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MOLECULAR-BASED STUDY OF THE SOLVATION BEHAVIOR OF SHORT-CHAIN POLYSTYRENE SULFONATE IN AQUEOUS ELECTROLYTE SOLUTIONS

Ariel A. Chialvo and J. Michael Simonson. Chemical Sciences Division
Aqueous Chemistry and Geochemistry Group. ORNL. Oak Ridge, TN
37831-6110, U.S.A.

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 polyelectrolyte and counterion should exhibit a marked ion selectivity resulting from a delicate balance between short-range (solvation) and long-range (electrostatic) forces that define the local environment. This local environment depends on the solvent's properties, the ionic strength, and the state conditions, and may be significantly different from the solvent's bulk properties. This situation points to the need for a more detailed understanding of the polyion-counterion interaction in aqueous solution. In particular, understanding the mechanism underlying the ion-selectivity of highly charged polyelectrolytes is central to quantitative interpretation of a variety of experimental measurements of physical and chemical properties.

With that purpose, in this presentation we seek answers to a few precise questions regarding the structural and conformational behavior of short polyelectrolyte chains in the presence of counterions and added salt in aqueous solutions. We focused our attention on short sulfonated polystyrene chains, composed of at least 8-mers, and modeled according to a united-atom description for the CH, CH₂, and CH₃ groups in the alkyl branches and the aromatic rings, as well as for the sulfonate groups.

The simulation study complements both theoretical and experimental investigations of aqueous polyelectrolytes carried out in our laboratory. First, we include

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an explicit and realistic description of water, its interaction with ionomers, and with other species in solution, as opposed to the traditional primitive dielectric continuum picture. This approach allows us to analyze specific solvation factors affecting the structure and dynamics of dissolved polyelectrolytes. Second, we include realistic representations of the salts in solution, based on the accurate parameterization for aqueous alkali halides, as compared with the equal-sized charged spheres of the primitive model approaches. Third, we address the link between the strength of all possible pairwise interactions and their effects on the equilibrium and time-dependent properties of the system, to suggest possible directions in the synthesis of new ionomers for further experimental studies. And fourth, we investigate the effect of the degree of sulfonation and its distribution along the PE chain on the resulting conformation and solvation structure, including the occurrence of ion-pair formation.

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