

Polyelectrolyte Association and Solvation

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The dynamic clustering of charged particles in solution is a ubiquitous, but poorly understood, phenomenon that underpins many biological processes. For highly charged polyelectrolytes, the counter-ions become dissolved into the solvent but continue to associate with the polyelectrolyte, leading to the formation of a diffuse “polarizable” cloud of counter-ions around the polymers. This effect has significant implications for the function of proteins and other natural occurring polyelectrolytes, as emphasized by Kirkwood and coworkers. To probe this general phenomenon, we perform molecular dynamics simulations of a model of polyelectrolyte solutions that includes an explicit solvent and counter-ions, where the relative affinity of the counter-ions and the polymer for the solvent is tunable. We find that the dispersion energies between the solvent and the ionic species greatly influences the nature of the association between the polyelectrolyte chains. In particular, we identify conditions in which three distinct types of polyelectrolyte association emerge. We rationalize these types of polyelectrolyte association based on the competitive association of the counter-ions with the solvent and the influence ion redistribution on the effective interactions between the polyelectrolytes. We calculate static and dynamic correlation functions to quantify the equilibrium structure and dynamics of these complex liquids.