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Ion- and pH-dependent volume transitions in biopolymer gels

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Swelling and collapse of polyelectrolyte gels are the result of a balance of different interactions that control the osmotic pressure and network elasticity. In biopolymer systems ions often play a central role in determining the phase behavior. For example, DNA condensation induced by multivalent cations is crucial for its packaging. It is known that biological processes, such as nerve excitation and muscle contraction, are mediated by divalent cations. In general, relatively little is known about the interaction between multivalent ions and charged biopolymers due to the lack of an appropriate theory and the absence of a sufficiently broad base of experimental data. Recent experimental observations made by anomalous small-angle X-ray scattering indicate that the spatial extent of the counterion cloud is significantly reduced in the case of divalent ions relative to the monovalent ions. An understanding of ion induced swelling/collapse transition in polyelectrolyte gels may shed light on the mechanism of important physiological processes. We compare the effects of pH, ionic strength and counterion valence on the structure and osmotic properties of biopolymer gels. Systematic studies made on DNA gels indicate that monovalent salts gradually reduce gel swelling but do not cause discontinuous volume transition. Introducing calcium ions into the gels produces a reversible volume change. Similarly, decreasing the pH in the surrounding environment leads to shrinkage of the swollen networks. Scattering observations reveal that cations mediate the equilibrium properties by modifying the local environment and the organization of the polymer chains. Osmotic pressure measurements detect significant differences between the effects of pH and ion valence.