CPP 13: Charged Soft Matter, Polyelectrolytes and Ionic Liquids

Time: Monday 15:00–17:00 Location: ZEU/0260

Invited Talk CPP 13.1 Mon 15:00 ZEU/0260

Modelling and simulation of pH-sensitive polyelectrolyte microgels — •Stefanie Schneider — Institute of Physical Chemistry, RWTH Aachen University, Aachen, Germany

For weak polyelectrolytes (PE) as well as for weak polyampholytes (PA), not only the pH-pKA value but also the local electrostatic environment of the ionisable group determines the degree of ionisation and structural properties of the polymer. The proximity of already ionised groups, which is enforced by the interconnectivity of the polymer chain, influences the probability of additional groups to become ionised. Therefore, the degree of ionisation for polymers with different architectures differs from the ideal value, obtained for monomers at low concentrations.

Polyelectrolyte and polyampholyte microgels of different topologies have been investigated using constant pH-Monte Carlo simulations. Ionisation, swelling as well as the uptake and release of guest molecules were studied. [1-5]

Especially, the interaction with guest molecules is an important aspect for the use of microgels for drug delivery.

[1] C. Hofzumahaus, P. Hebbeker, S. Schneider, Soft Matter, 2018, 14, 4087.

[2] C. Hofzumahaus, C. Strauch, S. Schneider, Soft Matter, 2021, 17, 6029.

[3] C. Strauch, S. Schneider, Soft Matter, 2023, 19, 938.

[4] C. Strauch, S. Schneider, Soft Matter, 2024, 20, 1263.

[5] C. Strauch, L. Roß, S. Schneider, Soft Matter, 2024, 20, 9664.

CPP 13.2 Mon 15:30 ZEU/0260

Beyond electrostatic screening: Effect of ion pairing on acid-base equilibria in complex electrolyte solutions — •Varun Mandalaparthy[1], Johannes Hunger[2], Mischa Bonn[2], and Nico van der Vegt[1] — [1]Technical University, Darmstadt — [2]Max Planck Institute for Polymer Research, Mainz

The modulation of acid-base equilibria by salts is central to solution chemistry, yet the molecular origins of these effects in multi-component electrolyte mixtures remain incompletely understood. Building on evidence that individual salts induce ion-specific shifts in the pKa values of weak acids, we combine experiments with constant-pH molecular dynamics simulations to examine how ion pairing and specific ion interactions regulate the pKa of acetic acid in single and mixed sodium salt solutions. Across anions of differing charge density (sulfate, chloride, iodide), we show that cation-anion association-rather than electrostatic screening alone-governs the observed pKa changes. In solutions containing mixtures of sodium chloride and sodium sulfate, the impact on acetic acid pKa deviates from simple additivity because of complex ion-ion interactions. We present an ion-pairing-enhanced Debye-Hückel model that quantitatively reproduces these behaviors, offering a predictive framework for pH regulation in multi-salt environments. This work provides a mechanistic foundation for interpreting and forecasting pH-dependent behavior in complex systems relevant to biochemistry and soft matter.

REF: Mandalaparthy et al. ChemRxiv. 2025; doi:10.26434/chemrxiv-2025-p2chl (under review at J. Phys. Chem. Lett.)

CPP 13.3 Mon 15:45 ZEU/0260

How polymer chain flexibility influences orientation and entanglements in polyelectrolyte solutions — Sascha Bartosch and •Ulrich Scheler — Leibniz-Institut für Polymerforschung Dresden e.V.

Entanglements in long-chain polymers are important for their mechanical properties and strongly impact the processability. In solutions the formation of entanglements depends on chain length, concentration and the chain flexibility. The flexibility of polyelectrolyte chains is influenced by the ionic strength of the solution that may screen the repulsive electrostatic interaction along the chain. That is reflected in the variation of the hydrodynamic radius of the polyelectrolytes measured by diffusion NMR. Upon shear polymers can orient or polymer chains maybe pulled out of entanglements. The NMR transverse relaxation time T2 is a good measure for the slow polymer-chain dynamics affected by polymer entanglements. Aligning polymer chains results in a shortened T2 while the loss of entanglements yielding longer chain segments between entanglements results in a longer T2. Short-chain polyelectrolytes under shear in a Searle cell show chain orientation. Long-chain polyelectrolytes at low ionic strength orient as well, while at higher ionic strength a loss of entanglements is observed. The transition from stiff to flexible entangled polymer is triggered solely by the electrostatic interaction modulated by the ionic strength under experimental control.

CPP 13.4 Mon 16:00 ZEU/0260

Molecular Mechanisms Underlying LCST and UCST Transitions in Thermoresponsive Ionic Liquids — •Hussen Oumer Mohammed[1,2], Abel De Cozar[1,2], and Ronen Zangi[1,2] — [1]Donostia International Physics Center (DIPC), Donostia, Spain — [2]University of the Basque Country UPV/EHU, Donostia, Spain

We investigate liquid-liquid phase separation (LLPS) of ionic liquid (IL)-water mixtures through atomistic MD simulations. Two model systems are studied: $[\mathrm{P}_{4444}]$ [TMBS], which exhibits a lower critical solution temperature (LCST) phase separation, and $[\mathrm{Hbet}][\mathrm{Tf}_2\mathrm{N}]$, which displays an upper critical solution temperature (UCST) behavior.

