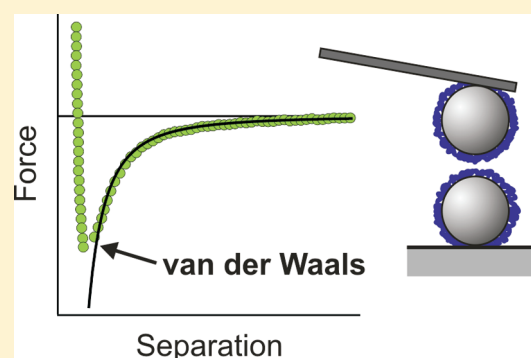


Charge Reversal of Sulfate Latex Particles by Adsorbed Linear Poly(ethylene imine) Probed by Multiparticle Colloidal Probe Technique

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ABSTRACT: Interactions between negatively charged latex particles in the presence of cationic linear poly(ethylene imine) (LPEI) were studied with atomic force microscopy (AFM) and electrophoresis. Forces were measured directly with the recently developed multiparticle colloidal probe technique, which permits colloidal particles to attach to the cantilever in aqueous dispersions in situ and ensures a large surface area during experiment. It was observed that the forces vary from repulsive to attractive and back to repulsive with increasing polymer dose. The repulsive forces are due to overlap of the diffuse layers around charged surfaces. The attractive forces are independent of the ionic strength and the molecular mass of the polymer and can be rationalized in terms of classical van der Waals interactions. Additional electrostatic attractive forces due to patch-charge heterogeneities observed in other particle–polyelectrolyte systems are absent here. Their absence indicates that the adsorbed layer of LPEI has a high lateral homogeneity.



INTRODUCTION

Polyelectrolytes adsorb strongly on oppositely charged particles, and thereby they modify the interparticle forces. For this reason, they are widely used as additives to control the stability and rheology of colloidal suspensions.^{1–6} Important applications include papermaking, wastewater treatment, preparation of ceramic materials, or food processing.^{1,7–10} More recently, it was realized that polyelectrolytes represent essential building blocks of functional multilayered structures.^{11–14} Many of these applications were developed empirically, and we still only have rudimentary understanding of the mechanisms of how interaction forces are influenced by adsorbed polyelectrolytes.

Information on the interparticle forces induced by adsorbed polyelectrolytes was frequently obtained from studies of particle stability. Gregory suggested that adsorbed polyelectrolytes modify particle stability in two ways.² First, the adsorption of polyelectrolytes leads to charge neutralization at the isoelectric point (IEP) and subsequent charge reversal. Near IEP, the forces are attractive as they are dominated by van der Waals attraction, and the suspension is unstable. Away from the IEP, the surface charge induces an electrical double layer, which leads to repulsive forces, and a stable suspension. Second, the polyelectrolyte adsorbs in a laterally heterogeneous fashion, which leads to additional electrostatic patch-charge attractions. These attractions manifest themselves in an acceleration of the aggregation near the IEP, and they become stronger with increasing molecular mass of the polyelectrolyte. This effect can be understood since larger polyelectrolytes lead to larger patches on the surface and thus to stronger attractions. The correctness of this mechanism was confirmed

in subsequent and more detailed stability studies for various systems in the presence of oppositely charged polyelectrolytes as discussed elsewhere.^{3,4,8,15–19} At higher polyelectrolyte doses, the adsorbed layer saturates and any excess polyelectrolyte remains dissolved in solution.^{4,18} In this regime, the particle stability becomes independent of the polymer dose and is determined by repulsive electrical double-layer forces.^{20,21}

Since the information on interparticle forces obtained from such stability studies is relatively indirect, researchers attempted to measure the resulting interaction forces directly. Popular techniques involve the surface forces apparatus (SFA) and variants thereof,^{22–24} total internal reflection microscopy (TIRM),²⁵ and the colloidal probe technique based on atomic force microscopy (AFM).^{26–28} Most of these studies were carried out when the polyelectrolyte was in excess, and therefore the measured forces were strongly repulsive and governed by electrical double-layer repulsion.^{22–24,26–31} Measurements of interaction forces between surfaces whose charge neutralized by adsorbed polyelectrolytes are scarce. Such conditions have been achieved with the SFA or related techniques by exploiting the kinetics of the adsorption process^{22,24} or with the colloidal probe technique by tuning the charge by means of solution pH.²⁶ Nevertheless, studies of the interaction forces of surfaces partially covered by polyelectrolytes are rare due to the difficulties to control the polyelectrolyte dose precisely.

