

Electrostatic Self-Assembly of Polyelectrolytes by Complex Coacervation

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Complex coacervation is a phase separation phenomena that occurs in aqueous environments.^{1,2} These effects have been studied in systems such as hydrogels, microencapsulation, and adhesives.^{3,4} The systems formed by complex coacervation have high biocompatibility as they are typically derived from biopolymers. Resultant materials have been proposed for use in a variety of applications including medicine, textiles, and food.⁴

Coacervation is the phase separation of a single, homogeneous solution of colloids into two liquid phases.^{1,3} The solution separates into one phase high in colloid concentration and another that is low in colloid concentration. Coacervation has been shown to aggregate into micelles before formation of separate liquid layers (Figure 1). The process of complex coacervation involves two oppositely charged polyelectrolytes as colloids of the system. The electrostatic attraction between the opposite charges leads to complexation of the polymers to induce phase separation of the solution. Bungenburg and Kryut discovered complex coacervation in

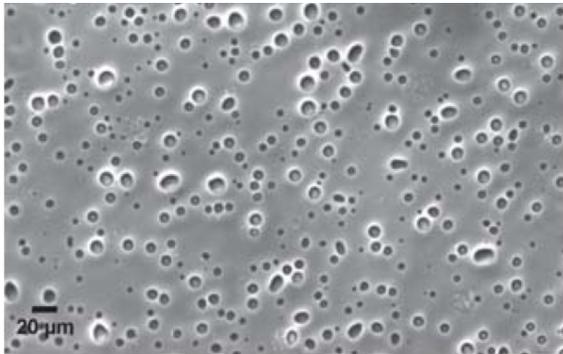


Figure 1. Micelles formed through coacervation.⁴

biologically derived polymers and the effects have derived into models such as the Voorn-Overbeek theory.^{2,3} The theory states that complexation of polyelectrolytes is strongly driven by release of counter ions to increase the overall entropy of the system. The spontaneity of complex coacervation has displayed high potential use as a method of self-assembly.

Salt effects are integral to phase separation conditions. A precipitate forms in the absence of any supporting salt but the addition of salt induces phase separation.^{4,5} At high salt concentration, complete solubility and miscibility of the polyelectrolytes is observed (Figure 2). There are two different category of salts that

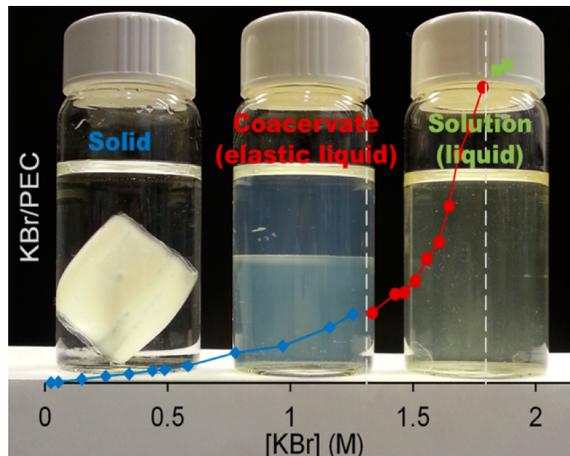


Figure 2. Images of polyelectrolyte solutions as a function of salt concentration.⁵

effect complexation, kosmotropic and chaotropic salts.^{5,6} Kosmotropic salts stabilize water interactions to improve solubility of electrolytes, favoring the formation of solutions. Chaotropic salts have the opposite effect and disrupt water interactions to favor phase separation or precipitation. These effects allow for use of different salts to control complexation conditions.

