

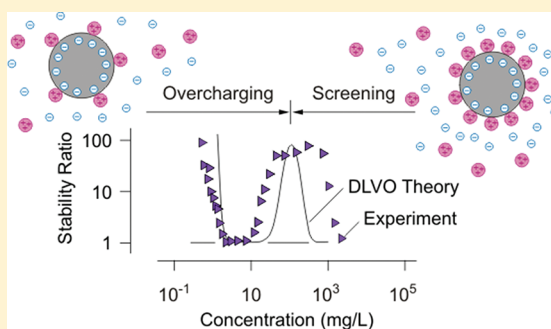
Destabilization of Colloidal Suspensions by Multivalent Ions and Polyelectrolytes: From Screening to Overcharging

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Supporting Information

ABSTRACT: The destabilization of charged colloidal suspensions is studied in the presence of polyelectrolytes and the corresponding oligomers. Two different systems are investigated, namely, negatively charged particles in the presence of polyamines and positively charged ones in the presence of polycarboxylates. Multivalent oligomers of low valence destabilize the particles by screening according to the Schulze–Hardy rule. Polyelectrolytes induce destabilization by overcharging. Both regimes can be observed for oligomers of intermediate valence. The stability data of any valence can be rather well described by the theory of Derjaguin, Landau, Verwey, and Overbeek (DLVO), indicating that the interactions are mainly governed by van der Waals and electrostatic double-layer forces.



INTRODUCTION

The great achievement of the theory developed by Derjaguin, Landau, Verwey, and Overbeek (DLVO) was to derive the Schulze–Hardy rule from first principles.^{1–4} This rule states that the critical coagulation concentration (CCC) scales as z^{-6} , where z is the valence of the counterion.^{5–7} DLVO theory accounts for the sharp transition between slow and rapid aggregation regimes located at the CCC by stipulating that interparticle forces are dominated by the van der Waals attraction and electrostatic double-layer repulsion.^{8–10} The latter forces have been deduced from Poisson–Boltzmann (PB) theory, which predicts a weakening of these forces due to increased screening at larger valence. This picture remained uncontested for almost half a century until theoretical evidence emerged that PB theory fails for multivalent ions because of ion–ion correlations.^{11–13} For multivalent ions, such correlation effects predict a charge reversal and additional attractive forces that are not captured within the classical DLVO framework. These effects were suggested to be responsible for the collapse of polyelectrolyte brushes¹⁴ or multilayers,¹⁵ but their role in colloidal stability has hardly been addressed so far.^{7,16}

Recently, the role of oppositely charged polyelectrolytes in the stability of colloidal suspensions has been investigated.^{17–21} Suspensions aggregate rapidly near the isoelectric point (IEP), whereas aggregation slows down away from this point. This characteristic behavior can be explained by a charge reversal induced by the adsorbed polyelectrolyte, which initially leads to charge neutralization at the IEP and subsequent overcharging. Such overcharging was attributed to ion–ion correlation effects or the presence of dispersion or hydrophobic forces.¹² In these systems, the aggregation is further accelerated by additional

attractive non-DLVO forces, which originate from the patchy distribution of the surface charge.^{17,18,22} However, the position of the IEP is typically independent of the valence (or the molecular mass) of the polyelectrolyte, which is in sharp contrast to the Schulze–Hardy rule.^{17,18,20,21}

Here, we clarify the nature of the transition between the Schulze–Hardy and polyelectrolyte regimes by studying particle aggregation induced by polyelectrolyte oligomers. By comparing negatively charged carboxylated latex particles in the presence of cationic linear poly(ethylene imine) (LPEI) oligomers and positively charged amidine latex particles in the presence of anionic poly(acrylic acid) (PAA) oligomers, we find that this transition is governed by a competition between screening and overcharging effects. We further show that the experimental data can be well rationalized within classical DLVO theory.

EXPERIMENTAL SECTION

Negatively charged carboxylated polystyrene latex particles with a diameter of 307 nm and positively charged amidine latex with a diameter of 220 nm were obtained from Interfacial Dynamic Corporation. Linear poly(ethylene imine) (LPEI) was purchased from Polysciences, and the respective oligomers were purchased from Sigma-Aldrich. Poly(acrylic acid) and its oligomers originate from Polymer Source Incorporation. Time-resolved dynamic light scattering was used to measure the particle aggregation rates. Each correlation function was repeatedly accumulated at a scattering angle of 90° with a compact goniometer system (ALV/CGS-3, Langen, Germany) for 20 s, and the apparent hydrodynamic radii were obtained through a

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cumulant fit. The stability ratio W was evaluated by normalizing the inverse rate of the increase in the hydrodynamic radius with respect to fast aggregation conditions in excess KCl at a particle concentration of about 11 mg/L.^{3,18} The electrophoretic mobility of the suspensions was measured by laser Doppler velocimetry with a Zetasizer Nano ZS (Malvern Instruments, Worcestershire, U.K.) under the same conditions as used for the stability experiments. Electrophoresis experiments were then used to estimate the partitioning between adsorbed and dissolved oligomers and polyelectrolytes by recording the mobility at two different particle concentrations.²³ Further details on materials and experimental methods are given in the Supporting Information.

