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Surface forces between highly charged cationic polyelectrolytes adsorbed to silica: how control of pH and the adsorbed amount determines the net surface charge

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KEYWORDS: poly(diallyl dimethyl ammonium chloride), charge reversal, pH dependent, adsorption conformation, atomic force microscopy, quartz crystal microbalance with dissipation

ABSTRACT. Atomic force microscopy (AFM) and quartz crystal microbalance with dissipation (QCM-D) were employed to investigate the pH dependent adsorption of poly(diallyl dimethyl ammonium chloride) (polyDADMAC) to silica surfaces as well as the surface forces between these layers. It was found that polyDADMAC adopted a relatively flat conformation when adsorbed to a silica surface, and that the adsorbed amount increased with increasing pH. From the surface force measurements it is evident that the surface undergoes a charge reversal upon saturation with polyDADMAC, at the three different investigated pH values and that some degree of charge regulation of the silica surface takes place during the adsorption process. Finally, the overcharging phenomenon is discussed in terms of a geometrical mismatch due to the different average spacing between the surface charges on the silica surface and the size of the polyDADMAC monomer.

1. INTRODUCTION

Polyelectrolytes are charged polymers, which bear electrolyte group attached to polymer chains and have strong interactions with oppositely charged surfaces in aqueous media^{1, 2, 3, 4}. Electrostatic attraction between charged surface groups is the main driving force for adsorption of polyelectrolytes to surfaces with an opposite net charge but various factors such as the ionic strength, the adsorbed amount of the polyelectrolyte, the charge densities of the polyelectrolyte and the surface as well as charge regulation effects influence the adsorbed amount⁵. For low ionic strength conditions, the strong repulsion between charged monomers makes highly charged polyelectrolytes assume extended conformation and fairly inflexible conformation at the interface, while at an increased salt concentration, the electrostatic intra-chain repulsions will decrease and the polyelectrolyte can adopt a more loosely bound conformation^{6, 7}. For surfaces or polyelectrolytes with acidic or basic groups the pH is further of particular importance for the adsorption process.

Poly(diallyl dimethyl ammonium chloride) (polyDADMAC) is a strong cationic polymer with permanent positively charged quaternary ammonium group in each monomeric unit and it can thus adsorb to negatively charged surfaces like silica (see Figure 1). This polyelectrolyte is applied in many industrial fields, such as paper manufacturing⁸, wastewater treatment⁹ and mining industry¹⁰ and the adsorption of polyDADMAC on solid surfaces has been studied using different methods. Cakara and coworkers¹¹ studied the charging behaviour of aqueous silica particle suspensions in the presence of polyDADMAC by potentiometric titrations and

electrophoretic mobility, and found that those particles experienced a charge reversal with increasing pH. Kim et al¹² employed sum frequency spectroscopy to investigate the molecular structural details of the adsorption of polyDADMAC at a quartz/water interface. Here it was found that polyDADMAC was not well aligned at the interface at below pH 9 but became well-ordered at higher pH-values. The kinetics of adsorption and monolayer of polyDADMAC were investigated by Michna et al., using quartz crystal microbalance (QCM) and streaming potential measurements¹³. They successfully interpreted the 3-dimensional electrokinetic model and quantitatively analysed their desorption kinetics. Popa et al¹⁴ examined the adsorption of polyDADMAC on planar silica substrates as a function of ionic strength and pH using reflectometry, atomic force microscopy (AFM) and ellipsometry. They found the adsorbed amount to increase with increasing ionic strength and pH. However, most of the research focuses on the adsorption kinetics of polyDADMAC on planar substrates or on particles, while the studies about the conformation on the surfaces are few.

In this work, we have studied the adsorption of polyDADMAC to silica surfaces using QCM-D and the interactions between silica surfaces after the adsorption of polyDADMAC using AFM colloidal probe, at different pH values and a background electrolyte solution containing 1 mM NaCl. The work has been focusing on the effect of overcharging which is observed when surface saturation of polyDADMAC is reached at a specific pH value; the charge reversal which is achieved when polyDADMAC is adsorbed at a lower pH value and the pH subsequently is increased; and the different nature of the surfaces forces between saturated and unsaturated polyDADMAC layers. Finally, the obtained data are used in a discussion about the general mechanisms for overcharging during polyelectrolyte adsorption to an oppositely charged surface.

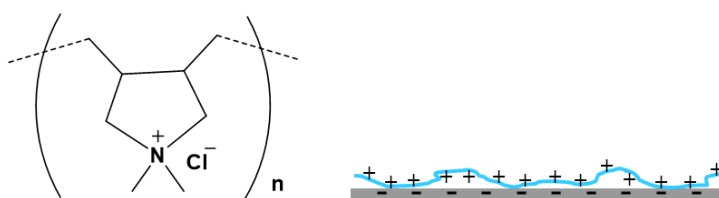


Figure 1. The molecule structure of polyDADMAC and its behavioural regime on an oppositely charged silica substrate

