Comparison of Polyelectrolyte Multilayers Built Up with Polydiallyldimethylammonium Chloride and Poly(ethyleneimine) from Salt-Free Solutions by in-situ Surface Plasmon Resonance Measurements

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Summary: Polyelectrolytes offer a widespread potential for the defined modification of planar inorganic or polymer surfaces. Essential parameters for the regular adsorption of subsequent polymer layers by electrostatic interactions are the charge of polyelectrolyte and of the outermost surface region, the surface of the substrate, and the molar mass of the polyelectrolyte.

To study such effects in mono- and multilayers we used poly(diallyldimethylammonium chloride (PD) with a molar mass from 5000 to 400000 g/mol as a strong polycation and poly(ethyleneimine) (PEI) with 75000 g/mol as a weak polycation and poly(sodium styrenesulfonate) (PSS) from 70000 to 1Mio g/mol in the diluted and semi-diluted region.

The characterization of the layers was performed by streaming potential, in-situ SPR and UV-Vis spectroscopy. Thereby the layer built up at the solid/liquid-interface could be followed and quantified at the molecular level. SPR revealed that the thicknesses of the multilayer depends strongly on pK values of the polyelectrolyte (strong or weak) and the molar masses. We observed a linear growth if both polyelectrolytes are strong and an exponential growth if one polyelectrolyte is weak. The thickness increased with higher molar masses of the polyelectrolytes. The process was followed in-situ in short time steps.

Keywords: layer thickness; multilayers; polyelectrolyte adsorption; self-assembly; SPR; streaming potential

Introduction

Polyelectrolyte (PEL) multilayers are materials obtained by sequential adsorption of two or more polymers onto a substrate. The technique introduced by Decher [1] is based on the alternating dipping of the substrate into solutions of polyelectrolytes of opposite charge. The method is called “Electrostatic self-assembly“ [2] because the primary forces for layer formation are the electrostatic interactions between polyelectrolytes and the substrate. However, secondary shorter range forces also play a role in determining such important parameters like film thickness, film morphology, surface properties and in

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some cases, can even determine whether stable multilayers form at all.[3] Because of the versatility and simplicity of the technique, there has been a fast growth of publications in this area.[3, 4] The proposed applications for the so prepared novel materials range from sensors,[5] particularly biosensors,[6] light emitting diodes,[7] non linear optical devices[8] and perm selective gas membranes,[9] to controlled release micro-capsules[10] and bioactive surfaces for implants and tissue engineering.[11]

Most studies so far focused on the equilibrium properties and behavior of single component and mixtures of polyelectrolyte.[12-22] These types of studies are crucial in order to understand the thermodynamics involved, and to provide means for determining the amount of material adsorbed. As the adsorption process is mainly driven by electrostatic forces, the surface charge density and the net charge of the polyelectrolyte molecules play the dominant roles. Considering the system more in detail, the molecular structure of the surfaces,[22] as well as their composition and the nature of the exposed chemical functionalities come into play. Control of those details may offer opportunities for designing surfaces for special applications.

The need for characterization of polyelectrolyte layers has generated a broad band of modern analytical techniques (UV spectroscopy, SPR). Many analytical methods are useful for the characterization of PEL layers on smooth surfaces. The electrostatic interactions influence strongly the conformation of the adsorbed polyelectrolyte molecules. The interactions of the polyelectrolyte-coated substrates are determined by the layer structure, the distribution of the adsorbed segments and the electrostatic charge distribution. The characterization of the charge conditions of surfaces is possible with electrokinetic measurements.

Here we report the formation of some layer-by-layer thin films using PD as a strong cationic and PEI as a weak cationic polyelectrolyte and PSS as an anionic polyelectrolyte, in dependence on the molar mass on different substrates as followed by UV spectroscopy, streaming potential measurements, and in-situ surface plasmon resonance measurements (SPR).

