

## Electrostatic Stabilization of Charged Colloidal Particles with Adsorbed Polyelectrolytes of Opposite Charge

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Repulsive electrostatic double-layer forces are responsible for the stabilization of charged colloidal particles in the presence of adsorbed polyelectrolytes of opposite and high line charge densities. This mechanism is revealed by studies of electrophoretic mobility and colloidal stability performed with dynamic light scattering as a function of the polyelectrolyte dose and the ionic strength for two different types of latex particles and four different types of polyelectrolytes. The dependence of these quantities is very similar for bare charged latex particles and the same particles in the presence of the different oppositely charged polyelectrolytes. Positively charged particles in the presence of anionic polyelectrolytes behave analogously to negatively charged particles in the presence of cationic polyelectrolytes.

Adsorption of polyelectrolytes to oppositely charged water–solid interfaces is relevant to control properties of colloidal suspensions (e.g., stability, rheology)<sup>1–4</sup> or to create nanostructured surface coatings (e.g., multilayers, patterning).<sup>5–8</sup> Suspension properties can be widely tuned by adding an oppositely charged polyelectrolyte to the suspension in question, which leads to the formation of an adsorbed polyelectrolyte layer. Surface coatings can be similarly obtained by exposing the surface to an appropriate polyelectrolyte solution, but in this case the stability of these layers and their desorption characteristics in polyelectrolyte-free solutions become crucial as well.

This Letter discusses the former situation of suspension properties, and focuses on the control of colloidal stability of aqueous suspensions of charged colloidal particles at higher doses of oppositely charged polyelectrolytes. At low polyelectrolyte dose, the situation is relatively well understood.<sup>1,2,4,9–14</sup> Added polyelectrolytes strongly adsorb on the particle surface and thereby neutralize the surface charge. According to the classical theory of

Derjaguin, Landau, Verwey, and Overbeek (DLVO),<sup>15–20</sup> attractive van der Waals forces acting between the neutral particles lead to rapid aggregation and floc formation. Increasing the polyelectrolyte dose leads to particle restabilization, but the corresponding mechanism is poorly understood. One knows that polyelectrolyte adsorption continues beyond neutralization point and that the particles reverse their charge when the polyelectrolyte is in excess.<sup>2,10–13</sup> However, no consensus on the nature of the forces responsible for the particle stabilization exists. Some authors have suggested that repulsive steric forces between the adsorbed polyelectrolyte layers are responsible for suspension restabilization.<sup>11,21</sup> Others have remarked the importance of electrostatic interactions and proposed the concept of electrosteric forces.<sup>22,23</sup>

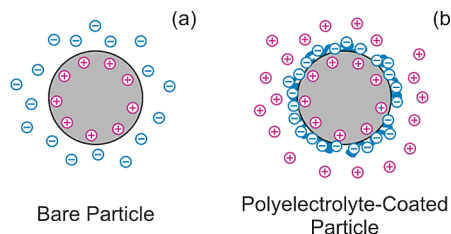
Here we show that repulsive electrostatic double-layer forces as expected from classical DLVO theory are mainly responsible for the stabilization of a colloidal suspension with an excess of polyelectrolyte of opposite charge and high line charge density (Figure 1). This finding follows from the dependence of aggregation rates in suspensions of latex particles on the polyelectrolyte dose and the ionic strength. The generic nature of the phenomenon can be established from the similarity between positively and negatively charged latex particles in the presence of four different types of oppositely charged polyelectrolytes.