2. MATERIALS AND METHODS

2.1. Chemicals. The cationic polyelectrolyte poly(diallyl dimethyl ammonium chloride) (polyDADMAC) was purchased from Polysciences, Inc. as an aqueous solution of a concentration of 20%. The supplier reports the weight-average molecular weight is 240 kDa and a polyDADMAC with a similar molecular weight from the same supplier has been reported to have a polydispersity of 2.0¹⁵. Sodium chloride (NaCl, 99.5%) was purchased from Sigma-Aldrich. The ultrapure water was purified by using a Milli-Q plus 185 system with a 0.2 μm Millipak filter at 25 °C. The resistivity of the purified water was 18.2 M Ω cm, and the organic contents were less than 5 ppb. PolyDADMAC solutions of 200 ppm were prepared by diluting the 20% polyDADMAC stock solutions in 1 mM NaCl aqueous solution. The pH of the solutions was measured with an 827 pH meter (Metrohm, Swiss) and adjusted by the addition of an appropriate amount of NaOH or HCl solutions to obtain 3, 5.6 and 9.

2.2. Quartz crystal microbalance with dissipation (QCM-D). The adsorption of polyDADMAC on silica as a function of pH was investigated employing a Q-Sense E1 quartz crystal microbalance with dissipation (QCM-D) equipped with a standard Q-Sense flow module (Biolin Scientific, Gothenburg, Sweden) with a volume of 40 μL . All measurements were performed on AT-cut quartz crystals with a SiO₂ top coating and a 5 MHz fundamental frequency from Q-Sense (QSX 303, Biolin Scientific, Gothenburg, Sweden). If the adsorbed mass is evenly distributed, rigid and small compared to the mass of the crystal, the frequency change Δf is related to the adsorbed mass per unit surface according to the Sauerbrey equation¹⁶:

$$\Delta m = -C \frac{\Delta f}{n} \quad (1),$$

Where Δm is the mass change, C is the mass sensitivity constant depending on the physical property of sensor, that is 0.177 mg·m⁻²·Hz⁻¹ for the crystals used, and n is the overtone number (in the present case $n=3$). For a polymer film in aqueous solution it should further be noted that the mass obtained from a QCM measurement is the so-called wet mass which includes the adsorbed polymer chains and the solvent molecules coupled to the oscillation.

Before using the silica crystal, it was repeatedly washed using acetone and copious amount of Milli-Q water, dried with compressed air, and ultimately plasma-cleaned for 1 min (PDC-32G plasma cleaner, Harrick Plasma). After mounting the quartz crystal in the flow module of the apparatus, a degassed electrolyte solution (pH adjusted) was injected at a steady flow of 100 $\mu\text{L}/\text{min}$ at 25 °C. After establishing a stable baseline for the frequency and dissipation, the

adsorption measurements were started by shifting from the electrolyte solution to a 200 ppm polyDADMAC solution with the same salt concentration and pH. After 40 min, the cell was rinsed with the pH adjusted salt solution in order to remove any residual polyelectrolyte. These experiments were conducted in duplicates and the largest difference in frequency shift between two replicates was 15 % which is a fair reproducibility considering the relatively low absolute values of the frequency shifts.

2.3. Atomic force microscope (AFM). Surface force measurements employing the colloidal probe technique^{17, 18} were conducted using a NanoWizard 3 atomic force microscope (JPK Instruments AG, Berlin, Germany). Thermally oxidised silicon wafers with a 100 nm thick SiO₂ layer (Wafer Net, USA) were employed as the flat substrate for the force measurements while a silica particle with a diameter of approximately 7 μm (Bangs Laborated Inc, USA) was used as the colloidal probe. The size of the particle was determined using a Nikon Eclipse LV100ND optical microscope and the Infinity Analyze image processing software. A tipless rectangular cantilever (CSC38/Cr-Au, Mikromasch, Estonia) was employed for AFM force measurement and a small amount of a two-component epoxy adhesive (Araldite, Rapid) was used to glue the particle on the end of the cantilever. The value of the spring constant was determined by the Sader method, before particle attachment^{19, 20}. The oxidized silicon substrate and all tools were repeatedly rinsed with acetone and copious amount of Milli-Q water before being dried with compressed air. The cantilever with the silica particle and the silica substrate were plasma-cleaned immediately before the experiments were conducted.

The normal forces between the bare silica surface and the bare silica probe in 1 mM NaCl were firstly measured at pH 3, 5.6 and 9. Then a 200 ppm polyDADMAC solution in 1 mM NaCl at pH 3 was injected and the polyelectrolyte was allowed to adsorb for 40 min. After rinsing with the same background electrolyte solution, the normal forces were measured at room temperature. The normal forces were repeated after increasing the pH using the 1 mM NaCl solution at pH 5.6. Hereafter, the polyDADMAC solution in 1 mM NaCl at pH 5.6 was introduced for 40 min before the 1 mM NaCl at pH 5.6 without polyDADMAC was injected. The above processes were repeated after increasing the pH to 9 and adsorbing at pH 9. After each adsorption step and subsequent rinsing as well as after increasing the pH, the system was subjected to 15 min of stabilisation time before the force measurements were conducted. For each measurement condition, more than 90 force curves were collected at various surface positions, where an area of 10 $\mu\text{m} \times 10 \mu\text{m}$ was adopted equally. As will be discussed further in the results section, these force curves show almost perfect reproducibility with respect to the

long-ranged electrostatic double layer repulsion measured during approach, but some spread in the adhesion measured during retraction. A constant approach and retraction speed of 400 nm/s were adopted for the normal forces, and it is sufficiently slow to allow us to neglect hydrodynamic effects²¹. The raw data and analysis of the force curves were processed and fitted using the standard software of the instrument (JPK SPM Data Processing), as described in detail elsewhere^{22, 23}.

