Effects of Charge Density and Counterions on the Assembly of Polyelectrolyte Multilayers

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Received: October 22, 2002; In Final Form: January 20, 2003

The kinetics of the electrostatic layer-by-layer adsorption of a weakly charged polycation, poly(allylamine hydrochloride), PAH, and a polyanion containing an azobenzene chromophore, P-Azo, was studied using UV−vis spectroscopy and ellipsometry. The thickness of the multilayer films was first measured over the adsorption pH range of 3 to 11, and the growth of multilayers was examined as function of time and concentration. Films assembled in bath pH near that of their pK_a value produced both the thickest films and displayed remarkably rapid adsorption isotherms. In some PAH/P-Azo films, a significantly large thickness was achieved in less than 5 s, which is more than 2 orders of magnitude faster than what is usually observed. We show that this anomalously rapid adsorption is a consequence of the weak acid−base nature of the layers. In addition, the role of counterion displacement in multilayer formation from weakly charged polyelectrolytes was explored by examining the rates of P-Azo adsorption in PAH/P-Azo multilayer formation from polymer solutions containing the counterion series F^-, Cl^-, Br^-, and I^-. Multilayers of PAH/P-Azo prepared from solutions containing I^- ions exhibited 21% greater adsorption at saturation ($t = 60$ s) than those containing an equal concentration of F^- ions. We provide a simple scaling rationalization relating the counterion binding energies with the observed rates of displacement by an adsorbing polymer segment.

I. Introduction

The sequential adsorption of charged polymers onto oppositely charged surfaces is a straightforward and versatile technique for the preparation of polymer thin films.[1] The layer-by-layer approach is suitable for designing functionalized polymer films over broad length scales ranging from angstroms to micrometers. Polyelectrolyte multilayer films have thus become useful for many applications, including capsules for drug delivery,[2] chemical sensors,[3] ultrathin ion-selective membranes,[4] electrochromic devices,[5] and all-optically patterned surfaces.[6,7] Such applications have fueled much experimental study of various thermodynamic aspects of multilayer formation with the aim of gaining better chemical control of film properties such as layer morphology,[8,9] interpenetration,[10−12] and thickness.[13,14]

Recent steady-state studies have shown that multilayers constructed from weakly charged polymers can exhibit rich and complex behavior, owing to their variable charge density. In particular, the thickness of the multilayer films has been shown to be highly dependent on the pH of the polymer solutions during assembly by over 2 orders of magnitude, as demonstrated in the now well-studied poly(allylamine hydrochloride) (PAH) and poly(acrylic acid) (PAA) systems.[15] Thus, by manipulating the charge fraction in adsorption baths of weakly charged polymers, one has good molecular control over the adsorption of polyelectrolyte chains, which can lead to variable layer structures and thickness transitions in the film.[16−18] An understanding of the kinetics of the electrostatic layer-by-layer assembly of polyelectrolytes onto solid supports is also necessary for the controlled preparation of functional polymer films and the optimization of their physical properties. However, many fundamental questions concerning multilayer formation remain unclear. Although several theoretical studies have provided some insight into the effects of adsorption variables for a single polyelectrolyte layer (i.e., concentration of counterions, pH, and surface charge density),[19−22] the predictions for adsorption behavior from the models are still poor in many systems, especially for weak polyelectrolytes. Furthermore, although the kinetics of polyelectrolyte adsorption onto an uncharged surface has been theoretically examined,[20,23] there remains a limited amount of detailed experimental data on the adsorption kinetics of oppositely charged polymers into multilayer assemblies, particularly for films made from weak polyelectrolytes. Recent results of the interplay between kinetic and thermodynamic contributions in the multilayer adsorption of weak polyelectrolytes have broadened our understanding of the process but have also prompted further studies of these systems.[24]

In an effort to examine some of the variables that govern the rate of polymer adsorption, we have conducted studies to determine the time-dependent thickness of a model weakly charged system. Specifically, we optically measured and mapped the growth profiles of weakly charged polycation PAH and a polyanion containing azobenzene dye moieties, P-Azo (poly{1-[4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamido]-1,2-ethanediyl, sodium salt}, as a function of various polymer concentrations. We then compared the thicknesses after just 1 s of adsorption of nine different multilayer systems to identify the origins of the substantial increase in film thickness observed over time in our model weak PAH/P-Azo system. Lastly, we examined the influence of counterion exchange on the rate of weak polyelectrolyte adsorption. This study involved comparing the time-dependent adsorption of P-Azo onto a weakly charged PAH surface in the presence of halogen salts F^-, Cl^-, Br^-, and I^-.