Experimental part

Materials

The poly(sodium styrenesulfonate) (PSS) and poly ethyleneimine (PEI) were purchased from Aldrich and Sigma, respectively, and used without further purification. The PEI is a highly branched product. The polydiallyldimethylammonium chloride (PD) is a linear product. The synthesis of PD is reported by Jaeger et.al.[23] Polymers with high (h) and low (l) molecular masses were used as follows: PSS(l) with Mw of 70 000 g/mol, PSS(h) with 1 Mio g/mol, PEI with 75 000 g/mol, PD(l) with 5 000 g/mol, and PD(h) with 400 000 g/mol. The polyelectrolyte concentrations for the adsorption studies were always 10^{-2} M related to the repeat unit of the polymer.

Water purified and deionized (reverse osmosis followed by ion exchange and filtration) by means of Milli-RO 5Plus and Milli-Q Plus systems (Millipore GmbH, Germany) was used as a solvent.

The quartz plates (Spektrosil B, Thermal Quarz-Schmelze GmbH, Germany) for investigations in the UV range had the dimensions of 76 mm x 26 mm x 1 mm. The plates were thoroughly cleaned by a mixture of sulfuric acid with potassium dichromate at 80 °C for about two hours in an ultrasonic bath prior to the deposition of such films for UV measurements.

For some experiments (surface plasmon resonance), high refractive index glass slides SF10 (Hellma Optic GmbH, Germany) covered by a thin evaporated gold layer with the thickness of 50 nm were used as the supports for the multilayers.

UV Spectroscopy

Multilayers were deposited from initial concentration c_0 of the cationic polyelectrolyte of 10^{-2} M related to the repeat unit of the polymer. The pH value of the solution was about 6. Adsorptions were carried out at room temperature in open glass beakers of 100 mL without stirring for 20 min. After every deposition layer, the substrates were rinsed three times (1 min each) with Millipore Milli-Q water. The substrates were not dried between the adsorption steps.

Absorbance spectra of the dried films were measured by means of a Lambda 800 UV/VIS spectrometer (Perkin Elmer Ltd., USA). The multilayers were dried at room temperature in air atmosphere prior to the spectroscopic investigation.

Electrokinetic Measurements

The samples were prepared as those for UV spectroscopy. Electrokinetic measurements for the PEL layers were carried out by means of an Electrokinetic Analyzer device (A. Paar KG, Austria). The values of ζ-potential were calculated according to the formula:

$$\zeta = \frac{\eta}{\varepsilon_0 \varepsilon_r} \cdot \frac{\Delta U}{\Delta p} \cdot \kappa$$

where ΔU is streaming potential measured between two Ag/AgCl electrodes located at the opposite ends of the substrates, η, ε_r, κ are dynamic viscosity, relative dielectric permittivity, and conductivity of the flowing electrolyte solution (0.001 M KCl) respectively, ε_0 is dielectric permittivity of vacuum, and Δp is the pressure applied (150 mbar). The 0.1 M solutions of KOH and HCl were used to change pH of the flowing electrolyte solution in the range from 9 to 3.

Surface Plasmon Resonance

Surface plasmon resonance data for the layers were obtained by means of the equipment consisting of a He-Ne laser with $\lambda = 632.8$ nm (Uniphase, USA), a semi-cylinder made of SF10 glass, a liquid flow cell with the volume of 2.5 mL, and a E10V large area silicon photodiode detector with an integral preamplifier (Linus GmbH, Germany). The laser emitted polarized light (polarization ratio was 500:1) with power of 3 mW onto a semi-cylinder whose plane face was coupled, via index matching fluid, to the substrate examined (SF10 glass slide covered by the gold layer and then by the polyelectrolyte layers). The liquid flow cell was attached to the other side of the substrate and sealed with a rubber O-ring. The light was reflected onto the gold layer to excite surface plasmons. The intensity of the reflected light was measured by the photodiode. Both the semi-cylinder and the detector were mounted in an in-house $\theta/2\theta$ goniometer in such a way that the laser beam was incident on the detector at any angle of incidence. The goniometer and the photodiode were interfaced (MotionMaster 3000, Newport Corp., USA) to a personal computer. An in-house 32-bit software package was used for goniometer control, data acquisition, curve modeling, and curve fitting. For scans over a certain range of incidence angles, a step width of 0.1° was used. The curves obtained were fitted according to Fresnel's equations for a four-layer model (glass/metal/dielectric/surrounding medium).