Theoretical force curves originating from the electrostatic double layer interaction were obtained by solving the non-linear Poisson-Boltzmann equation using constant charge and constant potential boundary conditions, respectively^{24, 25}. For a symmetric background salt, such as NaCl used in this study, the non-linear Poisson-Boltzmann equation is given as

$$\frac{d^2\psi}{dx^2} = \frac{2ze\rho_\infty}{\varepsilon\varepsilon_0} \sinh\left(\frac{ze\psi}{kT}\right) \quad (2),$$

where ψ is the double layer potential, x is the position of a plane of equal potential away from a flat surface, e is the elementary charge, ρ_∞ is the background salt concentration (number density), ε is the dielectric constant of the solution between the interacting surfaces, ε_0 is the permittivity of vacuum, and z is the ion valance (which is 1 in this case). For a more detailed discussion on how to derive the theoretical force curves from the non-linear Poisson-Boltzmann equation we refer to the previous work²⁶. However, from the non-linear Poisson-Boltzmann equation, the double layer pressure between two flat surfaces, ΔP , is obtained, and can subsequently be converted to the free energy of interaction per unit area, ΔG , by:

$$\Delta G(D) = - \int_\infty^D \Delta P(D)' dD' \quad (3).$$

Finally, the free energy of interaction can be related to the force between a sphere with radius R and a flat surface by the Derjaguin approximation²⁷:

$$F(D) = 2\pi R \Delta G(D) \quad (4).$$

In addition to the electrostatic double layer force, the experimental force curves will be influenced by van der Waals forces, hydration forces and steric forces. Hydration and steric forces will only kick-in at small surface separation and due to surface roughness effects we also only expect the contribution from the van der Waals forces to be short-ranged²⁸. Thus, our approach for comparing experimental force curves with the calculated double interactions, in order to determine the surface potentials, are as follows: First, the Debye length is kept fixed

(based on the ionic strength of the solution) leaving the surface potentials as the only adjustable parameters. Second, at large separations the forces calculated by the two set of boundary conditions overlays, and the surface potentials are adjusted to fit the experimental data in this region. However, at short separations the force calculated using constant charge boundary conditions is overestimating the real electrostatic double layer force while the force calculated using constant potential boundary conditions is underestimating the real electrostatic double layer force. This means that the experimentally obtained force always is found between the two calculated force profiles at short separations. Since none of the used boundary conditions is able to describe the force at short separations, it also means that the approach is insensitive to the before mentioned forces contributing to the experimental force profile at short separations.

3. RESULTS AND DISCUSSION

3.1. Adsorption of polyDADMAC layers. In order to obtain information about the amount and conformation of adsorbed polyDADMAC on silica surfaces at different pH values, QCM-D was employed. The change in frequency and dissipation as a function of time for adsorption of polyDADMAC at different pH values is shown in Figure 2. At pH 3 and 9, the frequency and dissipation values reach equilibrium after approximately 50 s, while a slow adsorption process followed the rapid increase in adsorption of polyDADMAC at pH 5.6. After approximately 40 minutes, the same background aqueous electrolyte solutions were used to rinse and to remove the excess polyelectrolyte from the cell. During the rinsing step, almost no decrease in the frequency was observed. At pH 3, the silica surface is carrying a relatively low surface charge density and the surface is rapidly saturated by polyDADMAC. Similarly at pH 9, where the surface charge density is high, the saturation is also fast. At pH 5.6 the surface charge density is also relatively high but here a slightly slower adsorption is observed. We speculate that the slower adsorption at pH 5.6 is due to conformational changes of the adsorbed polyDADMAC and increased charge regulation of the silica surface following the adsorption process but the exact adsorption mechanism is at this stage unknown.

The data in Figure 2B, also reveal very small changes in dissipation during adsorption of polyDADMAC layers, implying that the polyDADMAC molecules adopted a reasonably flat conformation on the silica surface. In previous investigations, it was found that for such a small dissipation shift (that is $\Delta D_n/(-\Delta f_n/n) \ll 4 \times 10^{-7} \text{Hz}^{-1}$ for a 5 MHz crystal), the film can be approximated as rigid, and the Sauerbrey equation can be used to calculate the areal mass

density of the film^{13,29}. In doing so we have determined the adsorbed amount of polyDADMAC and associated water molecules to be 0.09, 0.16 and 0.22 mg/m² at pH 3, 5.6, and 9, respectively. We will later relay these numbers to the effective surface charge densities for the adsorbed layers at the same pH values.

