Tunable Self-assembled Weak Polyelectrolyte Brushes

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Abstract: The authors have investigated the pH and ionic strength response of self-assembled layers formed by adsorption of amphiphilic weak polyelectrolytes. Using the SFA (Surface Forces Apparatus) the authors measured force-distance profiles of poly (isoprene)-poly (acrylic acid) block copolymers adsorbed on mica. Also by Atomic Force Microscopy the authors captured single polyelectrolyte molecule adsorbed on a surface. The effect of salt concentration (C_s) and pH upon the height of the brush layers was explored mainly by measuring the forces between two adsorbed polyelectrolyte brushes. At pH = 4 our results are in good agreement with the scaling prediction $L_0 \propto C_s^{-1/3}$. Changing the pH from 4 to 10 causes a remarkable swelling of the polymer layer, but only a weak dependence on salt concentration was detected at the higher pH. This can be attributed to the degree of dissociation, which depends on the local pH value. At low pH the polyelectrolyte chains have a low charge density, while on increasing the pH the degree of dissociation rises, and the increased charge density is followed by swelling of the adsorbed layer. The local concentration of ions in the brush is now greater than that of pH = 4 and approximately equivalent to 0.3 M. So the swelling is only weakly dependent on salt concentration in the range 0.01-1.0 M. The results demonstrate the tunable nature of such self-assembled polyelectrolyte brushes whose height and range of interactions, can be systematically controlled by adjusting the pH and ionic strength of the medium.

Key words: Polyelectrolytes, pH, self-assembled layers, surface forces apparatus, atomic force microscopy, tunable nature of such self-assembled polyelectrolyte brushes, ionic strength.

1. Introduction

Polyelectrolytes (charged polymer chains) remain among the least understood materials despite their importance in biology (proteins, DNA) and materials science. Their behavior and characteristics are not yet fully understood because of complicated correlations due to their charged nature that gives rise to long-range interactions. The counterplay of their properties as polymers and electrolytes with counterions around polyelectrolyte chains imposes additional difficulties on explaining their behavior. The association of counterions around polyelectrolytes and the pH of the solution are two parameters that can affect the properties of such systems [1, 2]. The degree of dissociation in weak polyelectrolytes (contrary to strong polyelectrolytes) is not constant, but depends on the local pH value. This is because the

amount of protons in the solution can adjust the charge density of the salt moieties.

Strong polyelectrolytes have been investigated recently [1, 3-7]. However weak polyelectrolytes are not so extensively investigated and that is why they remain among the least understood materials. Just recently chemically adsorbed weak polyelectrolytes have been investigated by ellipsometry [8, 9]. The authors although tried to adsorb physically weak polyelectrolytes onto mica substrate. The authors also imaged by means of A.F.M. the physically adsorbed polyelectrolytes. These systems are very important because of their technological applications. For example colloid stabilization, adhesion, lubrication, are some of them.

In this paper, the authors present force-distance measurements between two adsorbed layers of poly(acrylic acid)-poly(isoprene). The poly(isoprene) part of our polymer is the shortest one able to be adsorbed on a surface. The authors measured forces between two charged polymer layers of

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poly(isoprene-acrylic acid) diblock copolymers adsorbed on mica surfaces. Poly(isoprene-acrylic acid) diblock copolymers can be adsorbed from one end (poly-isoprene) which is shorter than the poly(acrylic acid) part.

The authors measured the force-distance profiles, at different salt concentrations and pH values, by the Surface Forces Apparatus [10, 11]. The adsorbed polymer layers tend to swell upon addition of small amounts of salt, while addition of large amounts of salt causes shrinking of the layers. From the force-distance profiles the authors can obtain information about the height of the adsorbed polymer layers as well as the changes induced by altering the salt concentration or the pH. Changing the pH of the ambient solution from pH = 4 to pH = 10, the aurhors increase the degree of dissociation so the authors can assume that all the moieties are charged. The protons of the COOH moieties on the polymer chain are forced to dissociate and combine with the OH^- groups. This causes swelling to the polymer layers because of increase in osmotic pressure induced by electrostatic repulsion. The authors measured the swelling of the polymer layer under three different salt concentrations of the ambient solution 0.01 M, 0.3 M and 1.0 M. For all three concentrations the authors observed essentially the same swelling. The results are in good agreement with current polyelectrolyte theories [12-16].