Multilayers were adsorbed in the measurements cell, and the measurements were done in-situ after adsorption onto the gold-covered glass plate. A peristaltic pump was used to circulate the solutions with a speed of 10 mL per minute. First, a SPR scan with the slide rinsed in water was performed. The pH of the PEI solution was pH = 9, all other polyelectrolyte solutions had pH of 6.5. Then a polyelectrolyte double layer was adsorbed according to the following procedure: circulation of the polycation solution, rinsing with pure water, circulation of the polyanion through the cell, and rinsing with pure water again. Then a SPR scan was performed. The procedure was repeated for each double layer.

All measurements were made at room temperature.

Results and Discussion

The adsorption of a polyelectrolyte molecule is mainly driven by electrostatic attraction to an oppositely charged surface. The adsorbed amount at the fist adsorption step must be so high that a charge overcompensation takes place which allows for the adsorption of unlike charged polyelectrolytes in the second step. It was often found[24] that the amount of adsorbed charges per adsorption step is approximately twice as much as the charge of the surface, half of which is attracted by the surface, the other half is repelled and distributed in the proximity of the surface. The density profile in this range depends on the solvent conditions. Repeating the adsorption steps would thus result in a constant adsorbed amount in each adsorption step. This result was found for a number of different polyelectrolytes, adsorbed under different conditions and measured with different approaches, ex-situ as well as in-situ.[25-30]

The first parameter to analyze is the charge density of the substrate used. The analytical techniques used to characterize the PEL layers required different substrates: quartz for UV spectroscopy and glass covered with a thin gold layer for SPR. The charge densities were characterized by the zeta potential which was measured over a certain range of pH values. The dependence of the zeta potential on pH for glass modified with a thin gold layer, and quartz glass are shown in Figure 1. The intersections with the lines at the working pH values (9 for PEI and 6.5 for the other) give the zeta potentials at which the adsorption occurred. All zeta potentials are negative at the working pH values. Consequently, multilayer built-up should start with a polycation as the first layer. The zeta potentials of quartz are close together at both pH values (approximately 40 mV and 45 mV for pH 6.5 and 9, respectively). Evaporation of a thin gold layer shifts the zeta potential to 15 mV and 25 mV.

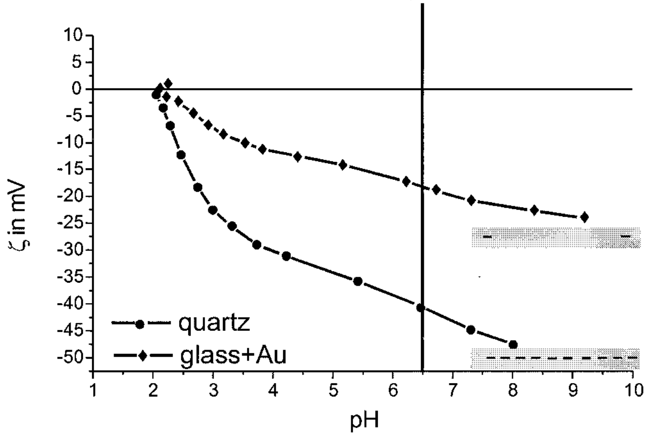

Figure 1. Dependence of zeta potential on pH for glass modified with a thin gold layer, and quartz glass.

