Acid−Base Equilibria of Weak Polyelectrolytes in Multilayer Thin Films

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Received September 2, 2002. In Final Form: January 17, 2003

In this paper, we report on the local apparent dissociation constants of poly(acrylic acid) and poly(allylamine hydrochloride) incorporated in polyelectrolyte multilayer thin films. We assembled 10 polyelectrolyte layers on colloidal silica by the sequential electrostatic adsorption of the polyacid and polybase from aqueous solutions at different pH values and then measured the zeta potential as a function of the solution pH to determine the $pK_{a(app)}$ of each surface layer. The results suggest that the dissociation constant decreases upon adsorption for poly(acrylic acid) and increases in the case of poly(allylamine hydrochloride). These deviations from ideal behavior can be substantial, changing by as much as 4 pH units, and the shifts become more pronounced as the number of adsorbed layers increases. In addition, we found that these $pK_{a(app)}$ shifts are influenced by the pH of the solution used to assemble the thin films but show little dependence on the salt concentration used in the assembly baths.

Introduction

Over the past decade, the layer-by-layer electrostatic adsorption technique introduced by Decher and Hong has received much attention as a route to prepare thin polymer films.[1,2] This self-assembly method involves the sequential adsorption of polyelectrolytes onto an oppositely charged substrate from dilute aqueous solution leading to charge reversal on the surface. This simple requirement makes layer-by-layer self-assembly applicable to a wide variety of polyelectrolytes ranging from complex biopolymers, such as proteins and DNA, to polyelectrolytes containing nonlinear optical functional groups.[3,4] The stratified structure of polyelectrolyte multilayer films has also been combined with small molecules to prepare more complex systems such as capsules for enzymes and nanoparticles, templates for nanoparticle growth, liquid crystal alignment, and nanowire assemblies.[5−9] In addition, polyelectrolyte multilayers have been assembled on substrates differing in size, composition, and geometry.[10] Consequently, the versatility of the layer-by-layer method makes this technique attractive for a number of potential applications such as electro-optic devices, microcapsules, and sensors.[11−13]

The thin films prepared using the layer-by-layer method are most frequently composed of strong polyelectrolytes because they remain fully charged over a wide pH range.[14] Although manipulating the ionic strength of the assembly solution can be used to control the morphology and thickness of such polyelectrolyte multilayer films to some extent, the effectiveness of using this parameter is limited to a small range of salt concentrations because increasing the ionic strength of the system can lead to either solubility problems or decomposition of the multilayer films.[15] However, more recent studies have shown that preparing multilayer thin films from weak polyelectrolytes can produce systems with a rich suite of properties because the behavior of this class of polyelectrolytes is sensitive not only to the ionic strength of the solution but also to its pH.[16−18] In fact, it was recently shown that even a single weak polyelectrolyte layer embedded at the bottom of a 10-layer film is greatly influenced by the local environment at the surface layer.[19]

One of the most studied polyelectrolyte combinations that yields multilayer thin films whose physical properties are strongly dependent on solution pH is that of poly(acrylic acid) (PAA) and poly(allylamine hydrochloride) (PAH). Surface wettability, surface roughness, film morphology, dielectric properties, and layer thickness are examples of such properties that experience significant variations with changes in pH of the system.[16−18,20−23] Perhaps most notably, bilayers with thicknesses ranging from less than 10 Å to more than 120 Å have been prepared from PAH/PAA at different pH values, while certain

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10.1021/la026500i CCC: $25.00

assembly pH combinations completely prevent multilayer assembly of PAH and PAA.[17] This wide diversity of film characteristics, due to the effect of pH on the charge density of the polyelectrolyte chains in solution, is not easily rationalized, and no existing adsorption models of single layers of weak polyelectrolytes are suitable to explain such phenomena, but it has been speculated that incorporating a polyelectrolyte into a multilayer thin film shifts the apparent dissociation constant ($pK_{a(app)}$) from its dilute solution value due to changes in the local electrostatic environment upon adsorption of the polymer chains, leading to unusual behavior.[17,18] Thus, it is particularly relevant to gain insight into these acid−base equilibria anomalies of PAH/PAA multilayer films because many of the potential applications for these systems, such as drug capsules and templates for nanoparticle growth, depend entirely on the charge density of the polyelectrolyte chains within the film.[7]