Received: April 15, 2011

Revised: June 17, 2011

Published: June 20, 2011

Such measurements are now substantially facilitated by the recently developed AFM-based multiparticle colloidal probe technique whereby forces between a pair of colloidal particles are studied.^{32,33} The advantages of this technique are 2-fold. First, the particles are attached to the cantilever and the substrate in solution, thereby avoiding the usual drying–rewetting process, which often leads to the formation of nanosized bubbles. Second, the experiments are carried out in a particle suspension, which offers a large surface area, and facilitates the precise control of the polyelectrolyte dose. With this technique it was possible to obtain detailed information on the forces induced by oppositely charged polyelectrolytes. In the two systems studied in detail, namely involving linear poly(styrene sulfonate) (PSS)³² and dentritic poly(amido amine) (PAMAM),³³ the generic picture discussed above could be confirmed. The forces are dominated by electrostatic forces, namely by repulsive double-layer forces and by attractive patch-charge forces.

In the present study, this technique is being used to study the interaction forces between sulfate latex particles in the presence of linear poly(ethylene imine) (LPEI). While some studies have been devoted to interactions induced by branched poly(ethylene imine) (BPEI),^{23,27,34} to the best of our knowledge no studies have been carried out with LPEI. Nevertheless, this polymer has some interesting properties, for example, LPEI is less toxic than BPEI.³⁵ Therefore, we investigated the resulting forces in this system in detail. We observe for the first time that interactions between adsorbed polyelectrolyte are dominated by repulsive electrical double-layer and attractive van der Waals interactions only and that patch-charge interactions are absent.

EXPERIMENTAL SECTION

Materials. Sulfate functionalized polystyrene latex particles were obtained from Interfacial Dynamics Corporation (Portland, USA). The mean diameter of 3.1 μm and polydispersity of 5.6% was determined with transmission electron microscopy by the manufacturer. They equally report a surface charge density of -67 mC/m^2 measured with conductometry. The sulfate latex particles were dialyzed against pure water with a cellulose membrane with a cutoff of 50 kg/mol molecular mass (Spectrum, No. 131378). The same latex particles were earlier used in related studies.^{33,36}

Two samples of linear poly(ethylene imine) (LPEI) with molecular mass of 2.5 kg/mol and 250 kg/mol from Polysciences (Eppenheim, Germany) were used. The polydispersity indices were 1.6 and 3.4, respectively. The polymers were dissolved in 1 M HCl in an ultrasonic bath at a temperature of 60 °C overnight and subsequently dialyzed against pure water with a cellulose ester membrane with a molecular mass cutoff of 10 kg/mol for the high molecular mass polymer and of 0.5 kg/mol for the low molecular mass. The polymer concentration was measured by total organic carbon and nitrogen analysis (TOC-V, Shimadzu). The concentration of stock solutions was about 1 mg/L. The Staudinger indices for both LPEI samples were obtained by capillary viscosimetry, and found to be 27 and 137 mL/g for the molecular masses of 2.5 and 250 kg/mol, respectively. These values agree reasonably well with earlier measurements on LPEI³⁷ and BPEI.^{38,39} The same LPEI samples were used in a related study focusing on colloidal stability.⁴⁰

All solutions were prepared with Milli-Q water adjusted to pH 4 with HCl and to the desired ionic strength by eventually adding KCl. The samples were prepared by mixing 2 mL of a stock

suspension of latex particles of a concentration of about 0.1 g/L. The ionic strength is then adjusted with a KCl solution, and finally 0.01–2 mL of LPEI of concentrations in the range 0.01–1 mg/L is added to obtain a final volume of 2–8 mL. Prior to measurements, the sample was equilibrated overnight. The same sample was used to carry out the electrophoresis and direct force measurements. All measurements were performed at room temperature.

Electrophoresis. The electrophoretic mobility of the latex particles were carried out with ZetaNano ZS (Malvern Instruments, UK) and a ZetaCompact (CAD Instrumentation, Les Essarts le Roi, France). The electric fields were about 4–15 kV/m. The suspension was directly injected into the measurement cell. Both techniques yielded the same electrophoretic mobilities within 15%. Electrokinetic surface potentials, or ζ -potentials, were calculated with the standard electrokinetic model developed by O'Brien and White.⁴¹

