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Electro-optics of colloid–polyelectrolyte complexes: Counterion release from adsorbed macromolecules

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Abstract

Complexation between sodium carboxymethylcellulose (NaCMC) and ellipsoidal particles of oppositely charged β-FeOOH is studied using electric light scattering and electrophoresis. We focus on the complex behavior for overcharging of the particle surface. In this case, the fraction of condensed counterions on NaCMC is found to remain unchanged during polymer adsorption onto a weakly charged particle surface. Using the theory of Sens and Joanny, we evaluate the fraction of condensed counterions and compare it with results for nonadsorbed NaCMC. The polarization of condensed counterions along the chain of the adsorbed macromolecule is proved to create the electro-optical effect in suspensions stabilized by NaCMC adsorption.

Keywords: Polyelectrolyte adsorption; Counterion release; Colloid–polyelectrolyte complexation; Electrical polarizability; Electro-optics; Overcharging

1. Introduction

The complexation of polyelectrolytes and oppositely charged colloidal particles has been the subject of intense theoretical and experimental research, strongly motivated by polyelectrolyte applications as colloidal stabilizers, flocculants, and rheological modifiers. Recent renewed interest in colloid–polyelectrolyte complexes comes from their potential application to gene therapy. The complexation of DNA with positively charged liposomes, for example, has been intensively studied in this context [1–3]. Repeated adsorption of anionic and cationic polyelectrolytes onto charged particles, on the other hand, permits formation of multilayers with well-defined characteristics. This widely used technique, based on complexation, was introduced by Decher and Hong [4], Decher [5] and its simplicity has triggered the current interest in layer-by-layer fabrication of nanomaterials with promising technological applications.

The process of colloid–polyelectrolyte complexation is rather complex. It depends on many parameters, such as charge density and size of the particles, charge density and flexibility of the polyion chain, pH, and ionic strength of the solution. One of the most peculiar effects that result from colloid–polyelectrolyte complexation is charge inversion (or overcharging) as more polyions adsorb onto the particle surface than are necessary to neutralize it [6,7]. This phenomenon seems to result from strong lateral correlations among the polyelectrolytes adsorbed onto the particle surface [7–12]. The scaling theory of Dobrynin et al. [8,9] includes the lateral correlations between weakly charged flexible chains to determine their adsorption onto a planar substrate. The adsorption of highly charged rodlike polyelectrolytes onto weakly charged surfaces has recently been analyzed by Cheng and Olvera de la Cruz [13], also including lateral correlations.

When a polyelectrolyte adsorbs onto an oppositely charged surface, the counterions on the particle surface and on the polymer play an important role. The counterion re-

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lease has been considered to be the true driving force for "charge-driven" polymer adsorption. This process increases the system's entropy. However, highly charged polyelectrolytes might not release all of their condensed counterions upon adsorption onto weakly charged substrate, because these counterions reduce the electrostatic repulsion among the adsorbed chains [13]. Sens and Joanny predict, on the other hand, that in the case of adsorption onto a substrate of low dielectric constant, the condensed counterions are not always released because of the major importance of the image-charge effect [14]. In their recent work, Bordi et al. [15] presented experimental evidence that a substantial fraction of condensed counterions remained unchanged after the adsorption of highly charged poly(acrylic acid) onto cationic liposomes. A similar conclusion was drawn earlier by Shin et al. [16] in their investigation of "charge-driven" polymer adsorption.