Acid−base equilibria deviations from ideal behavior have been observed previously in a number of different single-layer self-assembled organic films.[24−29] For example, the dissociation constant of poly((2-dimethylamino)-ethyl methacrylate-*b*-methacrylate) assembled in a monolayer film at the air−water interface was observed to experience a negative shift of ∼1 unit from the dilute solution value.[24] A similar shift in pK_a was observed for the small molecule species docosylamine incorporated into a free-standing film at the air−water interface.[25] In both cases, the pK_a shifts were attributed to changes in the dielectric permittivity of the local environment and a decrease in the degrees of freedom of the species immobilized at the interface. Larger shifts in the acid−base equilibria were reported for self-assembled monolayers (SAMs) of ω-substituted alkanethiol molecules chemisorbed to a gold surface.[26−29] The dissociation constants of ω-carboxyl alkanethiol molecules incorporated into self-assembled monolayers increase from the dilute solution value by 0.5−4.5 units, while in the case of ω-amino alkanethiols the pK_a values decrease by ∼3−4 units. It was concluded that the trend in the pK_a values resulted from a combination of effects including contributions from electrostatic repulsion between the charged moieties, a decrease in the permittivity at the interfacial layer, and strong lateral hydrogen bonding among the surface functional groups. Notably, acid−base equilibria shifts observed for functionalized alkanethiol molecules incorporated into SAMs are not surprising considering the extreme local environmental changes experienced by each individual molecule upon chemisorption from dilute solution into a densely packed surface film. In contrast, it is possible for many of the repeat units in a polyelectrolyte chain to maintain a similar local environment and mobility upon physisorption on a surface, particularly if the chains adsorb in a coiled state or with loopy conformations. Additionally, it is still unclear how the presence of multiple polyelectrolyte underlayers and the conditions used for polymer adsorption affect the dissociation constants of polyelectrolytes in multilayer thin films. Hence, it is of great interest to measure the acid−base equilibria of polyelectrolyte multilayer assemblies because of the many differences that exist between polymers and small molecules on surfaces.

One common technique used to determine the effect of various parameters (e.g., salt, polymer, pH) on the surface charge properties of colloidal particles is microelectrophoresis, from which zeta potential can be calculated using the electrophoretic mobility data.[30] The plots of zeta potential versus pH for colloidal particles containing acid−base functional groups represent titration curves, and such curves can be used to determine the dissociation constant of acid functional groups on colloidal particles by applying the basic principles of acid−base equilibria in solution, which indicate that $pK_a = pH$ at the inflection point on the curves.[31]

The acid−base equilibria of weak polyelectrolytes in solution have been a topic of investigation for many decades.[32−35] The dissociation behavior of weak polyelectrolytes in solution is commonly described as an apparent dissociation constant ($pK_{a(app)}$), which reflects the overall acid dissociation equilibrium of the polyelectrolyte. Due to the electrostatic interactions of the individual charged functional groups along the polyelectrolyte chain, the $pK_{a(app)}$ is strongly influenced by the degree of dissociation and the electrostatic screening of added salt molecules.[32,33] In the case of PAA for example, the $pK_{a(app)}$ has been shown to vary from 6.79 in the absence of added salt to 4.68 in the presence of 1.0 M NaCl.[33] In the present study, it is our goal to determine how such factors as the charge density on the surface (silica or polyelectrolyte), the degree of dissociation of the adsorbing polyelectrolyte, and the dissociation behavior of the polyelectrolyte underlayer as a function of pH influence the $pK_{a(app)}$ of the polyelectrolyte species terminating the surface of the multilayer films.

In this paper, we report measurements of the acid−base equilibria of PAA and PAH as part of a polyelectrolyte multilayer assembly. We layered PAH and PAA on colloidal silica at different pH values, and the resulting zeta potential of the particles was followed as a function of the solution pH to obtain an acid−base equilibrium profile for the surface after the deposition of each polyelectrolyte layer in the assembly, from which the $pK_{a(app)}$ was evaluated from the inflection point of the curve. Because the chains within each layer of the assembly have the ability to assume a variety of conformations and to penetrate into the neighboring layers,[16−18] we investigated the effect of layer accumulation, the assembly solution pH, and the salt concentration in the assembly bath on the dissociation behavior of the film surface. In addition, the dependence of the dissociation constants on the pH of the assembly solutions and the salt concentration in the assembly baths was evaluated.

Experimental Section

Multilayer Assembly. The multilayers were prepared by first depositing a PAH layer (MW = 60 000 g/mol, Polysciences) on Snowtex silica particles (70−100 nm) obtained from Nissan Chemical Industries. This involved adding an aqueous salt solution of PAH to a colloidal suspension. The salt was added to create sufficient electrostatic screening to promote polymer adsorption onto the particles. Both solutions were adjusted to the same pH with HCl or NaOH prior to mixing. The final solution concentrations were 0.01 M PAH, 0.1 or 0.2 M NaCl as required,

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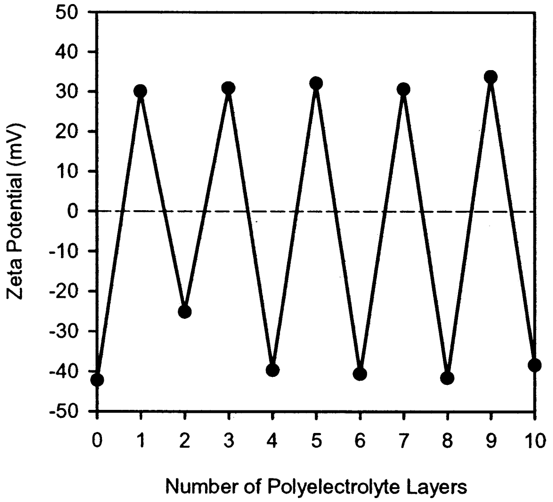

Figure 1. Alternation in zeta potential with layer number for PAH/PAA multilayer thin films assembled at pH = 7.0. Error in electrophoretic mobility, ±0.08–1.9%.