Force Measurements. Interaction forces between two sulfate latex particles were measured with a closed-loop AFM (MFP-3D, Asylum Research, Santa Barbara, USA) mounted on an inverted optical microscope (IX70, Olympus). A glass plate fitting the fluid cell was cleaned for 2–3 h in boiling piranha solution, which consists of a mixture of H_2SO_4 (98%) and H_2O_2 (30%) in a ratio of 3:1. After rinsing with Milli-Q water and drying with nitrogen, the plate was cleaned for 20 min in air plasma (PDC-32G, Harrick, New York) and finally silanized overnight in vacuum with 3-(ethoxydimethylsilyl)propylamine (Sigma-Aldrich). The silanization was verified by measuring the contact angle of water with a drop of water, which was approximately 36°. Tip-less AFM cantilevers (μMasch , Tallin, Estonia) were similarly cleaned in air-plasma and silanized. Prior to the experiment, the AFM fluid cell was rinsed with an electrolyte solution of the same pH and ionic strength of the sample to be investigated, which was previously degassed with a Gasstor degasser for 3 h. The particle suspension was injected into the AFM fluid cell and left overnight such that the particles would adhere to the substrate. To remove particles that did not stick to the substrate, the cell was flushed with a degassed electrolyte solution of the same ionic strength and pH as the suspension used. Subsequently, a colloidal spherical particle was picked up with the cantilever. This particle was centered above another particle on the substrate through the interference fringes observed with the optical microscope. The precision of this lateral centering is about 0.2 μm . The zero separation was obtained from the onset of the constant compliance region with a precision of about 0.3 nm. The cantilever deflection was converted into a force by applying the Hooke's law and force constant of the cantilever in the range of 0.01–0.3 N/m. Softer cantilevers were used to detect single molecule pulling events, while with the more rigid ones, the jump-in instabilities during the measurement of the attractive force profiles upon approach can be avoided. The force constants were obtained from the average of three independent methods,^{42–44} and these results agreed within 15%. The forces were mostly normalized to the effective radius defined as

$$R_{\text{eff}} = \frac{R_1 R_2}{R_1 + R_2} \quad (1)$$

where R_1 and R_2 are the radii of the interacting particles. The radii were obtained with the optical microscope with a precision of 0.2 μm . In a typical experiment, about 100 force curves were measured. The interaction forces were obtained by averaging

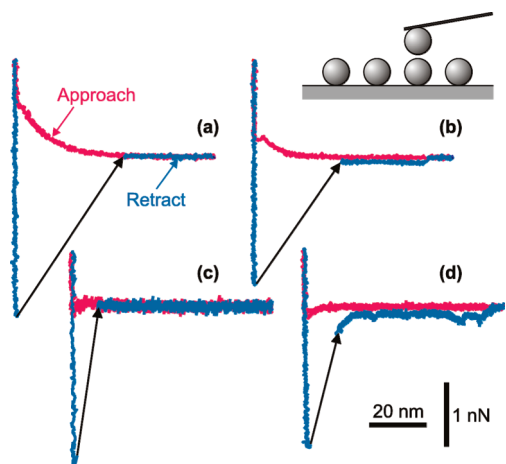


Figure 1. Typical individual approach-retract force curves between two sulfate latex particles with adsorbed LPEI of 250 kg/mol at pH 4. The jump-out instabilities are indicated with arrows. (a) Repulsive approach curve and short-range adhesion at a dose of 1.1 mg/g and an ionic strength of 1.1 mM. (b) Repulsive approach curve and peeling retraction event at a dose of 1.1 mg/g and an ionic strength of 3 mM. (c) Attractive approach curve and short-range adhesion at a dose of 0.28 mg/g and an ionic strength of 1.1 mM. (d) Attractive approach curve and multiple-chain retraction events at a dose of 0.28 mg/g and an ionic strength of 0.3 mM.

the approach profiles. The retraction part was analyzed for the presence of eventual single molecule pulling events. Forces were measured for 3–6 different pairs of particles.

Since the interaction forces near the IEP are extremely sensitive to minute variations in the polymer dose, the measured force profiles have often featured a minor repulsive part caused by a small but nonvanishing particle charge. These repulsive forces were subtracted by fitting the force profile at larger distances with the expected van der Waals and electrostatic force due to a diffuse layer overlap. The resulting force profiles were well reproducible for different strengths of the repulsive component and were in good agreement with the purely attractive forces observed. A similar approach was used to correct for the presence of such minor repulsive forces earlier.^{32,33,36,45–47}

RESULTS AND DISCUSSION

The multiparticle colloidal probe technique was used to measure interaction forces between pairs of sulfate latex particles with a diameter of 3.1 μm in the presence of linear poly(ethylene imine) (LPEI). This cationic polyelectrolyte strongly adsorbs on the negatively charged particles and induces a charge reversal. This reversal manifests itself through weakening of the repulsive forces with increasing polymer dose up to the isoelectric point (IEP) and its subsequent strengthening beyond that point. The experiments were carried out at pH 4.0, whereby about 65% of the secondary amino groups in the LPEI are charged in solution.³⁷ The ionic strength was adjusted by adding KCl.