2. Experimental Method

The authors used the mica force-balance technique, which has been described in detail previously [10, 11]. The experiment allows the force F(D) between two curved mica surfaces to be measured. Two mica pieces of identical thickness (typically 1.5-3 μm), and about 1 cm × 1 cm in area, are silvered on one side, and then glued onto cylindrical transparent lenses with mean radius of curvature $R \cong 1cm$ so that the silvered side faces the lens. The lenses are placed in the apparatus, facing each other in a crossed cylinder configuration. The force is measured as a function of the distance D between the mica surfaces. The surfaces can be driven together, with a mechanical drive or a piezoelectric crystal. One surface is mounted on a spring the deflection of which gives the force between the two surfaces. Separations are determined by white light interferometry (with an accuracy ± 3 Å). Prior to an experiment the glass and stainless steel components, which come in contact with the liquid, are exhaustively cleaned, as described previously [17]. The mica sheets are mounted, and brought into contact in air as a check that no contamination is present. The surfaces are then separated and triple distilled water introduced in order to measure forces in the absence of any polymer. The water is then replaced by a solution of poly (isoprene)-poly(acrylic acid) with different salt concentrations. After measuring the force-distance profile for each salt concentration the authors substitute the solution with a new one adjusting the pH to be 10 for each salt concentration. Polyelectrolyte solution without salt was also measured to confirm, that no adsorption is observed. This is because similar charged polyelectrolytes repeal each other, and cannot approach the surface. When salt added then the electrostatic repulsion is screened, allowing thus the polyelectrolyte chains to approach the surface.

3. Results

3.1 AFM Measurements

3.3.1 Experimental Procedure

The AFM measurements took place at the Institute for Polymer Research at Dresden Germany. The authors left freshly cleaved mica sheets to incubate for 14-16 hours into polyelectrolyte solution. The polyelectrolyte concentration was 0.1 mg/mL while the salt concentration was 0.1 M. The authors then left the mica sheets to dry under controlled conditions. After drying the authors measured the samples by means of tapping mode. The authors observed several

adsorbed polyelectrolyte chains onto the mica sheet. By cross section the authors measured the thickness of the adsorbed polyelectrolyte chains, which is in good accordance with our measurements in dry state. The authors will refer to these measurements later in this paper. In Fig. 1 the authors can see the AFM image and the cross section.

3.2 SFA Measurements

3.2.1 Pure Solvent

Before introducing polyelectrolyte solutions into the system, the interaction between the mica surfaces in pure water was first measured, as a check that the surfaces are uncontaminated.

3.2.2 Addition of Salt

Afterwards the authors introduced electrolyte (salt) solutions to measure the range of the DLVO interactions. The authors have measured KNO_3

solution with concentrations 10^{-3} M and 10^{-2} M. The resultant force-distance profiles revealed the range of the DLVO interactions and can operate as measure for our rest profiles. In Fig. 2 the authors present the measurement with salt concentration 10^{-2} M.