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10.1021/jp027278t CCC: $25.00

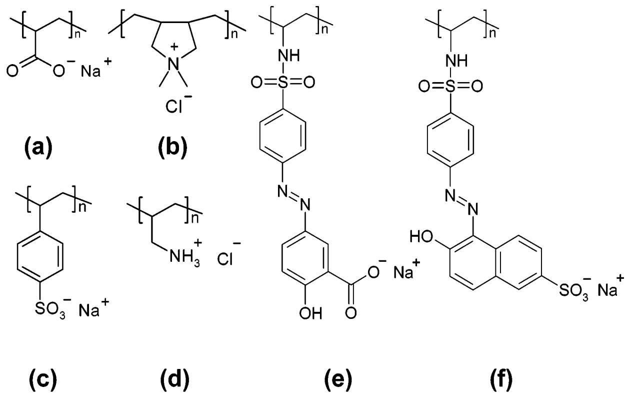

Figure 1. Repeat units of the polyelectrolytes used for multilayering: (a) PAA (weak polyanion), (b) PDAC (strong polycation), (c) PSS (strong polyanion), (d) PAH (weak polycation), (e) P-Azo (weak polyanion), and (f) P-S119 (strong polyanion).

II. Experimental Section

Materials. The principal polycation/polyanion combination investigated was PAH (Polysciences, M_w 60K) and P-Azo (Aldrich, M_w 90K), respectively. Other polyions employed were poly(diallyldimethylammonium chloride) (PDAC; Aldrich, M_w 200−350K), poly(acrylic acid, sodium salt) (PAA; Aldrich, M_w 90K), poly(sodium 4-styrenesulfonate) (PSS; Aldrich, M_w 70K), and an azobenzene containing poly(S119), (Aldrich). Figure 1 depicts the chemical structures of the various polyelectrolytes used. Unless otherwise indicated, aqueous solutions containing 10^{-2} M per repeat unit of polyion were prepared with 18 MΩ cm resistivity Millipore Milli-Q water. Where indicated, the pH of the solutions was adjusted using NaOH and HCl. For the counterion study, polymer solutions of concentrations 10^{-3} M were adjusted to pH 9, and a salt of concentration 5×10^{-2} M was added (NaF, NaCl, NaBr, or NaI from Fisher, used as received at minimum 99% purity). To prevent the replacement of the target ions, the quantity of NaOH used for pH adjustments was ensured to be at least 1 order of magnitude lower than the concentration of the examined salt.

Multilayer Film Preparation. Glass microscope slides (Fisherbrand) and silicon wafer substrates (Wafernet) were cleaned by immersion in a bath of 25% H_2SO_4 and 75% H_2CrO_4 for a minimum of 24 h. Substrates were subsequently washed with neutral Milli-Q water (pH ~7.5) in preparation for the electrostatic deposition of the initial polycationic layer. Except where specified, multilayer films were constructed with the aid of an automatic slide stainer (Shandon) using matched dipping times for both polycation and polyanion as indicated. The dipping protocol was a repeated and alternating immersion of substrates in polycation solution and then in the polyanion solution. Between each adsorption cycle of polymer layers, the films were rinsed thoroughly with neutral Milli-Q water.

