physik, Universität Tübingen — <sup>2</sup>Zentrum für Bioinformatik, Universität Tübingen

Charge regulation of proteins is a fundamental mechanism in biological systems, depending on the pH of the solution and condensation of counterions. We report on charge inversion and the related reentrant phase behavior in solutions of globular proteins with different multivalent metal cations [1,2], addressing the coupling of pH effects and charge regulation. For several proteins and both acidic and neutral metal salts, charge inversion as measured by electrophoretic light scattering is found to be a universal phenomenon, whose extent depends on the specific protein-salt combination. Reentrant phase diagrams show a much narrower phase-separated regime for acidic salts. The experimental findings are reproduced with good agreement by an analytical model accounting for ion condensation, pH effects due to metal hydrolysis and charge regulation of side chains. Using a DLVO picture, reentrant phase behavior can be explained. Finally, the relation of charge inversion and reentrant condensation is discussed, suggesting that pH variation in combination with multivalent cations provides control of both attractive and repulsive interactions between proteins.

[1] F. Zhang, et al., *Soft Matter* 8 (2012) 1313[2] F. Zhang, et al., *PRL* 101 (2008) 148101

CPP 33.3 Wed 16:30 Poster C

**Using Super-Heterodyne Laser Doppler Velocimetry for measurements in low concentration suspensions of charged colloids** — ●BASTIAN SIEBER and THOMAS PALBERG — Institut für Physik, Johannes Gutenberg Universität Mainz, Staudingerweg 7, D 55122 Mainz

Soft condensed matter is characterized both by its softness and an internal structure on a mesoscopic scale. This allows convenient optical access to system structure and dynamics in equilibrium. Among the various soft matter systems, charge stabilized colloidal dispersions have gained recognition as tremendously useful model condensed matter systems because of their structural ordering and rich phase behaviour. Experimentally, we studied electrokinetic flow in closed cells with electroosmotic solvent flow. Super heterodyning renders the data of interest free of homodyne contributions and low frequency noise. We used this method to study an aqueous charged sphere suspension driven under the influence of an external electric field. Measurements have been performed on suspensions of various concentrations by diluting the suspension further between measurements to reach very low

concentrations in the process. Preliminary results show an increase in the electro-osmotic velocity with lower concentration while the electrophoretic velocity is decreasing. Further data on this topic will be provided and discussed.

CPP 33.4 Wed 16:30 Poster C

**Small differences with big impact: Reentrant phase behavior induced by multivalent cations in protein solutions** — ●MARCELL WOLF, FAJUN ZHANG, FELIX ROOSEN-RUNGE, and FRANK SCHREIBER — Institut für Angewandte Physik, Auf der Morgenstelle 10, 72076 Tübingen

Subtle difference between proteins can lead to remarkably big differences in their resulting behavior. Using a multivalent cation, yttrium chloride (YCl<sub>3</sub>), a reentrant condensation (RC) with a liquid-liquid phase separation (LLPS) within the condensed regime has been established in a negatively charged protein system [1,2]. Here we compare the phase behavior of two serum albumins, BSA and HSA. They are highly similar in the primary structure but the comparison between the RC behavior of these two albumins shows that minor differences in the primary protein structure have a strong influence on such a system. The range of the condensed regime is much broader for HSA. Optical microscopy also shows a shift of the LLPS region to lower salt and protein concentrations in the case of HSA, where the LLPS region is much broader. The formation of clusters in the condensed regime and outside the LLPS region is systematically studied by SAXS, SLS/DLS and we observe that the cluster size is much smaller by using HSA. Differences of the primary structure between the two proteins leads to changes in the hydrophobicity and charge distribution of the proteins. These changes in BSA and HSA phase diagrams can be related to differences in protein structure. [1] F. Zhang et al., *PRL* 101, 2008, 148101; [2] F. Zhang et al., *Soft Matter* 8, 2012, 1313.

