

# A $^1\text{H}$ NMR relaxation study of hydration water in polyelectrolyte mono and multilayers adsorbed to colloidal particles

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## Abstract

The adsorption of polyelectrolytes to charged surfaces can be applied to build up multilayers of polyelectrolytes of alternating charge by layer-by-layer assembly. Here, poly-(allylamine hydrochloride) (PAH) is adsorbed to colloidal latex particles in aqueous solution, and to particles precoated with four layers of polyelectrolytes. The method of  $^1\text{H}$  NMR transverse relaxation is applied to monitor the hydration water in such layers, where relaxation rates  $R_2$  serve as a parameter describing the average immobilisation of water molecules. Electrophoretic and relaxation measurements are performed as a function of polymer coverage, surface precoating and salt content in the solution. While the zeta-potential increases monotonously with initial polymer concentration due to a charge reversal from a negatively to a positively charged surface, pronounced structures occur in the  $R_2$  curve for monolayers, which are attributed to the contributions arising from different water populations. For adsorption to multilayers, the electrophoretic curves are shifted to higher concentrations, and relaxation rates show an unexpectedly high water immobilisation. The electrophoretic and relaxation data are consistent with a molecular picture of rodlike chains in the absence of salt, and a coil shaped structure for adsorption from salt solution. In both cases, the properties of the fifth layer differ significantly from the first one, this is attributed to the entanglement of adsorbing chains in the precoated layers, leading to larger adsorbed amounts. © 2002 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The adsorption of polyelectrolytes to charged surfaces is a process of high relevance to applica-

tions requiring surface modification. In recent years, this has opened up a field of materials design, since self-assembly processes involving electrostatic interactions have been used in order to build up multilayers of polyelectrolytes of alternating charge [1–3]. Multilayer formation has not only been achieved by adsorption to planar substrates, but even to colloidal particles [4], which offers the possibility for investigations requiring a

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large internal surface area, such as NMR methods.

On planar substrates structural parameters like surface coverage, layer thickness etc. have been extensively characterised for mono or multilayers see e.g. [5–7]. The internal dynamics and the electrostatic coupling are of increasing interest, since these properties are determining the coupling strength between subsequent layers. The electrostatic interaction depends on the local dielectric properties, thus the local solvent environment and the degree of hydration of the layer are expected to have a substantial influence on the dynamics and stability.

In this work, we thus investigate the hydration water in polyelectrolyte mono- and multilayers. The polyelectrolytes are adsorbed to colloidal particles in aqueous or salt solution, and the  $^1\text{H}$  NMR relaxation rate of the water protons is determined in dependence of polymer surface coverage and preparation conditions. The relaxation of the solvent in colloidal dispersions is increased by solvent immobilisation in surface layers, and thus monitors the amount and motional dynamics of solvent molecules at the surface. The method of solvent relaxation in colloidal dispersions has been introduced by van der Beek et al., who studied the hydration water in a PDMS monolayer adsorbed to colloidal silica [8]. Solvent relaxation was further applied to investigate the physisorption of proteins [9], and of anionic polyelectrolytes to latex particles [10].

The aim of our work is to make use of the potential of this method to study the adsorption of polyelectrolytes to colloids, and for the first time apply it to multilayers to investigate their hydration in order to understand details of multilayer formation.

## 2. Materials and methods

### 2.1. Materials

Poly(allylamine hydrochloride) (PAH),  $M_w = 70.000$ , and Poly(sodium 4-styrenesulfate) (PSS),  $M_w = 70.000$  are purchased from Aldrich. PAH is used without further purification, while PSS is

dialysed ( $M_w$  cut-off 14.000) against Seradest water before use. Negatively charged sulphate-stabilised polystyrene latex nanoparticles (PS) (diameter 466 nm as determined from TEM, charge density =  $6.2 \mu\text{C cm}^{-2}$ ) are prepared in a surfactant-free synthesis [11]. Sodium chloride (NaCl) (AR grade) is obtained from Merck. The water used in all experiments is prepared in a Seradest USF 800 water purification system and has a resistance higher than  $18.2 \text{ M}\Omega \text{ cm}$ . The polymers are dissolved in  $\text{H}_2\text{O}$  without any adjustment or change of pH.

### 2.2. Sample preparation

The polyelectrolyte multilayer assembly is accomplished by adsorption from polyelectrolyte solutions of concentrations far above the saturation of the surface. Adsorption and subsequent washing cycles are carried out with the method of ultra-membrane pressure filtration [12]: The concentration of the polystyrene latex suspensions is kept low (about 1–3 vol.%) to reduce bridging coagulation to a minimum while coating. The ionic strength of the polymer solution is adjusted to be suitable for multilayer formation (0.25 M NaCl). The positively charged polyelectrolyte PAH is allowed to adsorb to the negatively charged polystyrene particles for 20 min under occasional stirring. As filter material polyamide with a pore size of 450 nm in diameter is used. Three washing cycles are carried out to ensure removal of free polyelectrolyte between coating subsequent layers. The procedure is repeated with PSS and PAH to obtain alternating layers, until a total of four monolayers is deposited.