Film Characterization. Optical absorbance measurements of P-Azo-containing multilayer films on glass microscope slides were performed with a UV−vis spectrophotometer (Varian Cary 300-Bio; scan rate 100 nm min^{-1}). The optical thickness of P-Azo-containing multilayers was quantified (an average of three measurements) by observing the $\pi \rightarrow \pi^*$ absorbance maximum of P-Azo at $\lambda_{max} = 365$ nm for the *trans* azobenzene isomer. Transmission results are represented as the calculated average of three replicate measurements and are blank-corrected. Reflective data for multilayers deposited on Si substrates were obtained using a Gaertner ellipsometer at 633 nm, solved for both refractive index and layer thickness. All total layer thickness values are reported as the statistical mean of 13 acquired measurements followed by a surface oxide subtraction of 27 ± 3 Å, determined independently. The average errors associated with the UV−vis absorbance and ellipsometry measurements were determined to be approximately ±5% and ±3%, respectively.

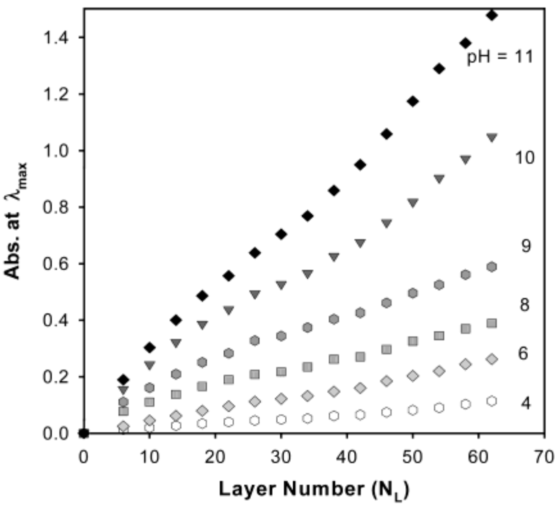

Figure 2. UV−vis absorbance at $\lambda_{max} = 365$ nm from 0 to 62 layers of PAH/P-Azo self-assembled under varying pH matched polycation/polyanion solutions.

III. Results and Discussion

A. Layer Thickness. Several recent studies have reported the pH-dependent thickness of weakly charged polyelectrolytes assembled into multilayer films.[21,22,25] In a similar manner, we characterized the growth of the PAH/P-Azo system prepared under conditions of varying charge density by assembling multilayers at matched solution pH values ranging from 3 to 11 and using a dipping time of 12.5 min. The optical absorbance resulting from variable P-Azo adsorption was measured as a function of the assembly bath pH at intervals of every 4 layers up to 62 layers, as displayed in Figure 2. A trend of increasing P-Azo adsorption with increasing assembly solution pH toward the pK_a was observed, in agreement with the previous studies. This effect was most prominent in the multilayer series assembled at pH 9 to 11, where a nearly 20-fold increase in optical absorbance was obtained by increasing the pH of the assembly bath from 3 to 10. Recent acid−base equilibria studies of layered colloids prepared from PAH and PAA indicate that the apparent local pK_a of the adsorbed polycation, as determined through ξ potential measurements, is approximately in the range of 9.9 and 10.8.[26] For PAH/P-Azo films made near the half-neutralization point of PAH (i.e., at pH 9 and 10), the measured average optical thickness of ~19 Å/layer corresponds to an intermediate value between the weakly charged (~35 Å/layer at pH 11) and strongly charged systems (~3 Å/layer at pH 4). To characterize the time-dependent thickness of the multilayers constructed from weakly charged PAH, we examined the effect of the assembly bath pH on the kinetics of PAH/P-Azo adsorption.

B. Time−Concentration Profile. Although there have been some kinetic studies on the formation of multilayer assemblies from strongly charged polyelectrolytes,[27] there is little information on the kinetics of the layer-by-layer adsorption of weakly charged polyelectrolytes. We performed static experiments to measure the multilayer growth for PAH/P-Azo prepared at pH 9 as a function of immersion time and concentration. Polyelectrolyte solutions of PAH and P-Azo were prepared at various

