Charging Mechanisms of the Composite Surfaces: Amphiphilic Block-Copolymer Micelles and Charged Surfaces with Adsorbed Polyelectrolytes

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The methodology for studying the pH-dependent charging of the composite polyelectrolyte/nanoparticle surfaces by means of high-precision potentiometric titrations with ionic strength control will be presented. The experimental charging isotherms can be interpreted in terms of models which take into account the dissociation reactions and the electrostatic interactions on the Poisson-Boltzmann level. The results will be demonstrated for several systems with different surface morphologies in which the forces that govern the charging behaviour are either purely electrostatic, or interplaying electrostatic and hydrophobic.

The weakly acidic nanoparticles with irreversibly adsorbed strongly cationic poly(diallyldimethylammonium chloride) (DADMAC) exhibit a charge reversal in a narrow pH-range, i.e. the point of zero charge, in which the system aggregates. The polyelectrolyte can induce both positive and negative excess surface charge, depending on the pH. This behaviour was studied for different DADMAC loadings, and at different ionic strengths [1,2]. In the first approximation, the results can be rationalized in terms of the Stern model, and the surface dissociation reactions.

The kinetically frozen micelles were prepared through self-assembly of the amphiphilic poly(styrene)-b-poly(N,N dimethylaminoethylmethacrylate) (pS-b-pDMAEMA) in water [3]. The representation of the titration data in terms of the effective $pK_a$ enables quantitative examination of the electrostatic and hydrophobic contributions to the protonation free energy. The results indicate a dominant influence of the hydrophobic interactions at high ionic strength, while the intramicellar electrostatic repulsions are dominant at low ionic strength. The collapse of the corona occurs upon deprotonation, which was detected in the static and dynamic light scattering experiments. At very low ionic strength, the intermicellar electrostatic repulsions may even cause a long-range ordering of the spheres, which are evidenced as structure factors.


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