The purpose of the present paper is to demonstrate (on the basis of electro-optical and electrophoretic measurements) that complexation between a highly charged polyelectrolyte and a weakly (oppositely) charged colloidal particle leads to overcharging of the particle surface. At the same time, the complexation does not lead to release of the condensed counterions from the adsorbed macromolecule. The latter causes the appearance of an additional low-frequency electro-optical effect, attributed to polarization of condensed counterions. The mobility of the condensed counterions was suggested to be lower than that of the free ions from the diffuse layer of the colloid–polyelectrolyte complex. A similar explanation has been given for the results obtained in our previous studies, but on a qualitative level [17–20]. Here, we apply the theory of Sens and Joanny [14] to estimate the release of the condensed counterions from highly charged NaCMC when it adsorbs onto the β-FeOOH particle surface. Since this theory examines the evolution of the effective charge of an infinitely long, charged rigid polyelectrolyte near an oppositely charged plane, our estimates can be considered as semiquantative.

In this study, the complexation of a semiflexible NaCMC polyion with a positively charged anisometric oxide particle was investigated in a wide polyion concentration range. The electrical properties of the complexes were compared after different charge densities of the NaCMC. Estimates have also been proposed for the electrical polarizability after overcharging of the particle surface, using Manning's equation for polarization of condensed counterions along the chain of a highly charged polyion in a solution [21]. Comparison with the experimentally obtained values for the electrical polarizability of the colloid–polyelectrolyte complexes allows us to emphasize the decisive role of the condensed counterions in the creation of the electro-optical effect at frequencies over the range of particle rotation.

2. Materials and methods

2.1. Materials

Anionic sodium carboxymethylcellulose (Na CMC) with molecular weight 250,000 was purchased from Aldrich. Three samples with degree of carboxyl substitution 1.2, 0.9, and 0.7 were used, which corresponded to charge densities ξ of 1.67, 1.25, and 1.00, respectively. (The charge density parameter $\xi = l_B/d$ is defined as the ratio of the Bjerrum length $l_B = e^2/(\varepsilon kT)$ to the charge spacing d, where e is the electronic charge, ε the bulk dielectric constant, and kT the Boltzmann energy term [22].) Aqueous solutions of NaCMC with concentrations in the range from 10^{-5} to 2×10^{-2} g dm^{-3} were prepared from a 1 g dm^{-3} stock solution.

β-Ferric hydrous oxide particles (β-FeOOH) were prepared by acid hydrolysis of a 1.8×10^{-2} M $FeCl_3$ solution containing 10^{-3} M HCl at room temperature over a period of 3 weeks [23]. The free Fe^{3+} ions were removed by repeated centrifugation of the particles in distilled water. This procedure gives prolate ellipsoids of narrow size distribution. The major a and minor b axes of the particle are determined by electron microscopy to be 285 ± 56 and 72 ± 14 nm, respectively. In aqueous solution, the β-FeOOH particles are positively charged, with surface charge density of ca. 0.015 C m^{-2} [24]. The concentration of the β-FeOOH particles was 8×10^{-3} g dm^{-3} (about 2×10^9 particles in 1 cm^3) in all experiments. The conductivity of this (very dilute) suspension was 2×10^{-6} S m^{-1} and its pH was 5.8. The colloid–polyelectrolyte complexes were formed by adding NaCMC at an appropriate concentration to the suspension of β-FeOOH particles and stirring for 20 min. The pH of the solutions after addition of 10^{-2} g dm^{-3} NaCMC was around 6.3.

2.2. Electric light-scattering measurements

The orientation of anisometric particles by an externally applied electric field is a result of interaction between the particle electric moments (permanent and induced) and the orienting field. As a consequence of the particle orientation, the light scattered by the suspension is changed.

The steady-state electro-optical effect α is defined as

$$\alpha = \frac{I_E - I_0}{I_0}, \qquad (1)$$

where I_E and I_0 are the intensities of the scattered light in the presence of an electric field E and without a field [25]. The electro-optical effect is a quadratic function of the electric field strength when the energy of particle orientation is lower than the Boltzmann energy kT [25]:

$$\alpha = \frac{A(Ka, Kb)}{I_0(Ka, Kb)} \left[\frac{p'^2}{kT} + (\gamma_a - \gamma_b) \right] \frac{E^2}{4kT}. \qquad (2)$$