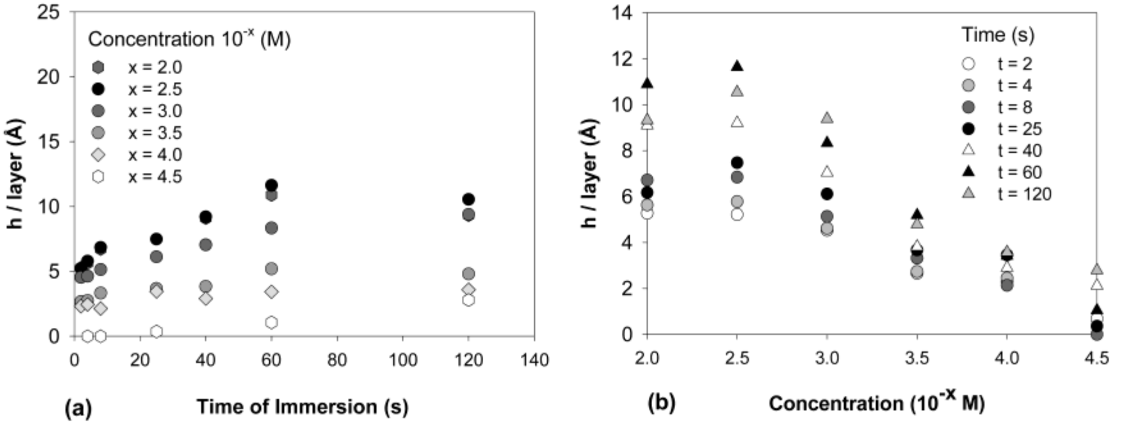

Figure 3. Layer thickness growth profiles for 30 layers of PAH/P-Azo adsorbed at pH 9 for both polyion solutions. Ellipsometric average height (*h*) per layer measured (a) as a function of time, using various matched concentrations of polycation/polyanion solutions and (b) as a function of concentration for various deposition times (*t*).

concentrations ranging from $10^{-2.0}$ to $10^{-5.0}$ M per repeat unit, and films of 30 layers were fabricated on Si substrates using various immersion times ranging from 1 to 120 s, matched for both the polycation and polyanion. The average layer thickness of films prepared using various dipping times was measured using ellipsometry. In this fashion, a layer growth profile was constructed and compared for seven sets of polycation/polyanion pairs at matched concentrations. Figure 3 illustrates the indirectly observed time-dependent growth of several PAH/P-Azo films prepared at concentrations ranging from $10^{-2.0}$ to $10^{-4.5}$ M. No significant growth was detected when the concentration of the assembly solutions was $10^{-5.0}$ M. The data indicate that when polymer solutions of at least $10^{-4.0}$ M are used multilayers adsorb and reach saturation (>80%) in approximately 60 s. Thus, saturated adsorption is rapidly achieved in the case of PAH/P-Azo assembled under conditions employing weakly charged polycations. At the saturation point, we also obtained the widest range in layer thickness for PAH/P-Azo films of 1 to 12 Å. Note that this static experiment suggests that a measurably thick layer of polymer is adsorbed within the first few seconds of substrate immersion into a polymer bath. However, the true thickness (which can be obtained from dynamic experiments) would not include experimental contributions to layer thickness, seen at short immersion times in Figure 3. For example, the adsorption of polyelectrolyte results from the presence of a concentration gradient, which exists on the surface of the film, during the rinse cycles.

Furthermore, experiments conducted using longer immersion times of 4 and 12.5 min revealed no significant increase in the average layer thickness beyond the 1 min saturation point (i.e., a maximum of 12.5 Å/layer). The highest layer thickness, determined to be 8 to 12 Å, is obtained with more concentrated solution baths on the order 10^{-3} and 10^{-2} M, respectively, whereas in more dilute systems significant reductions to $^{1}/_{2}$, $^{1}/_{3}$, and $^{1}/_{12}$ the maximum layer thickness occur at concentrations of $10^{-3.5}$, $10^{-4.0}$, and $10^{-5.0}$ M, respectively.

In a separate study, we deposited 30 layers for various adsorption times and examined the layer thickness as a function of solution concentration. Figure 3b illustrates the resulting concentration-dependent decay curves in layer thickness for a series of six different adsorption times. As previously determined from the variable-time experiments, Figure 3b confirms that the largest variation in layer thickness is between 1 and 12 Å, which is observed when multilayer films are prepared near the saturation point, $t = 60$ s. These results are presented in Figure 4 as sets of superimposed time and concentration variables, which provide a constant layer thickness in the early growth regime, in this case between 5 and 9 Å. The lines provided are intended to be visual guides only. Most notably, we observed a rapid increase in the film thickness of thin polymers layers after 1 s of substrate contact with the polymer solution.

