

Abstract: By means of molecular simulations, we study dissociative behavior of weak polyacids with added multivalent salt. Weak polyacids are macromolecules that bear weak acid groups, therefore, their ionization varies with pH. The titration curve of such an acid deviates from the ideal one – its ionization is suppressed because of the strong repulsion between charged groups on the polyacid contour. The presence of salt in solution of a polyacid enhances the ionization due to the effects of electrostatic screening and counterion condensation. Up to now, the influence of the salt valency on the weak polyacid ionization has not been explored, although it plays an important role in biological processes. In this thesis, we examine weak polyacid solutions with added salt of various cation valencies (+1,+2,+3) at fixed charge ratio of salt cations to polymer segments. We show that increasing the salt valency promotes the polyelectrolyte ionization in a manner which is different from the effect of increasing ionic strength. A higher counterion valency leads to a lower value of the critical Manning parameter, initiating strong counterion condensation which results in additional ionization due to ion-ion correlations between the condensed counterions and charged groups of the polyelectrolytes.