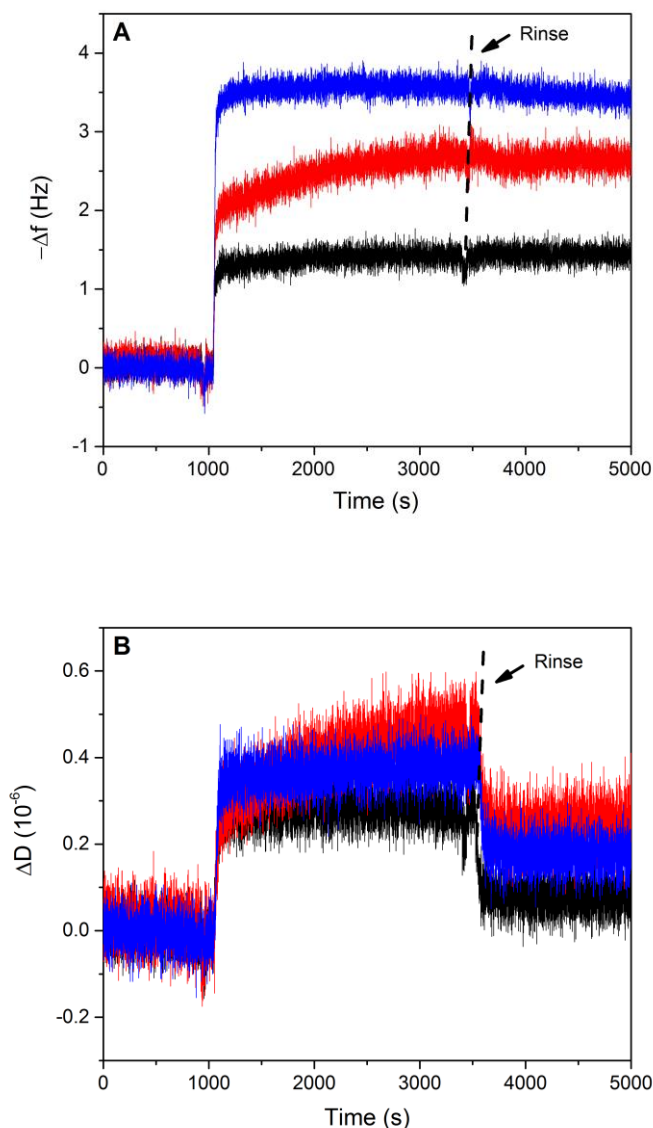


Figure 2. Change in frequency and dissipation as a function of time for adsorption of polyDADMAC on silica at different pH-values. Black, red and blue line and points represent pH 3, 5.6 and 9, respectively.

3.2. Interactions between bare silica surfaces. In order to evaluate the measured interactions between adsorbed polyDADMAC layers adsorbed to silica at different pH values, it is essential to first investigate the surface forces between bare silica surfaces. Thus, before addition of polyDADMAC to the AFM liquid cell, the force versus distance between the silica sphere and

substrate were measured. Figure 3 shows the approach force curves for the silica surfaces in 1 mM NaCl at pH 3, 5.6 and 9, respectively. From the DLVO calculations the surface potential of bare silica at pH 3 is determined to +/-20 mV, and the numerical value of the surface potential increases to +/-44 mV and +/-48 mV at pH 5.6 and pH 9, respectively. From the force measurements and the DLVO calculations, the sign of the surface potentials are not implicit, but it is well known that silica surfaces are negatively charged due to dissociation of some silanol groups^{30,31}. The dissociation is also the reason why the surface potentials increase with increasing pH and the results are in qualitative agreement with zeta-potential measurements which indicates a significant shift in potential in the pH-range 3-6 and a weaker pH dependence above pH 6^{12,32}. In the DLVO calculations, a Debye length of 6.8 nm was used at pH 3 while a Debye length of 9.6 nm, corresponding to the Debye length of the background 1 mM NaCl solution, was used at pH 5.6 and 9. This difference is rationalized by the extra ions added in for the pH adjustment ($[H^+] = 10^{-pH}$) which is increasing the total ionic strength at pH 3 to 2 mM.

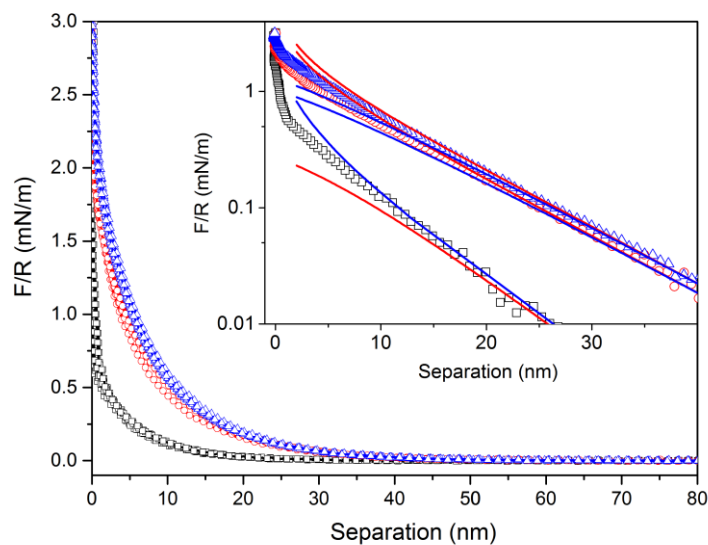


Figure 3. Surface forces between a bare silica substrate and a bare silica colloidal probe in 1 mM NaCl as a function of pH. Black open squares, red open circles and blue open triangles represent pH 3, 5.6 and 9, respectively. The graph shows in each case 10 consecutive approach force curves for each pH-value and the inset shows the approach curves plotted on a semi-log scale. The red and blue lines are fitted with DLVO forces using constant charge and constant potential boundary conditions, respectively.

