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Electrokinetic transport of a spherical gel-layer model particle: Inclusion of charge regulation and application to polystyrene sulfonate

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Abstract

An electrokinetic gel-layer model of a spherical, highly charged colloid particle developed previously [S. Allison, J. Colloid Interface Sci. 277 (2004) 248], is extended in several ways. The charge of the particle is assumed to arise from deprotonation of acidic groups that are present, in uniform concentration, over a portion (or all) of the gel layer. Free energy considerations coupled with Poisson–Boltzmann theory are used to estimate how the local electrostatic environment of a charged gel layer alters the local $\mathrm{p}K_\mathrm{a}$ of the acidic groups. This modulation of the charge of the colloidal particle, or "charge regulation," can be significant even for colloidal particles with strongly acidic groups at moderate pH if the ambient salt concentration is low. The methodology is applied to the viscosity and electrophoretic mobility data of a particular polystyrene sulfonate latex over a broad range of monovalent salt (NaCl) concentration [M.J. Garcia-Salinas, F.J. de las Nieves, Langmuir 16 (2000) 715]. The experimental data can be accounted for by a gel layer model that decreases in thickness, but does not vanish, as the salt concentration is increased. Viscosity data provides valuable information about the degree of solvation of the colloidal particle and the thickness of the gel layer. The mobility data is best explained by a model in which only the outermost portion of the gel layer is charged. Charge regulation is significant at a monovalent salt concentration of 3×10^{-3} mol/l and increases as the salt concentration decreases.

Keywords: Electrokinetic transport; Gel-layer modeling; Polystyrene sulfonate; Charge regulation

1. Introduction

Colloidal particles that consist of a solid core and a more diffuse surface layer have attracted considerable attention in recent years. These particles include biological cells [1], silica sols [2–4], crosslinked carbohydrates [5], and a wide variety of polystyrene latex particles [6–17]. The latex particles constitute a particularly rich and varied class with a divergence of surface properties depending on their composition and method of preparation. Variation in surface morphology can be achieved, but is not restricted to, varying the composition of the polymerization mixture. For example, emulsion copolymerization of hydrophobic monomers (styrene and butadiene) and a comparatively small amount of hydrophilic monomers (acrylic and fumaric acids) yields a particle with a hydrophobic core surrounded by a negatively charged hydrophilic layer [17]. The principal motivation for this interest in polystyrene latex particles is that they are simple model systems of electrosterically stabilized particles [7,8,10,14,16,17]. Suspension stability, in turn, is important in many industrial applications such as adhesives, coatings, and texture modification [18].

The electrokinetic methods of electrophoresis [6–11,13–15,17] and electroviscosity [13,15] have been useful in characterizing these latex particles. In past works, a number of investigators cited previously have noted "anomalies" in the electrophoresis and viscosity results of polystyrene latex particles. These include electroviscous effects that are difficult to reconcile with "hard sphere" modeling [13,15], and a significant dependence of mobility on pH, even when the disassociating groups are strongly acidic and the experiments are carried out well above the intrinsic $\mathrm{p}K_\mathrm{a}$'s of the charge groups [7,10]. The dependence of mobility on salt concentration depends on the nature of polystyrene surface properties [7]. For large latex particles with negatively charged surfaces that arise from dissociation of strong acidic groups, the observed trend is gen-

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erally a gradual decrease in absolute mobility with increasing monovalent salt at low concentration [6,7,13], a leveling off of mobility at a monovalent salt concentration of around 10^{-4}–10^{-3} molar [6,13], an increase in the absolute mobility to a maximum around 10^{-2} molar [11,13], and finally a sharp drop in absolute mobility at still higher salt concentration [11,13]. On the basis of electrokinetic theory of "hard" particles [19–22] that have surface or "zeta" potentials that are not too large, one would expect a steady decrease in mobility with increasing salt concentration provided the net charge of the particle does not change. If the absolute "zeta" potential of a "hard" particle at low salt is very large, it is possible the absolute mobility would be expected to increase, level off, and then decrease as the salt concentration is raised [11,21,22]. The characteristic rise in mobility below 10^{-2} molar salt is consistent with the presence of a "gel" or "hairy" layer on the particle surface [6,7,9–12]. Although the presence of a gel layer has been postulated in order to explain the electrokinetic behavior of particular latex particles, it has been difficult if not impossible to determine, in a quantitative manner, the thickness, composition, and charge of the gel layer. The objective of the present work is to present an electrokinetic model applicable to both electrophoresis and viscosity that is capable of yielding results that are consistent with experiment.