3.2.3 Addition of Polyelectrolyte Solutions with Different Salt Concentrations and pH

The authors then picked a new pair of mica sheets and the authors introduced a polyelectrolyte solution without any salt added into the bath. The concentration of the polyelectrolyte solution was 0.1 mg/mL and left to incubate typically for 12-14 h. It is known from previous studies that the chains attach to the surfaces via the hydrophobic part of the diblock copolymer, which in our polymer is poly(isoprene) [17, 18]. No measurable adsorbance detected because of the electrostatic (coulombic) repulsion forces between the polyelectrolyte chains and the surface.
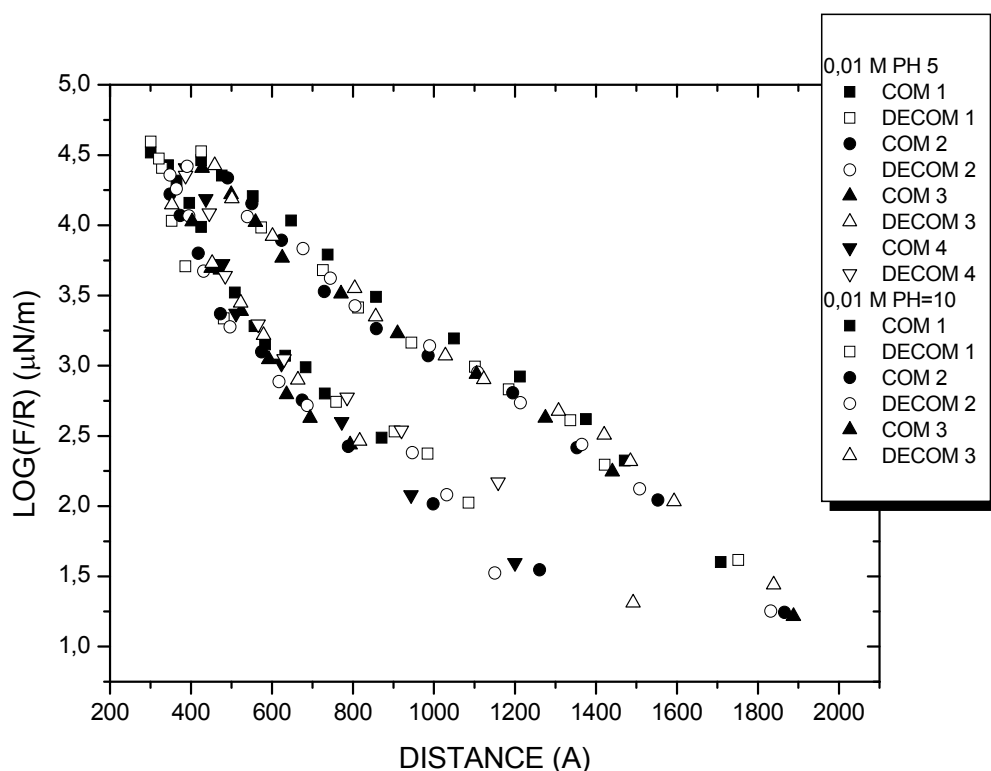

Fig. 1   Force-distance profiles between curved mica sheets following (14-16) h incubation in a solution (ca. 10^{-4} w/w) of PIAA at 0.01 M salt concentration. For pH = 5: first compression (■) and decompression (□), second compression (●) and decompression (○) third compression (▲) and decompression (△) and fourth compression (▼) and decompression (▽). For pH = 10: first compression (■) and decompression (□), second compression (●) and decompression (○) third compression (▲) and decompression (△).
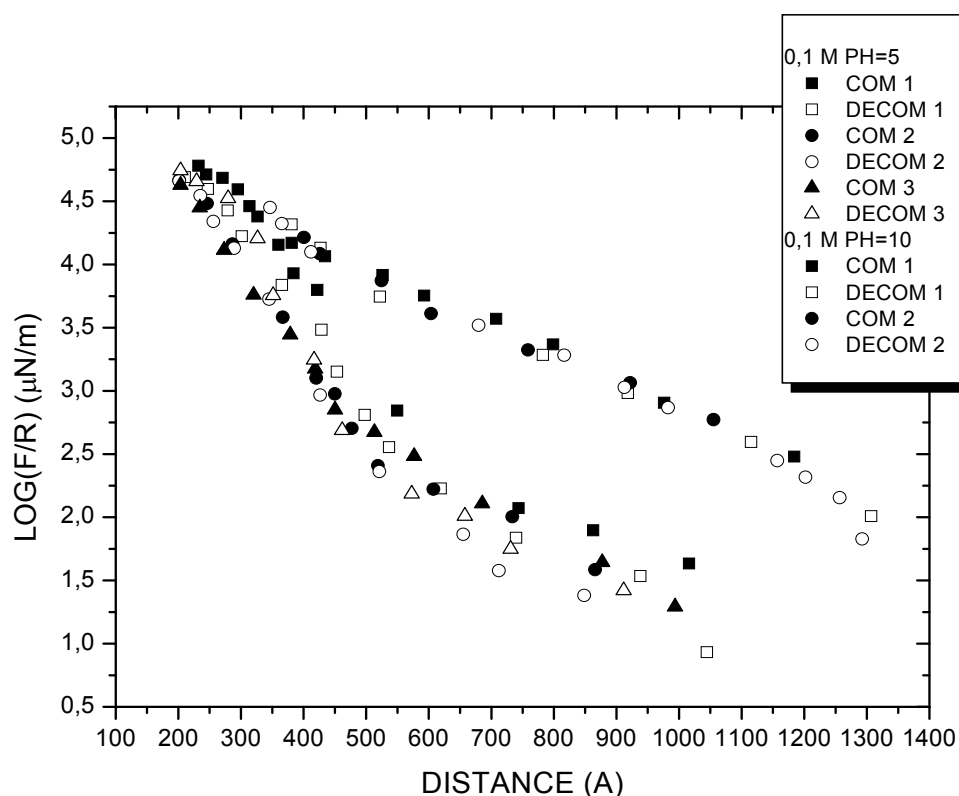
Fig. 2 Force-distance profiles between curved mica sheets following (14-16) h incubation in a solution (ca. 10^{-4} w/w) of PIAA at 0.1 M salt concentration. For pH = 5: first compression (■) and decompression (□), second compression (●) and decompression (○) third compression (▲) and decompression (△). For pH = 10: first compression (■) and decompression (□), second compression (●) and decompression (○).