First information on the multilayers, built up by the interaction between PD and PSS were obtained by the UV spectroscopy using the absorption band of PSS at 225 nm which is originated from the aromatic ring. As the commercial available branched PD types are known not to be suitable for the preparation of multilayers by the layer-by-layer adsorption technique, this special linear PD was tested for the preparation of multilayers. Figure 2 illustrates the absorbance of multilayers on quartz glass in dependence on the number of double layers. The absorbance is correlated to the adsorbed amount. The adsorbance for the low molecular mass polyelectrolytes as well as for those with high molecular mass increases with the number of double layers. It may be assumed from the linear rise of the adsorbance that the charge overcompensation in each adsorbed layer was approximately constant from the first layer.

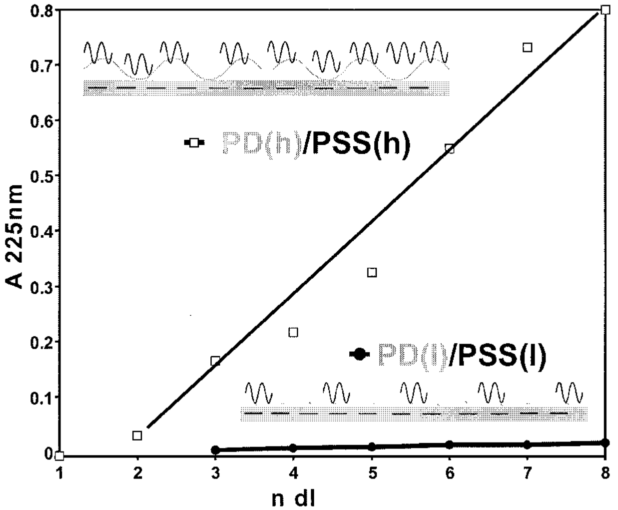

Figure 2. The absorbance of dried multilayers on quartz glass in dependence on the number of double layers for PD(l)/PSS(l) and PD(h)/PSS(h).

The adsorbed amount per double layer for the system PD(h)/PSS(h) is calculated to be 25 x 10^{-3} g/m^2, whereas this value for the system PD(l)/PSS(l) is only 0.5 x 10^{-3} g/m^2, 50 times lower. The molar masses of the polyelectrolytes thus have a big influence on the absolute amount of adsorbed material. However, the linear increase of the adsorbed amount with the number of double layers holds regardless of the molar masses. This linear increase was also found for the system PEI/PSS with the PEI solution adjusted to pH 3.

The SPR method allows to measure the amount of adsorbed material very sensitiv in-situ, taking into account any interaction with the aqueous phase, e.g. swelling. In the next section the system PD/PSS with different molar masses is investigated. The first steps of the adsorption of a multilayer were followed by a time dependent measurement at which the angle of incidence was fixed to 55.7 and the reflectivity was measured over the time. The angle of incidence was choosen so that the slope of the SPR curve in that angle range is almost linear. According to own model calculations, a small change of the reflectivity is then correlated to the adsorbed amount. The time dependent measurements in Figure 3 show a fast adsorption process for all polyelectrolytes. The adsorption process is finished after some seconds. The rinsing with water does not lead to a desorption and does not prevent the next adsorption step, pointing to a stable multilayer. The comparison of the time dependent measurements of the layers made from PD(l) and PSS with low and high molar mass shows that the adsorbed amount for PSS with a high molar mass is larger. However, the relation between the both values is much lower than that obtained for the system PD(h)/PSS(h). For both systems the adsorbed amounts for the polycation layers and for the polyanion layers are approximately equally large. The adsorbed amount of PEI in the first layer is much higher than that for PD(l). According to [24] it may be assumed that the adsorption is not only driven by electrostatics, but non-electrostatic forces are responsible for that behavior. This assumption was supported by Monte-Carlo simulations,[31] which shows a large increase of the amount of adsorbed polyelectrolyte chains in the first layer and a higher stability of the total multilayer if a non-electrostatic interaction parameter was

