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Surface potential of spherical polyelectrolyte brushes in the presence of trivalent counterions

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ABSTRACT

We consider the ζ-potential and the effective charge of spherical polyelectrolyte brushes (SPBs) in aqueous solution in the presence of trivalent europium ions. The SPB consists of a polystyrene core of ca. 250 nm diameter onto which long chains of the strong polyelectrolyte poly(styrene sulfonate) are grafted (contour length: 82 nm). At low concentration of $EuCl_3$ the chains are stretched to nearly full length. If the concentration of the trivalent ions is raised, the surface layer of the polyelectrolyte chains collapses. The ζ-potential of the SPB is calculated from the electrophoretic mobilities measured at different concentrations of $EuCl_3$. At the collapse, ζ decreases by the partial neutralization of the charges by the trivalent ions. The experimental ζ-potential thus obtained agrees with the theoretical surface potential Ψ_{theo} calculated for the effective shear plane by a variational free energy model of the SPB.

1. Introduction

The electrostatic stabilization of colloids by surface charges is among the best-studied problems in colloid science [1,2]. It is by now well-understood that the high electric field resulting from the bare charge Q_b leads to partial condensation of the counterions onto the surface and the electrostatic stability will be provided only by the effective charge Q^*. If Q^* on the surface is known, the corresponding surface potential Ψ is accessible and the repulsive potential between two colloidal spheres can be calculated quantitatively. The effective charge will also determine the electrophoretic mobility μ of the particles in suspension as well as the ζ-potential in an electric field. As a convention, the ζ-potential is defined as the electrostatic potential at a shear plane [3–5]. The ζ-potential has been used to assess the strength of electrostatic repulsion and thus the colloidal stability of the suspensions [1,2].

Early studies of Hückel [6], von Smoluchowski [7] and Henry [8] provide analytical expressions for $\mu(\zeta)$ at low surface potentials but neglect the relaxation effect of the electric double layer. For highly charged rigid particles in mono- or multivalent salt, the theory of O'Brien and White (OW) [9] can be applied for the conversion of the electrophoretic mobility into the ζ-potential. This theory includes double layer relaxation which originates from the polarization of ions within the diffuse layer around the particle by the applied electrical field. A careful comparison of theory and experiment demonstrates that the OW model provides a good description for highly charged sulfonated polystyrene spheres [10,11]. The obvious practical importance of the ζ-potential has led to a large number of theoretical [12–15] and experimental studies [5,16]. Experimental data obtained with polystyrene sulfate colloids in the presence of divalent ions are discussed in Ref. [17]. The relevance of ion size correlations especially for di- and trivalent ions on the mobility of sulfonated latexes is demonstrated in Ref. [18]. It is fair to state that the relation of the electrophoretic mobility and of the ζ-potential to Q^* and the colloidal stability of charged spherical colloids seems to be well-understood by now. A comprehensive review of this problem has been given recently [5].

However, an entirely different situation arises if long polyelectrolyte chains are appended to the surface of the spherical particles. These "soft particles" can be made either by adsorption from the solution, by grafting to the surface [5,19–22], or by affixing a polymeric network to solid core particles [23,24]. The effect of particle coating with polyelectrolytes complicates the calculation of the electrophoretic mobility in a significant manner: First of all, the polymer layer may immobilize or release a certain fraction of its counterions depending on the ionic strength in the system. In this way the effective charge and the thickness of the coating become a function of the concentration and valency of the added salt as recently discussed by Hill, Saville, and Russel [19,20]. Moreover, the hydrodynamic permeability has a profound influence on the mobility [25,26]. If counterions in the soft layer exhibit a non-zero mobility they can induce an electro-osmotic flow in the presence of

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an external electric field. Thus, the soft layer becomes permeable to the solvent. The resulting fluid flow is impeded by the hydrodynamic drag exerted by the polymer segments [20]. The extent to which solvent convection develops within the soft layer is given by the penetration length $\lambda_0^{-1} = (\eta_W/K)^{1/2}$ (η_W dynamic viscosity of water, K friction coefficient exerted by the polymer segments) [27] or the Brinkman screening length $l_B = (n_S 6\pi a_S F_S)^{-1/2}$ (a_S Stokes radius of a polymer segment, n_S polymer segment density, F_S dimensionless drag coefficient for random sphere configuration [19,28]) as expressed by Hill [19]. Duval and Ohshima derived a theory for soft particles [15,27]. In this model, the electrophoretic mobility is calculated for a given distribution of polymer segments at diffuse soft interfaces. As shown by Dukhin *et al.*, the internal structure of polyelectrolyte layers (PL) may be inferred from surface conductivity measurements in order to calculate the Donnan potential and the intrinsic charge [29–32]. Furthermore, measurements of the streaming potential were conducted to investigate the electrokinetic properties of thin films of crosslinked charged polyacrylamide copolymer gels [33] or of planar poly(acrylic acid) brushes [34].