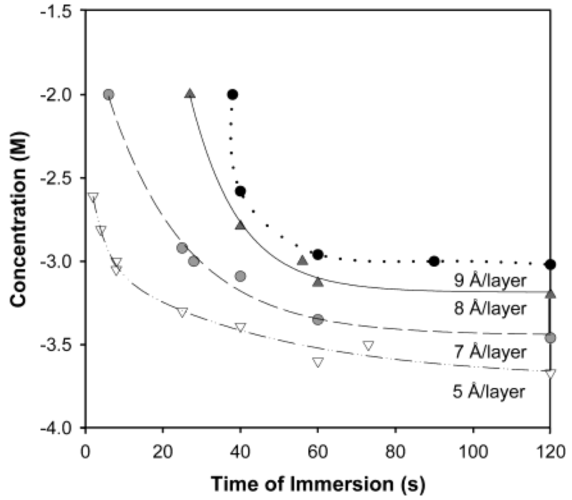

Figure 4. Concentration−time plot of the growth of PAH/P-Azo multilayers with both polyion adsorption baths set to pH 9.

Whereas many previously studied multilayer combinations typically report adsorption times on the order of minutes or even tens of minutes,[28] our data for the PAH/P-Azo system indicate unusually rapid adsorption within the first few seconds of substrate immersion into a polymer bath adjusted to pH 9.

C. Dependence of Adsorption Kinetics on Charge Density. In an effort to understand the source of the anomalously rapid growth observed in PAH/P-Azo films constructed at pH 9, we examined various other polyelectrolyte multilayers on Si prepared from 1-s immersions and measured the resulting thicknesses by ellipsometry every five layers. We first obtained the 1-s layer growth of a model PAH/PAA system over 25 layers, in which the charge density of either the polycation or the polyanion was selectively altered by suitable pH adjustments of the polymer solutions. The resulting 1-s thickness of the PAH/PAA films made from polyelectrolyte solutions at matched pH values of 7 and 9 is displayed in Figure 5. At assembly pH 9, we observed a large 1-s thickness of ∼20 Å/layer. Conversely, we did not detect a significant increase in the 1-s layer thickness when PAH/PAA films were prepared from solutions set to pH 7. The anomalously fast 1-s growth observed for the PAH/PAA

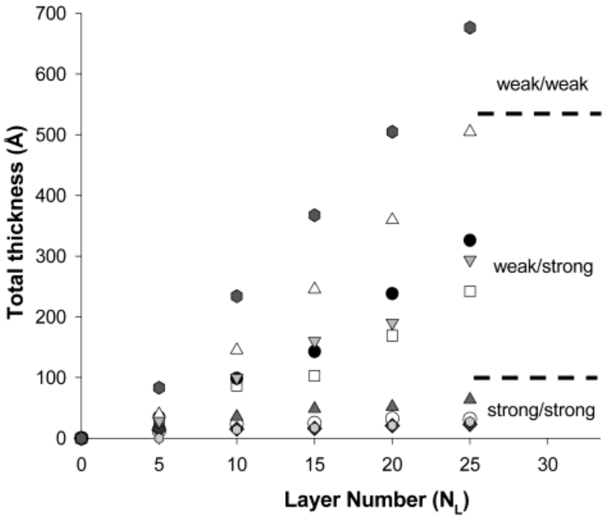

Figure 5. Multilayer film growth using 1-s adsorption times for variously charged polycation/polyanion combinations. A weak/weak system demonstrating unusually large 1-s thickness is (⬢) $PAH_{pH\ 9}$/$PAA_{pH\ 5}$. Intermediate 1-s thicknesses are observed in weak/strong systems including (●) $PAH_{pH\ 9}$/P-$S119_{pH\ 9}$ and (▼) $PAH_{pH\ 9}$/P-$Azo_{pH\ 9}$, which contain azobenzene chromophores, as well as in (△) $PAH_{pH\ 9}$/$PAA_{pH\ 9}$ and (□) $PAH_{pH\ 9}$/$PSS_{pH\ 9}$. Strong/strong systems displaying minimal 1-s thickness include (▲) $PAH_{pH\ 5}$/P-$Azo_{pH\ 5}$, (○) $PAH_{pH\ 5}$/$PSS_{pH\ 5}$, (⬡) $PAH_{pH\ 7}$/$PAA_{pH\ 7}$, and (♦) $PDAC_{pH\ 9}$/$PSS_{pH\ 9}$.

