Opposites attract in Soft Matter: Mechanisms and Applications

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Recent studies have pointed the importance of electrostatic assembly in the elaboration of innovative nanomaterials [1]. Beyond their structures, many important questions on the thermodynamics of association remain to be answered. Here, we investigate the complexation between oppositely charged polymers chains using a combination of different techniques, isothermal titration calorimetry (ITC), static and dynamic light scattering and electrophoresis. Upon addition of polycation to polyanion the results obtained by the different techniques reveal a two-step process [2]. The primary process is the formation of highly charged polyelectrolyte complexes of sizes 100 nm. The secondary process is the transition towards a coacervate phase made of rich and poor polymer droplets. The binding isotherms measured are accounted for using a phenomenological model that provides the thermodynamic parameters for each reaction. Small enthalpies and large positive entropies consistent with a counterion release scenario are found throughout this study. Applications of the above strategy to other charged nanosystems, including inorganic nanoparticle [3], natural organic matter [4] or phospholipids [5] have shown strong similarities with polymer complexation. Beyond. this work stresses the importance of the underestimated formulation pathway or mixing order in charged systems [1].

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