After that a new pair of mica sheets prepared and solution of poly(acrylic acid)-poly(isoprene) with 0.01 M salt concentration added into the bath. The polyelectrolyte concentration and the incubation time were the same as before. Force-distance profiles were measured following adsorption. No attractive interactions were found. The authors used different compression and decompression rates and the force-distance profiles were measured for various cycles. No hysteretic behavior was observed. Then the authors removed the solution from the bath and the authors added KOH solution increasing the pH value to pH = 10. After few minutes the authors measured the force-distance profile again. The authors detect swelling at the polyelectrolyte layer, no hysteric behavior and no differences because of the rates of compression-decompression. Fig. 3 shows force-distance profiles for pH = 4 and pH = 10 for salt

concentration 0.01 M.

Continuously, the authors have repeated the measurements for different salt concentration: 0.3 M at pH = 4. The polyelectrolyte solution left to incubate for 12-14 h and then the authors measured the force-distance profiles. After that the authors have substituted the solution with pH = 10 KOH solution. Fig. 4 shows the measurements for 0.3 M at pH = 4 and pH = 10. The authors can easily notice no hysteretic phenomena for all compression-decompression cycles, but the thickness of the polyelectrolyte layer adsorbed from 0.01 M solution is greater than the layer conformed after adsorption under salt concentration 0.3 M. After changing the pH to 10 the adsorbed layers in both salt concentrations swell to almost the same thickness.