system assembled at pH 9 is in agreement with the rapid adsorption kinetics observed in the case of PAH/P-Azo films, which were also prepared using weakly charged polycations (Figure 3a).

In a more broad study, we similarly obtained the 1-s thickness profile of various other polyelectrolyte pairs, each assembled with their unique pH-dependent charge densities. The results, shown in Figure 5, suggest that all films made from both a strongly charged polycation and polyanion exhibit considerably less or negligible 1-s thicknesses in comparison to multilayers prepared using at least one weakly charged component. For example, no significant 1-s thickness was detected for PDAC/PSS films (i.e., ~1 Å/layer) prepared from polycation/polyanion solutions at matched pH values of either 5 or 9. Notably, both PDAC and PSS are strongly charged polyelectrolytes in the pH range of 3 to 11. Similarly, a reduced 1-s thickness of ~2 Å/layer was detected in both cases of PAH/PSS and PAH/P-Azo multilayered at pH 5. The estimated pK_a of P-Azo is ~3.3 based on observations of precipitation near this pH value and is in agreement with a recent report of the dissociation constant of P-Azo in multilayer thin films.[29] Since both PAH and P-Azo remain strongly charged at pH 5, we did not observe the usual weakness effect, which appears to give rise to the adsorption of thick polymer layers at a short immersion time.

In contrast, multilayer films prepared using one weakly and one strongly charged polyelectrolyte exhibit much greater 1-s thicknesses of 8 Å/layer and 10 Å/layer, respectively, for both the PAH/PSS and the PAH/P−S119 systems assembled at pH 9. Although both PSS and P-S119 (an alternate azobenzene-containing polyanion) are fully charged polyanions, the polycation here remains weakly charged, which leads to thicker layers after only 1-s immersion times. Our result is also in agreement with the rapid adsorption recently noted in the assembly of PAH/P-S119 multilayers.[30] Notably, when we changed the assembly solution pH to a value of 5 in the PAH/PSS system, the 1-s thickness value was reduced by 5-fold. All 1-s thickness results reported here are consistent with the hypothesis that reduced charge density in adsorbing polyelectrolytes is mainly responsible for larger film thicknesses observed at short immersion times. Although previous *in situ* studies, through second harmonic generation, indicate fast adsorption of PDAC/PSS multilayers (<10 s),[31] our 1-s thickness studies suggest that considerably thicker layers are a consequence of the reduced charge fraction in the assembling polymers. This is supported by the fact that all strongly charged polycation/polyanion multilayer combinations examined here demonstrate little or negligible adsorption on the time scale of 1 s. Furthermore, the largest 1-s growth is expressed in a system assembled with both a weakly charged polycation (PAH at pH 9) and a weakly charged polyanion (PAA at pH 5), resulting in films of ~28 Å/layer. Since the weakness effect is most pronounced in a system prepared using both a weakly charged polycation and polyanion, we suggest that the degree to which the 1-s thickness is increased is therefore related to the extent to which the charge fraction may be reduced in the assembly of both of the polyelectrolytes. We speculate that this effect may arise from a variable "effective" charge density of weak polyelectrolytes upon approaching the surface for adsorption. This charge readjustment of the polymer near the surface can consequently result in a net larger degree of charge overcompensation and therefore yield greater layer thicknesses at low immersion times. The ability of weak polyelectrolytes to alter their charge because of an "effective" local pH in the interphase, which is different from that in the bulk solution, has previously been shown both experimentally[26,32] and theoretically.[33] In addition, it has been demonstrated that the local pH during adsorption is influenced by the ionization fraction of the underlying polymer layers, which oscillates with the number of layers deposited. Thus, the extent to which the 1-s layer thickness increases (observed in our studies as large differences between a purely weak polyelectrolyte system and a purely strong one) is influenced not only by the alteration of local charge density at the surface during adsorption but also by the changing ionization fraction of the relevant underlying polymer layers.[34]