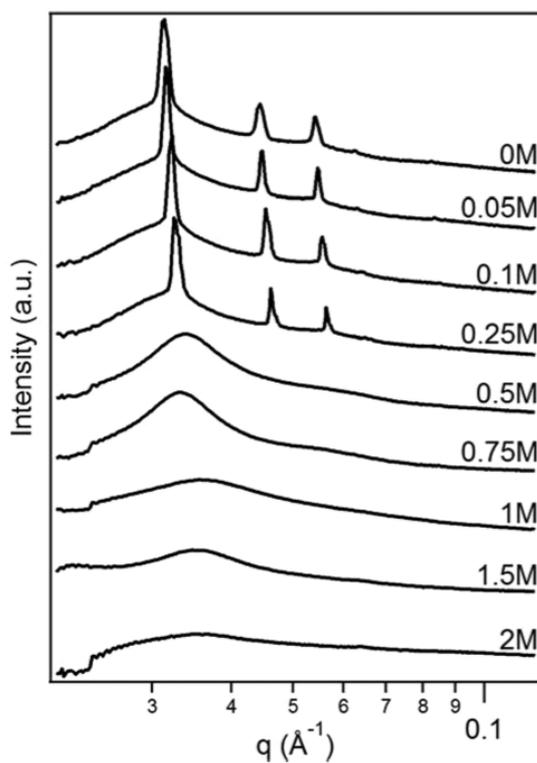


Figure 3. SAXS patterns of oppositely charged triblock polymers under different salt (NaCl) concentrations.⁸

salt concentration effects discussed earlier (Figure 3). Ordered domains exist at low salt concentration as the ionic domains are tightly bound. Increasing the salt concentration breaks up the domains and leads to full dissolution of polymer chains.

Outside of synthetic materials for hydrogels, complex coacervates have been observed as a material in nature. The sandcastle worm forms its home from adhering grains of sand with complex coacervates (Figure 4. B).⁹ The mixture of post-functionalized proteins, used to form the complex, gives an adhesive with quick curing time. The catechol group is a motif in the amino acid L-dopa used to bind the grains of sand together. This functionality was utilized by the Stewart group to affix fragments of live rat skulls together and encourage proper healing of removed bone. L-dopa motifs in the complex coacervate mixture were able to adhere to bone surfaces and allow for new bone growth. The results showed biodegradability and biocompatibility for the healing of rat skulls and no impairment or damage from coacervate use was observed in the specimens.¹⁰

Complex coacervation has been proposed as a method of producing hydrogels for tissue engineering and drug delivery. The van der Gucht group proposed the use of synthetic triblock polyelectrolytes to form transient networks with the oppositely charged homopolyelectrolytes. These results were analyzed by Small Angle X-ray Scattering (SAXS) to reveal that ordering was observed.⁷ The resulting material was a weak gel but the Hawker group was able to expand on this concept to make a higher ordered hydrogel and greater mechanical properties.⁸ Oppositely charged triblock copolymers were used to form ordered hydrogels. The resultant gels displayed superlattice ordering with body centered cubic unit cells.⁸ Mechanical properties of the gels varied depending on salt and polymer concentrations. The ordering correlates with proposed

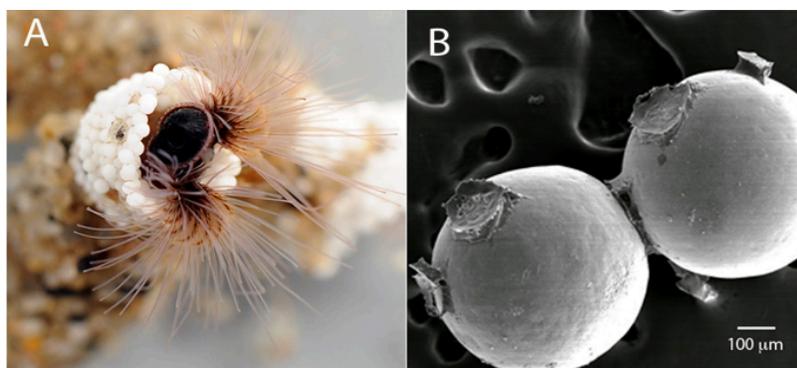


Figure 4. A) Image of the sandcastle worm, B) two sand grains bound by complex coacervate adhesive.⁹

Previous complex coacervates relied heavily on biopolymers that were non-uniform and heterogenous. The lack of homogenous and functionalizable biopolymers made the properties of previous systems inconsistent. Improvements in synthetic techniques have opened doors to new functionalities and access to monodisperse polymers that were not previously available. Recent research utilizing synthetic complex coacervates have displayed that the phenomena displays great potential for many applications. The use of different polyelectrolyte architectures could offer desirable mechanical properties to improve feasibility of complex coacervates for commercial applications. Biodegradable hydrogels with the ability to encapsulate cells have great potential as skin graft materials. Adhesive materials offer uses in medicine as replacements for metal in bone fracture repair and in sutures after surgeries.⁹ The utility of complex coacervates have potential in other applications such as conductive coatings and batteries.⁴

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