

MOLECULAR-BASED STUDY OF THE SOLVATION BEHAVIOR OF SHORT-CHAIN  
POLY-ELECTROLYTES IN AQUEOUS SOLUTIONS. LI-PSS VERSUS LI-PPS

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ABSTRACT

Polyion-counterion interactions play an essential role in determining the stability and solubility of polyelectrolytes in aqueous solutions. These interactions are particularly strong for multivalent counterions, common in biological systems, where the negatively charged biopolymer interacts with divalent metal ions. The nature of the counterion, including its electrostatic charge and polarizability, as well as the short-range (non-electrostatic) interaction with the binding site of the polyelectrolyte, appears to be as important as the location of the binding site. Consequently, the binding between polyion and counterion can exhibit a marked ion selectivity resulting from a delicate balance between short-range (solvation) and long-range (electrostatic) forces that define the local environment, and can also give rise to unexpected like charge interactions. This local environment depends on the solvent's properties, the ionic strength, and the state conditions, and consequently may be significantly different from the solvent's bulk properties. This situation points to the need for a more detailed analysis of the polyion-counterion interaction in aqueous solution, with particular emphasis on understanding the mechanism underlying the ion-selectivity of highly charged polyelectrolytes as a prerequisite for the quantitative interpretation of a variety of experimental measurements of physical and chemical properties.

With that purpose, in this presentation we analyze the solvation behavior of short-chain polystyrene (PSS) and polyphenylene sulfonate (PPS) in aqueous electrolyte solutions by molecular dynamics simulation, to determine the solvation effects on the structure and conformation of the polyion as a function of the aqueous environment and the backbone rigidity. To that end, we study these aqueous systems involving the explicit atomistic description of water, the chain backbones, and their interactions with all species in solution. In addition, we investigate the effect of the degree of sulfonation and its

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distribution along the chain backbone on the resulting conformation as well as solvation structure. Moreover, we assess the impact of added salts ( $\text{BaCl}_2$  and  $\text{LaCl}_3$ ) on the net charge of the chain backbone, placing emphasis on the valence of the counterion, and the extent of the ion-pair formation between the sulfonate group and the counterions. Finally, 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.

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