RESULTS AND DISCUSSION

Let us first discuss the experimental results for the stability of negatively charged particles in the presence of cationic polyelectrolytes or its oligomers. Figure 1a shows the stability ratio W of carboxylated latex particles in 1 mM KCl electrolyte at pH 4.0 in the presence of methylamine (N1), diethylenetriamine (N3), tetraethylenepentamine (N5), and LPEI with molecular masses of 2.5 kg/mol (N58) and 250 kg/mol (N5800). Sequence N1 and N3 illustrates the classical Schulze–Hardy rule. The particles aggregate slowly at low salt concentration, and the aggregation becomes rapid at higher concentrations. The CCC separates these two regimes, and its value shifts to substantially lower concentrations when N1 (1×10^4 mg/L) is replaced by N3 (30 mg/L).

Re-entrant fast aggregation behavior is observed with N5, however. At low concentration, the aggregation is slow but reaches a first fast aggregation regime at concentrations above 2 mg/L. The aggregation slows down again around 10 mg/L. The stability ratio remains at an intermediate plateau with $W \approx 80$ and decreases near 2×10^3 mg/L to reach the second fast aggregation regime. The first fast regime is induced by overcharging due to adsorbing N5, as can be confirmed by electrophoresis (Figure 1b). The electrophoretic mobility indeed reverses its sign at 5 mg/L, and this IEP lies within the first fast regime. The onset of the second fast regime is dictated by screening by the monovalent chloride anions because the particles are now positively charged. The stability in the presence of the polyelectrolytes is dominated by the overcharging, and the aggregation rate goes from slow to fast and back to slow. Indeed, the regime of fast aggregation coincides well with the position of the IEP observed by electrophoresis, and its position is independent of the molecular mass.

One encounters an entirely analogous situation for positively charged particles in the presence of an anionic polyelectrolyte and its oligomers. Figure 2 summarizes the results with amidine latex particles in 1 mM KCl electrolyte at pH 5.8 in the presence of acetic acid (C1), glutaric acid (C2), 1-(2-methylbutyl)heptane-1,3,5,7-tetracarboxylic acid (C4) and PAA with molecular masses of 5.7 kg/mol (C88) and 88 kg/mol (C1200). One observes very similar trends as for the oligomeric amines discussed above. Simple screening behavior is observed for C1, whereas C2 shows a small intermediate plateau due to overcharging. The overcharging effect is very pronounced for C4, whereby the intermediate plateau is no longer measurable. The first aggregation regime is located near the IEP around 1 mg/L, and the onset of the second fast aggregation regime is shifted to 8×10^4 mg/L. Under these conditions, the particles are negatively charged and the counterions are now the monovalent potassium cations. The PAA analogs adsorb more strongly to the oppositely charged

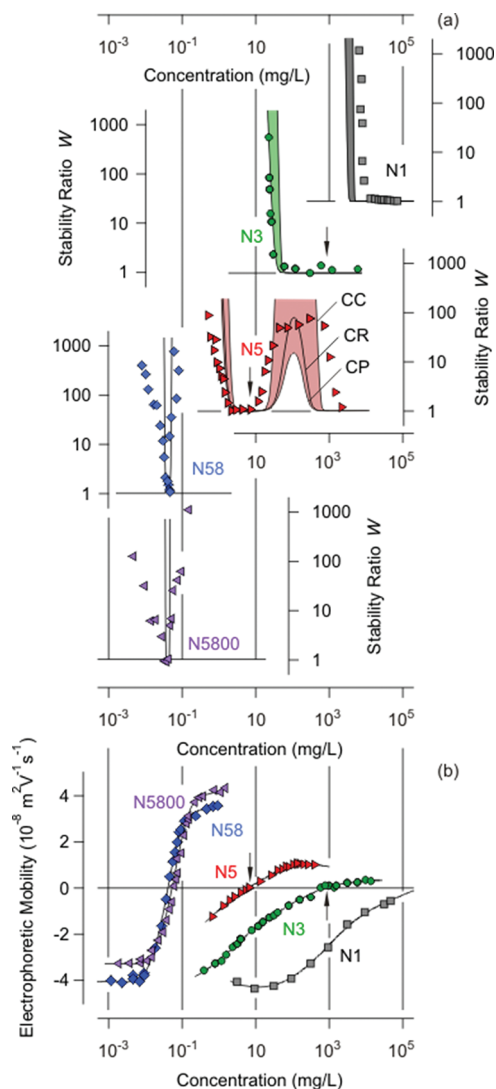


Figure 1. Properties of suspensions of carboxylated latex particles in the presence linear aliphatic amines at pH 4 and an ionic strength of 1.0 mM. Comparison of (a) colloidal stability and (b) electrophoretic mobility versus the oligomer or polyelectrolyte concentration. Solid lines are interpolations in b, and calculations are based on DLVO theory in a. Boundary conditions are the constant charge (CC), constant potential (CP), and constant regulation (CR). Isoelectric points (IEPs) induced by the oligomers are indicated by arrows. Horizontal grid lines indicate $W = 1$, and the vertical ones indicate the same concentrations.

