

FROM COACERVATION OF OPPOSITELY CHARGED POLYELECTROLYTES TO SUPRAMOLECULAR BOTTLEBRUSHES AND GELS

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Key Words: coacervation, polyelectrolytes, gels, supramolecular, solutions

We develop a scaling model of coacervates formed by oppositely charged polyelectrolytes. The intramolecular electrostatic interactions in dilute polyanion or polycation solutions are characterized by the so-called electrostatic blobs, D_- or D_+ respectively. Polyelectrolyte sections of electrostatic blob size repel neighboring sections of the same chain with electrostatic energy on the order of thermal energy kT . Conformations of polyanion or polycation chains in their respective dilute solutions with no added salt can be described as stretched arrays of their corresponding electrostatic blobs of size D_- or D_+ . The structure of a coacervate formed upon mixing polyanion and polycation solutions depends on the electrostatic attraction between oppositely charged polyelectrolytes balanced by the short-range repulsion. In the symmetric case with $D_- = D_+ = D_e$ the coacervate is a dense packing of these electrostatic blobs with neighboring oppositely charged blobs of size D_e attracting each other with energy on order kT . This attraction is stabilized by short-range non-electrostatic repulsion with energy on the same

order kT between all chain sections of size D_e . In the asymmetric case with stronger polyanion intramolecular repulsion $D_- < D_+$ the structure of coacervate is more complex. The highest energy in the coacervate is intramolecular repulsion within polyanions that on scales smaller than inter-polyanion distance $\xi_- \approx D_-^{1/2} D_+^{-1/2}$ keeps their conformation of stretched arrays of electrostatic blobs of size D_- . Here ν is the scaling exponent describing interactions of uncharged chain section with solvent ($\nu=1/2$ in theta solvent and $\nu=3/5$ in good

solvent). Conformation of polyanions in coacervate is similar to their conformation in semidilute polyanion solutions with the same correlation length ξ_- – stretched array of electrostatic blobs D_- on length scales smaller than correlation length ξ_- and a random walk of chain sections on larger length scales. Weaker charged polycation adsorbs on stronger charged polyanion forming a screening “coat” around it analogous to a semidilute solution of uncharged polymers. The electrostatic attraction of polycations to polyanions is the second largest energy in coacervate and is balanced by the short-range repulsion between sections of polycations of size ξ_+ with energy on the order of thermal energy kT . This attraction slowly decreases in strength with increasing distance from polyanion within the polycation “coat” resulting in a slow (logarithmic) decrease of coat concentration. The inter-polyanion correlation length ξ_- is determined by the length scale at which the polycation “coat” compensates the polyanion charge. This compensating polycation coat of coacervates plays the role of counterions of semidilute polyanion solution with the essential difference of negligible translational entropy and important short-range inter-polycation repulsion balancing electrostatic attraction and reducing osmotic pressure of coacervates to zero. The order of interactions from strongest to weakest corresponding from the order of length scales from the smallest to the largest is $D_- < \xi_+ < D_+ < \xi_-$. Opposite charges form bound pairs and larger ionic clusters at higher strength of electrostatic interactions resulting in a formation of first mixed ionic/screening coat coacervate and eventually at the highest electrostatic strength – ionic network of comb/bottlebrush-like polyanion backbones with polycation loops and bridges. We describe how supramolecular assemblies of oppositely charged molecules can form similar bottlebrushes and networks.