Figure 1 shows illustrative force profiles measured upon approach and retraction as a function of the separation distance for LPEI coated particles. At high LPEI dose, the forces are repulsive upon approach. Upon retraction, the profiles mostly show short-range adhesion and a jump-out of the cantilever, see Figure 1a. Rather infrequently, some single molecule events are observed, such as a peeling event characterized by a force plateau, see Figure 1b. At lower LPEI doses, the forces can be attractive

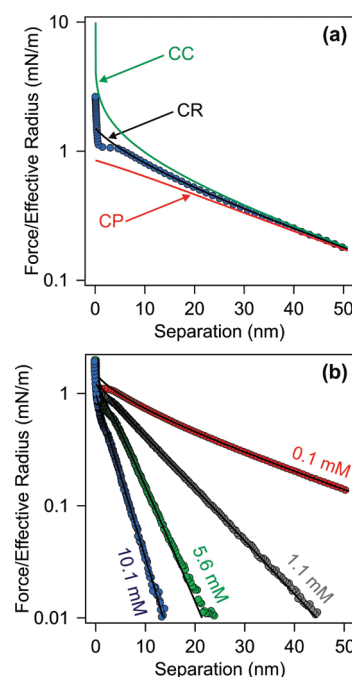


Figure 2. Interaction forces between sulfate latex particles as a function of the separation distance measured in KCl electrolyte solution of pH 4 with AFM. The forces have been fitted with PB theory. (a) Forces at an ionic strength of 0.1 mM compared with PB model with constant charge (CC), constant regulation (CR), and constant potential (CP) boundary conditions. (b) Different ionic strengths compared to the constant regulation boundary condition.

upon approach, and again mostly show short-ranged adhesion, see Figure 1c. In some cases, single molecule events reappear, including multiple chain events, see Figure 1d.

The short-range adhesion upon retraction is about 5 mN/m when the forces are repulsive, and this value is somewhat larger when the forces are attractive. Single molecule events are rare, and mostly consist of peeling events characterized by plateau forces in the range of 80–200 pN. Such events were observed only in <2% of all force profiles. Due to the few events observed, trends with the salt level or the polymer dose could not be established. Nevertheless, this finding clearly suggests that bridging forces are unimportant in this system.

The forces upon approach were analyzed in more detail. To improve the signal-to-noise ratio, few hundred of such force curves were recorded and averaged. The forces were further normalized to the effective radius of both particles.

Repulsive Forces. Forces between the bare sulfate latex particles are strongly repulsive and they are shown in Figure 2. One observes that the forces are nearly exponential, and that their range decreases with increasing ionic strength. These observations indicate that these forces originate from the overlap between the diffuse parts of the electric double layer. Indeed, the measured forces can be interpreted within Poisson–Boltzmann (PB) theory. This theory predicts that the force decays exponentially at larger distances, whereby its amplitude is related to the diffuse layer potential ψ_d while its range is given by the Debye length κ^{-1} . The latter quantity is related to the ionic strength I as⁴⁸

$$\kappa^2 = \frac{2e^2 N_A I}{kT \epsilon \epsilon_0} \quad (2)$$

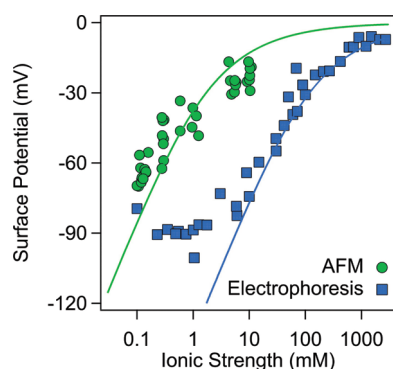


Figure 3. Surface potentials as a function of the ionic strength for the bare sulfate latex particles at pH 4. The solid lines are fits by PB theory. Potentials obtained by AFM are fitted with a charge of -3 mC/m^2 and the electrophoresis data with -25 mC/m^2 .