latex particles than do the polyamines, which could be related to weaker dispersion or hydrophobic interactions in the latter system. The polyelectrolytes are dominated by overcharging only, and the position of the IEP is again independent of the molecular mass.

Because these two oppositely charged systems behave entirely analogously, we suspect that the observed trends are generic and that particle interactions are dominated by electrostatics. Screening dominates the destabilization in the presence of counterions of low valence. As the concentration of the salt is increased, the dissolved ions screen the electrostatic double-layer repulsion. With increasing valence, screening becomes more effective, and the CCC decreases. At the same time, however, a larger valence leads to an increasingly strong adsorption to the surface and to overcharging. This over-

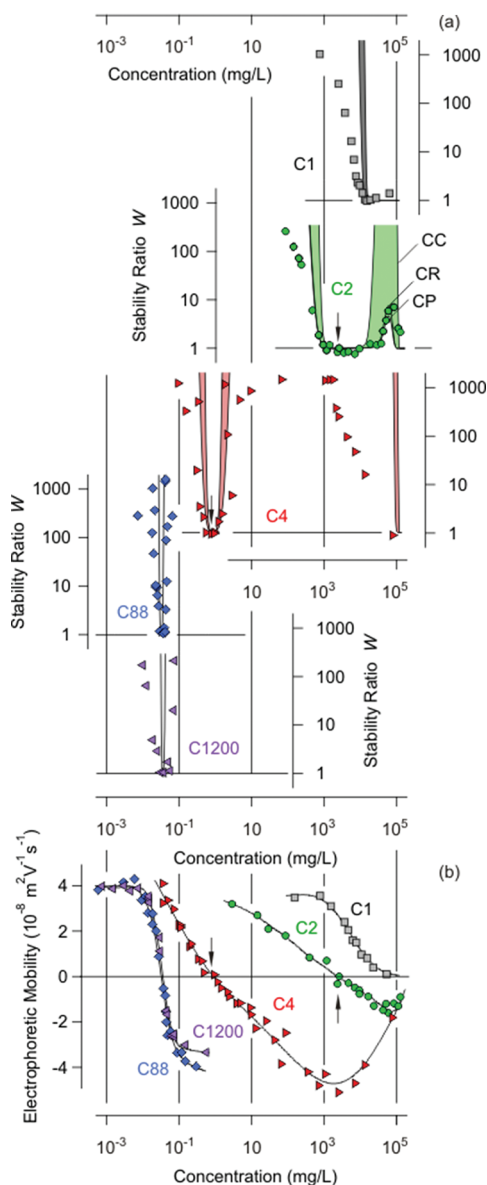


Figure 2. Properties of suspensions of amidine latex particles in the presence linear carboxylates at pH 5.8 and an ionic strength of 1.0 mM. Comparison of (a) colloidal stability and (b) electrophoretic mobility vs the oligomer or polyelectrolyte concentration. Solid lines are interpolations in b and predictions of linearized DLVO theory in a. Boundary conditions are the constant charge (CC), constant potential (CP), and constant regulation (CR). Isoelectric points (IEPs) induced by the oligomers are indicated by arrows. Horizontal grid lines indicate $W = 1$, and vertical ones indicate the same concentrations.

charging is responsible for the intermediate first aggregation regime, which finally entirely dominates the stability in the presence of polyelectrolytes. Under these circumstances, the valence of the polyelectrolyte no longer influences the position of the IEP. This “polyelectrolyte rule” has been previously reported for LPEI,²⁰ PAA,²¹ and other polyelectrolytes.^{17,18,24} In the latter case, polyelectrolytes adsorb quantitatively and screening originates only from the salt ions dissolved in solution, which is KCl in the present case. For the oligomers investigated, however, they partition principally into solution and screening is determined by the dissolved multivalent ions. As detailed in the Supporting Information, this characteristic

partitioning behavior has been confirmed by studying the electrophoretic mobility at different particle concentrations.²³