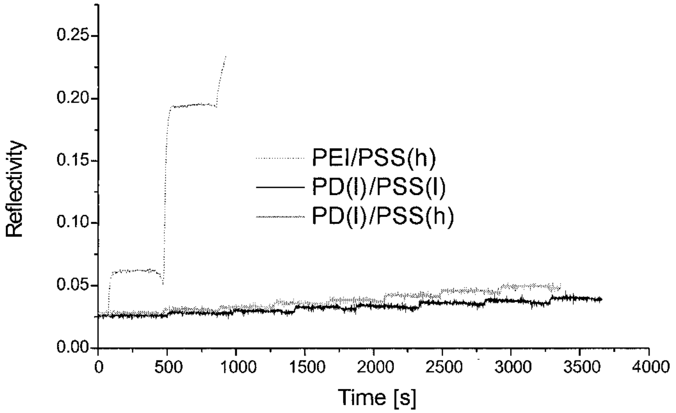

Figure 3. Time dependent measurements for multilayer systems of PEI/PSS(h), PD(l)/PSS(l) and PD(h)/PSS(h), angle of incidence 55.7°.

introduced for the polyelectrolyte in the first layer. In our experiments the adsorption of PEI in the first layer leads to a much higher compensation of the surface charge, which than supports an enhanced adsorption of the next layers. The high change in reflectivity in the time dependent measurement due to the adsorption of PSS points to an overcompensation, which is higher again. Since a time dependent measurement with those large reflectivity changes off the linear range cannot be correlated to the adsorbed amount, SPR scans were recorded for more detailed investigations of that system.

The SPR curve with pure water in the measurement cell is shown in Figure 4 a (most left line). The typical values of the best fit to the Fresnel's equations were: dielectic permitivity of the gold layer = -12 + 1.3*i, thickness = 50 nm. These values agree with other data in the literature.[5] Measurements were done after adsorption of each double

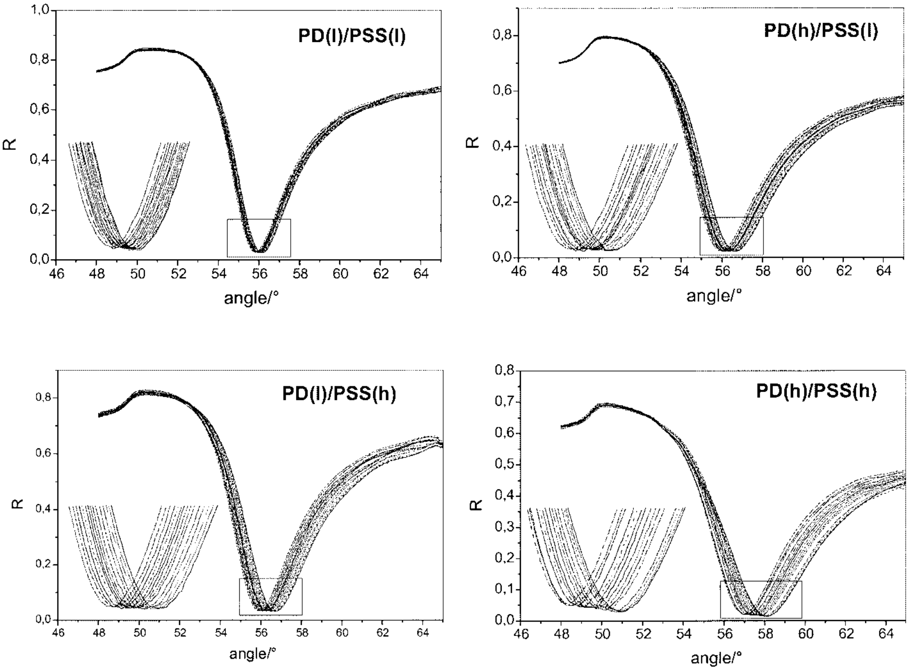

Figure 4. SPR curves measured after the adsorption of multilayers for the systems PD(l) or PD(h) and PSS(l) or PSS(h).
Shift of the SPR minimum to higher angle from 0 to 15 double layers in water.