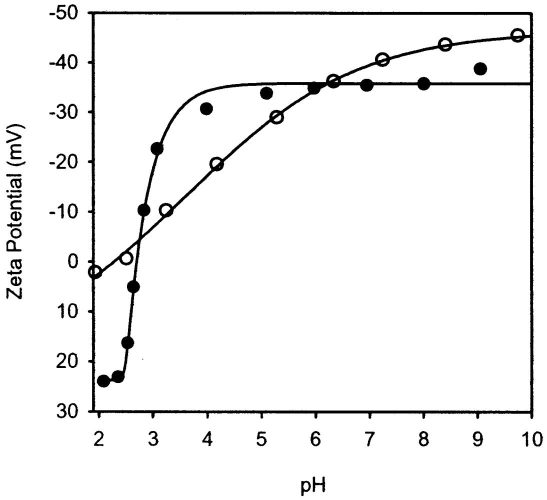

Figure 2. Acid–base equilibrium profile for a 10-layer PAH/PAA film assembled at pH = 7.0 (●) and bare silica (○). Uncertainty in electrophoretic mobility, ±1.9%.

and 0.5 g/L of silica particles. After 30 min, the solution was centrifuged, followed by removal of the supernatant. The sample was washed with water (Millipore, Milli-Q 18.2 MΩ cm) adjusted to the same pH as the preparation solutions. The particles were redispersed by sonication, and the suspension was allowed to stand for 30 min followed by centrifugation. This wash procedure was completed three times to remove unabsorbed polyelectrolyte to prevent the formation of polyelectrolyte complexes in solution. A small sample of particles (~30 mg) was then removed for characterization and dried at 65 °C for 12 h. The remaining colloidal particles were added to a solution of 0.02 M PAA (M_w ~90 000 g/mol, Polysciences)/0.2 or 0.4 M NaCl for the deposition of PAA on top of the PAH layer. The adsorption and washing procedures for the PAA layer were similar to those used for the deposition of the PAH layer. Alternate polyelectrolyte layers were assembled on the colloidal silica to a maximum of 10 layers.

Titration with Strong Polyelectrolyte. For the titration experiments, an aqueous stock solution of 2.0 g/L of PAH/PAA layered particles (assembled at pH = 9.0) and 1.0 mM NaCl was prepared at pH = 9.0. The stock was divided into several 15 mL samples. A variable amount of stock poly(diallyldimethylammonium chloride) (PDADMAC, Aldrich, MW = 200 000–350 000 g/mol) solution containing 1.0 mM NaCl and adjusted to a pH value of pH = 9.0 was added to each colloid sample to create a series of titrant solutions differing in PDADMAC concentration ranging across the point of half neutralization for the PAH/PAA layered particles.

Zeta Potential Measurements. Solutions of 30 mg of dry colloidal particles in 15 mL of 1.0 mM NaCl were prepared for the electrophoretic mobility measurements, which were determined using a Microelectrophoresis Apparatus Mk II (Rank Brothers, Bottisham, U.K.). We calculated the zeta potential of our assemblies from the Smoluchowski equation using an average mobility value based on 20 measurements. The concentration of NaCl in the colloidal solutions was maintained at 1.0 mM because higher salt concentrations lead to flocculation of the colloidal suspension.

Results and Discussion

Multilayer Buildup. In the field of polyelectrolyte multilayer thin films, zeta potential measurements are commonly employed to determine whether the electrical charge on the film is positive or negative as a means of monitoring the stepwise growth of sequential polymer layers.[36] An example of this is shown in Figure 1 for the assembly of 10 layers of PAH and PAA on colloidal silica at neutral pH = 7.0. Bare silica displays a zeta potential of −42 mV, reversing to +30 mV with the addition of 1 layer of the polycation PAH. The sign of the zeta potential then shifts back to negative with the addition of the first PAA layer. This alternation in the sign of the zeta potential occurs with each additional layer. Notably, the change in the sign of the zeta potential does not indicate whether adsorption or desorption has occurred with each polyelectrolyte cycle. However, ^{13}C cross-polarization/magic-angle spinning (CP-MAS) NMR and elemental analysis studies were used to confirm the sequential addition of each polyelectrolyte layer.[37,38] It has previously been determined that the thickness of the PAH/PAA multilayer films grows in a linear fashion under constant pH conditions, but that the average thickness of the layers varies depending on the pH of the assembly solutions.[17] Changing the solution pH affects the charge density of these weak polyelectrolytes, and this influences the film characteristics such as the surface roughness, the layer thickness, and the electrical properties. Since the zeta potential is a reflection of the electrical character of the colloidal particles, it is used in this case to monitor the changes in the electrical properties of weak polyelectrolyte films with variations in the pH of the colloidal suspension. The resulting plots represent acid–base titration curves from which the local apparent dissociation constant of the surface after the deposition of new polyelectrolyte layer is obtained from the inflection point of the curve.[31] An example of this is illustrated in Figure 2 for a 10-layer PAH/PAA film assembled at pH = 7.0 for which the $pK_{a(app)}$ was found to be 2.76 ± 0.06. Reversibility was confirmed by increasing the pH back up to pH = 7.0 and recovering the original strongly charged film. The titration curve for bare silica is shown for comparison.