The charge reversal phenomenon is easily illustrated by electrophoresis. Figure 2a (top) shows the electrophoretic mobility of positively charged amidine latex particles of 200 nm in diameter upon addition of negatively charged poly(styrene sulfonate) (PSS) in a KCl electrolyte at pH 4. The mobility is initially positive, then passes through the isoelectric point (IEP), and finally becomes negative, indicating that the adsorbed polyelectrolyte has reversed

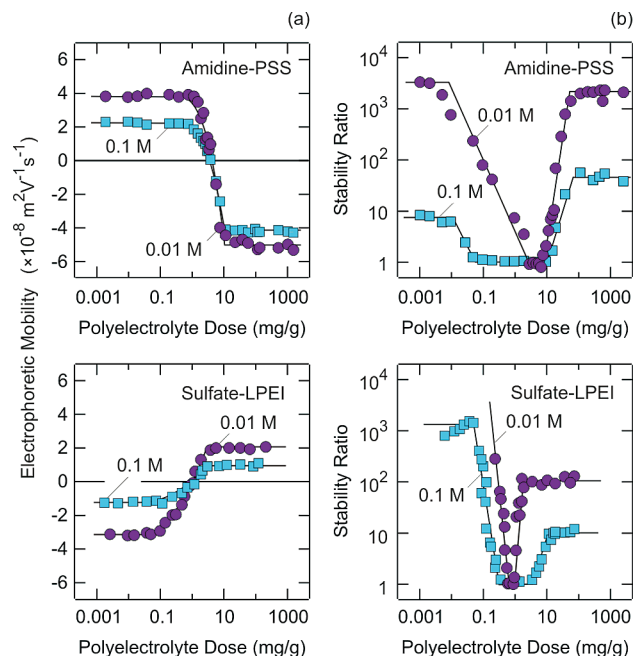
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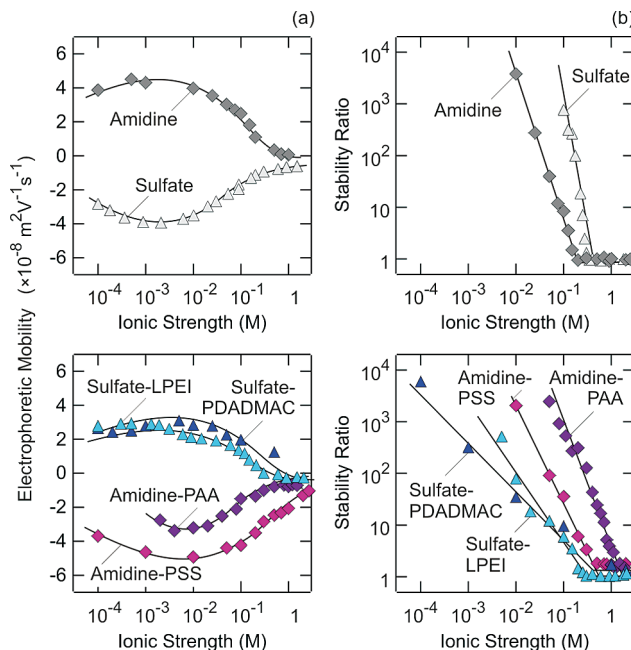
**Figure 1.** Schematic representation of the electrostatic stabilization mechanism whereby the overlap of the diffuse layers generates strong repulsive forces at low ionic strengths. (a) Positively charged particle with a diffuse layer, which mainly consists of anions. (b) Positively charged particle with adsorbed saturated layer of a highly charged anionic polyelectrolyte, which makes the particle negatively charged. In this case, the diffuse layer mainly consists of cations. An analogous scenario applies to negatively charged particles and a highly charged cationic polyelectrolyte.



**Figure 2.** Electrophoretic and stability data for charged latex particles as a function of the dose of an oppositely charged polyelectrolyte for two different ionic strengths of 0.01 and 0.1 M in KCl electrolyte at pH 4.0. (a) Electrophoretic mobility is shown in the left column, while (b) the stability ratio is in the right one. (top) Amidine latex and poly(styrene sulfonate) (PSS). (bottom) Sulfate latex and linear poly(ethylene imine) (LPEI). The solid lines serve to guide the eye.

the particle charge. The adsorption process stops when the plateau in the mobility is reached. Beyond this plateau, the adsorbed amount remains constant and the excess polyelectrolyte is dissolved in the solution. Prior to the onset of the plateau, the adsorption of the polyelectrolyte is quantitative and there is basically no free polyelectrolyte in solution.<sup>13</sup>

