Nonmonotonic Effect of Ionic Strength on Surface Dye Extraction during Dye−Polyelectrolyte Multilayer Formation

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Abstract: Multilayer formation between organic dyes and polyions is complicated by the possible competition between dye extraction from the surface by the polymer solution instead of polymer adsorption. We study the effects of salt concentration (NaCl, Na_2SO_4, $MgCl_2$, and $MgSO_4$) on this process and note that significant fractions of the dye are removed from the surface at intermediate salt concentration but that at lower or higher salt concentration less surface dye extraction occurs. Polymer solutions with intermediate NaCl concentrations show more than 60% dye extraction, while those of $MgCl_2$, Na_2SO_4, and $MgSO_4$ show approximately 30%, 25%, and 20% dye extraction, respectively. The maximum in dye extraction for all of these salts occurs when the solution Debye length is approximately 2 Å. The reduced efficiency of dye complexation away from the maximum is interpreted in terms of the polymer's expected increase in persistence length (low salt concentration) and the reduced electrostatic interactions between the charged dye and polymer (high salt concentration). The absorbance of poly(styrenesulfonate) remains roughly constant or slightly increases for the 1:1 and 2:2 salts but decreases with increasing 2:1 salt concentration. We propose that this decrease is due to charge reversal on the polymer or surface by the salt. Small shifts in dye peak positions suggest changes in the polarity of the surrounding matrix.

Introduction

Layer-by-layer growth of polyelectrolyte polymers is an effective way of preparing ultrathin polymer films that provides a high degree of control over structure, composition, and thickness.[1,2] It is believed that adsorption occurs through the interaction of a charged surface with an oppositely charged polyion, where polyion adsorption changes the surface charge. Alternating exposures of the surface to polycations and polyanions lead to multilayer formation. As an important extension of this method, other charged species can take the place of one of the polyions so that charged clays,[3] proteins or DNA,[4] viruses,[5] or semiconducting nanoparticles[6] can be included in these polymer films.

Recent reports have further demonstrated that small charged organic molecules, such as dyes,[7−9] can be incorporated into these layers. However, it was found that, under certain conditions, and especially at high polymer concentration,[8] multilayer formation from dyes and polyions did not proceed cleanly. In other words, rather than simply adsorbing at the surface, the polymer may extract some of the dye from the surface, decreasing the efficiency of multilayer formation. No mention of the influence of the ionic strength of the polymer solution on the extraction process was made in these reports. It is reasonable that the polymer, especially at high concentration, can extract dye from the surface because an equilibrium should exist between dye that is adsorbed on the surface and dye in solution:

$$\text{dye}_{\text{adsorbed}} + \text{polymer}_{\text{solution}} \leftrightarrow \text{dye−polymer complex}_{\text{solution}} \quad (1)$$

Under the conditions of equilibrium described in eq 1, raising the solution polymer concentration should increase the amount of dye−polymer complex that is formed in the solution. This simple statement of equilibrium should be complicated by the competing process of polymer adsorption. Polymer that adsorbs onto the surface may kinetically trap dye and thereby hinder its complexation and the attainment of equilibrium that is described in eq 1.

Polyelectrolyte−dye complexation in solution has been extensively studied.[10−14] It is believed that these interactions depend strongly on electrostatic forces between the polymer and

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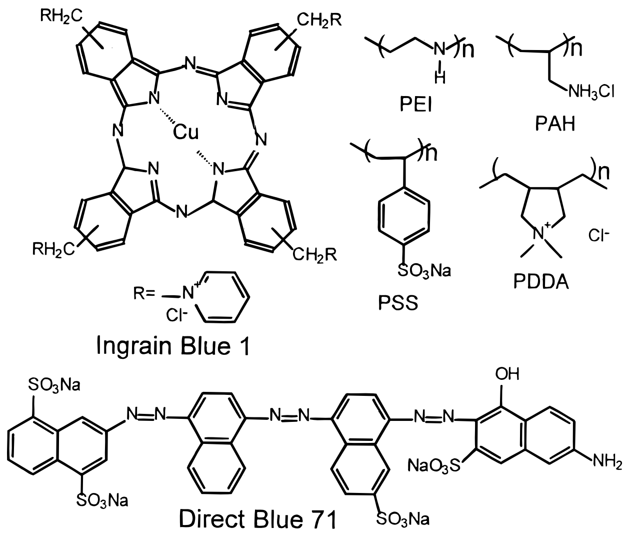

Figure 1. Molecular structures of copper phthalocyanine dye (Ingrain Blue 1), poly(ethylenimine) (PEI), poly(allylamine hydrochloride) (PAH), poly(styrenesulfonate sodium salt) (PSS), poly(diallyldimethylammonium chloride) (PDDA), and Direct Blue 71.

the dye,[10] on the polymer's persistence length or conformational adaptability,[14] and on the polymer's degree of cross linking.[10,13] In general, a linear polymer complexes dye less efficiently than a coiled or cross-linked polymer.[10] These factors probably influence dye extraction from a surface by the polyion during multilayer formation.

