

Charge Inversion and Layer-by-Layer Assembly of Flexible Polyelectrolytes

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We have applied a continuum self-consistent field (SCF) theory to flexible polyelectrolytes on flat surfaces which are either uncharged or carrying the opposite charge as the polyelectrolytes. We examined in detail the effects of various parameters on the polyelectrolyte adsorption and surface charge compensation by the adsorbed polyelectrolytes. The ground-state dominance approximation (GSDA) was used to explore the large parameter space involved, including the charge distribution and degree of ionization of the polyelectrolytes, surface charge density, short-range (non-Coulombic) surface-polymer interactions, solvent quality, and bulk polymer and salt concentrations. The numerical results under the GSDA were also compared to the full SCF calculations in order to examine the effects of the molecular weight of the polyelectrolytes. Strong charge inversion is found for relatively long polyelectrolytes on oppositely charged, attractive surfaces in poor solvents at high salt concentrations. At the mean-field level, the adsorption behavior of polyelectrolytes at high salt concentrations can be understood by that of neutral polymers in good solvents.

Based on the above results, we have further modeled the process of the layer-by-layer assembly of flexible polyelectrolytes on flat surfaces. The multilayer has a three-zone structure. An exponential growth is found for the first several layers, followed by a linear growth for subsequent layers, evolving towards a steady state. While adjacent layers are highly interpenetrating, stratification can be seen for every four or more layers. We have also examined the effects of surface charge density, bulk salt concentration, and solvent quality on the thickness and internal structure of the multilayer. Our results agree with most experimental findings on polyelectrolyte layer-by-layer assembly.