where e is the elementary charge, N_A Avogadro's number, I the ionic strength, k Boltzmann constant, T the absolute temperature, and $\epsilon\epsilon_0$ is the permittivity of water. At shorter distances, these forces are sensitive to the boundary conditions. While the classical boundary conditions of constant charge (CC) and constant potential (CP) are insufficient to account for the detailed distance dependence, a quantitative fit can be obtained by introducing the constant regulation (CR) approximation.⁴⁹ This approximation introduces the so-called regulation parameter p ($-\infty < p \leq 1$), and includes as special cases the classical boundary conditions of CC ($p = 1$) and CP ($p = 0$). Note that the regulation parameter can become negative as CP boundary condition does not represent a lower bound to the force.⁵⁰

The best fit of the force at an ionic strength of 0.1 mM is shown in Figure 2a. The decay length extracted from the force curve is $29.4 \pm 0.2 \text{ nm}$ and the diffuse layer potential is $-70.0 \pm 0.3 \text{ mV}$. The negative sign can be inferred from the presence of the sulfate groups on the surface of the latex particle. The regulation parameter is 0.51 ± 0.01 , which indicates that the surface charge regulates strongly upon approach.

When the decay length was converted to the ionic strength with eq 2, the values always agreed within 20% with the known value from the solution composition. Larger deviations were only observed at the lowest ionic strengths, probably due to traces of dissolved carbon dioxide. The regulation parameters were about 0.34 ± 0.08 and were roughly independent of the ionic strength.

The diffuse layer potential obtained from the force curves is shown in Figure 3. One observes that the magnitude of the potential decreases with increasing ionic strength as suggested by PB theory. The diffuse layer potential is expected to follow the Gouy–Chapman equation⁴⁸

$$\psi_d = \frac{2kT}{e} \operatorname{asinh}\left(\frac{e\sigma}{2kT\epsilon\epsilon_0\kappa}\right) \quad (3)$$

where σ is the surface charge density. The diffuse layer potential yields a charge density of about -3.0 mC/m^2 . The magnitude of this value is substantially smaller than the one of the charge -67 mC/m^2 obtained by conductometry. The difference is probably due to specific adsorption of potassium ions to the particle surface.

The electrophoretic mobility of these particles was also measured, and the data confirm clearly that the particles are negatively charged. The surface potential can be extracted from

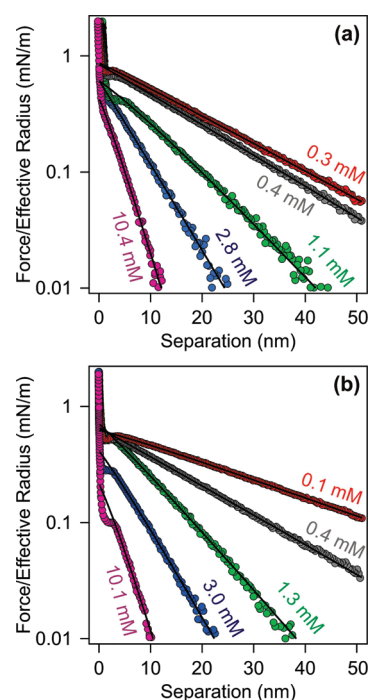


Figure 4. Interaction forces between sulfate latex particles as a function of the separation distance in the presence of LPEI at a dose of 1.1 mg/g measured at different ionic strengths at pH 4 with AFM. The forces have been fitted with PB theory with constant regulation (CR) approximation. Molecular mass of (a) 250 and (b) 2.5 kg/mol.

the mobilities with the standard electrokinetic model introduced by O'Brien and White.⁴¹ The resulting potentials are also shown in Figure 3. While the overall trend of the surface potentials obtained from direct force measurements and electrophoresis is similar, the magnitudes of the surface potentials obtained by electrophoresis are substantially higher. At higher ionic strengths, they can be fitted with a surface charge of -25 mC/m^2 . This observation is at odds with the notion that an immobile layer at the particle surface shifts the plane of origin of the electrokinetic potential away from the one of the diffuse layer, and therefore the magnitude of the electrokinetic potential (ζ -potential) should be smaller than of the diffuse layer potential. We suspect that the discrepancy originates from existing surface charge heterogeneities on the surface of the latex particles.⁵¹ Such heterogeneities induce additional rotational motion of the particles in an external electric field and will result in electrophoretic mobilities that are higher than the ones predicted by the standard electrokinetic model.

At doses of 1.1 mg/g of LPEI or higher, the forces become again highly repulsive and they depend no longer on the polymer dose. Typical results are shown in Figure 4. The range of the forces depends strongly on the ionic strength, suggesting that they originate from double layer overlap. The forces are somewhat weaker for LPEI of the lower molecular mass than for the higher one. The forces can be quantitatively interpreted with PB theory. The best fits with the CR approximation are shown in Figure 4. The resulting Debye lengths agree within 15% with the expected value based on the ionic strength. The regulation parameters are 0.3 ± 0.1 .