In order to perform comparable relaxation experiments the particle concentration in each sample has to be identical. Particle concentrations of bare and coated particle suspensions used as stock solutions are determined both gravimetrically and by Single Particle Light Scattering (SPLS) [13]. Samples are prepared from a fixed volume of stock solution, to which the same volume of polyelectrolyte solutions of varying concentration is added. The polyelectrolyte is allowed to adsorb to the particles for at least 20 min followed by gentle shaking, and NMR measurements are then performed without further washing.

### 2.3. Zeta-potentials

$\zeta$ -potentials of freshly prepared dispersions are determined after further dilution. The electrophoretic mobility of bare, coated and partially coated PS latex particles is measured using a Malvern Zetasizer 4. The mobility  $\mu$  is converted into a  $\zeta$ -potential using the Smoluchowski relation  $\zeta = \mu\eta/\epsilon$ , where  $\eta$  and  $\epsilon$  are the viscosity and dielectric constant of the solvent, respectively.

### 2.4. NMR experiments

For all experiments a Bruker 400 MHz Avance spectrometer is used. The sample volume is adjusted to match the internal volume of the RF coil to avoid artefacts.

For determination of the relaxation time  $T_2$  the Carr–Purcell–Meiboom–Gill (CPMG) sequence, described as  $d1 - 90_x^\circ - (d2 - 180_{x'}^\circ - )_n$ , is applied [14,15]. The  $90^\circ$  pulse length is 14.2  $\mu$ s, the delay  $d2$  is 10 ms, and the sample temperature is set to  $25.0 \pm 0.3$  °C. Relaxation rates are evaluated from the integral of the  $H_2O$  signal by a monoexponential fit of the echo decay. In all experiments it is confirmed that the fits result in the same  $R_2$  value as those evaluated from the intensity of the  $H_2O$  signal.

## 3. Theoretical basis of NMR solvent relaxation

In heterogeneous systems molecules can often occupy different sites with different properties, such as for example free molecules as opposed to bound sites in a colloidal particle sample. In such cases the parameters measured by NMR depend on the time scale of the exchange of molecules between the sites,  $\tau_{ex}$ , with respect to the time scale of the experiment. The time scale of exchange is often determined by the diffusion coefficient of the molecular species: Polyelectrolytes exhibit slow adsorption/desorption kinetics [16], and are irreversibly bound to charged surfaces, thus bound and free polymers are in slow exchange. Surfactants exhibit faster exchange dynamics, and are found to be in intermediate exchange for a diffusion experiment with  $\tau_{ex}$  on

the order of 10 ms [17]. Small solvent molecules have even faster adsorption dynamics, determined by the fast diffusion and low binding energy, thus their exchange time scale at a surface is usually fast compared with any experimental NMR time scale [18]. In this regime of ‘fast exchange’ the relaxation rates of molecules in two sites are averaged quantities, weighted by the fractions  $f_A$ ,  $f_B$  of molecules in the respective site A or B [19]:

$$R_2 = f_A R_{2A} + f_B R_{2B} \quad (1)$$

Relaxation measurements of water in heterogeneous samples containing several sites thus are expected to exhibit one relaxation rate only. In agreement with fast exchange, for all samples investigated in this work, a monoexponential decay of the echo is observed.

To facilitate the evaluation of relaxation rates in composite systems, a specific relaxation rate  $R_{2sp}$ , normalised on  $R_2^0$  of free water, has been introduced [8], and is defined as:

$$R_{2sp} = \left( \frac{R_2 - R_2^0}{R_2^0} \right) \quad (2)$$

$R_{2sp}$  monitors the relative change of the relaxation rate due to the presence of water binding sites. It can be shown that  $R_{2sp}$  is an additive quantity in samples containing several water binding components. In adsorption samples, the quantity  $\Delta R_{2sp}$  is calculated from the experimentally determined  $R_{2sp}$  by:

$$\Delta R_{2sp} = R_{2sp} - (R_{2sp}^{CP} + R_{2sp}^{Pol}) \quad (3)$$

Here, the water immobilisation of a noninteracting system, given by the specific relaxation rates of the particle solution,  $R_{2sp}^{CP}$ , and of the polymer solution,  $R_{2sp}^{Pol}$ , is subtracted.

Throughout this paper, we consider  $R_{2sp}$  as a measure of water immobilisation, as reflected by the quantities  $fR_2$ . The term immobilisation will thus refer to either an increasing amount of immobilised water,  $f$ , or further reduced dynamics of a fixed fraction of water, as monitored by  $R_2$ . Both effects can not be separated in the relaxation measurement. Additional effects such as relaxation induced by diffusion close to susceptibility discontinuities, or cross relaxation can further increase the relaxation rate, but are here in a first

approximation assumed to be compensated by the subtraction in Eq. (3).