layer. Each curve in Figure 4 a for the system PD(l)/PSS(l) exhibit a very small but significant shift of the SPR minimum (shown in the inset), whereas the angle of total reflection stayed at the same value. This demonstrates the reliability and sensitivity of the setup and allows for measuring of very small adsorption amounts. The thickness of this double layer was received as a result of the best fit of a four layer model to the data. Since it is not possible to fit the refractive index and the thickness at the same time under these conditions, the refractive index was fixed to be 1.5 for the fit of the thickness. This value is close to that measured for a series of polyelectrolyte multilayers with the Scanning Angle Reflectometry as an independent method. The refractive index determined with that method varied between 1.48 to 1.49.[18] The adsorbed amount is related to the optical parameters according to Feijters equation[33]

$$\Gamma = \frac{d * \Delta n}{\frac{dn}{dc}}$$

with thickness d, Δn = n(layer) - n(solution), refractive index n, and the refractive index increment dn/dc with c being the polyelectrolyte concentration of the solution. For the calculation of the adsorbed amount an average value of dn/dc = 0.18 ml*g^{-1} was used.

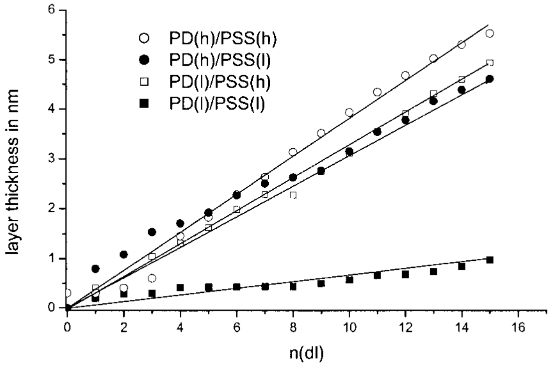

Figure 5. Layer thickness as a function of the number of double layers for the systems PD(l) or PD(h) and PSS(l) or PSS(h).

The resulting thicknesses, which obviously are averages over the beam spot, are presented as a function of the number of double layers in Figure 5. The multilayer thickness increases almost linearly with the number of double layers, the final thickness after 15 cycles being approximately 1 nm. This gives an averaged thickness per double layer of app. 0.07 nm or an adsorbed amount of $7*10^{-8}$ $g*m^{-2}$. The SPR curves of systems with PD(h) or PSS(h) exhibit larger shifts, see Figure 4 b-d. The resulting average thicknesses and adsorbed amounts per double layer are almost the same for all systems, 0.3 nm and $30*10^{-8}$ $g*m^{-2}$, respectively. The effect of the molar mass of PSS is almost negligible here. It should be remarked that the increase of the multilayer thickness is linear to the number of double layers for all the systems, as found for UV measurements. However, the absolute adsorbed amounts differ considerably between the SPR and the UV measurements. This may be attributed to the different processing conditions (stirring, dry, wet) and substrate surface charges.[34]

The SPR curves for the system PEI/PSS(l) measured after adsorption of each double layer are shown in Figure 6a. On a first glance the differences of the curves are considerably larger compared to the systems with PD as polycation, pointing to larger thicknesses of the multilayers with PEI as a polycation. This agrees with the observation of the reflectivity in Figure 3. At higher number of double layers not only the SPR minimum shifts but also the reflectivity at angles lower than the critical angle is reduced, whereas the critical angle was constant for all curves. This is in agreement with the model at large layer thickness. The fringes at higher angles are artifacts and stems from interferences as the beam spot becomes broad. The curves for the system with PSS(h) show an additional minimum in front of the critical angle, pointing to the exciting of waveguide modes. Exciting of waveguide modes is possible for large layer thicknesses if the layer is smooth and homogeneously. The fitted thicknesses are presented in Figure 7 as a function of the number of double layers. In contrast to the multilayers with PD as polycation, the increase of the layer thickness is not linear but exponential. The effect was not found for the system PEI/PSS on a fixed pH by UV measurements and for a similar system (poly(allylamine*HCl)/PSS(h))[18] although both polycations are weak. The thickness of the multilayer after 10 double layers is approximately 150 nm and 25 nm for PSS(h) and PSS(l) as polyanions, respectively.