Much of the previous work has been done in order to use electrophoretic measurements to elucidate the structure of polymeric surface layers. The present study aims at a different approach of this problem by investigating the electrophoretic mobility of a model system where the static structure and the thermodynamics is well-established. Fig. 1 displays this model system termed spherical polyelectrolyte brush (SPB; [22]). The particle consists of a solid polymer core with known size R_c onto which long linear chains of poly(styrene sulfonate) of length L are densely grafted (σ). Hence, the appended chains interact strongly (brush-limit; cf. Ref. [35–37]) and most of the counterions are immobilized within the polyelectrolyte layer [38–40]. For salt-free solution the osmotic pressure of the confined counterions leads to a strong stretching of the chains (osmotic brush) [22,35,36,41–43]. If the ionic strength is raised by adding monovalent salt, the brush layer shrinks gradually until the limit of the salted brush is reached [22,35–37]. A similar effect has been observed in studies of charged microgels [23]. However, trivalent ions lead to a much more pronounced shrinking at the same ionic strength since the osmotic pressure within the brush layer is strongly reduced [43,44]. This leads to a collapse of the brush layer at a given concentration of trivalent ions that can be followed precisely by dynamic light scattering (DLS; see Ref. [43]). The SPBs may be used to remove multivalent ions in the treatment of radioactive waste water [45]. However, such applications require the precise control of particle stability.

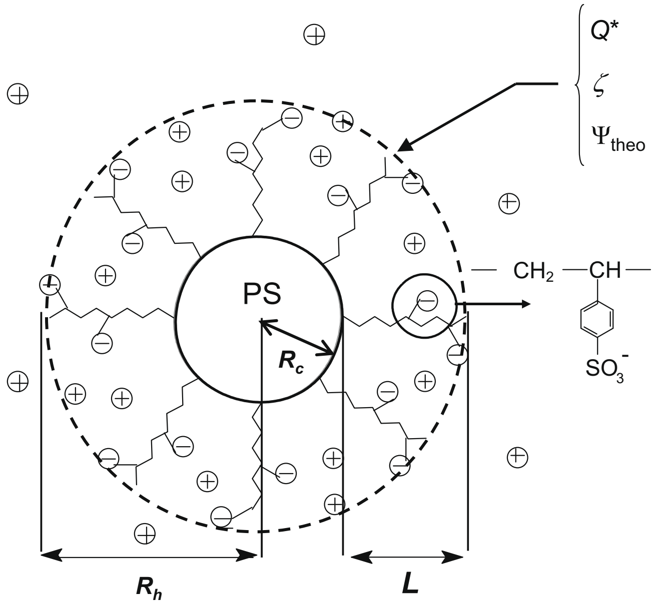

Fig. 1. Schematic representation of the spherical polyelectrolyte brush under consideration. The core of radius R_c consists of polystyrene and a thin layer of photoinitiator, from which polyelectrolyte chains made of sodium styrene sulfonate are densely grafted (σ). L denotes the thickness of the brush shell, R_h the hydrodynamic radius. The effective particle charge Q^*, the experimental ζ-potential and the calculated surface potential Ψ_{theo} in this model are ascribed to the hydrodynamic shear plane of the particle located at a distance R_h from the center of the core (dashed line).

Here we present the analysis of the electrophoretic mobility μ and ζ-potential of spherical polyelectrolyte brushes in the presence of trivalent europium counterions. The present study has been prompted by the success of the theoretical description of the SPB in presence of trivalent ions [43,44]: The reduction of the height L of the surface layer as the function of salt concentration can be quantitatively understood when considering the balance of the osmotic pressure of the counterions within the brush layer and the retracting force of the polymer chains [43,44]. Thus, the thickness L of the surface layer (see Fig. 1) can be modeled as the function of the concentration of the added trivalent ions. An important ingredient of this theory is the partial neutralization of the SPB by the trivalent counterions that are fully condensed onto the polyelectrolyte chains [44]. These ions do not have translational entropy and do not contribute to the osmotic pressure inside the brush [44]. The loss of osmotic pressure inside the layer of polyelectrolyte chains is followed by a marked collapse of the surface layer [43,44]. Concomitantly, the colloidal stability of the particles is expected to decrease very much which is found indeed [46]. As a consequence of this, the partial neutralization of the chains by the trivalent ions should be followed by a strong decrease of the effective charge Q^* and the ζ-potential. Up to now, however, no experimental data are available for the ζ-potential and Q^* of these model SPB in presence of trivalent counterions. The problem at hand can be divided in two parts:

(i) In the first step the hydrodynamic radius R_h and the electrophoretic mobility μ are measured for the SPBs in various concentrations of $EuCl_3$ [47] (see Section 4.1). From the electrophoretic mobilities, the ζ-potential can be deduced using the theory of O'Brien and White [9]. For this we assume that the effective shear plane [5] coincides for both diffusion as well as for the electrophoretic mobility (see Section 4.2).

(ii) In a second step the surface potential Ψ_{theo} at the shear plane defined by R_h is calculated from theory without adjustable parameters. Here, R_h is obtained from the theory delineated in Ref. [48]. The same approach gives the effective charge Q^*. The effective charge can be related to the effective shear plane and used for the calculation of the surface potential Ψ_{theo} (see Section 3).

A comparison of Ψ_{theo} thus obtained with the experimental ζ may then serve for a test of the underlying assumptions (see Section 4.3).

2. Materials and methods

2.1. Materials

The core particles as the precursor for the SPB were synthesized in an emulsifier-free emulsion polymerization of styrene together with the functional monomer sodium(styrene sulfonate) (NaSS) using a solution of $NaHCO_3$, Na_2SO_3 and $K_2S_2O_8$ (KPS) as redox-initiator as described in Ref. [49]. The synthesis of the photoinitiator 2-[p-(2-hydroxy-2-methylpropiophenone)]-ethylenglycol methac-