#### 4. Results and discussion

In order to investigate the immobilisation of water in adsorption layers, the effect of water binding to either particles or polymers in solution has to be considered. As reference data, relaxation measurements of binary systems of particles in water ( $R_{2sp}^{CP}$ ), and polymer solutions ( $R_{2sp}^{Pol}$ ) are performed. Fig. 1 gives the results of relaxation measurements on solutions of latex particles in  $H_2O$  and 0.25 M NaCl solution, respectively, at varying particle concentration. The specific relaxation rates scale approximately linearly with surface area. This is reflecting the increase of the fraction of water bound to the particle surface,  $f_B$ , with surface area, which is linear. Stabilising charges on the latex surface attract a hydration shell of ordered water. This fraction of water exhibits a reduced mobility, and the increased rotational correlation time leads to an increased

relaxation rate. In the presence of salt  $R_2^0$  is increasing from 0.50 Hz for pure water to 0.53 Hz in 0.25 M NaCl.  $R_{2sp}$  values of particle solutions containing salt are normalised to the  $R_{2sp}^0$  value of the salt solution. The increase of  $R_{2sp}$  observed for particles in salt solution is larger than in aqueous solution. Sodium ions form a screening layer around the particle, where obviously the water immobilisation, as monitored by the product  $f_B R_{2B}$ , is increased as compared with unscreened charges.

In polymer solutions the water relaxation rate is increasing with concentration in a similar way, as shown in Fig. 2. At polymer concentrations below about  $0.5 \text{ mg ml}^{-1}$  the increase is linear within experimental error (detailed data not shown), corresponding to the linear increase of the fraction of water bound to noninteracting polymer coils. At higher concentrations, especially above the overlap concentration ( $c^*$  estimated to about  $3 \text{ mg ml}^{-1}$ ) deviations from the linear behaviour are occurring due to structural changes in the polymer solutions. Generally,  $R_{2sp}$  reaches rather large values as compared with the particle solutions:

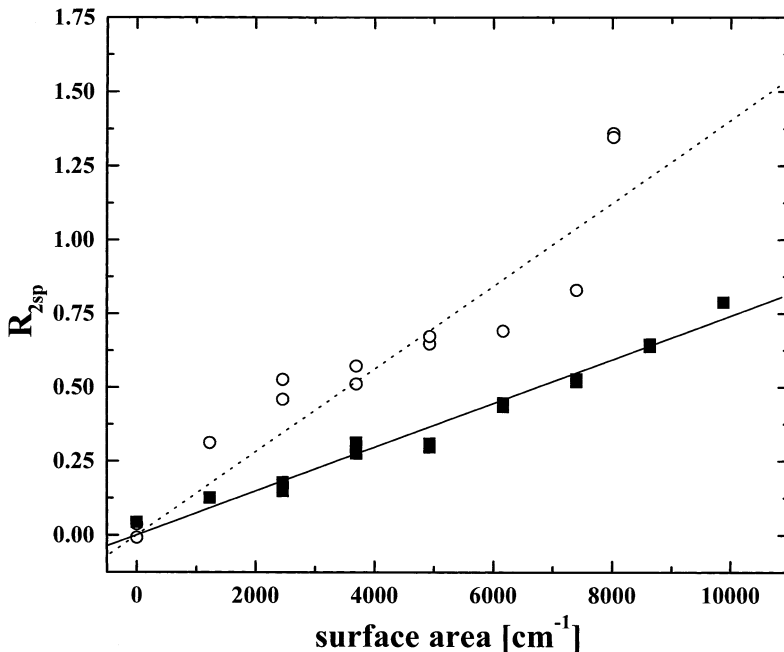


Fig. 1.  $R_{2sp}$  of particle solutions. Filled symbols/straight line: in water, open symbols/dotted line: in 0.25 M NaCl. The lines are linear fits of the data.

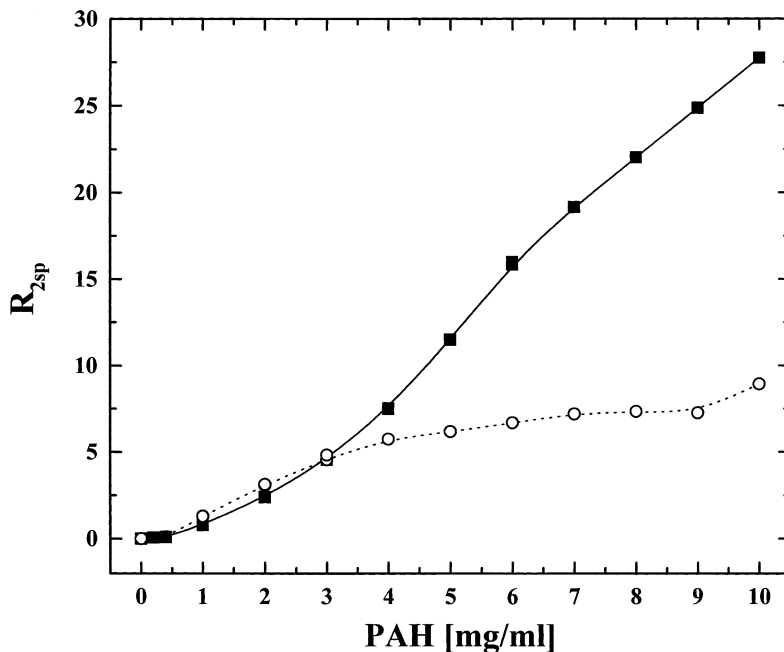


Fig. 2.  $R_{2sp}$  of polymer solutions: Filled symbols/straight line: PAH in H<sub>2</sub>O, open symbols/dotted line: PAH in 0.25 M NaCl. The lines are guides to the eye.