Dependence of $pK_{a(app)}$ on Layer Number. To investigate the effect of the number of underlying polyelectrolyte layers on the $pK_{a(app)}$ of the surface layer, we assembled films at pH = 7.0 containing 1–10 layers of polyelectrolyte on colloidal silica. Both PAH and PAA were found to be fully charged at neutral pH when adsorbed onto a surface.[17] Thus, by comparing the $pK_{a(app)}$ of similar layers (i.e., PAH layers: 1, 3, 5, 7, and 9), we are able to isolate the effects of layer number on the acid–base equilibria of PAH and PAA. Figures 3 and 4 illustrate the trends in the $pK_{a(app)}$ as a function of layer number for

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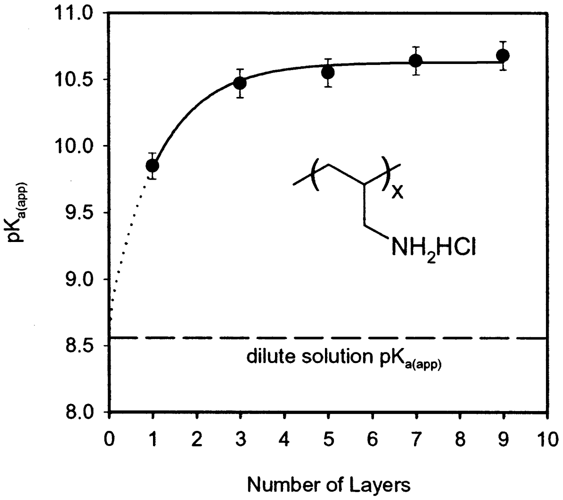

Figure 3. Dependence of the apparent dissociation constant of PAH on the total number of layers in PAH/PAA multilayer films assembled at pH = 7.0. The dashed line indicates the dilute solution p$K_{a(app)}$. The dotted and solid lines are visual guides.

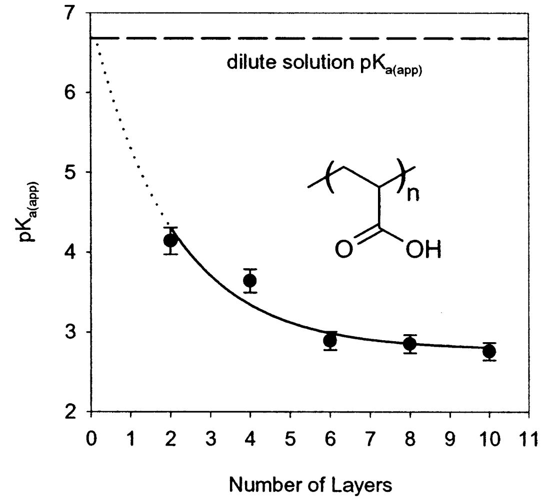

Figure 4. Dependence of the apparent dissociation constant of PAA on the total number of layers in PAH/PAA multilayer films assembled at pH = 7.0. The dashed line indicates the dilute solution p$K_{a(app)}$. The dotted and solid lines are visual guides.

