Specific Binding of Cations to Poylacrylates in Dilute Solution –

a Combined SAXS add ASAXS Study

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Organic polyelectrolytes are highly charged water soluble polymer chains. The subtle interplay of their electric charges and the hydrophobic chain backbone make these polyelectrolytes extremely sensitive to variations of solvent conditions and to the addition of Specifically Interacting Cations (SIC). In the absence of SICs, the polyelectrolytes are highly flexible and adopt an extended coil conformation. Once SICs have been added to such solutions, the SICs are decorating the anionic chains and at the same time are modulating the structure of the anionic coils. At characteristic threshold concentrations formation of SIC-polyelectrolyte even precipitation does occur.

In the present report, diluted sodium polyacrylate chains (NaPA) are investigated with respect to their specific interactions with Pb²⁺ ions, Sr²⁺ ions and Ag⁺ ions. Whereas light scattering revealed the global dimensions of the decorated NaPA coils, small angle x-ray scattering (SAXS) experiments gave an insight into the size and structure of the polyelectrolyte-SIC complexes. The SAXS data were interpreted with carefully developed new model formfactors based on hybrid coil-particle systems. It could be demonstrated, that the coil dimensions shrink while SICs assemble into small nodule-like pearls. These features are attributed to structural intermediates being subdued to an intra-molecular collapse of PA-SIC complex chains while approaching the precipitation threshold.

Additional recording of SAXS curves with at least three different X-ray energies (i.e. wavelengths) - all being close to an absorption edge of the SIC - establishes anomalous SAXS (ASAXS). ASAXS enabled us to successfully retrieve the isolated scattering contribution from
the condensed SICs. Aside from this, ASAXS provides a quantitative measure of the fraction of SICs sticking to the PA chains.[1] Hence SAXS and ASAXS do not only give insight into the manner the PA-chains redistribute the SICs under consideration while shrinking their dimensions but may also yield the amount of SICs being bound to the PA chains.

The present contribution will introduce into the features of quantitative ASAXS, established in the present work in order to investigate condensation of counterions to polyelectrolytes and will compare the impact of Pb$^{2+}$, Sr$^{2+}$ and Ag$^{+}$ ions, thereby providing an overview on common features of SIC – PA interactions and on differences among the three SICs. Along with the new results from selected ASAXS experiments the present contribution outlines the proper requirements for successful ASAXS and demonstrates that ASAXS is an important tool to address the structure of components in complex systems both qualitatively and quantitatively once the system merges with these requirements.[2]

References

[1] Günther Goerigk; Klaus Huber; Ralf Schweins; Probing the extent of Sr$^{2+}$ ion condensation to anionic polyacrylate coils: A quantitative anomalous small angle x-ray scattering study Journal of Chemical Physics (2007), 127, 154908