Aiming to elucidate the driving forces governing the two types of phase separation, we performed a detailed analysis of energy decompositions, HB networks, and microstructural organizations. We find that for $[\mathrm{P}_{4444}]$[TMBS]/water phase demixing, increasing temperature weakens IL-water HB, augments the enthalpic penalty of hydration, and favors ion pairing and mesoscale segregation. Conversely, for $[\mathrm{Hbet}][\mathrm{Tf}_2\mathrm{N}]$/water demixing, cooling enhances water self-networking and suppresses ion hydration, promoting like-like association, while heating disrupts the water network and re-establishes miscibility through stronger ion-water HB.

By shedding light on these molecular-level mechanisms underlying those behaviors in distinct ILs, this study offers a predictive simulation-based framework for the rational design of thermoresponsive draw solutes in FO desalination, enabling tunable and energy-efficient regeneration cycles.

CPP 13.5 Mon 16:15 ZEU/0260

Machine-Learning Prediction of Ionic Conductivity from Short-Time Structural Data in Ionic Liquids — •David Bienek — Helmholtz-Institut Münster, Münster, Germany

Molecular dynamics (MD) simulations are a powerful tool for studying electrolyte materials, but the reliable calculation of ionic conductivities and transference numbers requires long trajectories. In this project, we explore whether machine-learning (ML) models can predict dynamic properties of ionic liquids (ILs) from structural information obtained in much shorter simulations. ILs are chosen as model systems because prior work has demonstrated links between structure and hydrodynamic behaviour. Their simple cation-anion composition also allows systematic generation of simulated systems. As structural descriptors, we employ radial distribution functions (RDFs), which are physically interpretable.

We test linear regression, random forests, and neural networks for predicting ionic conductivity. After feature engineering we find substantial improvements in accuracy. A peak-based representation proves particularly helpful for identifying structure-dynamics relations. Feature-importance analyses consistently indicate that the dominant information originates from the first coordination shell. Moreover, simpler models (random forest, linear regression) outperform neural networks, highlighting the necessity to use appropriate model complexity. Overall, our results show that ML can support the identification of structure-dynamics correlations in electrolytes and may help estimate transport properties from short MD trajectories.

CPP 13.6 Mon 16:30 ZEU/0260

Dissociation of weak polyacid systems in solution and brush coatings determined by IR titration — •Martin Müller[1,2], Luise Wirth[1,2], Birgit Urban[1], Leo Dagand[1,2], Alexander Münch[1], and Petra Uhlmann[1] — [1]Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Str. 6, Dresden D-01069, Germany — [2]Technische Universität Dresden, Dresden D-01062, Germany

The dissociation degrees a of poly(acrylic acid) (PAA) and propionic acid (PA) solutions were determined by infrared (IR) titration and potentiometric (POT) titration concept. Stepwise increasing pH value from 2 to 12 by adding NaOH portions, IR spectra of PAA and PA show decrease of n(C=O) band due to carboxyl (COOH) and increase of n(COO-) band due to carboxylate (COO-) groups. From the respective normalized band integrals A, dissociation degree was calculated according to a=A(COO-)/(A(COOH)+A(COO-)). Plotting pH versus a and fitting by modified Henderson-Hasselbalch equation according to pH=pKa+B*log(a/(1-a)) the parameters pKa and B were determined. The slight pKa deviation found for IR and POT titration, the respective deviation between monomeric PA and polymeric PAA and the PAA molecular weight trend (PAA-2K, PAA-50K, PAA-450K) are discussed considering the two-phase model of polyelectrolyte solutions and Gibbs-Donnan theory. Furthermore, a and pKa of thin PAA brush coatings under aqueous ambient and the influence of metal ion type (Na+, Ca++, Ce+++) and concentration were determined by FTIR titration revealing higher pKa values compared to solution state and significant effects of ion valency on a.

CPP 13.7 Mon 16:45 ZEU/0260

Unconventional Layer-by-Layer Assembly of Films with PEDOT: Write, Read, and Delete — •Muhammad Khurram, Martin Hunger, and Christiane A. Helm — muhammad.khurram@uni-greifswald.de

PEDOT:PSS films are widely used because they offer high conductivity & tunable electro-optical properties. We present an unconventional layer-by-layer (U-LbL) method for PEDOT:PSS/PDADMA multilayers. Masking was used to create either homogeneous coatings or narrow conductive strips. Each bilayer is only 7-9 nm thick, indicating that films form by adsorption of PSS-linked PEDOT, with unbound nanoparticles removed during rinsing. Flow-cell produces higher conductive films (260 kS/m) than dip coating. The U-LbL process also provides a natural framework for repeated Write/Read/Delete modulation, including PEDOT addition, partial & controlled PEDOT removal, forming molecular cavities that rebind PEDOT & restore percolative pathways.