Due to the chemical equilibrium between the protonated and unprotonated amino group of PAH, this polyelectrolyte contains exchangeable protons at its nitrogen atom, and these contribute to  $R_{2sp}$  of water protons. The relaxation rate of covalently bound protons is much larger than that of the water protons in the hydration shell of a charged polymer segment, since the rotational mobility is significantly reduced, and cross-relaxation can further enhance  $R_{2sp}$ . Thus the exchangeable protons deliver a substantial contribution to  $R_{2sp}$ , and lead to  $R_{2sp}$  values, which are large compared with those determined for water in polystyrene sulfonate solutions [10].

The increase of the slope of  $R_{2sp}$  for PAH in water at high concentrations probably arises from a reduced mobility of the polymer backbone, induced by chain entanglements, which is reducing the motion of exchanging water protons. The addition of salt to PAH solutions leads to no differences at low polymer concentrations below the overlap, but to a less pronounced increase of  $R_{2sp}$  at high concentrations. Due to electrostatic screening PAH in salt solution forms coils with a

smaller radius of gyration, which might account for a larger mobility of the polymer at high concentrations. Additionally, at high polymer concentrations, changes of the equilibrium of dissociation will have an influence on both  $R_{2sp}$  curves, since the fraction of covalently bound protons is changing.

The polymer concentrations used for adsorption samples are in the range of  $c < 0.5 \text{ mg ml}^{-1}$ .  $R_{2sp}^{\text{Pol}}$  values of polymer solutions are evaluated from a linear interpolation of the curves in Fig. 2 at low concentration.

The adsorption of PAH to polystyrene latex particles is monitored by electrophoretic measurements and relaxation rates in samples of fixed particle concentration (4% wt., corresponding to about  $4900 \text{ cm}^{-1}$  surface area per volume) and varying polymer concentration. The zeta-potential (see Fig. 3) is negative for uncoated particles, due to the negative stabilisation charges. On addition of positively charged polymer, the zeta-potential is monotonously increasing with increasing polymer concentration. The increase is finally resulting in a charge reversal and a plateau when the

surface is saturated with polymer. The zeta-potential is thus monitoring the adsorption process in a qualitative way.

In Fig. 4, the horizontal line marks  $\Delta R_{2sp} = 0$ , which is corresponding to a noninteracting system, where  $R_{2sp}$  would equal the sum of the values for the particle solution and the polymer solution at the respective concentrations, as determined from Figs. 1 and 2. Any deviation from this line arises from differences in the water immobilisation due to polymer-particle interactions. In water as well as in salt solution, a decrease of  $\Delta R_{2sp}$  is observed with increasing polymer concentration, followed by a maximum and a further decrease at higher PAH concentrations. Finally, around the saturation level detected by the zeta-potential measurement,  $\Delta R_{2sp}$  forms a plateau, since further added polymer does not interact with the particles and, therefore, does not cause further deviations from zero. For the salt free solution, the results point at a net increase of mobility of water due to adsorption (filled symbols).

The open symbols in Figs. 3 and 4 show the same experiments for the adsorption of PAH from a 0.25 M NaCl solution. The presence of salt is causing no significant difference in the shape of the zeta potential curve. Similarly, the relaxation rate curve has the same structure at low polymer concentrations as compared with adsorption from water solution. At high polymer concentrations, a plateau is formed as well, however, in salt solution the plateau value is at positive  $\Delta R_{2sp}$ , indicating a net decrease of water mobility.

The structure of the  $R_{2sp}$  curves in dependence of polymer concentration can be interpreted taking into account the contributions of water in different sites. The water fractions which contribute to  $R_{2sp}$  in samples containing polymers and particles, are the following (see Fig. 5):  $f_A$ : free water,  $f_B$ : water bound to the particle surface (hydration shell of the stabilisation charges),  $f_C$ : water bound to free excess polymer in solution,  $f_D$ : hydration water in an adsorbed polymer layer.

