

Ion Pairing and Counterion Condensation in Aqueous Polyelectrolyte Solutions. Why bother with them?

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ABSTRACT

Polyion-counterion, and more generally ion-coion, interactions play a relevant role in determining the thermophysical properties of aqueous polyelectrolyte solutions. These interactions become increasingly important as salt of multivalent counterions is added, by giving rise to a rather complex interplay between short-range (solvation) interactions characterizing the local environment and long-range (though partially screened by the presence of ions) electrostatic interactions, that leads to ion-pair association and counterion condensation. The nature of the counterion in these systems, including its electrostatic charge and the short-range interaction with the binding site of the polyelectrolyte, appears to be as important as the location of the binding site in the backbone as well as its local environment. The local environment around the charged species depends strongly on the solvent's properties, the ionic strength, as well as the state conditions, and therefore, it is significantly different from that characterized by a solvent as a continuum dielectric.

In this presentation, we address some of those issues by molecular simulation of precisely defined models of aqueous (poly) electrolytes. In particular, we analyze the solvation behavior of short-chain polystyrene (PSS) and polyphenylene sulfonates (PPS) in aqueous electrolyte solutions by molecular dynamics simulation, to determine the solvation effects on the structure and conformation of the polyions as a function of the aqueous environment and the backbone rigidity. Moreover, we assess the impact of added salts (BaCl_2 and LaCl_3) on the net charge of the chain backbone, placing emphasis on the valence of the counterion, and the extent of the counterion condensation. Subsequently, we present evidence for the so-called *like charge attraction* between

sulfonate groups through the formation of counterion-mediated interchain sulfonate-sulfonate and water-mediated intrachain sulfonate-sulfonate bridges, as well as between unlike counterion-counterion interactions. Finally, we discuss some recent developments on the molecular-based interpretation of the signature of ion pair formation in raw data from neutron diffraction with isotope substitution, as well as propose a method to isolate the ion-pairing peak from the neutron weighted distribution functions and then measure its magnitude

This research was sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences under contract number DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

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