D. Ion Displacement and Adsorption Kinetics. The finding of anomalously fast adsorption kinetics in multilayer assemblies prepared from weakly charged polyelectrolytes leads to questions regarding the mechanism of adsorption, such as the role of ion displacement in the formation of polymer layers. It is known that when a polyion segment approaches a surface containing an oppositely charged polyelectrolyte layer a displacement of the salt ion must occur to allow for segment adsorption.[35] This exchange of salt ions for the repeat units of strongly charged polyelectrolytes has been confirmed by direct observation with radio-labeled ion probes.[36] Results from X-ray photoelectron spectroscopy studies have shown that the residual ion content trapped within formed multilayers made from strongly charged polymers is negligible.[37] However, there is a lack of experimental data on the effect of counterion displacement on the kinetics of polyelectrolyte adsorption into layer-by-layer assemblies. In addition, these effects cannot be generalized to the adsorption behavior of weakly charged polyelectrolytes.

The role of ion exchange in the adsorption kinetics of multilayers was investigated here by comparing the relative rate of P-Azo adsorption on partially charged PAH (pH 9) for a series of polyelectrolyte solutions containing either NaF, NaCl, NaBr, or NaI of concentration $5 \times 10^{-2.0}$ M. Multilayer films containing 30 layers were assembled onto glass slides using various adsorption times ranging from 1 s to 15 min for the P-Azo component whereas the saturated adsorption of the

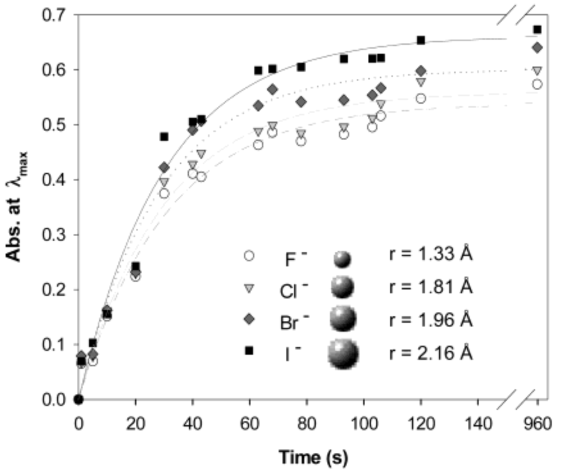

Figure 6. Effect of ion exchange on the adsorption kinetics of PAH/P-Azo multilayers (at a constant pH of 9 for both polyelectrolyte solutions).

polycation was ensured by maintaining a constant immersion time of 15 min. Reported optical measurements on multilayer films were time-corrected for prolonged polyelectrolyte adsorption resulting from significant polymer concentration at the surface of the film during rinse cycles initially, which was quantified using UV−vis. As shown in Figure 6 for the UV−vis absorbance of the various PAH/P-Azo films prepared, immediate adsorption of P-Azo results for all ion solutions within 5 s of immersion.

The optical thickness measurements show that saturation is nearly achieved in approximately 60 s of adsorption time. The results from this time-dependent study of film thickness for PAH/P-Azo on glass slides is in agreement with the thickness values obtained from reflective ellipsometry measurements obtained for the thickness of PAH/P-Azo (Figure 4), which suggests that maximum polyelectrolyte adsorption is obtained upon approaching 1 min of immersion time. No distinguishable difference in the kinetics of P-Azo adsorption for the films prepared with varying halogen ion salt films was observed up to 20 s. After 20 s, significant differences in the optical thickness revealed a reduced adsorption of P-Azo when the multilayers were prepared in the presence of small F^- counterions. Conversely, an increase of 21% in the UV−vis absorbance of multilayer films prepared from I^--containing solutions suggests that polymer solutions containing larger counterions exhibit a faster adsorption of P-Azo than those containing an equivalent number of F^- counterions. The analogy to weak polymer systems is that lower charge density similarly facilitates rapid adsorption by effectively reducing the number of ionic interaction sites required for adsorption and hence lowering the energy barrier.