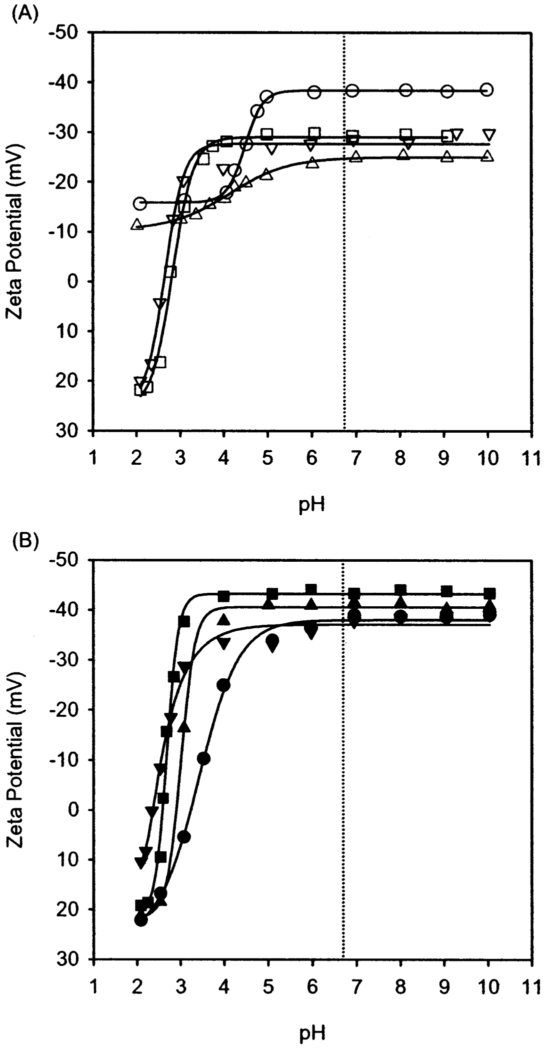

Figure 5. Acid–base equilibria curves for PAA surface layers in PAH/PAA multilayer films assembled at different pH values: (A) 2-layer film assembled at pH = 3.0 (▽), pH = 5.0 (□), pH = 7.0 (△), and pH = 9.0 (○); (B) 8-layer film assembled at pH = 3.0 (▼), pH = 5.0 (■), pH = 7.0 (▲), and pH = 9.0 (●). The dotted lines indicate the isoelectric point of PAA in dilute solution. Uncertainty in electrophoretic mobility, ±1.0–2.1%.

PAH/PAA multilayer films assembled at pH = 7.0. The complete set of titration curves is provided as Supporting Information. Both PAH and PAA experience a shift in their dissociation constants upon adsorption onto the colloid surface from the dilute solution values 8.56 ± 0.08 and 6.68 ± 0.05, respectively, in the presence of 1.0 mM NaCl (Figures A and B, Supporting Information);[40] these values are in good agreement with the reported literature values of 8.7 and 6.71 (Figure C, Supporting Information).[33,39]

It is clear that the acid–base equilibria shifts are layer dependent and that with increasing the total number of layers the dissociation constants for both polyelectrolytes appear to level off to a constant deviation from the dilute solution values. The dissociation constant of PAH assembled in a multilayer film increases from the dilute solution value, but this change levels off after layer 3. In the case of PAA, the p$K_{a(app)}$ shifts to smaller values upon adsorption and continues to do so up until the fourth layer is reached. The variable shifts in p$K_{a(app)}$ observed for the first 3–4 layers are attributed to influences from the charged silica substrate or to inhomogeneous polyelectrolyte coverage on the surface in agreement with previous suggestion.[41] Notably, in the titration curve for the first PAA layer (assembled at pH = 7.0), the zeta potential remains negative over the entire pH range investigated (Figure 5A). It is speculated that the zeta potential neither reaches a value of zero nor switches sign because of a combination of effects. First, it is believed that there is sparse coverage of the substrate by the first PAH layer, which is consistent with the finding that the average incremental thickness contribution from PAH is fairly low when the multilayer assembly is carried out at pH = 7.0.[17] Therefore, one might expect there to be little to no contribution to the overall surface charge from the first PAH layer, otherwise the zeta potential would become

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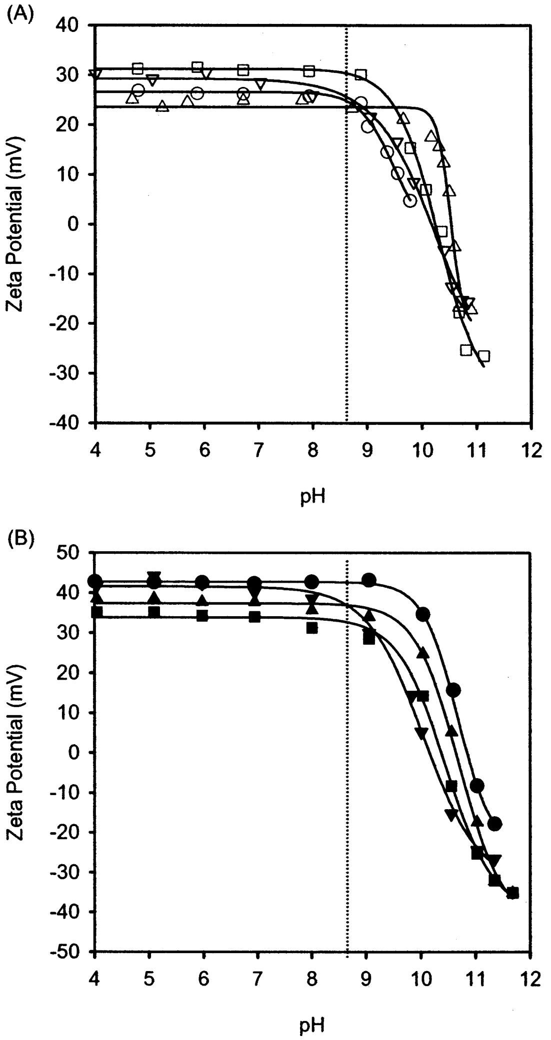

Figure 6. Acid−base equilibria curves for PAH surface layers in PAH/PAA multilayer films assembled at different pH values: (A) 3-layer film assembled at pH = 3.0 (▽), pH = 5.0 (□), pH = 7.0 (△), and pH = 9.0 (○); (B) 7-layer film assembled at pH = 3.0 (▼), pH = 5.0 (■), pH = 7.0 (▲), and pH = 9.0 (●). The dotted lines indicate the isoelectric point of PAA in dilute solution. Uncertainty in electrophoretic mobility, ±0.9−2.0%.