Stability ratios are determined by time-resolved dynamic light scattering in the early stages of the aggregation.<sup>2,13,17</sup> This quantity represents the ratio between the aggregation rate of the bare particles in excess salt and the actual aggregation rate. This ratio is close to unity for an unstable suspension and increases with increasing suspension stability. Figure 2b (top) shows the stability ratio for amidine particles as a function of the PSS dose. Around the IEP, particles are neutral and they aggregate rapidly due to attractive van der Waals forces. Away



**Figure 3.** Electrophoretic and stability data for bare latex particles as a function of the ionic strength in KCl electrolyte with a saturated layer of adsorbed polyelectrolyte and without. (a) Electrophoretic mobility is shown in the left column, while (b) the stability ratio is in the right one. (top) Bare amidine and sulfate latex particles. (bottom) Amidine particles in the presence of poly(styrene sulfonate) (PSS) and poly(acrylic acid) (PAA) and sulfate latex particles in the presence of linear poly(ethylene imine) (LPEI) and poly(diallyldimethyl ammonium chloride) (PDADMAC). The latter data were obtained at a polyelectrolyte dose of 30 mg/g. The data shown were measured at pH 4.0, except the PAA data at pH 5.8. The solid lines serve to guide the eye.

from the IEP, the suspension is stabilized by repulsive electrostatic double-layer forces. At low doses, the stability ratio reaches a plateau corresponding to the aggregation rate of the bare particles. At higher doses, surprisingly, one observes a similar plateau. The latter plateau corresponds to the aggregation rate of the particles with a saturated adsorbed polyelectrolyte layer. As the ionic strength is increased, the stability ratio decreases substantially. This strong decrease indicates the importance of repulsive electrostatic interactions, which are progressively being screened as ionic strength is increased.

Negatively charged sulfate latex particles of 135 nm in radius in the presence of the cationic polyelectrolyte linear poly(ethylene imine) (LPEI) behave analogously. Figure 2a (bottom) shows that, with increasing LPEI dose, the mobility of the particles passes the IEP and saturates at a positive value of the mobility. This positive value indicates that a charge reversal did take place too. Figure 2b (bottom) shows that, near the IEP, the suspension is unstable, and the stability increases away from the IEP. At low and high doses, the stability ratio reaches a plateau. With increasing ionic strength, the suspension becomes less stable, indicating the importance of electrostatic interactions. The fact that negatively charged particles in the presence of a cationic polyelectrolyte behave analogously to positively charged particles in the presence of an anionic polyelectrolyte strongly suggests that electrostatic forces govern the interactions in these systems.

The electrostatic origin of the stabilization mechanism becomes fully obvious when mobility and stability are studied as a function of the ionic strength. Recall the classical case of electrostatic stabilization described by DLVO theory<sup>15–20</sup> illustrated here with

bare latex particles. Figure 3a (top) shows the electrophoretic mobility of both latices as a function of the ionic strength. With decreasing ionic strength, the magnitude of the mobility initially increases due to the increase in the magnitude of the electrostatic surface potential. While the magnitude of surface potential continues to increase, the maximum or minimum in the mobility originates from the polarization effect and can be quantified with the standard electrokinetic model.<sup>18</sup> Figure 3b (top) shows the corresponding stability data. At high ionic strength, the suspension becomes unstable with a stability ratio close to unity. The rapid aggregation is induced by van der Waals forces, since electrostatic interactions are fully screened. With decreasing ionic strength, the suspension stability increases. The slowdown of the aggregation is induced by the onset of repulsive electrostatic forces, whose strength increases with decreasing ionic strength. The sharp transition between fast and slow aggregation regimes is indicated by the cusp in the stability plot and is referred to as critical coagulation concentration (CCC).<sup>15,24</sup> For monovalent electrolytes, DLVO theory predicts the CCC between 0.1 and 1.0 M, in agreement with experiment. The electrostatic stabilization mechanism is well established for latex and oxide particles.<sup>15–20,25,26</sup> For weakly charged particles, DLVO theory even describes the aggregation rates quantitatively.<sup>17,20</sup> For highly charged particles, as the ones used here, the agreement with DLVO theory is only semiquantitative.<sup>16,18,25,26</sup> The existing discrepancies are probably due to lateral charge heterogeneities or discrete charge effects.

