

Probing oppositely charged surfactant and copolymer interactions by isothermal titration microcalorimetry

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The complexation between charged-neutral block copolymers and oppositely charged surfactants was investigated by light scattering experiments and by isothermal titration calorimetry (ITC) [1]. The copolymer was poly(sodium acrylate)-b-poly(acrylamide) and the surfactant dodecyltrimethylammonium bromide (DTAB). In a previous report, we had shown that the copolymers and the surfactants co-assembled spontaneously into colloidal complexes. Depending of the charge ratio Z , the complexes were either single surfactant micelles decorated by copolymers, or core-shell hierarchical structures. ITC was performed in order to investigate the thermodynamics of the complex formation. Titrations of copolymers by surfactants and of surfactants by copolymers revealed that the electrostatic co-assembly was an endothermic reaction, suggesting a process dominated by the entropy of the counterions. Here we found that the thermodynamic quantities associated with the reaction depended on the mixing order. When surfactants were added stepwise to copolymers, the titration was associated with the formation of single micelles decorated by a unique polymer. Above a critical charge ratio, the micelles rearranged themselves into 100 nm colloidal complexes in a collective process which displayed the following features : *i*) the process was very slow as compared to the timescale of Brownian diffusion, *ii*) the thermodynamic signature was a endothermic peak and *iii*) the stoichiometry between the positive and negative charges was modified from $n = 0.48$ (single micelles) to 0.75 (core-shell complexes). When copolymers were added stepwise to surfactants, the titration resulted in the formation of the core-shell aggregates only. In both experiments, the amount of polyelectrolytes needed for the complex formation exceeded the number required to compensate the net micellar charge, confirming the evidence of overcharging in the complex formation [2].

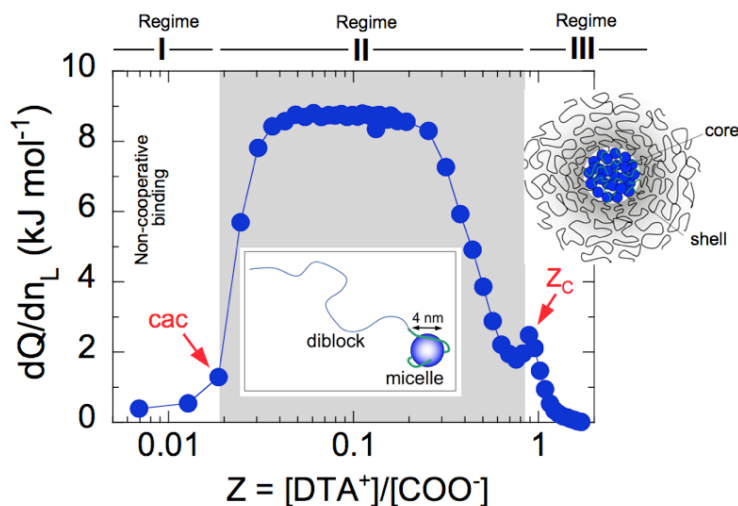


Fig. 1: Illustration of the complexation scenario between oppositely charged surfactants and anionic-neutral block copolymers. Regime I is characterized by a non-cooperative binding of the surfactants on the polymers. In Regime II, above the cac , the binding is cooperative and individual micelles made from surfactants and from the polyelectrolyte block form spontaneously. Regime III corresponds to the formation of core-shell complexes of large sizes, $D_H \sim 100$ nm.

Références

- [1] Courtois J, Berret J-F. *Langmuir*. 2010;26(14):11750-8.
- [2] Berret J-F. *Colloid and Polymer Science*. 2009;287(7):801-10.