Table 1. Dependence of the p$K_{a(app)}$ Values of PAH and PAA on the pH of the Assembly Solutions

polymer	layer no.	assembly pH	p$K_{a(app)}$
PAA	2	3.0	2.75
PAA	2	5.0	2.83
PAA	2	7.0	4.14
PAA	2	8.0	4.26
PAA	2	9.0	4.48
PAA	8	3.0	2.46
PAA	8	5.0	2.59
PAA	8	7.0	2.85
PAA	8	8.0	3.01
PAA	8	9.0	3.16
PAH	3	3.0	10.10
PAH	3	5.0	10.27
PAH	3	7.0	10.47
PAH	3	8.0	10.62
PAH	3	9.0	9.91
PAH	7	3.0	10.32
PAH	7	5.0	10.46
PAH	7	7.0	10.64
PAH	7	8.0	10.80
PAH	7	9.0	10.94

positive once all of the COO^- groups from PAA were protonated at low pH. Furthermore, assuming sparse coverage of the first few layers, it is possible that the negative zeta potential at low pH from the 2-layer coating may result from contributions from the low residual charge of PAA and the silica substrate. Although the silanol groups of the particle substrate are weakly acidic, the isoelectric point does not occur until pH = 2.4. It is possible that this value may even be lower in the presence of polyelectrolyte on the surface, which has been shown to be the case for colloidal silica in the presence of a copolymer of acrylamide and ((3-methacrylamido)propyl)trimethylammonium chloride.[42] This would also explain why the zeta potential is slightly more negative than that observed for subsequent layers.

The overall increase in the base strength of PAH from dilute solution to the adsorbed state may be attributed to the fact that the influence of the negatively charged functionality of the PAA or silica underlayer in promoting the protonation of the amino groups of PAH is greater than the resistance to protonation from electrostatic repulsion of neighboring groups. In the case of PAA, it was previously speculated that the presence of the fully protonated PAH underlayer may increase the ease of dissociation of the adsorbing PAA layer and thus facilitate the increase in the acid strength of the adsorbing PAA chains.[17] Our results do indeed indicate that the surface charge strongly influences the acid−base equilibrium of the adsorbing polyelectrolyte layers.

Dependence of p$K_{a(app)}$ on the pH of the Assembly Solutions. One means of investigating the nature of the influence of the surface charge of the polyelectrolyte-coated particles on the p$K_{a(app)}$ of the adsorbing polyelectrolyte is to vary the degree of dissociation of the surface (i.e., silica or polyelectrolyte layer(s)) on which it assembles. We chose to alter the surface charge by changing the pH of the solutions used to assemble the layers since pH affects the degree of dissociation of both polyelectrolytes and the charge density on the silica particles. The dissociation constants were determined for PAH/PAA multilayers assembled at pH = 3.0, 5.0, 7.0, 8.0, and 9.0. Covering a large pH range is particularly important because the polyelectrolytes in dilute solution are fully charged at one pH extreme but only partially charged at the other extreme, with the polyacid and polybase showing opposite trends in dissociation with respect to the solution pH.

Figures 5 and 6 contain plots of zeta potential versus pH for four different total layer numbers (2, 3, 7, and 8) within multilayer films assembled using a range of pH conditions. The resulting apparent dissociation constants are summarized in Table 1. These findings indicate that for all assembly pH conditions studied, the p$K_{a(app)}$ values of the films terminated with PAA (layers 2 and 8) are substantially lower than those observed in dilute solution, while the opposite is true for the surface of films composed of a total of 3 and 7 layers whose composition is dominated by PAH.

For both of the films investigated that have surface layers terminated with PAA, the apparent dissociation constant decreases with decreasing assembly solution pH. To rationalize these findings, one needs to consider the influence of the charge density of the surface (silica or polyelectrolyte) on which the polyelectrolyte adsorbs, the degree of dissociation of polyelectrolyte in solution, and the average incremental thickness contributions from both PAH and PAA. For example, at low assembly solution pH values (i.e., 2.5 < pH < 5.5), Shiratori and Rubner found that the average incremental thickness contribution from PAH is larger than that from PAA.[17] Therefore, there is

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a higher concentration of amino functional groups in the underlayer than carboxylic acid groups on the surface for films assembled in this pH regime. PAH/PAA films are also known to experience interpenetration between layers and to undergo rearrangement of their counterions when exposed to solutions of variable pH.[16-18] During the titration of films terminated in PAA, the charge density of the PAA chains decreases with decreasing pH, but the PAH chains from the previously adsorbed layer become more protonated. Since the concentration of amino groups in the underlayer is higher than that of the carboxylic acid groups on the surface, the underlying PAH strongly promotes the dissociation of the COOH groups to neutralize the high residual positive charge obtained with decreasing pH, leading to a decrease in the $pK_{a(app)}$ of the PAA-terminated surface. However, when the films are assembled at higher pH values (pH > 5.5), the average incremental thickness contributions from PAA and PAH are essentially the same at matched assembly solution pH values.[17] Therefore, since the ratio of amino groups to carboxylic acid groups is lower when the films are assembled at high pH values, the underlying PAH chains have less of an influence on the dissociation of the surface COOH groups going from high to low pH on the titration curves.