CPP 33.5 Wed 16:30 Poster C

**Thin films of lithium containing block copolymer electrolyte** — ●SIMON BRUNNER<sup>1</sup>, EZZELDIN METWALLI<sup>1</sup>, MARTIN BAUMANN<sup>1</sup>, WILLIAM HEFTER<sup>1</sup>, MAN NIE<sup>1</sup>, VOLKER KÖRSTGENS<sup>1</sup>, JAN PERLICH<sup>2</sup>, STEPHAN V. ROTH<sup>2</sup>, and PETER MÜLLER-BUSCHBAUM<sup>1</sup> — <sup>1</sup>TU München, Physik Department, LS Funktionelle Materialien, James-Frank-Str. 1, 85748 Garching, Germany — <sup>2</sup>HASYLAB at DESY, Notkestr. 85, 22603 Hamburg, Germany

In the light of an increasing demand on power sources for portable electronic devices, nano-scaled lithium based membranes pave the way for new opportunities regarding design, application and integration of rechargeable batteries. In this work, thin hybrid films [1] based on block copolymer electrolytes and lithium salt are investigated using grazing-incidence small angle x-ray scattering (GISAXS) and real space techniques such as SEM, AFM and optical microscopy. In both bulk and thin film format of the lithium-polymer nanocomposite, lithium ions were found to prevent the crystallization of PEO and an enhanced micro-phase separation is observed as evident by both SAXS and GISAXS investigations. Probes of lithium containing thin films sandwiched between two metal electrodes were prepared and the film conductivity is measured using impedance spectroscopy. The effects of salt concentration and membrane morphology on the ionic conductivity are demonstrated.

[1] E. Metwalli, M. Nie, V. Körstgens, J. Perlich, S.V. Roth, P. Müller-Buschbaum, *Macromol. Chem. Phys.* 212, 1742-1750 (2011).

CPP 33.6 Wed 16:30 Poster C

**Adsorption Behavior of Oppositely Charged Polyelectrolyte/Surfactant Mixtures: Neutron Reflectivity from Alkyltrimethylammonium Bromides (CTABs) and poly[tris(hydroxymethyl)methylacrylamide (PAMPS) mixtures at the Air/Water Interface** — ●HEIKO FAUSER, NORA KRISTENHOCHREIN, MARIN UHLIG, and REGINE VON KLITZING — Technische Universität Berlin, 10623 Berlin, Deutschland

If a polyelectrolyte and a surfactant of opposite charge are mixed, the two ions associate forming a large variety of complexes. Different interfacial adsorption behavior leads to different foaming properties.

Former studies done in our group on mixtures of the negatively charged polyelectrolyte PAMPS with the positively charged CTAB revealed a different adsorption behavior in foam film lamellas and at the

air-water interface.

To gain a detailed insight into the structure and composition of the film interfaces, we performed neutron reflectometry measurements at the air/water interface.

Our approach focusses on a fixed surfactant concentration while varying the amount of polyelectrolyte. In order to get information about the composition and layer structure we investigated mixtures of different isotopic contrast. Also the influence of different surfactant chain lengths (C12,C14) and variation in electric charge of the polyelectrolytes are investigated.

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**Charge transport and electrode polarization at the interface between glass forming ionic liquids (ILs) and metal electrodes**

— •LUDWIG POPP, CIPRIAN GHIORGHITA IACOB, WYCLIFFE KIPROP KIPNUSU, MARTIN TRESS, JOSHUA RUME SANGORO, and FRIEDRICH KREMER — Institute of Experimental Physics I, Leipzig, Germany

Charge transport and electrode polarization phenomena are investigated in a homologous series of imidazolium-based ionic liquids by broadband dielectric spectroscopy (BDS) in a large temperature (190 - 300 K) and frequency range ( $10^{-3}$  -  $10^5$  Hz). The dielectric spectra are dominated – on the low frequency side – by electrode polarization, while, for higher frequencies, charge transport (in a disordered matrix) is the underlying physical mechanism. The absolute values of dc conductivity vary over 5 decades upon systematic variation of ILs structure and electrode material. A microscopic model is applied to quantitatively describe the electrode polarization. The applicability of the model to the experimental data in a broad frequency range is discussed in more details [1-4].