The observed variances in the rate of polyanion adsorption based on the presence of either F^-, Cl^-, Br^-, or I^- can be rationalized using a simple electrostatic argument considering the binding energies of the tested anions with various cations (Table 1). The Arrhenius equation (eq 1) is used to compare the adsorption rates at constant temperature qualitatively. The rate constant k here is exponentially proportional to the chemical bond strength of ionic dissociation.

$$k = A\mathrm{e}^{-E_a/RT} \tag{1}$$

As a first approximation, we assume first-order kinetics. The rate of dissociation for the anions thus scales with k, suggesting a slower displacement of the smaller F^- counterion, with a relative rate ∼53% of that of the larger I^-, as shown in Table 1.

TABLE 1: Calculated and Experimetnal Relative *k* for Multilayer Formation with Target Counterions

target counterion	ionic radius (Å)	av E^* [a] (kcal mol^{-1})	E^* rel to I^-	rel k	k rel to I^-	exptl rel k
F^-	1.33	137.5	1.63	0.20	53	81
Cl^-	1.81	111.9	1.32	0.27	73	84
Br^-	1.96	100.2	1.19	0.30	83	91
I^-	2.16	84.6	1	0.37	100	100

[a] E^* was determined from the average ionic binding energies of the target counterion with Li^+, Na^+, K^+, and Rb^+.[38]

Since P-Azo must exchange with the bound counterions existing on the PAH surface for adsorption to occur, systems with larger I^- ions (i.e., more loosely bound) would be expected to exchange more rapidly than those of the more tightly bound F^- ions, as observed. In comparing the relative rates of adsorption, it is also important to consider the effect of the hydrated radii of the counterions when they are displaced from their countercharge on the polyelectrolyte. For example, fluoride ions, while having the smallest ionic radius, have the largest hydrated radius and are therefore much slower to diffuse away into water than chloride, bromide, and iodide ions, which have smaller hydrated radii. As indicated in Table 1, a trend of faster counterion dissociation (and thus thicker polymer layers at equivalent time) with increasing counterion radius (decreasing hydrated radius) is indeed observed qualitatively. The expected variance in the counterion diffusion rates due to the different sizes of the hydrated radii combined with the effect of the binding energies (proportional to the ionic, not hydrated, radius) both further support our experimental finding of more rapid adsorption with larger halide counterions. However, the scaling argument based on counterion binding energies alone does not adequately describe the full increase in the rate of layer-by-layer adsorption observed for weakly charged polyelectrolytes. Thus, whereas our kinetic study of counterion displacement suggests that this process may not necessarily be the rate-limiting step in multilayer formation, it has a significant and measurable effect on the rate at which weakly charged polyelectrolytes adsorb.

IV. Conclusions

We observed anomalously rapid adsorption for the formation of PAH/P-Azo multilayers, on the order of seconds. This was attributed to the reduced charged density on the polyelectrolytes since significantly large 1-s thicknesses could be obtained only with weak polyelectrolytes. The resulting 1-s film thickness of polyelectrolyte multilayers prepared using weakly charged polycations or polyanions can be approximately 10-fold greater than that obtained from similar polyelectrolytes, which are strongly ionized. Furthermore, when both the polycation and the polyanion are assembled at low charge fraction, this weakness effect gives rise to much thicker 1-s films, by a factor of up to 30, as compared to both strongly charged polyelectrolytes. Our studies have also shown that the process of counterion displacement makes a significant and easily measurable contribution to the time-dependent growth of multilayers up to the point of saturation. The time-dependent thickness of weakly charged polymers appears to be sensitive to the variables of concentration, charge fraction, and counterion species and demonstrates that the layer-by-layer technique can be highly advantageous from the point of view of achieving a precise control of thickness in multilayer assemblies.

Acknowledgment. This work was financially supported by NSERC Canada and the Center for the Physics of Materials at McGill University. We are also grateful to Professor David Ronis for helpful discussions and Professor Hanadi Sleiman for the use of equipment.

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