

CPP 45: Charged Soft Matter, Polyelectrolytes and Ionic Liquids I

Time: Wednesday 11:00–13:00

Location: C 243

Invited Talk

CPP 45.1 Wed 11:00 C 243

Double-Semidilute Liquid and Gel Coacervates formed by Oppositely Charged Polyelectrolytes — ●MICHAEL RUBINSTEIN¹, SERGEY PANYUKOV², and QI LIAO³ — ¹Duke University, Durham, NC, USA — ²P. N. Lebedev Physics Institute, Moscow, Russian Federation — ³Chinese Academy of Sciences, Beijing, China

We develop a scaling model for two qualitatively different classes of coacervates formed by oppositely charged polyelectrolytes. The weakly interacting coacervates are liquids with electrostatic interaction energy per charge less than thermal energy kT . The strongly interacting coacervates are gels with cross-links formed by ion pairs of opposite charges attracting each other with energy stronger than kT . The liquid coacervate is a double-semidilute solution with two correlation lengths and two qualitatively different types of conformations of weaker and stronger charged polyelectrolytes. Weaker charged chains form a screening "coat" around stronger charged chains. The conformations of weaker charged chains in this screening coat is analogous to a semidilute solution of uncharged polymers. The conformation of stronger charged polyelectrolytes in liquid coacervates is similar to their conformation in semidilute polyelectrolyte solutions. The strongly interacting coacervates form bottlebrush gels for longer polyelectrolytes with higher charge density and star-like gels for shorter higher charge density chains.

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Dendritic polyelectrolytes and their interaction with proteins: Simulation perspective — ●ROHIT NIKAM^{1,2}, XIAO XU^{1,2}, QIDI RAN¹, MATEJ KANDUC¹, RAINER HAAG³, MATTHIAS BALLAUFF¹, and JOACHIM DZUBIELLA^{1,2} — ¹Institut für Weiche Materie und Funktionale Materialien, Helmholtz-Zentrum Berlin, Hahn-Meitner-Platz 1, 14109 Berlin, Germany — ²Institut für Physik, Humboldt-Universität zu Berlin, Newtonstr. 15, 12489 Berlin, Germany — ³Multifunctional Biomaterials for Medicine, Helmholtz Virtual Institute, Kantstr. 55, 14513 Teltow-Seehof, Germany

Dendritic polyelectrolytes constitute high potential drugs and carrier systems for biomedical purposes, yet their interaction modes with biomolecules have not been microscopically characterized. We investigate key electrostatic, hydration and structural features of dendritic polyglycerol sulfate (dPGS) and its interaction with biologically important serum proteins using molecular simulations complemented by isothermal titration calorimetry (ITC) and electrophoretic measurements. We demonstrate that the driving force for the strong complexation originates mainly from the release of only a few condensed counterions from dPGS upon binding. The binding constant shows surprisingly weak dependence on dPGS size (and bare charge) which can be explained by charge-renormalization effects and by the fact that the magnitude of the dominating counterion release mechanism is sensitive exclusively to the interfacial charge structure of the protein-specific binding patch. Our results open new perspectives for the rational design of charged polymeric drugs and carrier systems.

CPP 45.3 Wed 11:45 C 243

The effect of weakly and strongly interacting cations on phase behaviour of protein solutions — ●OLGA MATSARSKAIA¹, FELIX ROOSEN-RUNGE², GUDRUN LOTZE³, JOHANNES MÖLLER³, FAJUN ZHANG¹, and FRANK SCHREIBER¹ — ¹Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen — ²Division of Physical Chemistry, Lund University, Lund, Sweden — ³ESRF, Grenoble, France

Multivalent cations can induce a rich phase behaviour including reentrant condensation, clustering, liquid-liquid phase separation with a lower critical solution temperature (LCST-LLPS) and crystallisation [1], [2] in aqueous protein solutions. Interestingly, these phase behaviours strongly depend on cation-specific properties. Comparing different rare-earth metals, we find a strong decrease of an LCST-related transition temperature (T_{trans}) with decreasing cation radius. This result is complemented by a thermodynamic characterisation of cation-protein binding revealing a decrease in the point of zero charge for smaller cations. Finally, significant differences in cation-induced protein-protein interaction strengths are observed using small-angle x-ray scattering (SAXS). Importantly, these point towards the fact that in addition to their radius, other cation-specific effects such as polarisability and orbital occupation can play a crucial role in cation-protein

interactions. Our findings thus indicate that a careful choice of a suitable multivalent salt can help tailor protein phase behaviour [3].