The main result of this Letter is that the colloidal stability of latex particles with and without an adsorbed polyelectrolyte layer behaves entirely analogously. Figure 3a (bottom) shows the electrophoretic mobilities of polyelectrolyte-coated particles as a function of ionic strength. While the corresponding signs are reversed due to polyelectrolyte adsorption, the overall behavior remains the same. The mobilities increase in magnitude with decreasing ionic strength and then pass through the corresponding maximum or minimum as observed for the bare particles. Figure 3b (bottom) shows the stability as a function of the ionic strength. At high ionic strength, the aggregation is rapid with a stability ratio close to unity. With decreasing ionic strength, it shows an analogous slowdown to the one of bare particles. The CCC lies again between 0.1 and 1.0 M.

To illustrate the generic nature of the phenomenon, we have further investigated similar amidine latex particles in the presence of poly(acrylic acid) (PAA) at pH 5.8 and sulfate latex particles in the presence of poly(diallyldimethyl ammonium chloride) (PDADMAC) at pH 4.0. As illustrated in Figure 3, one observes analogous dependence of the mobility and stability on the ionic strength. Again, the stability ratio is close to unity at high ionic strength and shows the characteristic transition between fast and slow aggregation with a CCC located between 0.1 and 1.0 M. The latter feature indicates that the repulsive forces are mainly of electrostatic nature, as they can be fully screened by addition of salt.

However, there is one difference between the stability of the bare particles and those with an adsorbed polyelectrolyte layer. When comparing the top and bottom panels of Figure 3b, the slopes of the stability plot in the slow aggregation regime are smaller for the polyelectrolyte coated particles than for the bare ones. We suspect that this difference originates from the lateral heterogeneity of the adsorbed polyelectrolyte layer. When this layer is heterogeneous, an additional attractive electrostatic force will be operational.<sup>27,28</sup> When a patch with an adsorbed polyelectrolyte will be interacting with a patch of the bare surface, the resulting attractive electrostatic force will lead to a decrease in the suspension stability. Similar patch-charge effects are suspected to decrease the stability of bare colloidal particles and to weaken the dependence of the stability ratio on pH or salt concentration.<sup>16,25,26</sup> Patch-charge effects are likely to play an important role for adsorbed polyelectrolyte layers due to their lateral heterogeneity.<sup>8,28</sup> They are also suspected to be responsible for the decrease of the stability of colloidal particles with increasing molecular mass of added oppositely charged polyelectrolytes.<sup>29,30</sup> Nevertheless, the electrostatic double-layer repulsion remains the principal stabilization mechanism in these systems. The importance of electrostatic forces was also suggested by atomic force microscopy (AFM) for amidine latex particles in the presence of PSS. Direct force measurements with AFM confirmed the importance of electrostatic repulsion at high polyelectrolyte dose, while imaging with AFM revealed the lateral heterogeneity of the adsorbed polyelectrolyte layers.<sup>8,28</sup>

We conclude that repulsive electrostatic double-layer forces are principally responsible for the stabilization of charged colloidal particles with excess of adsorbed polyelectrolytes of opposite charge and high line charge densities. This classical DLVO stabilization mechanism is evidenced through the analogous ionic strength dependence of the stability of bare charged latex particles and of the same particles with adsorbed oppositely charged polyelectrolytes at saturation. In the presence of highly charged polyelectrolytes, the stability ratio remains close to unity at high ionic strength. Moreover, positively charged particles behave analogously in the presence of anionic polyelectrolytes to negatively charged particles in the presence of cationic polyelectrolytes. This conclusion is based on the congruence of experimental data for two different types of latex particles and four different highly charged polyelectrolytes. For the polyelectrolytes investigated, repulsive steric forces between the adsorbed polyelectrolyte layers remain unimportant in stabilizing these systems. However, such forces could become relevant in the case of weakly charged polyelectrolytes.

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**Supporting Information Available:** Details on the materials and experimental protocols. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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