The solid lines shown in Figures 1a and 2a refer to modeling results based on DLVO theory within the Derjaguin approximation. The concentration dependence of the electrophoretic mobility was interpolated and converted to surface potentials (ζ potential) with Henry’s model.³ The resulting electrostatic potentials were used to estimate the double-layer interaction on the Debye–Hückel level by invoking the boundary conditions of constant charge (CC) and constant potential (CP). For the oligomers, the ionic strength was calculated by taking the partial dissociation of the oligomers into account. The stability ratios were obtained by considering the hydrodynamic interactions and van der Waals forces. The latter were quantified with a Hamaker constant of 9.0×10^{-21} J for the carboxylated latex particles and 2.0×10^{-21} J for amidine particles. One should note that for the calculated stability ratios shown in Figures 1 and 2 the magnitude of the surface potential obtained from the mobility experiments is always below 25 mV, which is a condition that must be satisfied such that Henry’s and Debye–Hückel theory are applicable. Further details on the DLVO calculations are given in the Supporting Information.

One observes that results of such DLVO calculations agree with the experimental data rather well. Because the plateau value in the stability ratio for N5 is very sensitive to the boundary conditions, we found that the data can be rationalized with a charge regulation (CR) model with a regulation parameter of 0.3. A similar situation arises with C2, and the observed peak in the stability ratio can be well described with a regulation parameter of 0.1.

A substantial discrepancy between the experimental data and DLVO calculations can be observed for C4 at higher concentrations. In this case, the experimentally observed dependence of the stability ratio on the concentration is much weaker than modeled by DLVO theory. This discrepancy is probably related to the fact that monovalent potassium cations are responsible for the screening and the barrier in the interaction potential lies at small separation distances, in fact, below 1 nm.^{8,9} When multivalent ions act as counterions, the barrier shifts toward larger separations, making DLVO theory more accurate.⁷ Similar effects may be responsible for analogous but less important discrepancies for C1 and C2. One also observes that suspensions are less stable in the presence of polyelectrolytes than DLVO theory suggests. This decrease in stability is probably related to the presence of electrostatic patch–charge attractions, which originate from the heterogeneous charge distribution within adsorbed polyelectrolyte layers.^{18,21,22}

The overall good agreement between experimental stability data and DLVO calculations indicate that forces operating between the particles are well approximated within DLVO theory and that the ζ potential provides a good estimate of the strength of the electrostatic double-layer interactions. This aspect may seem surprising from the point of view of modern theories of the electrical double layer, which predict additional attractive forces due to ion correlations.^{11,12} Such attractions seem not to play a dominant role in the systems investigated here. A possible explanation of this inconsistency might be that ion correlations remain relevant for the adsorption process and the resulting extent of overcharging within the compact layer but that they are of minor importance within the diffuse layer, which appears to be well described by classical DLVO theory.

However, such forces could well represent the origin of the discrepancies observed for C1, C2, and, in particular, C4.

We conclude that the destabilization of charged colloidal suspensions occurs by screening in the case of small ions and by overcharging in the case of polyelectrolytes. With increasing counterion valence, the CCC corresponding to the first fast aggregation regime shifts toward lower concentrations according to the Schulze–Hardy rule. However, the position of the IEP is independent of the valence or the molecular mass of the polyelectrolyte, which is in line with the polyelectrolyte rule. Figure 3 illustrates this trend with additional data for oligomers

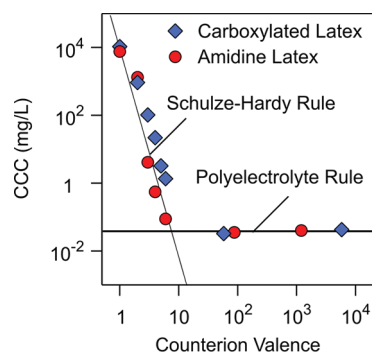


Figure 3. Variation of the critical coagulation concentration (CCC) of the first fast aggregation regime with the valence for carboxylated latex particles in the presence of linear aliphatic amines and for amidine latex particles in the presence of linear carboxylates. Full dissociation is assumed for simplicity. The solid lines show the dependencies expected from the Schulze–Hardy and the polyelectrolyte rules.

obtained at different valences. The transition between these two regimes occurs at a valence of about 10. The intermediate regime situated between valences 3–6 is characterized by two fast aggregation regimes. The first regime is located near the IEP and is governed by overcharging, and the second one is induced by the screening of the overcharged particle by the oligomer counterions. The fact that the suspension stability can be well described with DLVO theory has two main implications. First, non-DLVO forces are of minor importance in colloidal stability. Second, DLVO theory can be used to assess the suspension stability in systems containing multivalent ions and/or polyelectrolytes rather well. The latter finding could be of substantial importance for the design of novel flocculating agents that rely on mixtures of multivalent ions and polyelectrolytes.

■ ASSOCIATED CONTENT

Supporting Information

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

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Notes

The authors declare no competing financial interest.

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