The resulting diffuse layer potentials are shown in Figure 5, and they decrease with increasing ionic strength. The positive

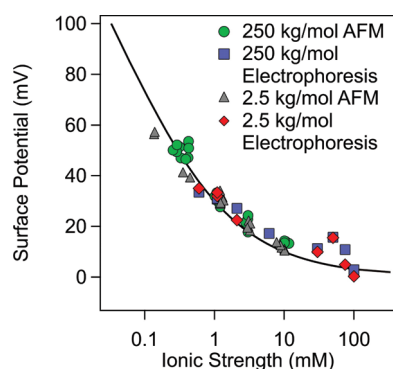


Figure 5. Surface potentials as a function of the ionic strength of the sulfate latex particles in the presence of LPEIs with a molecular mass of 2.5 and 250 kg/mol at a concentration of 1.1 mg/g and pH 4. Comparison between potentials obtained by AFM and electrophoresis. The solid line is the result of the PB theory.

sign of the potential can be inferred from the fact that the adsorbed LPEI is a cationic polyelectrolyte. One observes that the diffuse layer potentials are the same within experimental error for both molecular masses of LPEI. The ionic strength dependence can be again rationalized with eq 3. Best fit of the data yields a surface charge density of 2.3 mC/m^2 . This value is identical to the surface charge density found by direct force measurements for saturated BPEI layers adsorbed on silica.²⁷

In spite of some scatter in the experimental data points, the potentials obtained from electrophoretic mobilities agree very well with the ones obtained from direct force measurements. The reason for the good agreement between these two data sets can be rationalized by the fact that the adsorbed LPEI layer is laterally homogeneous, and for that reason the standard electrokinetic model is valid. Similarly good agreement between surface potentials obtained from electrokinetics and direct force measurements was found for saturated PSS layers adsorbed on amidine latex particles.⁴⁷

Charge Reversal and Attractive Forces. Although the measurements of the forces in the absence and excess of LPEI could have also been carried out with the classical two-particle colloidal probe technique, the use of the multiparticle technique becomes essential for measurements at intermediate LPEI doses. Under these conditions, the added LPEI adsorbs quantitatively and the adsorbed amount can be only controlled with sufficient precision when the available surface area is sufficiently high. Although the control of this quantity is basically impossible with two particles of a surface area of few μm^2 , this quantity can be accurately tuned when working in a suspension, where the surface exceeds several m^2 .

Figure 6 shows the force profiles for different doses of LPEI with a molecular mass of 250 kg/mol. In the absence of LPEI, the particles are negatively charged and their force is strongly repulsive due to diffuse layer overlap, see Figure 6a. With increasing LPEI dose, the negative surface charge is progressively neutralized by the positively charged adsorbed LPEI, which reduces the magnitude of the surface potential and the strength of the repulsive force. As this strength is being reduced, an attractive force becomes apparent at short distances. At a dose of 0.28 mg/g, the repulsive force disappears and the force is now purely attractive, and the adsorbed polyelectrolyte precisely neutralizes the surface of the particle and a diffuse layer is no longer present. At this point, about 3 charges on the LPEI

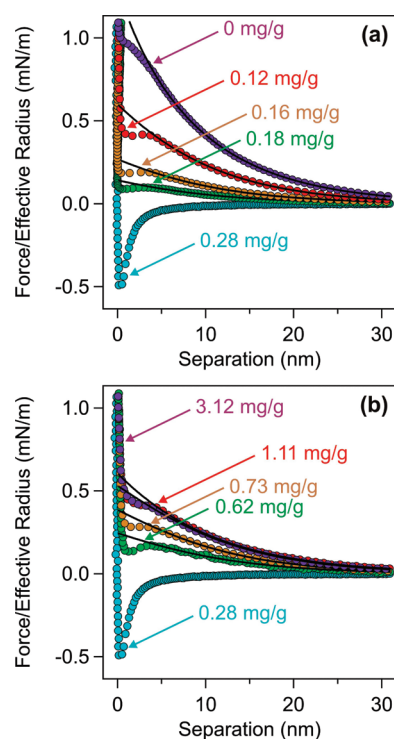


Figure 6. Interaction forces between sulfate latex particles as a function of the separation distance for various doses of LPEI of a molecular mass of 250 kg/mol at an ionic strength of 1.1 mM and pH 4. The forces are fitted with PB theory with constant regulation (CR) approximation. Polymer dose (a) below and at IEP and (b) at IEP and above.

neutralize one charge on the particle surface. Such superstoichiometric charging ratio indicates that during the adsorption of LPEI coadsorption of anions occurs.¹⁸ The short-range attractive forces are equally apparent in Figure 2, but they are masked by the strongly repulsive double-layer forces and jump-in instabilities.