Fig. 5 shows a new cycle of measurements where adsorption now takes place from solution with 1 M
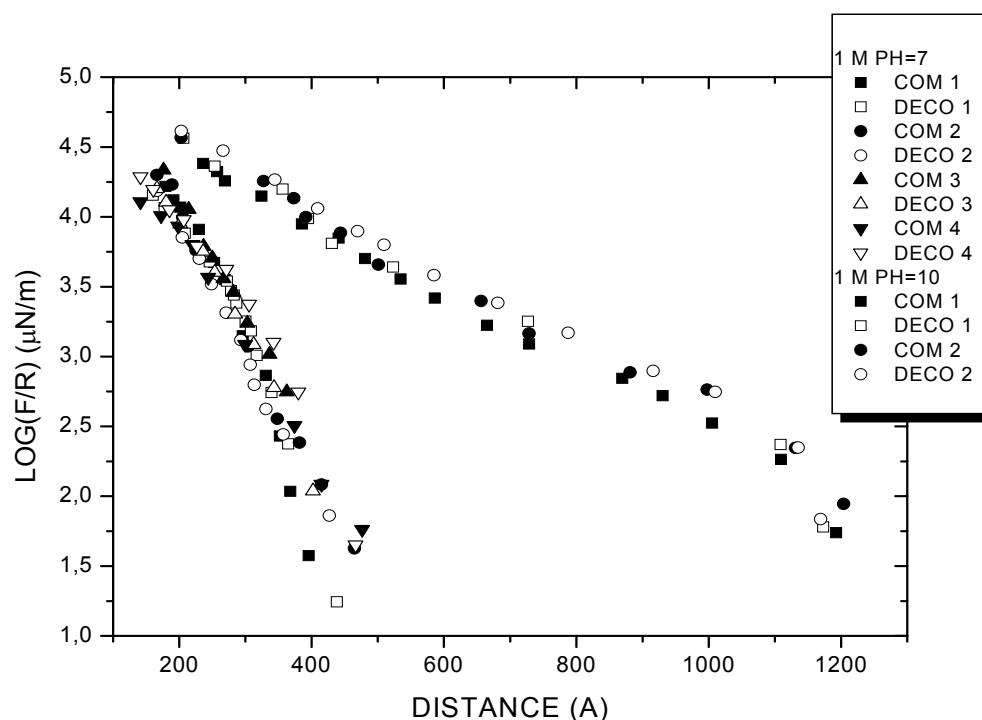
Fig. 3 Force-distance profiles between curved mica sheets following (14-16) h incubation in a solution (ca. 10^{-4} w/w) of PIAA at 1 M salt concentration. For pH = 5: first compression (■) and decompression (□), second compression (●) and decompression (○) third compression (▲) and decompression (△) and fourth compression (▼) and decompression (▽). For pH = 10: first compression (■) and decompression (□), second compression (●).
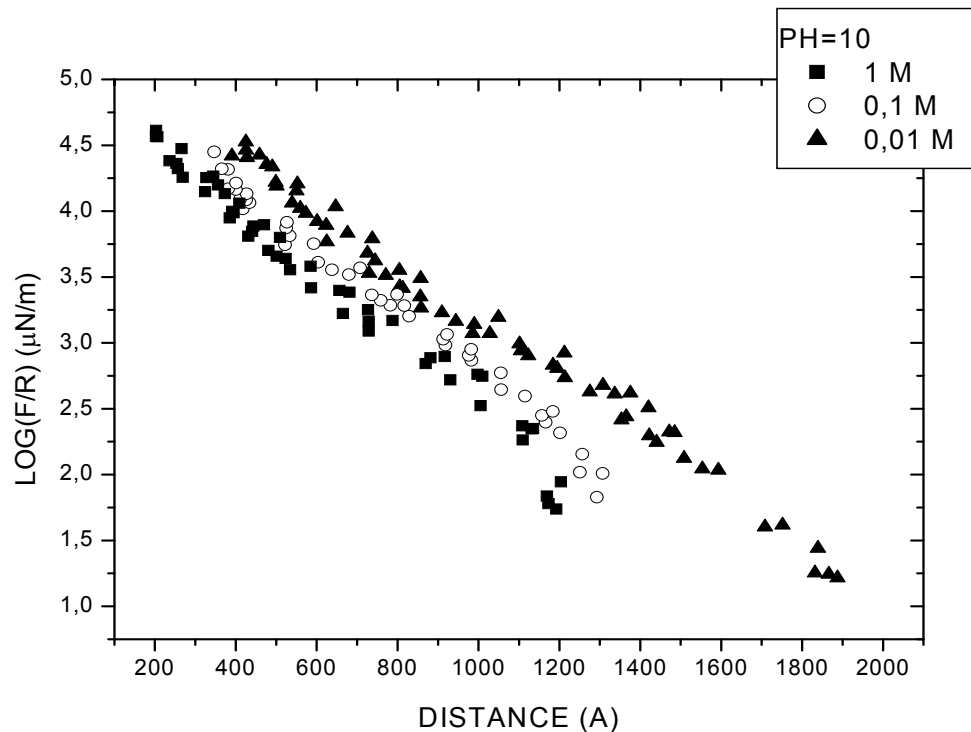

