Adsorption and Aggregation of Cationic Amphiphilic Polyelectrolytes on Silica

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The adsorption of two cationic amphiphilic polyelectrolytes, which are copolymers of two charged monomers, triethyl(vinylbenzyl)ammonium chloride and dimethyldodecyl(vinylbenzyl)ammonium chloride (which is the amphiphilic one) with different contents of amphiphilic groups (40% (40DT) and 80% (80DT)), onto the hydrophilic silica—aqueous solution interface has been studied by in situ null ellipsometry and tapping mode atomic force microscopy (AFM). Adsorption isotherms for both polyelectrolytes were obtained at 25 °C and at different ionic strengths, and the adsorption kinetics was also investigated. At low ionic strength, thin adsorbed layers were observed for both polyelectrolytes. The adsorption increases with polymer concentration and reaches, in most cases, a plateau at a concentration below 50 ppm. For the 80DT polymer, at higher ionic strength, an association into aggregates occurs at concentrations at and above 50 ppm. The aggregates were observed directly by AFM at the surface, and by dynamic light scattering in the solution. The adsorption data for this case demonstrated multilayer formation, which correlates well with the increase in viscosity with the ionic strength observed for 80DT.

1. Introduction

Hydrophobically modified polyelectrolytes (HMPEs) can be divided into three main classes: block copolymers, associating polyelectrolytes and polymeric surfactants (including copolymers with different densities of amphiphilic segments), or polyelectrolytes. They are used in many industrial applications to modify surface properties as the adsorption behavior can be adjusted both by chemical modification and by manipulating the ionic strength of the solution. The HMPEs are therefore currently used in several industrial products such as paints, cosmetics, and pharmaceutical formulations in order to control the rheology and stability of complex fluids. These types of polymers have also come into use for building core—shell morphologies at surfaces with potential use in drug delivery systems. Polymeric surfactants (with different densities of the amphiphilic segments) dissolved in aqueous solutions are known to adopt micelle-like microphase structures, where hydrophobic substituents form the interior domains and charged segments form outer layers. These structures are often referred to as unimolecular micelles. For large enough polymers one polymer molecule can contain several unimolecular micelles. The distribution of the hydrophobic moieties along the polymer backbone determines the behavior of the polymer in aqueous solution. Polymers surfactants have a random distribution of amphiphilic segments and tend to form intramolecular aggregates, while associative polyelectrolytes and block copolymers mainly form intermolecular aggregates.

The two amphiphilic polyelectrolytes used in this investigation are copolymers of two charged monomers, triethyl(vinylbenzyl)ammonium chloride and dimethyldodecyl(vinylbenzyl)ammonium chloride. The two polymers used, 40DT and 80DT, contain 40 and 80 mol % monomers with dodecyl side chains, respectively. These copolymers can be referred to as polyelectrolytes. Each amphiphilic unit is surfactant-like and contains both an alkyl chain and a polar cationic headgroup. Such copolymers exhibit solubility in water even for high content of amphiphilic groups, and the associative properties are controlled by the content and distribution of amphiphilic groups. Few studies of the interfacial behavior of these types of polyelectrolytes have been published. The forces acting between mica surfaces across a dilute solution of 40DT, one of the copolymers under our investigation, in 0.1mM KBr were monitored by Dedinaite et al. The results indicate that the adsorbed layer formed consisted of an inner part that is strongly anchored to the surface and an outer part that is weakly anchored to the inner layer.

One objective of the present study is to correlate bulk solution behavior with interfacial properties of amphiphilic...