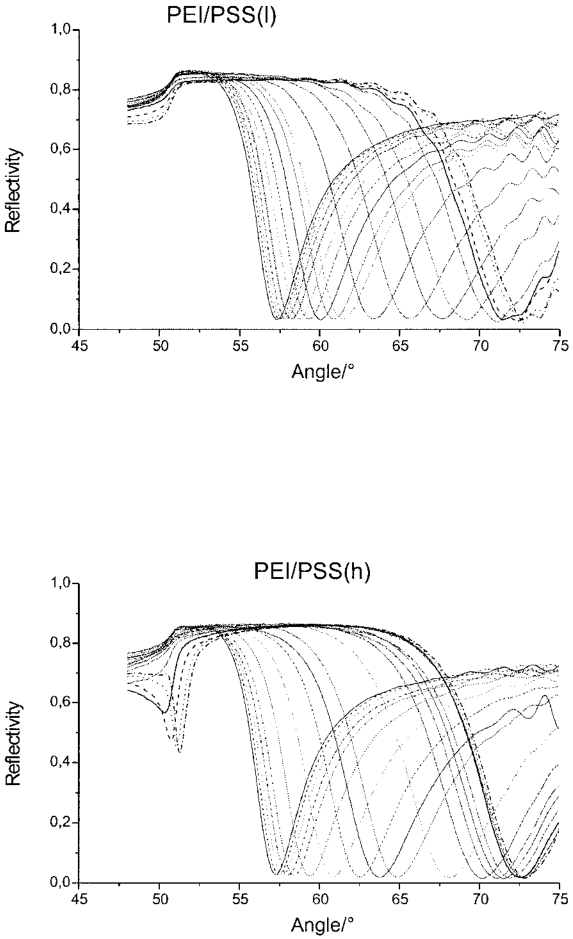

Figure 6. SPR curves measured after the adsorption of PEI/PSS(l) double layers. Shift of the SPR minimum to higher angle from 0 to 20 double layers in water.

Larger thicknesses could not be fitted satisfactory. The increase of the double layer thickness (adsorbed amount) was approximately 1 nm (10^{-6} g*m^{-2}) at the beginning and 100 nm (10^{-4} g*m^{-2}) for the 15th double layer for the system PEI/PSS(h). The lowest double layer thickness was even more than that in the systems with PD as polycation, even though the zeta potential of the substrate is smaller. The exponential increase of the double layer thickness points to an extended overcompensation of the charge of the underneath layer by the adsorbed double layer. This extension must increase itself after each double layer, and it may be caused by the change of the pH value from 6.5 to 9 on the change from the PSS to the PEI solution and vice versa. The protonization and, thus, the charge of PEI is higher at pH 6 than at pH 9. For PD and PEI the fraction of charges per repeat unit are approximately 1 and 0.36, respectively, whereas the value for PEI was measured at pH 9, and the value for PD is nearly independent of the pH value. The adsorbed amount may scale to the fraction of charges per chain f and the charge σ of the surface formed by adsorption of the previous layer approximately as $\Gamma \sim \sigma^* f^1$.[24] For PSS and PD the absolute σ and f are the same for every adsorption step. According to the model of the built-up of PEL multilayers explained above, half of the charges of every polycation molecule are complexed with the previously adsorbed polyanion, the other half forming the attractive force for the next layer and are exposed to the environment according to the solvent conditions.