When the dose is increased beyond 0.28 mg/g, the forces become again repulsive due to diffuse layer overlap, see Figure 6b. In this regime, the LPEI continues to adsorb to the surface beyond the charge neutralization point due to electrostatic correlation forces and attractive hydrophobic interactions. As a consequence, a charge reversal takes place and the surface now becomes positively charged. A diffuse layer builds up again near such a charged surface and its presence manifests itself by repulsive forces due to diffuse layer overlap.

As the LPEI dose is increased further, the adsorption process saturates, and a maximum adsorbed amount is reached. When LPEI is added beyond this dose, the adsorbed amount does not increase any further and excess polymer remains dissolved in solution. Due to the constant adsorbed amount, the surface charge density remains constant as well, and thus the forces no longer vary with increasing the polymer dose. This aspect is illustrated in Figure 6b as the forces remain constant beyond a LPEI dose of 1.1 mg/g. The short-range attractive forces remain visible in the force profiles all the way up to saturation, but they are probably blurred by jump-in instabilities, see also Figure 4.

The repulsive part of these forces was fitted with the solution of PB equation within the CR approximation as discussed above. The fitted decay lengths agreed with the expected one based on the ionic strength within 10%. The regulation parameters were in

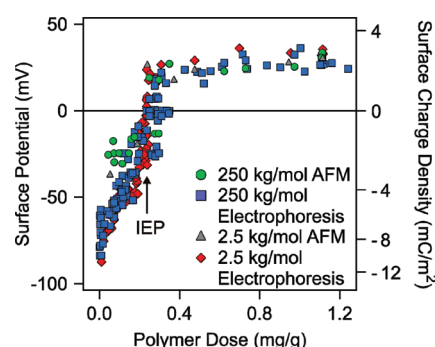


Figure 7. Surface potentials of sulfate latex particles as a function of polymer dose at an ionic strength of 1.1 mM and pH 4 obtained by AFM and electrophoresis. The surface charge density obtained from PB theory in indicated on the left axis in a nonlinear scale.

the range of 0.3 ± 0.1 . The resulting diffuse layer potentials are compared with the electrokinetic potentials in Figure 7. One observes that the surface potentials obtained by the different techniques give very similar results. In particular, the dose needed to reach the IEP, at which the electrophoretic mobility is zero, coincides perfectly well with the dose at which repulsive diffuse layer overlap force vanishes. The only disagreement between the surface potentials obtained from direct force measurements and electrophoresis occurs at low LPEI dose. Recall that a similar disagreement was observed for the bare latex particles in the absence of any added LPEI, and interpreted in terms of surface charge heterogeneities. When the dose of LPEI remains low, these charge heterogeneities are not completely covered up by adsorbed LPEI, and the discrepancies persist up to a dose of about 0.1 mg/g. When the adsorbed amount increases beyond this point, the adsorbed LPEI generates a relatively homogeneous surface and good agreement between the surface potentials obtained from force measurements and electrophoresis is found. On the basis of the electrophoresis results, one observes that surface potential increases slowly with the polymer dose, and near the IEP makes a sudden transition up to the plateau. Similar behavior was observed during the charge reversal of amidine latex particles with PSS and of sulfate latex with PAMAM dendrimers.^{47,52} This effect was interpreted by the lateral overlap of the diffuse layers around the individual polyelectrolyte chains.

Figure 8 shows the attractive forces at IEP. The maximal attractive force observed at short distances is lower when the surface charge is neutralized with the high molecular mass LPEI than for the low molecular mass. At larger distances, however, the distance dependence of these forces is remarkably independent of the ionic strength and the molecular mass. The latter behavior suggests that the attractive force is due to van der Waals dispersion interactions. Neglecting retardation effects, attractive dispersion force can be written as⁴⁸

$$\frac{F}{R_{\text{eff}}} = -\frac{H}{6} \frac{1}{(h + \delta)^2} \quad (4)$$

where H is the Hamaker constant and δ an eventual shift of the plane of origin of the van der Waals force with respect to the contact plane. The observed forces are fitted with $H \approx 9.0 \times 10^{-21}$ J as was predicted from the dielectric spectra of polystyrene and water.⁵³ To obtain good agreement with the observed force profiles, a shift of $\delta \approx 0.85$ nm must be chosen. This shift is likely to be related to surface roughness, whose root-mean-