3.3. Electric double layer forces between polyDADMAC layers. Measurements of the interaction between adsorbed polyDADMAC layers at different pH values followed a procedure with a stepwise change in pH and adsorption/resorption of polyDADMAC to the

silica surfaces. First polyDADMAC was adsorbed at pH 3 and the surface forces were measured after rinsing the system in order to remove nonadsorbed polymers. Hereafter the pH was increased to 5.6 and the surface forces were measured. Then the solution containing polyDADMAC at pH 5.6 was reintroduced in order to saturate the surface at this pH value and the surface forces were again measured after rinsing. The same procedure was followed when the pH was increased to 9. This means that we have measured the interaction between fully saturated adsorbed layers at pH 3, 5.6 and 9, while we have also measured the surface forces between unsaturated adsorbed layers at pH 5.6 and 9. All adsorption, rinsing and force measurements were conducted at a 1 mM NaCl solution (but at different pH values). Figure 4 shows representative forces curves from the different steps following this experimental procedure. The insets in Figure 4 provide the force curves on approach in a semi-log together with calculated DLVO force curves.

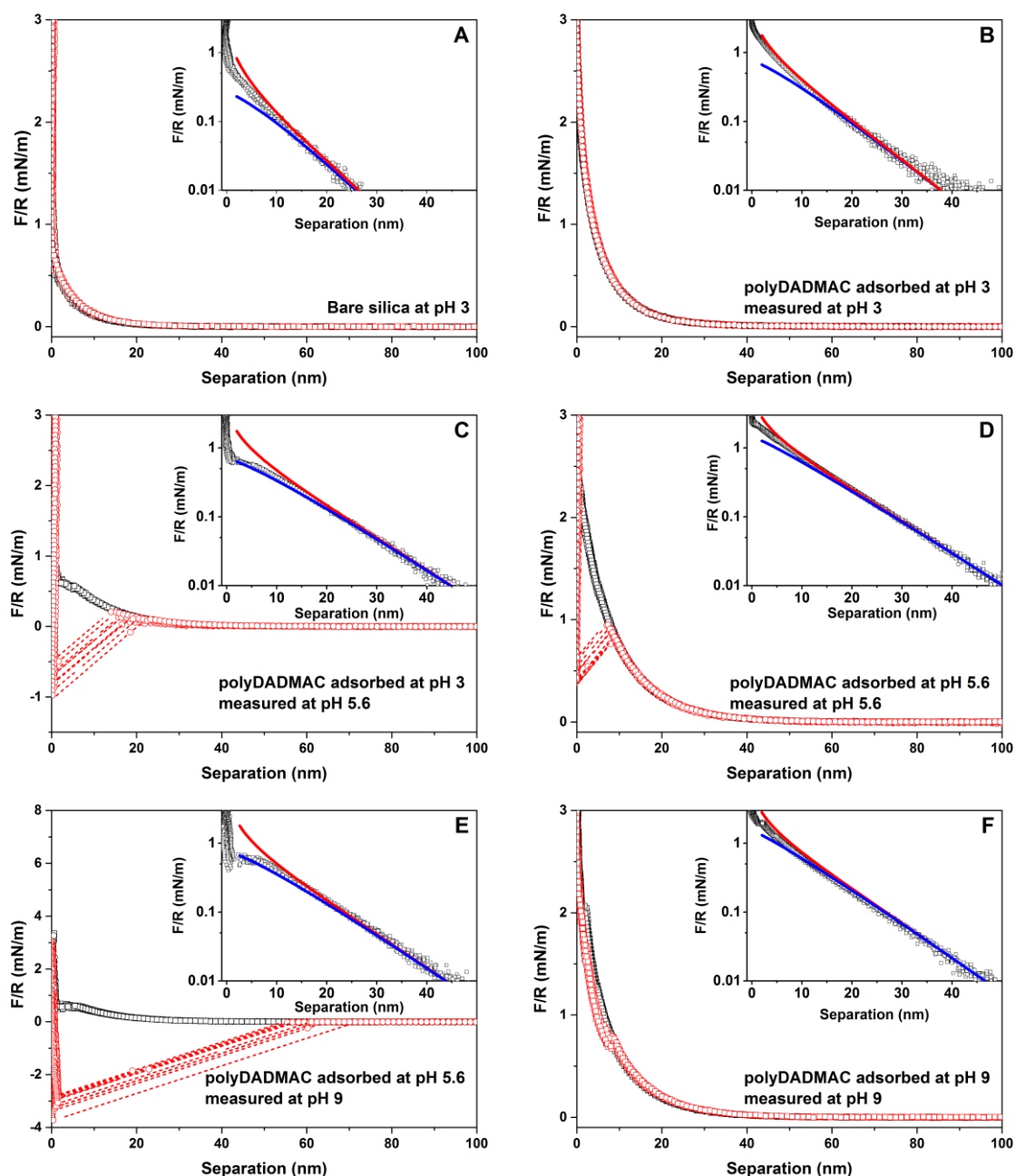


Figure 4. Forces normalised by radius as a function of separation between silica surfaces coated with PolyDADMAC in 1 mM NaCl solutions. Black open squares and red open circles represent data obtained on approach and retraction, respectively. The graphs show in each case 10 consecutive approach and retraction force curves and the insets show 10 consecutive approach force curves plotted on a semi-log scale. The red and blue lines in the insets are the DLVO forces calculated using constant charge and constant potential boundary conditions, respectively. The background electrolytes are 1 mM NaCl. (A) Force curves obtained between bare silica surfaces at pH 3. (B) Force curves obtained at pH 3 for polyDADMAC adsorbed at pH 3. (C) Force curves obtained at pH 5.6 for polyDADMAC adsorbed at pH 3. (D) Force curves obtained at pH 5.6 for polyDADMAC adsorbed at pH 5.6. (E) Force curves obtained at pH 9 for polyDADMAC adsorbed at pH 5.6. (F) Force curves obtained at pH 9 for polyDADMAC adsorbed at pH 9.

9. The figures on the left panel are assigned to unsaturated adsorbed layers with net negative charges, while the figures on the right panel belong to saturated adsorbed layers with net positive charges.

From Figure 4 it is observed that all the approach force curves show monotonically repulsive interactions with a close to exponential decay, which is consistent with electrical double-layer forces. Since the measured interaction lies between the values obtained using constant surface charge and constant surface potential boundary conditions, we conclude that some charge regulation occurs as the surface separation decreases. The surface potential obtained from the DLVO calculation are presented in Tabel 1 where the arrows indicated the experimental route and the letters in brackets refer to the subfigures in Figure 4 from where the numbers are deduced.

Table 1. Surface potentials of silica at different conditions and pH. The arrows and letters (A to F) refer to order in which the measurements were conducted and the corresponding results are shown in Figure 3A-F.

	pH 3	pH 5.6	pH 9
Surface potential of bare silica	-20 mV (A) ↓	-44 mV	-48 mV
Surface potential of silica saturated with polyDADMAC	+36 mV (B) ↓	+53 mV (D)	+52 mV (F)