Starting from the zero value at zero polymer concentration,  $\Delta R_{2sp}$  is first decreasing. At this

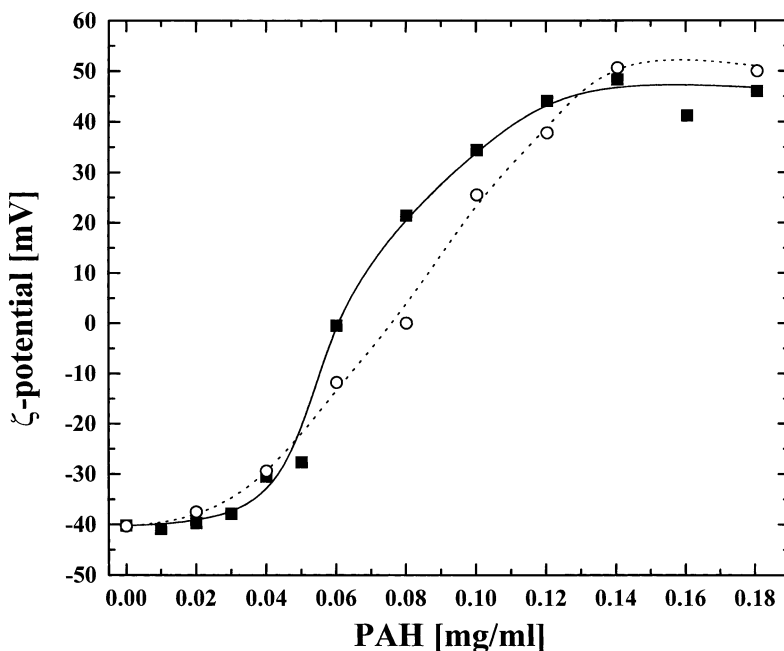


Fig. 3. Zeta-potential of particles coated with PAH at varying polymer concentration: Filled symbols/straight line: in H<sub>2</sub>O, open symbols/dotted line: in 0.25 M NaCl. The particle concentration before dilution prior to the electrophoretic measurement is 4% wt (about 4900 cm<sup>-1</sup> surface area per volume). The lines are guides to the eye.

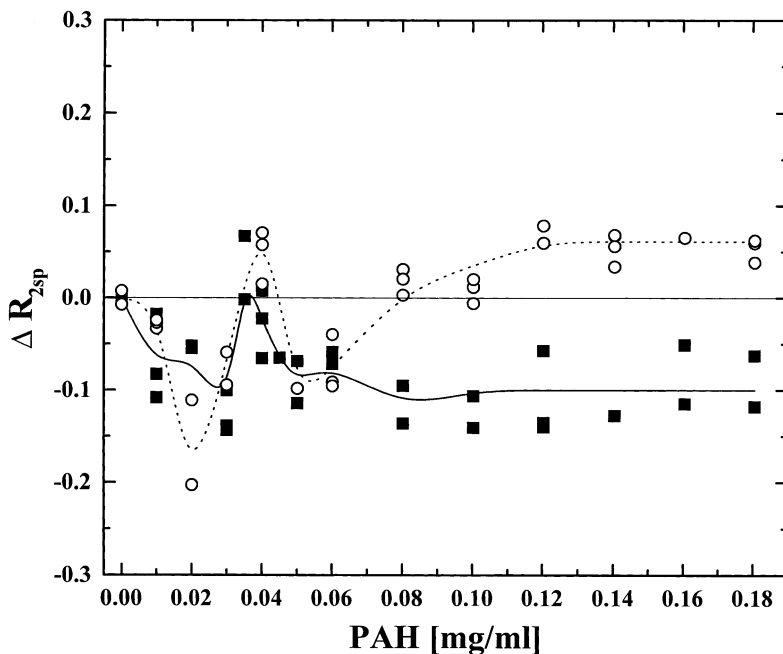


Fig. 4.  $\Delta R_{2sp}$  of the adsorption of a 1st layer to latex particles. Filled symbols: PAH in  $H_2O$ , open symbols: PAH in 0.25 M NaCl. The particle concentration is 4% wt. (about  $4900 \text{ cm}^{-1}$  surface area). The lines are guides to the eye.

low polymer amount the dominant effect which the interaction of polymer and particles has on the water mobility is the replacement of surface bound water molecules by polymer segments. This leads to a decrease of  $f_B$  and an increase of  $f_A$ . Since it is  $R_{2B} > R_{2A}$ , the result is a net decrease of  $R_{2sp}$ , reflecting a net ‘mobilisation’ of water. Simultaneously, however, an immobilisation of water is expected to take place, since the motional dynamics of adsorbing polymer chains are changing. This is causing an increase of the relaxation rate of the hydration water of the polymer as it is adsorbed, or, in other terms, an increase of  $f_D$  while  $f_C$  is decreasing. In a first approximation the immobilisation should scale linearly with the adsorbed amount of polymer, assuming that the hydration of adsorbed and free chains is identical. This immobilisation is starting to compensate the decrease of  $f_B$  at a coverage where additional polymer segments adsorbing do not release further water from site B. In the case of adsorption from water solution (filled symbols in Fig. 4), the net effect at high coverage is an increase of water mobility, while in the presence of salt the contri-

bution from  $f_D$  is overcompensating that of water release from the particle surface. This result is consistent with the formation of a layer of higher thickness in the presence of salt.