References: [1]. Serghei, A. et al. (2009), Phys. Rev. B, 80(18), 184301-5, [2]. Dyre, J. C. (1988), Phys. Rev. B, 37(17), 10143-10149, [3]. Sangoro, J. R., Ph.D. Thesis, (2010), University of Leipzig, [4]. Kremer, F., Schönhals, A. (2003), Broadband Dielectric Spectroscopy, Springer, Berlin.

CPP 33.8 Wed 16:30 Poster C

**Manning condensation on DNA fragments with monovalent and divalent counterions**

— •DAMIR VURNEK<sup>1,2</sup>, MARIJA SORIC<sup>2</sup>, and TOMISLAV VULETIC<sup>2</sup> — <sup>1</sup>Institut für Theoretische Physik and Cluster of Excellence: EAM, Universität Erlangen-Nürnberg, Erlangen, Germany — <sup>2</sup>Institut za fiziku, Zagreb, Croatia

We obtained the Manning free (uncondensed) counterions fraction  $\theta$  for dilute aqueous solutions of rodlike polyions: 150 bp DNA fragments, across a range of concentrations,  $c(\text{monomer}) = 0.03 - 8$  mM. Conductometric measurements were done on  $\text{Na}^+\text{DNA}$  and  $\text{Mg}^{++}\text{DNA}$ , in 1mM added salt (NaCl and  $\text{MgCl}_2$ , respectively) as well as in pure water conditions.

We remind that the high linear charge of polyions Manning condenses a fraction of counterions close to the polyion. This partly neutralizes polyion charge, and reduces the effective solution conductivity. Our conductivity study of DNA in added salt confirms theoretical values  $\theta = 0.24$  and  $0.12$  for  $\text{Na}^+\text{DNA}$  and  $\text{Mg}^{++}\text{DNA}$ , respectively. However, in pure water conditions, towards lower DNA concentrations the effective  $\theta$  increases well above the Manning values. UV-absorbance measurements showed that this is not due to DNA denaturation. Denaturation may occur in pure water conditions due to a reduction in the electrostatic screening; as single stranded DNA has a lower linear charge it also has a correspondingly higher  $\theta$  fraction. We concluded that in dilute solutions more counterions must become decondensed as the entropy gain overcomes the electrostatic cost, as Deshkovski et al. (Phys.Rev.Lett. 2001) indeed have discussed.

CPP 33.9 Wed 16:30 Poster C

**The effects of reactive oxygen species on single polycation layers**

— •FLORIAN BERG<sup>1</sup>, STEPHAN BLOCK<sup>2</sup>, STEFFEN DRACHE<sup>1</sup>, RAINER HIPPLER<sup>1</sup>, and CHRISTIANE A. HELM<sup>1</sup> — <sup>1</sup>Inst. für Physik, Uni Greifswald, D-17487 Greifswald — <sup>2</sup>ZIK HIKE, D-17487 Greifswald

Positively charged, branched polyethylenimine (PEI) adsorbed onto silicon wafers are attacked by free hydroxyl radicals. With AFM Colloid Probe technique, the surface forces between the PEI layers are measured. The force profiles show that freshly deposited PEI layers are flat, i.e., electrostatic repulsion dominates the interaction. After radical attack both, surface potential and surface charge density, are reduced by a factor of about two, while the Debye length remains unchanged. Force volume measurements show a homogeneous distribution of the surface charge on the  $\mu\text{m}$  scale. To probe the nm-scale,

negatively charged gold nanoparticles (NP) are adsorbed. After radical attack we find a 10 % decrease of saturation coverage consistent with the decreased surface charge density if the electrostatic three-body interaction is considered. Nevertheless, the NP adsorption kinetics is slowed down suggesting that the PEI-layer is inhomogeneous on the nm-scale after radical attack.