[1] Zhang *et al.* *Pure & Appl. Chem.* 2014, 86, 191-202; [2] Matsarskaia *et al.* *JPCB* 2016, 120, 7731-7736; [3] Matsarskaia *et al.* *in preparation.*

CPP 45.4 Wed 12:00 C 243

Effects of anions on the reentrant phase behavior in protein solutions induced by multivalent salts — ●MICHAEL K. BRAUN¹, ANDREA SAUTER¹, SIMON SCHOENBERG¹, MICHAEL SZTUCKI², FAJUN ZHANG¹, and FRANK SCHREIBER¹ — ¹Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen — ²ESRF, Grenoble, France

Interactions between ions and proteins are a highly active research field. They are important both in metabolic processes and to more generally understand protein phase behavior [1]. Model globular proteins in solution with trivalent salts exhibit a reentrant phase behavior where in the condensed regime the cation serves as a linker between two proteins [2, 3]. The nature of the condensates is tunable by the specific cations and anions that are employed. The microscopic role of the anion is not yet fully understood. However, it has now been observed that NO_3^- salts lead to a stronger attraction compared to Cl^- salts. This result is consistently obtained by visual inspection of the sample solutions, by monitoring the protein concentration in the supernatant using UV-vis absorption spectroscopy and by extracting potential parameters from model fits to small angle x-ray scattering data. This suggests a different affinity of Cl^- vs. NO_3^- to the protein surface. Possible microscopic reasons such as Hofmeister effects and different entropy contributions of the anions will be discussed.

[1] Gunton *et al.*, *Protein Condensation*, 2007 [2] Zhang *et al.*, *Pure Appl. Chem.*, **86**, 191, 2014 [3] Matsarskaia *et al.*, *J. Phys. Chem. B*, **120**, 7731, 2016

CPP 45.5 Wed 12:15 C 243

The influence of co-solutes on the chemical equilibrium - a Kirkwood-Buff theory for ion pair formation processes in ternary solutions — ●ANAND NARAYANAN KRISHNAMOORTHY, CHRISTIAN HOLM, and JENS SMIATEK — Institute for Computational Physics - University of Stuttgart

We present a theoretical framework for ternary solutions in order to describe the influence of co-solute species on the chemical equilibrium of ion pair formation. The theory relies on the use of Kirkwood-Buff integrals and the introduction of a local/bulk partition model. We can show that either ion pair formation or ion dissociation is favored with regard to a more pronounced co-solute accumulation around the corresponding ion state. The co-solute molecules can be either charged or uncharged and the theory is applicable for ideal and weakly non-ideal solutions in combination with low ion concentrations. The corresponding implications of our theory are useful in order to optimize the efficiency of electrolyte solutions in electrochemical applications. All theoretical results are verified by atomistic molecular dynamics simulations of sodium chloride ion pairs in dimethylacetamide (DMAc)/water mixtures.

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Binary mixtures of ionic liquids and co-solutes: the local structure at uncharged walls in presence of dimethyl sulfoxide and water — TAKESHI KOBAYASHI¹, MARIA FYTA¹, and ●JENS SMIATEK^{1,2} — ¹University of Stuttgart, Institute for Computational Physics, D-70569 Stuttgart, Germany — ²Helmholtz Institute Münster (IEK-12 HI MS), Forschungszentrum Jülich, D-48149 Münster, Germany

We study the local structure of binary ionic liquid mixtures, namely 1-ethyl-3-methylimidazolium dicyanamide (EMIM/DCA) in combination with varying mole fractions of co-solutes dimethyl sulfoxide (DMSO) and water in front of uncharged and purely repulsive walls. In agreement with recent experimental results [1], we observe significant differences in our atomistic molecular dynamics simulations between the local accumulation behavior of the co-solutes at the interfaces. The corresponding bulk solvation structure provides more insights into these effects, which can be attributed to non-idealities in the local dis-

tribution of the molecules. Our recently introduced Kirkwood-Buff approach for ionic liquids [2] helps us to shed more light on the corresponding findings.

[1] M. Jitvisate et al., *J. Phys. Chem. C* **121**, 18593 (2017)

[2] T. Kobayashi et al., *Phys. Chem. Chem. Phys.* **19**, 18924 (2017)

CPP 45.7 Wed 12:45 C 243

Competing interactions and the formation of dynamic protein clusters — ANITA GIRELLI¹, MICHAL K. BRAUN¹, FELIX ROSEN-RUNGE², MARCO GRIMALDO³, TILO SEYDEL³, FAJUN ZHANG¹, and FRANK SCHREIBER¹ — ¹Institut für Angewandte Physik, Universität Tübingen, 72076 Tübingen — ²Physical Chemistry, Lund University, Sweden — ³ILL Grenoble, France

Protein clusters are potential precursors for protein crystallization. The question of their formation and transient, dynamic or permanent

nature is of high relevance to structural biology and biomedicine. Here we report on protein clusters in bovine serum albumin (BSA) - trivalent salt (YCl₃, LaCl₃) systems. The protein clusters are most probably held together by ion bridges and precede a condensation regime [1, 2]. The clusters are characterized by dynamic light scattering (DLS). For a molar ratio of salt concentration and protein concentration, c_s/c_p , equal to 4, we can observe the formation of clusters with a lifetime longer than 1 ms. Based on a comparison with self-diffusion data from neutron back scattering experiments [3], we assume that dynamic clusters form for c_s/c_p between 2 and 4. Furthermore, SAXS measurements for samples under these conditions demonstrate the competing interactions, which support the formation of dynamic clusters.

[1] Soraruf et al., *Soft Matter*, **10**, 894, 2014

[2] Zhang et al., *J. Appl. Cryst.*, **44**, 755, 2011

[3] Grimaldo et al., *J. Phys. Chem. Lett.*, **6**, 2577, 2015