Additional contributions to  $\Delta R_{2sp}$  can arise from an increase of the polymer density in the layer with increasing coverage, leading to an increased net water mobility due to release of a fraction of the water from the layer. Such effects might account for the decrease of  $\Delta R_{2sp}$  observed

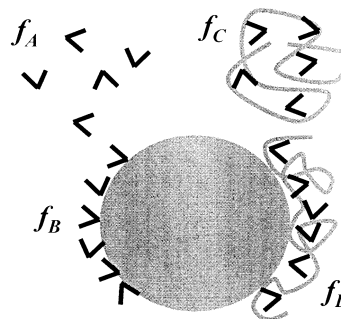


Fig. 5. Scheme defining the sites of water molecules contributing to the relaxation rate.

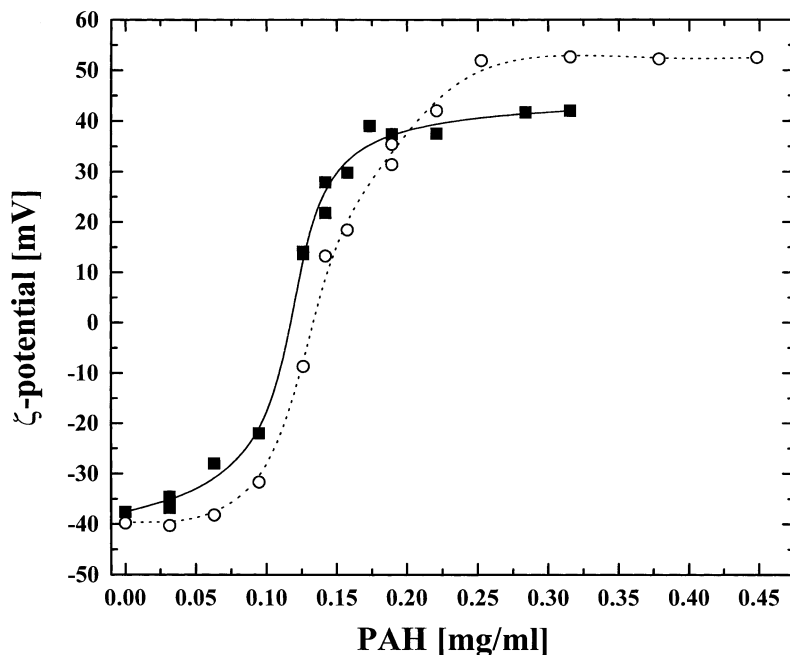


Fig. 6. Zeta-potential of particles precoated with four polyelectrolyte layers at varying coverage of PAH (5th layer): Filled symbols: in H<sub>2</sub>O, open symbols: in 0.25 M NaCl. Samples are initially prepared at a particle concentration of 2% wt. and the data have been rescaled to 4% wt. to facilitate comparison with Fig. 3. The lines are guides to the eye.

after the maximum at about  $0.04 \text{ mg ml}^{-1}$ . On the other hand, in this region of rather low surface coverage a polymer chain might be attracted by different particles, leading to bridging flocculation. This would cause water immobilisation due to a strong motional restriction of water molecules bound to bridging polymer chains. Assuming that bridging occurs in a narrow concentration regime, it might account for the formation of a maximum in  $\Delta R_{2\text{sp}}$ .

In their relaxation study of NaPSS on cationic polystyrene particles, Cosgrove et al. observe a plateau of  $\Delta R_{2\text{sp}}$  indicating net water immobilisation at high coverage as well, and a very pronounced maximum at low concentration [10]. In their system, however, the maximum is clearly attributed to bridging, since the particle concentration is much higher than in the present investigation.

It is interesting to note that both plateaus in Fig. 4 are reached already in the region of charge reversal (compare to Fig. 3). From scaling theory [20], a picture has been put forward where the

polymer is adsorbing in a flat configuration, with different chains overlapping to form a 2D network. Within such a model, our data imply that the addition of further chains does not change the hydration water properties in the network layer, once charge reversal is achieved. The addition of polymer after charge reversal probably leads to a closer packing within the adsorption layer, such that the immobilisation of the hydration water of additional chains, which would cause an increase of  $\Delta R_{2\text{sp}}$  can be compensated by a release of water from the layer.

The adsorption of a layer of PAH onto multi-layers of PAH/PSS on colloidal particles has been followed in a similar way. Relaxation measurements are performed on solutions containing 2% wt. particles, but the data are rescaled to 4% wt. solutions to be comparable to the data shown above. Figs. 6 and 7 give the results for the adsorption from aqueous solution and salt solution. Zeta potential curves are similar to those in Fig. 3, however, charge reversal is achieved only at higher polymer concentrations. The plateau

values of  $\zeta$  reached in saturation are similar to those of the first layer. Close to saturation, the positive potential is preventing the adsorption of further chains, since it is forming a potential barrier. Saturation is, therefore, achieved at the same potential values for the first and fifth layer. In the presence of salt, however, the outer layer charge is screened, leading to saturation at higher zeta-potential values.