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**Polyelectrolytes Adsorbed onto Oppositely Charged Lipid Monolayers - Reduced Charge Densities**

— THOMAS ORTMANN<sup>1</sup>, •HEIKO AHRENS<sup>1</sup>, ANDREAS GRÖNING<sup>1</sup>, FRANK LAWRENZ<sup>1</sup>, ANDRE LASCHEWSKY<sup>2</sup>, and CHRISTIANE A. HELM<sup>1</sup> — <sup>1</sup>Inst. für Physik, Uni Greifswald, D-17487 Greifswald — <sup>2</sup>Fraunhofer Institute for Applied Polymer Research, Potsdam-Golm, Germany

Polyelectrolytes in dilute solutions ( $10^{-5}$  monoMol/L) adsorb in a two-dimensional lamellar phase to oppositely charged lipid monolayers at the air/water interface. To investigate the influence the electrostatic interaction, a statistic copolymer with 90% and 50% charged monomers and mixtures between charged and uncharged lipids are used. With grazing incidence diffraction the separation between stretched polyelectrolyte chains is determined. The monomer/lipid ratio is calculated. When the fraction of charged monomers is reduced to 50%, the chain distance decreases from 4.5nm to 3nm (at an area per lipid of  $80\text{\AA}^2$ ) i.e. less than proportional and the ratio of lipids to charged monomers decreases from 0.7 to 0.5. Similarly, when the fraction of charged lipids is decreased the distance of the polyelectrolyte chains is increased sub-proportionally.

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**Quaternized Brushes of Weak Polyelectrolytes (PE): Brush Structure Studied with Neutron Reflectometry**

— •ZULEYHA YENICE<sup>1</sup>, JAN GENZER<sup>2</sup>, REGINE V.KLITZING<sup>1</sup>, and RALF KÖHLER<sup>1,3</sup> — <sup>1</sup>Stranski Lab, Inst. of Chemistry, TU Berlin, Germany — <sup>2</sup>Dept. of Chemical & Biomolecular Engineering, NCSU, Raleigh, USA — <sup>3</sup>Inst. of Soft Matter and Functional Materials, HZB Berlin, Germany

PE-brushes are used for surface modifications because of properties as specific adsorption, permeability and stimuli responsive behavior. PDMAEMA\* is a weak PE with pH-dependent properties, giving room for further modifications like protonizing by varying the pH, or turning them into strong PE by quaternization. The PDMAEMA-brush was gradually quaternized with deuterated iodomethane. Deuterium simultaneously labels the brush for neutron reflectometry (NR) without altering its chemistry. NR was applied to detect the inner structure, density, and thickness after partially quaternizing the brush, to see the iodide distribution in the brush, lateral and vertical to the substrate. First results indicate an increase of the iodide content at the surface in lateral direction what is paralleled by an increase of brush thickness. Up to now, the vertical distribution of iodide is still unclear but is probed by incorporation of charged gold nanoparticles (Au-NP) along the charge gradient. Penetration depth and distribution of deposited Au-NP was investigated with ellipsometry. Specular and off-specular NR will be used to determine possible internal structures to clarify the potential of PE-brushes as functionalized substrate and as tool for nano-templating. \*poly[2-(dimethylamino) ethyl methacrylate]

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**Polyelectrolyte Multilayers (PEM) of different charge densities in humid atmospheres: Structural changes and swelling mechanics**

— INGO DÖNCH<sup>1</sup>, PATRICK OTT<sup>2</sup>, ANDRÉ LASCHEWSKY<sup>2</sup>, ANDREAS FERY<sup>3</sup>, RUMEN KRASSTEV<sup>4</sup>, and •RALF KÖHLER<sup>1,5</sup> — <sup>1</sup>Interfaces, MPI-KGF Potsdam/Golm — <sup>2</sup>Applied Polymer Chemistry, University of Potsdam — <sup>3</sup>Physical Chemistry II, University of Bayreuth — <sup>4</sup>Biomaterials, NMI at University of Tübingen — <sup>5</sup>Soft Matter and Functional Materials, HZB Berlin: Germany