Surface potential of silica unsaturated with polyDADMAC		-38 mV (C) ↑	-39 mV (E) ↑
Charge density of silica saturated with polyDADMAC	$1.77 \times 10^{16} \text{ e}\cdot\text{m}^{-2}$	$2.83 \times 10^{16} \text{ e}\cdot\text{m}^{-2}$	$2.76 \times 10^{16} \text{ e}\cdot\text{m}^{-2}$

As discussed for the interaction between bare silica surfaces, electric double layer calculations with respect to the interaction between symmetric surfaces do not distinguish between a positive or a negative surface potential. Thus, additional information or rational arguments are needed to determine the sign of the surface potential. Compared to the bare silica surfaces where the surface charge could only originate from dissociated silanol groups (and thus only be negative), the surface charges will now both originates from dissociated silanol groups and from the permanent charges on polyDADMAC (and the total surface charge can thus be either negative or positive). However, in the present case it is relatively easy to determine the sign of the surface charge in each step. If the sign of the surface potential after polyDADMAC adsorbed at pH 3 should be negative, the numerical value should be smaller than the value for bare silica at pH 3 (because we are adding positive charges). Thus, since the numerical value of the surface potential is higher after adsorption of polyDADMAC it can be concluded that the surface potential must be positive. By similar arguments, it can also be concluded that the

signs of the surface potentials at pH 5.6 and 9 are negative for the surfaces with unsaturated layers of polyDADMAC and positive for the surfaces with saturated layers of polyDADMAC. For the saturated layers of polyDADMAC, this implies overcompensation of the surface charge and hence charge reversal resulting in net positively charged surfaces which is consistent with many previous reports^{26,33}. It is, however, interesting that the sign of the net charge of surface layers reverses back to the negative value when the pH is increased and an unsaturated polyDADMAC layer is obtained. When the pH increased from 3 to 5.6, the adsorbed amount of polyDADMAC is fixed (and thus the amount of positive charges are fixed) but the silica substrate turns more negative due dissociation of silanol groups resulting in an overall charge reversal from positive to negative. When the pH is adjusted from 5.6 to 9, the conclusion about the overall sign of the surface charge is less obvious since the measured net charge of +/-39 mV is below the numerical value of the surface potential measured for the saturated layer at pH 5.6. However, we argue that the net charge of the unsaturated layer at pH 9 should be negative since no significant further adsorption of polyDADMAC would be possible if the surface was carrying a high net positive charge. It should further be noted that the observation of a charge reversal depending on the degree of surface saturation with polyDADMAC at a given pH value is in agreement with previously reported observation for adsorption of polyDADMAC to different substrates. Michna et al¹³ used streaming potential measurement to study the effect of surface coverage of polyDADMAC on mica at constant pH. Here it was found that the streaming potential was changing from negative to positive as the coverage was gradually increased. Schwarz et al³⁴ measured the ζ -potential of silica, mica and acidic polymer latex particles with different adsorbed amount of polyDADMAC. In this study, they found a gradual increase in the isoelectric point of the particles as the adsorbed amount of polyDADMAC on the particles was increased.