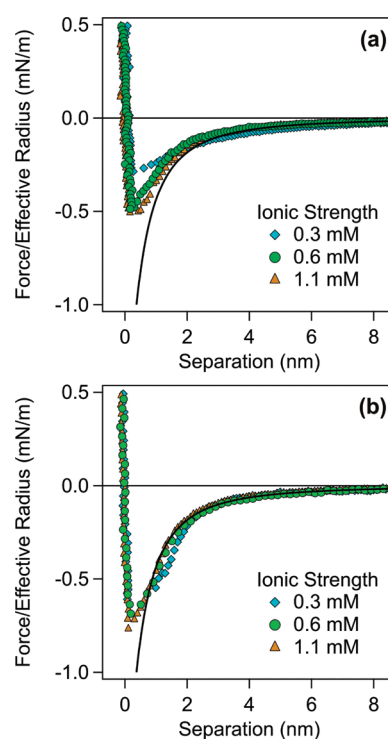


Figure 8. Interaction forces between sulfate latex particles as a function of the separation distance at different KCl concentrations at a LPEI dose of 0.28 mg/g (IEP) and pH 4. The solid line is the best fit with van der Waals theory. Molecular mass of (a) 250 and (b) 2.5 kg/mol.

square variation is about 1.3 nm as estimated from AFM topographic images.³⁶ The attractive force can be equally rationalized without a shift ($\delta = 0$) but with a Hamaker constant of about a factor of 3–4 smaller. Therefore, the attractive forces are governed by van der Waals forces and there is no evidence of any additional attractive forces due to adsorbed LPEI. When the van der Waals force is determined in this way, one can also rationalize the short-ranged attractive part in the force profiles away from IEP in an approximate way.

The insensitivity of the attractive force to the ionic strength and molecular mass of the polyelectrolyte is in marked contrast to previous measurements of attractive forces between charged latex particles and oppositely charged polyelectrolytes at IEP.^{32,33,36,47} These studies have focused on sulfate latex particles in the presence of PAMAM dendrimers and amidine latex particles in the presence of PSS. Both systems revealed substantially stronger attractive forces than the ones observed here, especially for high molecular mass polyelectrolytes at low ionic strength. The additional attractions were interpreted by lateral patch charge heterogeneities induced by the charged adsorbed polymers on the oppositely charged particle surface. These patch-charge heterogeneities were most pronounced for high molecular mass adsorbed PAMAM dendrimers. This regime is probably reminiscent to the dilute 2-d Wigner regime proposed by Dobrynin et al.⁵⁴ In this regime, the adsorbed layer consists of individual polyelectrolyte chains with minimal overlap.

From this point of view, the present results suggest that the layer of adsorbed LPEI is relatively homogeneous. Therefore, the LPEI molecules have to adsorb in an extended state. This regime could be similar to the semidilute 2-d Wigner regime introduced by Dobrynin et al.⁵⁴ Thereby, the individual chains lie flat on the

surface and they cross many times, which leads to denser network of adsorbed polyelectrolyte chains. Such a network would be much less laterally heterogeneous than the dilute 2-d Wigner regime, and could be the reason why no forces due to patch-charge attraction are observed. The polydispersity of LPEI could represent another reason for this behavior, at least partially. This novel observation is in contrast with previous reports that attractive forces between adsorbed polyelectrolyte layers exceed van der Waals forces substantially.^{24,33,47}

CONCLUSIONS

Direct force measurement between negatively charged latex particles in the presence of cationic linear poly(ethylene imine) (LPEI) were carried out with the AFM-based multiparticle colloidal probe technique. With increasing polymer dose, the forces vary from repulsive to attractive and back to repulsive. The remarkable point is that the attractive forces are independent of the ionic strength and the molecular mass of the polymer, and they are well described with classical van der Waals interactions. This behavior has not been described before and is in contrast with earlier reports in similar systems where additional electrostatic attractive forces due to patch-charge heterogeneities were observed.^{36,47} Stability studies in a very similar system involving LPEI confirm the absence of patch-charge interactions independently.⁴⁰ The fact that these forces are unimportant in the present system indicates that the adsorbed layer of LPEI is unusually homogeneous and probably resembles the semidilute 2-d Wigner regime.

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ACKNOWLEDGMENT

This work was supported by the COST Action D43, State Secretariat for Education and Research, Swiss National Science Foundation, and the University of Geneva. We thank Mihail Popescu to pointing out the role of surface charge heterogeneities on electrokinetic effects.

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