Fig. 4 Force-distance profiles between curved mica sheets following (14-16) h incubation in a solution (ca. 10^{-4} w/w) of PIAA at 0.01 M (■), 0.1 M (○) and 1 M (▲) salt concentrations at pH = 10. Different compressions and decompressions are shown from different experiments.
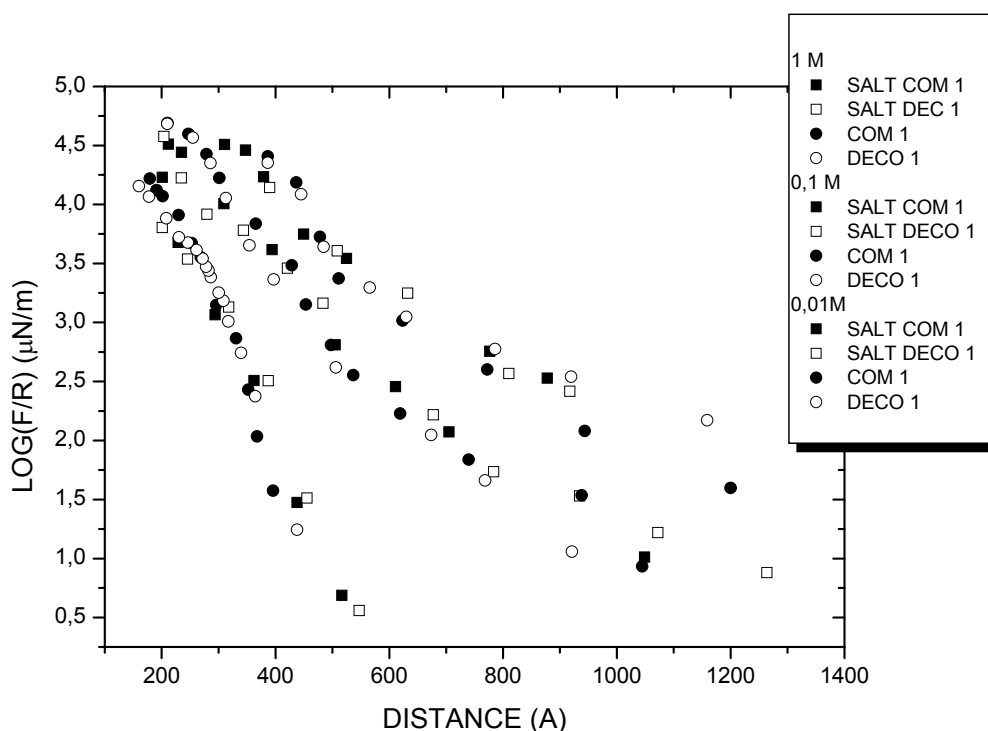
Fig. 5   Force-distance profiles between curved mica sheets following (14-16) h incubation in a solution (ca. 10^{-4} w/w) of PIAA at different salt concentrations for pH = 5. Comparisons between measurements after adsorption of PIAA at each salt concentration and after changing the salt concentration are shown. Compressions (■) and decompressions (□) after changing the salt concentration (first adsorption at 0.01 M). Compressions (●) and decompressions (○) after adsorption at each different salt concentration.

salt concentration. The authors follow the same procedure as before. The thickness of the polyelectrolyte layer is now lower than those measured for 0.01 M and 0.3 M salt concentrations. This is in agreement with earlier observations for strong polyelectrolytes [19, 20] and it is expected to be the same for weak polyelectrolytes upon addition of large amount of salt. Continuously the authors substituted the polyelectrolyte solution with pH = 10 KOH solution 1 M salt concentration. The results are shown in Fig. 5. The authors can see the swelling of the adsorbed layer after increasing the pH of the ambient solution. Comparing the force-distance profiles for all different salt concentrations at pH = 10, the authors realize that the qualitative features of all profiles are similar. The authors observe a long-range repulsion, increasing monotonically with decreasing inter-surface separation.

As a check of reproducibility the authors have repeated all the measurements at least twice and often

several times using different pairs of mica. For each experiment with freshly cleaved mica the authors measured different contact positions. The results were reproducible within the scatter of the data. The authors can finally suggest that the swelling or shrinking of the polyelectrolyte layer depends only on the salt concentration and the pH value of the ambient solution.