Ohshima has developed a detailed theory of the electrophoresis of spherical colloid particles containing a gel layer [23–26]. This theory is applicable under quite general conditions and under certain conditions, can be put into the form of convenient analytical expressions. This work has been of considerable value in enabling scientists to understand the essential physics of colloid electrophoresis when a gel layer is present. On the other hand, this theory is only applicable if the colloidal particle is weakly charged, since the "relaxation effect" [18–22] is not accounted for. The relaxation effect refers to the distortion of the ion atmosphere around a charged particle due to the presence of an external electric field. Even for highly charged "hard" (lacking a gel layer) colloidal particles, however, it has been necessary to resort to intensive numerical calculations in order account for the relaxation effect [21,22]. Hill et al. [27] accounted for the relaxation effect in modeling the electrophoresis of spherical particles containing a gel layer. Recently, we developed a spherical gel layer model that numerically determines both the electrophoretic mobility and viscosity of highly charged spherical particles of arbitrary size [28]. Basically, this model extends the "hard sphere" model of O'Brien and White [22] (electrophoresis) and Watterson and White [29] (viscosity) to include the presence of a gel layer of uniform composition.

In the present work, we shall apply this model to the polystyrene sulfonate latex studied by Garcia-Salinas and de las Nieves [13,15]. The reason for focusing on this particular latex is that both electrophoresis and viscosity data are available over a wide range of monovalent salt concentrations. In addition, the titration charge is known. The viscosity data is particularly useful in modeling the thickness of the gel layer. Another factor that is dealt with in the present work is accounting for how environmental considerations influence the pK_a of charge groups in the gel layer. This "charge regulation" phenomenon [30] is a long recognized problem in charge studies of peptides [31]. Physically, the pK_a of an acidic group in the environment of a peptide or gel layer of a colloid particle will be influenced by the presence of neighboring charge(s). When the gel layer is highly charged, the pK_a of a particular acidic group is altered due to the presence of charge neighbors, and this, in turn, alters the net charge of the colloid. In the present work, how charge regulation affects the pK_a and hence the charge state of the colloid is examined using free energy arguments and solution of the Poisson–Boltzmann equation (Appendices A and B). Since high absolute electrostatic potentials are involved, it is appropriate to ask whether or not Poisson–Boltzmann theory should even be used for highly charged polystyrene latex particles. A number of groups [32–34] have investigated ionic distributions around high molecular weight duplex DNA. They have shown that the non-linear Poisson–Boltzmann equation gives reasonable electrostatic potentials and ion distributions for both co- and counter-ions that are univalent and not small compared to the diameter of DNA. Since the electrostatic potentials around highly charged latex particles are roughly comparable to DNA, we may assume that the non-linear Poisson–Boltzmann equation can be used here as well for monovalent co- and counter-ions. More sophisticated modeling such as using the hypernetted chain equation [35] is not carried out in the present work. Using the non-linear Poisson–Boltzmann equation to determine electrostatic potentials and ion distributions, our analysis predicts substantial protonation of the acidic residues in the gel layer may occur due to the high absolute electrostatic potentials that are present. This is particularly true at low ($\leqslant 10^{-3}$ M) monovalent salt concentrations.

2. Model

The colloidal particle considered in the present work is a generalization of the model considered previously [28]. The model consists of an unhydrated core particle of radius a made up of "segments" of volume v_c per segment. The gel layer, which lies outside of the core and may be hydrated, is made up of potentially different material. For example, the core of the particle may consist primarily of styrene [13] or styrene and butadiene [17] whereas the gel layer may consist primarily of sulfonated styrene [13] or acrylic and fumaric acids [17]. Let v_{gl} denote the volume of an individual (unhydrated) segment in the gel layer. It is assumed that the segment density within the gel layer, ρ_s, is uniform and that it drops abruptly to 0 at a distance, b, from the center of the colloidal sphere. If the gel layer were fully collapsed, then $b = b^*$. The number of segments making up the core, N_c, and gel layer, N_{gl}, are then

$$N_c = \frac{4\pi a^3}{3v_c}, \tag{1}$$

$$N_{gl} = \frac{4\pi(b^{*3} - a^3)}{3v_{gl}}. \tag{2}$$