Abstract Submitted
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Theory of competitive counterion adsorption on flexible polyelectrolytes: Divalent salts[1] ARINDAM KUNDAGRAMI, M. MUTHUKUMAR, Polymer Science and Engineering, University of Massachusetts Amherst — Counterion distribution around an isolated flexible polyelectrolyte in the presence of a divalent salt is evaluated using the adsorption model [M. Muthukumar, J. Chem. Phys. **120**, 9343 (2004)] that considers temperature, salt concentration, and local dielectric heterogeneity as physical variables in the system. Self consistent calculations of effective charge and size of polymer show that divalent counterions replace condensed monovalent counterions in competitive adsorption. The theory further predicts that at modest physical conditions, polymer charge is compensated and reversed with increasing divalent salt. Consequently, the polyelectrolyte collapses and reswells, respectively. Lower temperatures and higher degrees of dielectric heterogeneity enhance condensation of all species of ions. Complete diagram of states for the effective charge is calculated as functions of temperature and salt concentration. A simple theory of ion-bridging is also presented which predicts a first-order collapse of polyelectrolytes. The theoretical predictions are in agreement with generic results from experiments and simulations.

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