3.3 Measurement of Thickness in Dry State

Finally the authors have measured the thickness of the adsorbed polyelectrolyte layer in dry state. After incubation of 12-14 h the authors removed the solution, and the authors introduced triple distilled water into the bath at least twice in order to remove totally the polyelectrolyte solution. The authors then left the adsorbed layer to dry under flux of Nitrogen. The authors have measured the dry thickness for adsorbed layers under three different salt concentrations.
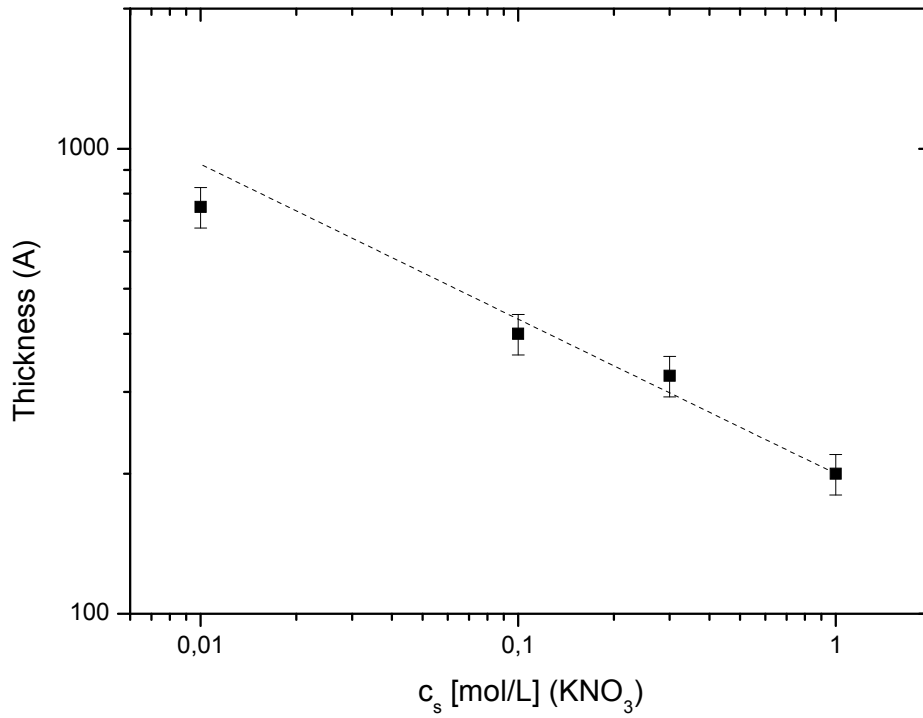
Fig. 6   Logarithmic plot of thickness against salt concentration for pH = 5. The filled symbols are measured thickness calculated as half the distance of the onset of forces. The dashed line is the theoretically predicted behaviour for weak polyelectrolytes at high salt concentrations.

The authors can then calculate the total adsorbed amount of polyelectrolyte. Table 1 shows the measured thickness for each salt concentration and the calculated values of the adsorbed amount. The results are in agreement with what the authors have measured by A.F.M. The thicknesses in dry state are almost identical in both experimental techniques.

4. Discussion

According to Lyatskaya et al. [14], addition of large amounts of salt, will affect weak polyelectrolyte in the same manner as strong polyelectrolytes. Both weak and strong polyelectrolyte layers shrink according the same power law. Actually the height of strong polyelectrolyte brushes decreases by a weak power law:

$$L_{salt} \propto c_s^{-1/3}$$

An explanation for this behavior can be the

penetration of ions into the brush. Due to dissociation of ions from the polyelectrolyte moieties, inside the brush the authors have a specific salt concentration. When the salt concentration of the ambient solution is lower than the inner concentration then screening takes place only at the outer edge of the brush. The osmotic pressure inside the brush remains unaffected forcing the chains to stretch from the surface. Increasing the salt concentration the osmotic pressure is changing by a power law [3]:

$$p \propto 1/c_s$$

suggesting a decrease at the height of the polyelectrolyte layer. When the salt concentration of the ambient solution reaches the interlayer concentration then the osmotic pressure reduces causing consequently reduction at the brush height. The screening is now extended to the whole brush and the polyelectrolyte chains behave like a neutral brush

with enlarged excluded volume.

If the authors increase the pH from 4 (self pH for PIAA) to 10 then the degree of dissociation increases causing almost totally charging of the polymer chains. When the authors changed the salt concentration, the authors observed no difference in the height of the polymer layer although a remarkable swelling at the brush measured. This is logical while increasing the concentration of OH^- groups the free protons are associated with them. The increase in charge density over the polyelectrolyte chains causes swelling to the layer. The authors have assumed that if the authors change the salt concentration the swelling might change or disappear, because of the screening. Surprisingly the authors have observed no difference after changing the salt concentration at constant pH = 10.