The specific relaxation rates differ significantly from those of Fig. 4: For the 5th layer, no minimum at low polymer concentrations is observed, but a monotonous increase of  $\Delta R_{2sp}$ , which reaches a plateau at rather high positive values (observe even the different scales of  $\Delta R_{2sp}$  in Figs. 4 and 7). It should be noted that the  $\Delta R_{2sp}$  values in Fig. 7 reflect water immobilisation due to the addition of the 5th layer only, and do not contain contributions from water immobilised in the layers beneath, since the particles coated with four layers are considered as reference system to calculate  $\Delta R_{2sp}$  from  $R_{2sp}^{CP}$ . This demonstrates a much larger net water immobilisation of the 5th layer as

compared with the first. Part of this difference can be attributed to the fact that no contribution of water release from the particle surface occurs for the 5th layer. The following estimate quantifies this contribution: Assuming that both layers, first and fifth, are identical in their structure and hydration properties, the difference of the plateau values  $\Delta R(\text{Surf}) = \Delta R_{2sp}(5\text{th}) - \Delta R_{2sp}(1^{\text{st}})$  should account for the contribution of water released from the particle surface. It is  $\Delta R(\text{Surf}) = 2.30$  and 2.54 without and with salt, respectively. The water immobilisation in the uncoated particle solution, however, only leads to  $R_{2sp} = 0.36$  and 0.69, respectively (taken from Fig. 1). Therefore, the difference in the plateau values of  $\Delta R_{2sp}$  can not be attributed to the contribution from particle bound water. Furthermore, neither the slightly increased surface area of pre-coated particles (about 7%) at identical latex weight fraction, nor the small change of the curvature can account for the difference in  $\Delta R_{2sp}$  between the first and the fifth layer. It thus has to be concluded that the 5th layer (a) either has a significantly larger hydration

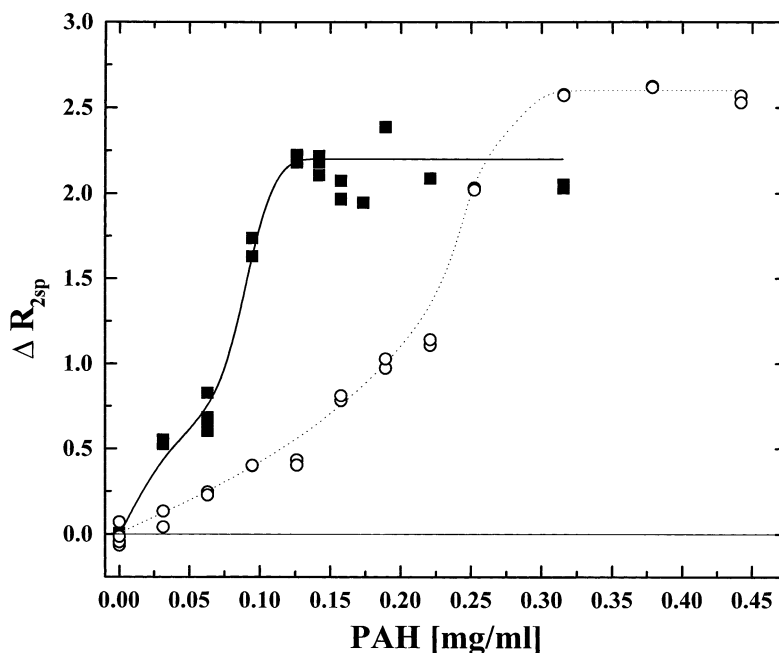


Fig. 7.  $\Delta R_{2sp}$  of the adsorption of a 5th layer to pre-coated latex particles: Filled symbols: PAH in H<sub>2</sub>O, open symbols: PAH in 0.25 M NaCl. Samples are initially prepared at a particle concentration of 2% wt. and the data have been rescaled to 4% wt. to facilitate comparison with Fig. 4. The lines are guides to the eye.

Table 1

Polymer concentration required to achieve charge reversal ( $\zeta = 0$ ), the onset of saturation of the  $\zeta$ -potential and of the relaxation rate, respectively; and  $\Delta R_{2sp}$  saturation value

	$c$ ( $\zeta = 0$ ) (mg ml <sup>-1</sup> )	$c$ ( $\zeta$ -saturation) (mg ml <sup>-1</sup> )	$c$ ( $\Delta R_{2sp}$ -sat.) (mg ml <sup>-1</sup> )	$\Delta R_{2sp}$ (in plateau)
PAH, 1st layer	0.06	0.12	0.08	-0.1
PAH, 1st layer in salt	0.08	0.14	0.12	0.06
PAH, 5th layer	0.12	0.18	0.12	2.2
PAH, 5th layer in salt	0.13	0.25	0.28	2.6