3.4. Polymer induces forces between adsorbed polyDADMAC layers. Beside the long-ranged electrical double layer forces measured when the surfaces are approaching each other, short-ranged polymer induced surface forces are in some cases observed in both the approach and retraction force curves.

For the saturated layer of polyDADMAC at pH 3 (Figure 4B), the short-range interaction is purely repulsive, and no hysteresis is observed between forces measured on approach and on retraction. The lack of a steric repulsive barrier and no short-ranged compressive component to the interaction profile implies a low amount of adsorbed polyelectrolytes which have adopted

a relatively flat conformation at the surfaces. Similar observations have previously been reported for other polyelectrolytes adsorbed on mica and silica^{35, 36}.

When the pH is increased from 3 to 5.6, more silanol groups dissociate and more available binding sites for polyDADMAC becomes available on the silica surface. Thus, when two unsaturated polyDADMAC layers are approaching at pH 5.6, at some separation distance, polymers adsorbed on one of the surfaces will be able to extend and bind to available spots on the opposite surface. In Figure 4C traces of such bridging interactions are seen at a separation of approximately 5 nm. After the surfaces have been in contact more bridges will form which is resulting in the dominating adhesion force seen in the retraction force curve. A similar condition has been observed in experimental studies which polyethyleneimine was adsorbed to silica³⁷ and by model results on the interaction between surfaces containing adsorbed polymers³⁸. In Figure 5 a histogram of adhesion forces, based on more than 90 consecutive force curves, for the unsaturated surface at pH 5.6 shows an average adhesion force of 0.88 mN/m. The presence of bridging forces upon approach suggests that the polyDADMAC molecules are not fixed in an entirely immobile flat conformation but might show some flexibility with an ability to extend slightly into the solutions. Such a slightly extended conformation might also explain the significant overcharging seen from the long-ranged forces.

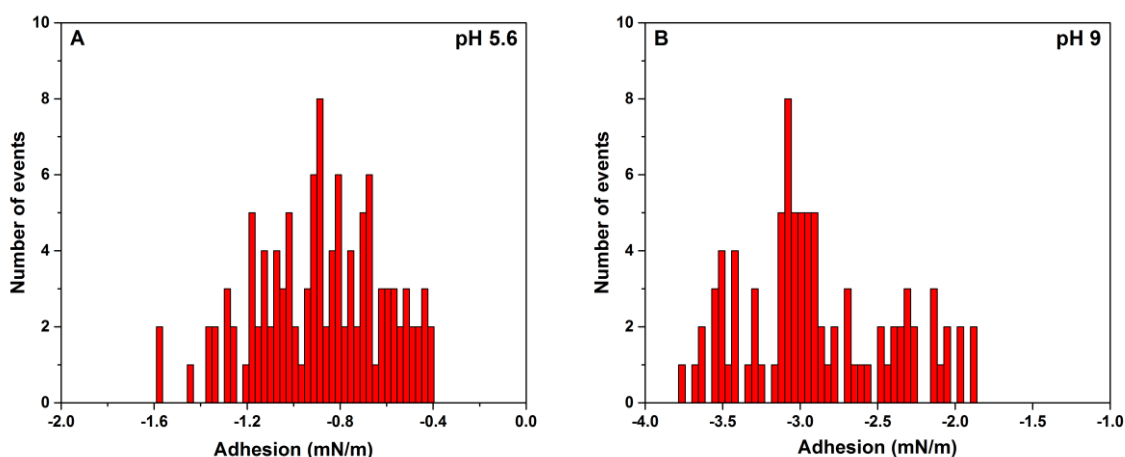


Figure 5. Histograms showing the distribution of adhesion forces (normalized by radius) between unsaturated polyDADMAC coated silica surfaces at pH 5.6 (A) and pH 9 (B), respectively. These two conditions are corresponding to the conditions in Figure 4C and Figure 4E and the adhesion forces correspond to the maximum adhesion forces observed in the two sets of retraction force curves.

After reintroducing the polyDADMAC solution at pH 5.6, all the new available binding sites will again be occupied, thus effectively preventing bridging interaction between these saturated layers. In the approach curve in Figure 4D no “bump” appears but a small force minimum observed upon retraction reveals that a minor degree of polymer bridging can take place after

the surfaces have been in hard contact, although, still to a much smaller extent as for the unsaturated layers.

A very similar trend as seen when increasing the pH from 3 to 5.6 was found when increasing the pH from 5.6 to 9. However, a significant difference is a stronger adhesion force observed for the unsaturated layers at pH 9 (Figure 4E) compared to the unsaturated layers at pH 5.6 (Figure 4C). As seen from Figure 5 the adhesion force at pH 9 possesses an average value of 2.87 mN/m which is more than three times higher than the adhesion force found for the unsaturated layers at pH 5.6.

