

Effect of the Charge Regulation Behavior and Chemistry of Polyelectrolytes on their Nonequilibrium Complexation with Oppositely Charged Surfactants

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The complexation of hexadecyl trimethylammonium bromide (CTAB) with sodium poly[(vinyl alcohol)-co-(vinyl sulfate)] (PVAS) copolymer and poly(acrylic acid (PAA) samples of low charge density has been investigated using electrophoretic mobility, turbidity and dynamic light scattering measurements. The results indicate considerable impact of the applied mixing procedures on the PAA/CTAB mixtures. In contrast, for the PVAS/CTAB mixtures the effect of solution preparation protocols is less pronounced and limited to a narrow concentration range of CTAB excess. This marked difference in the nonequilibrium behavior is attributable to the different surfactant binding mechanism at the same linear initial charge density of the polyelectrolytes. In the case of PAA, the binding of CTAB charge up the macromolecule which leads to decreased solubility of the polyion/surfactant complex and elevated tendency for the formation of charge stabilized colloidal dispersions at surfactant excess. On the other hand, the PVAS molecules cannot adjust their low charge density, therefore the bound amount of surfactant to the oppositely charged groups is much lower compared to the PAA/CTAB system. Furthermore, contrary to the homopolyelectrolyte/surfactant mixtures, there is an additional binding step on the nonionic vinyl-alcohol units of PVAS at higher surfactant concentrations [1]. This leads to the reswelling of the PVAS/CTAB complexes and the disappearance of kinetically arrested states at appropriately large surfactant excess. Our study clearly reveals that the charge regulation feature of the polyelectrolytes and their chemistry can be successfully used to tune the nonequilibrium characteristics of macromolecule/surfactant association.

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[1] K. Bodnár, E. Fegyver, M. Nagy and R. Mészáros, *Langmuir*, 2016, **32**, 1259.