Similar rationale can be used to explain the trends in the $pK_{a(app)}$ values for the films terminated in PAH as a function of assembly solution pH. In this case, the base strength of PAH increases with increasing assembly solution pH. When the films are assembled using the low-pH regime, the ratio of the carboxylic acid groups of the underlayer to the amino groups in the surface PAH layer is low in comparison to its value when the films are assembled using the high-pH regime because of the differences in the average incremental thickness contributions from PAH and PAA.[17] Hence, in the high solution pH region of the titration curve where the COOH groups of the underlayer become dissociated and the PAH chains on the surface become weakly charged, the ability of the PAA chains to promote the protonation of the amino groups on the PAH-terminated surface is greater in films assembled at higher pH values because of the higher ratio of COOH to NH_2 functionality making up the surface composition of the film.

Because of the prevalence of the substrate effects and inhomogeneous polyelectrolyte coverage in the first 3−4 layers within the multilayer film, we examined the effect of the assembly pH on the acid−base equilibria of PAH and PAA at both low and high layer numbers. We determined the apparent dissociation constants for layers 2 and 8 as well as layers 3 and 7, which are composed of PAA and PAH, respectively. For both polyelectrolyte species, the trends in the $pK_{a(app)}$ with increasing assembly pH are the same for the two comparable films examined. However, the apparent dissociation constants depend on the layer number for all assembly pH values studied. These results are in agreement with those found in the study of $pK_{a(app)}$ as a function of layer number for films assembled at neutral pH = 7.0.

In the case of the 2-layer film terminated with PAA, the titration curves do not pass through zero zeta potential for films assembled at pH = 7.0, 8.0, and 9.0. As mentioned earlier, this anomaly is attributed to inhomogeneous coverage of the first PAH layer on silica and the residual charge on the silica particles since the charge density of the silica is known to increase in the presence of positively charged polyelectrolyte.[42] In addition, due to the decreasing surface charge of the PAH layers at higher pH values and PAA layers at lower pH values, the stability of the colloidal suspension is reduced under these conditions, resulting in flocculation of the suspension in some cases. This was observed at high solution pH values for a 3-layer film assembled at pH = 9.0. This behavior was not observed for a 7-layer film assembled at pH = 9.0, suggesting that the flocculation of the 3-layer film may be attributed to inhomogeneous coverage of the polymer on the particle surface, which is common for the first few layers assembled. This explains the discrepancy in the trend of $pK_{a(app)}$ for 3-layer films assembled at different pH values (Table 1).

Table 2. Summary of the Effect of the Salt Concentration in the Assembly Solutions on the Dissociation Constants of PAH and PAA in Multilayer Films

			$pK_{a(app)}$	
polymer	layer no.	assembly pH	PAH/PAA 0.2 M/ 0.4 M NaCl	PAH/PAA 0.1 M/ 0.2 M NaCl
PAH	3	7.0	10.47	10.44
PAH	7	3.0	10.32	10.34
PAA	2	3.0	2.75	2.69
PAA	8	7.0	2.85	2.81

Salt Effect on the Acid−Base Equilibria. In addition to examining the dependence of the acid−base equilibria of PAH/PAA multilayer films on the number of polyelectrolyte layers in the film and the pH of the assembly solutions, we also investigated the effect of varying the salt concentration in the assembly solutions. This parameter is of interest because the presence of salt in the assembly step screens the electrical charge in the system, which influences such factors as the amount of polyelectrolyte adsorbed, the conformation of the chains on the surface, and the stability of both the multilayer film and the particle suspension.[15,21,43] In addition, studies have shown that the salt concentration directly affects the acid−base equilibria of both PAH and PAA in solution.[44,45] To determine the effect of the NaCl concentration in the assembly solutions on the $pK_{a(app)}$ of the multilayer films, we assembled films at two combinations of salt concentrations. The results discussed so far are for films assembled using a salt concentration of 0.2 M NaCl in the PAH solution and 0.4 M NaCl in the PAA solution. Four other films were assembled using a reduced salt concentration of 0.1 M NaCl in the PAH solution and 0.2 M NaCl in the PAA solution. The resulting $pK_{a(app)}$ values are summarized in Table 2. Notably, the salt concentration does not have a significant effect on the acid−base equilibria of the four films investigated. One way to account for this observation is to note that most of the Na^+ and Cl^- ions present from the adsorption bath are rinsed away in the three consecutive wash cycles. Therefore, it is reasonable to believe that any of the changes in the film caused by the presence of salt in the adsorption step may be altered by the salt-free wash solutions preventing us from observing any salt effects on the acid−base equilibria of the surface layer. However, assembling the multilayers on colloidal particles from salt-free polyelectrolyte solutions led to instable films that desorbed from the particles after 3 layers were deposited. In this study, the concentrations of NaCl used in the assembly solutions were chosen because they yielded the most robust films for which growth was possible for many layers. In