as compared with the first one, or (b) is strongly influencing the hydration of the precoated layers. In case (a), a possible molecular picture is the formation of a very flat first layer, and a significantly larger roughness and/or thickness of the fifth layer. For the adsorption of the first layer, the hydrophobic interaction with the latex particle probably plays a role and induces a flat adsorption, since the interaction of the hydrophobic polymer backbone with the hydrophobic regions of the particle surface is favoured over interactions with water. In contrast to the assumption of different thicknesses, SPLS measurements result in a linear increase of total layer thickness with increasing number of double layers, however, the method is not sensitive enough to resolve any thickness differences between the first and subsequent layers. The scenario (b) would imply an increased immobilisation of water in the precoated layers, i.e. either an increase of the amount or relaxation rate, induced by adsorption of the 5th layer. As dominant effect, however, rather a decrease of the water amount due to charge complexation would be expected. Though in principle processes leading to an increased water immobilisation are possible, at the current stage they are too complex to be discussed on the basis of the current data and remain the subject of further investigations.

The picture of a higher surface coverage of the fifth layer is not only put forward by the large water content, but additionally supported by the fact that charge reversal and the onset of saturation require a higher polymer concentration as compared with the first layer (see Table 1). The concentration data in Table 1 reveal further details in the formation of the first and the fifth

layer in H<sub>2</sub>O: While  $\zeta = 0$  is reached at half the saturation concentration ( $c_0 = 0.06$  mg ml<sup>-1</sup>) for the first layer, a larger amount of polymer is needed to achieve  $\zeta = 0$  in the fifth layer (0.12 mg ml<sup>-1</sup>), while the concentration difference required to reach saturation from the point of charge reversal is identical. It is interesting to note that this does not correspond to a stretching of the zeta-potential curve due to a higher adsorbed amount, but to a shift of the curve to higher concentrations. It appears that about the first third of polymer chains of the fifth layer is needed to compensate charges located deeply within the fourth layer (see Fig. 8), and thus does not significantly change  $\zeta$ , which is defined at the shear plane, i.e. far outside the adsorption layer. A strong intercalation of subsequent layers had been proved for planar multilayers as well by neutron reflectivity [6].

Contrary to this, in the presence of salt the  $\zeta$ -potential curves of the first and fifth layer can be identified rather by a stretching than a shift in

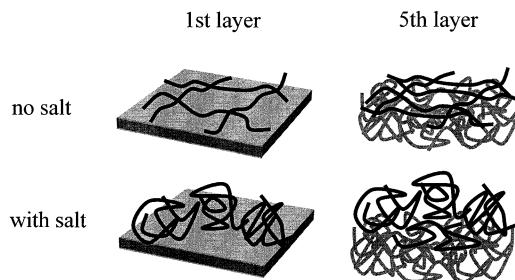


Fig. 8. Sketch of the structure of PAH in adsorbed layers: Flat adsorption from water solution and coil-shaped adsorption from salt solution. Intercalation into precoated layers in the case of the fifth layer leads to a higher surface coverage.

polymer concentration, with  $c$  ( $\zeta = 0$ ) amounting to around half the concentration required for saturation in both cases. Such a picture would be expected for the adsorption of a monolayer of globular coils rather than a network of overlapping rods, since the surface charge would scale with the fraction of surface covered by polymer coils (see Fig. 8). It is reasonable that the polymer should adsorb in a coil-like geometry from salt solution, since the hydrodynamic radius is smaller due to electrostatic screening, and it has been argued before for planar layer systems, that with increasing salt content a transition from adsorbed rods to coils occurs [21]. Further support of a lateral arrangement of coils in the case of adsorption from salt solution is obtained from the fact that the saturation concentrations of the zeta-potential and the relaxation rate are similar. Thus even close to saturation, additional adsorbing chains add immobilised water to the layer, since they adsorb to previously uncovered parts of the surface. In contrast to this, on adsorption without salt, saturation of the relaxation rate is achieved at a lower coverage than saturation of zeta (see Table 1). This can be understood in terms of an increase of polymer density within the layer at a constant water immobilisation value, i.e. further adsorbing rods can intercalate into the outer layer in such a way that no additional water is immobilised. Fig. 8 gives a simple model of the polymer configuration in adsorption layers in dependence of the surface properties and the salt content. In both cases, for the first as well as the fifth layer, the water immobilisation and probably the final thickness of the layer are determined already around the point of charge reversal, as we had discussed above for the case of the first layer.

## 5. Conclusions

We have demonstrated here, that solvent relaxation, which had so far been applied to simple polymer adsorption layers, is a suitable tool to resolve details of the adsorption process in complex processes such as multilayer formation. The molecular picture suggested is a network of overlapping rods in the case of adsorption from water

solution, which is very flat for the first layer and partly intercalates with the precoated layers in the case of the fifth layer, leading to a larger adsorbed polymer amount and a surprisingly high water immobilisation.

On adsorption from salt solution, the results point at the formation of a layer of laterally organised coils, where again for the fifth layer the surface coverage and the water content are much larger than for the first layer. The details resolved here for layers on colloidal particles are consistent with previous results on the structure of multilayers on planar support.

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