One probable reason is possibly the ion concentration into the brush. In order to calculate the ion concentration the authors have to measure the adsorbed amount in dry state (Table 1). The authors calculated the adsorbed amount around 1.5 mg/m^2 which gives an ion concentration around 0.3 M into the brush. Measuring the force-distance profile for 0.01 M and 0.3 M, the authors detected no differences. It seems that the conformation of the layer is mainly determined by the ion concentration into the brush, while this is much greater than the ion concentration of the ambient solution. Increasing the ion concentration of the ambient solution to 1 M in order to exaggerate the inter-brush concentration the authors measured no significant differences. This can attribute to the Debye length of the charged moieties on the polyelectrolyte chain [21]. At 25 °C the magnitude of the Debye length is:

$$1/\kappa = 0,304 \big/ \sqrt{[KNO_3]} \quad \text{nm}$$

This form is valid for 1:1 electrolytes such as NaCl and KNO₃. Where [KNO₃] is the salt concentration in M. Calculating the Debye length for 0.3 M, which is the inter-brush salt concentration the authors find

0.556 nm. This magnitude is less than the distance between two charged moieties on the chain so the length of the brush is not determined by the salt concentration into the brush. Increasing more the salt concentration to 1 M the Debye length reduces further. The Debye length for 1 M salt concentration is 0.304 nm and can hardly affect the length of the layer.

Recently Rühe et al. [8, 9] have measured the thickness of the layer conformed under different salt concentrations. These measurements are showing a remarkable increase in the thickness of the layer for small salt concentrations and subsequently a decrease for higher salt concentrations. Specifically for salt concentrations smaller than 0.01 M they have measured an increase to the layer thickness. This increase is following the power law [4, 5, 7, 14-16]:

$$L \propto c_s^{1/3}$$

which has predicted theoretically by Zhulina et al. When the salt concentration of the ambient solution is greater than 0.01 then by increasing the salt, the authors observe a decrease in the thickness of the adsorbed layer. This was also predicted by Zhulina et al. and follows the law [14]:

$$L \propto c_s^{-1/3}$$

The authors plotted the thickness of the adsorbed layer, which is half the distance of the onset of the forces and calculated the slope of the logarithmic plot of L against c_s. The logarithmic plot is shown in Fig. 6. The slope is 0.3 ± 0.05, which is in well accordance to the theoretically predicted 0.33.

Small differences can be attributed to the fact that salt concentration value 0.01 M is the "borderline" point, where the behavior of the brush changes. For salt concentrations smaller than 0.01 M the thickness of the layer follows the law $L \propto c_s^{1/3}$ while for concentrations greater than 0.01 M the thickness follows the law $L \propto c_s^{-1/3}$. In well accordance to previous measurements the authors detected no

differences in the thickness of the adsorbed layer for pH = 10. Rühe et al. [8, 9] also measured no differences at high pH by changing the salt concentration in the regime of high salt concentrations.

5. Conclusions

The authors have investigated the swelling behavior of weak polyacids by changing the salt concentration and the pH of the ambient solution. The authors used the Surface Forces Apparatus and AFM to measure the force distance profiles the thickness of the adsorbed layer in dry state and to detect single polyelectrolyte macromolecules physically adsorbed on mica surface. The authors estimated the degree of dissociation at high pH and the adsorbed amount of the polyelectrolyte on the surface.

The authors have measured the force distance profiles for the PIAA at three different salt concentrations 0.01, 0.3 and 1.0 M at pH = 4 and pH = 10 in order to investigate the swelling degree. The thickness of the adsorbed layers at pH = 4 follow the theoretically predicted law: $L \propto c_s^{-1/3}$ while the swollen thickness is almost inert to changes concerning the salt concentration.

Changing the pH from 4 to 10 and keeping the salt concentration the same the authors measured the swelling behavior of the layer. The swollen thickness is greatest in the occasion of 1 M while for 0.01 M is lowest. Finally the authors measured the force distance profiles for pH = 10 by changing the salt concentration in order to ensure that no pronounced differences were detected.

By AFM measurements the authors have detected single adsorbed macromolecules. By cross section the authors estimated approximately the thickness of the adsorbed layer in dry state. The calculated values are in good accordance with our measurements by SFA.

Acknowledgment

The authors wish to thank the Greek General

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