3.5. The effect of overcharging. As evident from the AFM-based force measurement and the derived values of surface potential and surface charge densities presented in Table 1, adsorption of polyDADMAC is not only neutralizing the negative surface of silica but leading to a significant overcharging of the surface. Noteworthy, almost an exact charge reversal is observed at all three investigated pH value, however with a slightly higher numerical value of the surface potentials and surface charge densities of the adsorbed polyDADMAC layers compared to the bare silica surface.

By assuming that the adsorption of polyDADMAC first neutralizes the charges on silica and next lead to an overcharging, one can in principle estimate the amount of adsorbed polyDADMAC and compare the values with the sensed mass derived from the QCM-D measurements. However, the sensed masses from the QCM-D measurements are at all three pH values approximately one order of magnitude higher than the masses derived from the surface charge densities. A similar discrepancy is described in a paper by Notley³⁹ reporting the adsorption of polyDADMAC in cellulose gels and several factors could be the reason for this. Firstly, the assumption that the total amount of adsorbed polyDADMAC can simply be determined by the summation of the surface charge densities of bare silica and an adsorbed layer of polyDADMAC (multiplied by the mass of one DADMAC monomer), will likely underestimate the adsorped amount due to charge regulation of the silica surface. This charge regulation process which was already discussed in relation to the QCM-D data obtained at pH 5.6 (see Figure 2) means that more silanol groups dissociate as a response to the polyDADMAC and that more positive charge thus are required for charge neutralization. Secondly, the adsorbed amount for polyDADMAC determined from the surface potential measurements might further by underestimated due to co-adsorption of chloride ions. According to the classical theory such an ion condensation process, also often refer to as Manning condensation^{40, 41, 42}, will take place when the distance between two charges is smaller than the

Bjerrum length ($l_B = e^2 / (4\pi\epsilon_0\epsilon k_B T)$). In the present case of the heavily charged strong polyelectrolyte, polyDADMAC, the distance between two charges will compare with the Bjerrum length, which is approximately 7 Å in water, and some minor degree of ion condensation can thus be expected. Thirdly, it is well-known that the sensed mass obtained by QCM-D is overestimating the real mass since it also includes water entrapped in the adsorbed polymer layer^{39, 43, 44}. Thus, taking these two factors into account will bring the values obtained from surface force measurements and QCM-D closer to each other.

After arguing that the true amount of adsorbed polyDADMAC probably lies in between the values derived from the AFM and QCM-D measurements, respectively, the next step will be to discuss the physical reason for the large overcharging of the surface. Here, we believe that the main reason is a mismatch of the charge densities on the silica and polyDADMAC which is making a 1:1 charge neutralization impossible. E.g. at pH 9 where we have the highest charge density of silica, the electrical double layer calculations returned a value of 2.48×10^{16} charges per m^2 , which corresponds to an average distance of approximate 6-7 nm between two charges. In comparison will the distance between two charges on the polyDADMAC chain correspond to the size of one DADMAC monomer which is below 1 nm. Thus, for a polyDADMAC molecule to neutralize neighboring charges on the silica surface it will have to bring several extra positive charges due to this geometrical mismatch. On the regard, Kim and coworkers⁷ investigated the adsorption of polyDADMAC at the quartz/water interface employing IR-visible sum frequency spectroscopy. They found that only at pH values higher than 9.6, polyDADMAC chains were sufficiently well aligned at the interface to elicit a sum frequency. Thus, at lower pH values it is reasonable to assume that segments of adsorbed polyDADMAC layer extend slightly into the solutions even though our results generally suggest that polyDADMAC molecules adopt a relatively flat conformation on silica surfaces. This is possible also evidence from Figure 2B where the adsorbed polyDADMAC layer at pH 5.6 hold bigger dissipation than that at pH 9 even though the sensed mass of adsorbed polyDADMAC layer at pH 9 was bigger. By combining this knowledge, it is suggested that the pH influences on not only the surface coverage but also the conformation of the adsorbed layer.

4. SUMMARY AND CONCLUSION

In this work, we first studied the adsorption of polyDADMAC on silica at different pH values by QCM-D and secondly measured the surface forces between adsorbed layers as a function of pH and adsorbed amount by colloidal probe AFM. The first part revealed a significant increase in the adsorbed amount of polyDADMAC with increasing pH due to the dissociation of silanol

groups but also some pH dependence of the adsorption kinetics - especially at intermediate pH values where the surface charge density is most pH sensitive. The surface force studies demonstrated that the negative surface charge of bare silica was overcompensated for saturated layers of polyDADMAC resulting in a surface charge reversal at all three investigated pH-values. However, when polyDADMAC was first adsorbed at a lower pH-value whereafter the pH was increased, the surface charge again changed to a negative value due to the increased deprotonation of the silanol groups and the unsaturated nature of the polyDADMAC layer. The difference between saturated and unsaturated polyDADMAC layers also manifested itself in the short-ranged interaction and in the retraction force curves where attractive bridging interactions are observed between the unsaturated polyDADMAC layers while purely repulsive interactions were observed between the saturated layers. Finally, a discussion about the reason for the large overcompensation of saturated polyDADMAC layers suggests that the charge reversal and the adsorbed amount likely can be tuned by the degree of geometric mismatch between the charge densities of the surface and the polyelectrolyte.

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