Thermodynamics of Ion Pair Formation Between Charged Poly(Amino Acid)s and Detergents

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Proteins show a variety of specific interactions with macromolecules and ligands resulting from their unique composition and structure. Real protein-ligand systems are often complicated and hinder energy contributions of the interacting counterparts. The systems of charged amino acid homopolymers and detergents can serve as a models of protein-ligand system. However, it can be difficult to dissect energy contributions even in such relatively simple systems, because of various contributions present in these interactions, including ionic and hydrophobic interactions, cooperativity, aggregation, and spatial rearrangements.

Here we present a study on charged polyamino acid interaction with ionic detergents. We report isothermal titration calorimetry data obtained in two polymer–surfactant systems: 1) cationic alkylamines (decylamine, undecylamine, dodecylamine, tridecylamine) and anionic poly(amino acid)s (poly(aspartic acid), poly(glutamic acid)) and 2) anionic alkylsulfates (octyl sulfate, decyl sulfate, undecyl sulfate, dodecyl sulfate, octyl sulfonate, nonyl sulfonate, decyl sulfonate) and cationic poly(amino acid)s (poly(arginine), poly(lysine), poly(ornithine)). Titration of poly(amino acid)s with charged side groups by oppositely charged surfactants shows that binding occurs until the charge neutralization point is reached, which means that one surfactant molecule binds to one amino acid molecule. The increased ionic strength inhibits the interaction due to weakened ion pair formation. Surfactants with longer aliphatic tail demonstrated more negative enthalpy contribution to the binding energy. All studied interactions had negative constant pressure heat capacities resulting from the association of hydrophobic tails.