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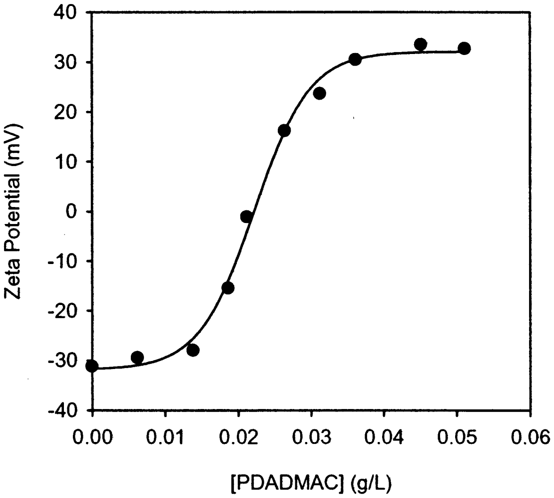

Figure 7. Acid−base equilibrium profile for a 2-layer PAH/PAA multilayer film assembled at pH = 9.0 and titrated with PDADMAC. Uncertainty in electrophoretic mobility, ±9.6%.

addition, the salt concentration in the solutions used for the microelectrophoresis studies was maintained at 1.0 mM because the colloidal suspensions are unstable in the presence of higher salt concentrations.

Titration with a Strong Polyelectrolyte. As a second and independent test to confirm the suitability of our method for determining the apparent dissociation constant of polyelectrolyte multilayer films, we carried out an additional experiment that allowed us to evaluate the point of half neutralization of our multilayer films. This experiment involved titrating a solution of the particles wrapped with a polyelectrolyte multilayer film with a strong polyelectrolyte. We chose to use PDADMAC for this study because of its high binding affinity.[46] The titration experiment was carried out at pH = 9.0 for a 2-layer film assembled at pH = 9.0 (Figure 7). From knowledge of the concentration of functional groups at the point of half neutralization (inflection point on the curve), we were able to determine a corresponding concentration of protons required to reach half neutralization of the surface. The charge density of functional groups on the surface was calculated based on manufacturer-supplied data of the surface area of the coated colloidal particles, and the relative size of the repeat units based on usual bond lengths. The resulting inflection point was found to be 4.4 ± 0.4 for the surface of a 2-layer film, terminated in PAA. This result is in close agreement with the $pK_{a(app)}$ of the film obtained from the zeta potential versus pH study ($pK_{a(app)} = 4.48 \pm 0.08$). Notably, there is a higher uncertainty associated with the strong polyelectrolyte titration method for determining the dissociation constant than with the variable-pH zeta potential curves used for the study reported here.

Conclusion

We reported here direct measurements of the local acid−base equilibria of polyelectrolytes incorporated into multilayer assemblies on solid supports. We found significant deviations in the dissociation constants of PAH and PAA incorporated into multilayer thin films in comparison to the dilute solution values. We also investigated the influence of the layer number, the assembly pH, and the assembly salt concentration on the apparent dissociation constants for PAH and PAA surfaces. In all cases, PAA was found to be a stronger acid and PAH a stronger base by 1−4 units when incorporated into multilayer assemblies. The acid strength of PAA and the base strength of PAH both increase with an increase in the total number of layers in the films. The $pK_{a(app)}$ of PAA increases with an increase in the pH of the assembly solutions but always remains lower than the dilute solution value, while the $pK_{a(app)}$ of PAH increases with an increase in the pH of the assembly solution. In addition, the salt concentration in the assembly solutions has no detectable influence on the acid−base equilibria of the multilayer films. However, salt is required in the assembly solutions for successful assembly of PAH/PAA multilayer films on colloidal silica. Knowledge of acid−base anomalies in weak polyelectrolyte systems may be important for polyelectrolyte multilayer thin films employed as pH sensors, drug delivery vehicles, and selective membranes.

Acknowledgment. The authors thank NSERC Canada and McGill University for financial support in the form of grants and scholarships. Professors D. Ronis and T. van de Ven are acknowledged for helpful discussions, and Professors van de Ven, Reven, and Kazlauskas are also appreciated for use of equipment.

Supporting Information Available: Plots showing the layer-dependent acid−base titration curves for 10 films assembled at pH = 7.0 and a plot showing the titration curves for PAH and PAA in dilute solution. This material is available free of charge via the Internet at http://pubs.acs.org.

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