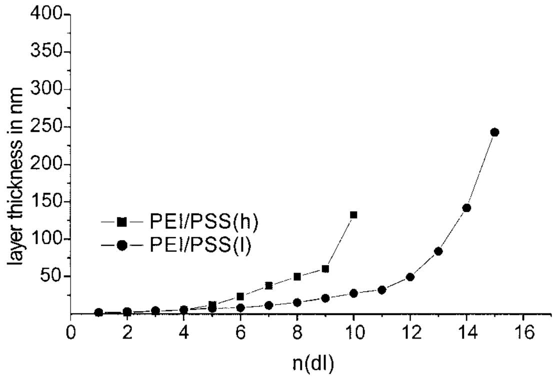

Figure 7. Fitted thickness as a function of the number of double layers for the systems PEI/PSS(l) and PEI/PSS(h).

In our experiments, however, the conditions are different, particularly due to the change of the polyelectrolyte charge density with the pH of the solution. A qualitativ approximation of the adsorbed amount Γ with the number n of double layers is given in this section. On the adsorption of PEI half of the available charges at pH 9 and the corresponding repeat units interact with the surface with charge σ and leads to an adsorption. Since f(PEI, pH 9) = f_A = 0.36, the adsorbed amount of repeat units is higher, the other repeat units being non-charged at pH 9. On adsorption of the next PSS layer the pH value has changed to 6.5, resulting in an increase of f of the adsorbed PEI layer to f(PEI, pH 6.5) = $f_B = z^* f_A$ with z being app. 1.5. This leads to an increase of the charge of the surface formed by the PEI layer to $z^*\sigma$, resulting in a high adsorbed amount of PSS, providing the multilayer is still stable. In the first double layer the adsorbed amount may be estimated roughly as

$$\Gamma_1 \sim \frac{\sigma}{f_A} + \frac{\sigma}{f_A},$$

where the left term is for the polycation layer and right term for the polyanion layer. Since f of PSS does not depend on pH the charge of the surface formed by the PSS layer is constant at pH 9, and the adsorbed amount of PEI increases compared to the previous PEI layer. On adsorption of PSS, again, the lower pH leads to a higher surface charge, resulting in a larger amount of adsorbed PSS. The adsorbed amount in the second layer is, thus,

$$\Gamma_2 \sim \frac{\sigma \cdot z_A}{f_A} + \frac{\sigma \cdot z_B}{f_A}.$$

This cycle is repeated on each adsorption step. The adsorbed amount in the ith layer is than, assuming $z_A = z_B$

$$\Gamma_i \sim \frac{2\sigma \cdot z^{i-1}}{f_A}.$$

After repeating the cycle n times the total adsorbed amount is

$$\Gamma_n \sim \frac{2\sigma}{z \cdot f_A \cdot \ln z}(z^n - 1)$$

for $z > 1$.

According to this rough model to Γ_n, which does not take into account any effects of solvatization, charge screening and non-uniform distribution of the adsorbed material in one layer, lg Γ is correlated to n. The correlations holds also if Γ scales as $\sigma^a * f^{-b}$ [35] with any a, b. As this was found experimentally for the multilayers with PEI, further detailed investigations will reveal the reasons for the unusual multilayer adsorption more precisely at different pH values and salt concentrations.

Conclusions

The adsorption of PEL multilayers from salt-free solutions was investigated by UV spectroscopy and SPR. These methods ensure a high sensitivity required for the small amounts of adsorbed material. The multilayers were built with PSS with different molar masses as polyanions. As polycations PD with different molar masses and PEI were used. Experiments with the strong polyelectrolytes exhibited a linear increase of the adsorbed amount with the number of double layers. The adsorbed amount per double layer was dependent on the substrate, the adsorption procedure and the molar masses. For the multilayers with PEI as polycation an exponential increase of the adsorbed amount with the number of double layers was found. This behavior was correlated to the charges of PEI at the different pH values of the solutions.

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