PEM consist of complexed layers of two organic polyions of opposite charge build-up by layer-by-layer deposition. They are known for a high tunability of their structural properties, e.g. thickness and roughness on nanoscale. The interplay of internal interactions and structure of PEM is investigated by means of swelling experiments, i.e. an internal mechanical stress in the films is induced by incorporation of solvent molecules from adjacent solvent vapour (H<sub>2</sub>O). Neutron reflectometry is used to test for structure parameters of the sample and its specific material content of polymer and solvent. Three different PEM systems made from PSS/PDADMAC\* by spraying technique are investigated; each containing a derivative of the polycation PDADMAC of 75, 89, or 100% charge density (ChD) along the molecular chain, also the number of adsorbed layers of polyions, i.e. the film thickness,

is varied. The swelling characteristics changes continuously and systematically with the number of adsorbed bilayers indicating internal transitions of structure and swelling. Lower ChD results in thicker films. \* poly-(styrene sulphonate)/ poly-(diallyldimethyl ammonium)

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**The structure of fluids with impurities** — ●MARKUS BIER and LUDGER HARNAU — Max Planck Institute IS, Stuttgart, Germany, and University of Stuttgart, Germany

The influence of dilute impurities on the structure of a fluid solvent is investigated theoretically. General arguments, which do not rely on particular models, are used to derive an extension of the Ornstein-Zernike form for the solvent structure factor at small scattering vectors. It is shown that dilute impurities can influence the solvent structure only if they are composed of ions with significantly different sizes. Non-ionic impurities or ions of similar size are shown to not alter the solvent structure qualitatively. This picture is compatible with available experimental data. The derived form of the solvent structure factor is expected to be useful to infer information on the impurity-solvent interactions from measured scattering intensities.

Reference:

[1] M. Bier and L. Harnau, *Z. Phys. Chem.* **226**, 807 (2012).

CPP 33.14 Wed 16:30 Poster C

**molecular dynamics simulations of polyelectrolyte brushes under poor solvent conditions** — ●GUILI HE<sup>1</sup>, HOLGER MERLITZ<sup>2</sup>, and JENS-UWE SOMMER<sup>1</sup> — <sup>1</sup>Leibniz-Institut fuer Polymerforschung Dresden, 01069 Dresden, Germany — <sup>2</sup>Department of Physics and ITPA, Xiamen University, Xiamen 361005, P.R. China

Molecular dynamics simulations have been applied to investigate salt-free planar polyelectrolyte brushes under poor solvent conditions with respect to the molecular backbone under the variation of the chain degree of polymerization, the brush grafting density and the charge

fraction (strength of the electrostatic interaction). We found that, with decreasing the system temperature (changing solvent quality) far below the theta point, the brush first displays lateral phase separation with respect to the solvent and eventually collapses vertically [see also J.-M. Y. Carrillo and A. V. Dobrynin, *Langmuir* 2009, 25(22)]. The lateral phase separation leads to cylindrical morphologies (bundles of chains) which has been observed for different charge fraction, degree of polymerization and grafting density. Even changing the size and solvent selectivity of the counterions cannot prevent lateral structure formation in the poor solvent state. This phenomenon can be explained by an entropy gain of counterions in the cylindrical state as compared to the homogeneously collapsed state at the same temperature.

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**Charge and Mobility of Polyelectrolyte Complex Nanoparticles** — KARSTEN GELFERT, UWE LAPPAN, SIMONA SCHWARZ, and ●ULRICH SCHELER — Leibniz-Institut für Polymerforschung Dresden e.V.

Polyelectrolyte Complex nanoparticles formed from poly(maleicanhydride-coethylene) and poly(diallyldimethylammonium chloride) have been studied by a combination of NMR, EPR and light scattering under variation of the overall composition of the complexes. Dynamic light scattering and PFG NMR yield complementary information on the hydrodynamic size, where PFG NMR is more sensitive to primary complexes and DLS to the nanoparticles. The importance of primary particles for the total stability of the system has been shown. Electrophoresis NMR permits the measurement of the effective charge of both the primary complexes and nanoparticles. In conjunction with the NMR spectroscopic on the chemical species involved, free polyelectrolytes are excluded all excess material is contained in primary complexes. Selective placements of spin labels on the polyanion permits the investigation of molecular dynamics by EPR lineshape analysis showing strong hinderance of the local mobility in the minority component.