We show here that, under conditions of high polymer concentration, the ionic strength in the polymer solution significantly alters the amount of dye that is extracted from a surface. Understanding this effect adds an additional degree of control to multilayer formation between polyions and small charged molecules. We consider here the effects of four different salts: a 1:1 electrolyte (NaCl), two 2:1 electrolytes (Na_2SO_4, $MgCl_2$), and a 2:2 electrolyte ($MgSO_4$) on multilayer formation between a polyanion (poly(styrenesulfonate); see Figure 1) and an organic dye with four positively charged groups (a copper phthalocyanine; see Figure 1). Copper phthalocyanines have been studied extensively in thin organic films including polyelectrolyte multilayers[7] and Langmuir–Blodgett films.[15–17] We observe decreased amounts of dye extraction at both low and high ionic strength. But at intermediate ionic strength significantly more extraction occurs (greater than 50% for NaCl). Ionic strength can alter both a polyelectrolyte's persistence length (a stretched out polymer is expected to complex small molecules less effectively than a coiled one[14]) as well as the double-layer thickness of charged objects in solution (interactions between charges are believed to strongly influence complexation[10]). We also show preliminary results that indicate that the polymer composition strongly influences the efficiency of polyion–dye multilayer formation and that extraction of negatively charged dyes by polycations is also dependent on the salt concentration in the polymer solution. We finally note here the possibility of future work that would consider other ions at different positions in the Hofmeister or lyotropic series, e.g., K^+ or Li^+ instead of Na^+. Such information would add even greater control to the dye–polymer adsorption/complexation process.

Experimental Section

Materials. Poly(styrenesulfonate) (PSS) (Cat. No. 24,305-1), poly(diallyldimethylammonium chloride) (PDDA) (Cat. No. 40,902-2), poly(allylamine hydrochloride) (PAH) (Cat. No. 28,321-5), poly(ethylenimine) (PEI) (Cat. No. 18,197-8), Direct Blue 71 (Cat. No. 21,240-7), Ingrain Blue 1 (Cat. No. 23,655-1), magnesium chloride hexahydrate (99.99%) (Cat. No. 21,240-7), and magnesium sulfate heptahydrate (98+%) (Cat. No. 23,039-1) were obtained from Aldrich Chemical Co. and were used as received. Sodium chloride (99.5%) and sodium sulfate (99.5%) were obtained from Merck and Reachim, respectively, and were used as received. All water used in experiments was from a Millipore Milli-Q Plus 185 system and had a resistivity of 18.2 MΩ. Quartz slides (1.25 × 12 × 46 mm) were obtained from Hellma Optik.

Substrate Cleaning and Multilayer Preparation. Quartz and silicon substrates were rinsed with water, sonicated in ethanol for ~15 min, rinsed again with water, immersed in ~50:50 NH_4OH (concentrated)–H_2O_2 (30%) for ~30 min (***warning:*** *mixtures of ammonium hydroxide and hydrogen peroxide are extremely corrosive and should be handled with great care*), and rinsed again with copious amounts of water. Following this cleaning procedure, the samples were completely wet by water. Multilayers were prepared by immersing the dry substrates in an aqueous solution of poly(ethylenimine), 0.1 M (monomer), for 30 min followed by alternating 20 min immersions in solutions of polyions and dyes. Following these immersions, the surfaces were rinsed by consecutively dipping them three times (or four times for the dye) for 1–1.5 min in vials of Millipore water (pH ~5.5) and then dried with a jet of argon or nitrogen. The concentration of the dye solutions was 10^{-3} M. The concentration of the polymer solutions was 0.2 M (monomer).

Instrumentation and Data Handling. Ultraviolet–visible (UV–vis) spectra were taken with a Cary Model 4E UV–vis spectrophotometer. Peak positions in the UV–vis spectra were determined by smoothing the derivative of the spectra with a 13-point Savitzky–Golay routine and observing where the resulting curve crossed the x-axis. The derivative and smooth spectra were obtained with a plotting program (Origin 4.1). The resulting peak positions appear to be accurate to better than ±1 nm. Specular X-ray scattering was performed with a commercial $\theta/2\theta$ instrument (STOE & CIE GmbH Darmstadt, Germany, $U = 40$ kV, $I = 50$ mA, $\lambda = 1.54$ Å (Cu K_α)). The divergence of the incoming beam was 0.1°. The analysis of the X-ray data was performed with a box model using software described elsewhere.[18]

Results and Discussion

We show here that the ionic strength of a concentrated polyion solution strongly influences the amount of charged organic dye that it extracts during multilayer formation. We first consider a multilayer formed by alternating exposures of poly(styrenesulfonate) in 2 M NaCl and Ingrain Blue 1 (see Figure 2). Ultraviolet–visible (UV–vis) absorption spectroscopy was used to follow this process. Figure 2a shows the absorbance of a poly(styrenesulfonate) film (note the strong peaks at 195 and 225 nm due to the pendent aromatic groups of this polymer) on top of a poly(ethylenimine) sticking layer (lowest spectra). Figure 2b next shows the absorbance of this surface following immersion into a solution of Ingrain Blue 1 (a positively charged copper phthalocyanine dye; see Figure 1). In these spectra we note peaks at 335, 625, and 680 nm due to the dye. After this surface is reimmersed into the original poly(styrenesulfonate) solution, more than half (56%) of the intensity of the peak at 335 nm is lost, suggesting that this fraction of the dye has been extracted from the surface (see Figure 2c). The peak at 225 nm, which has contributions from both the dye and poly(styrenesulfonate) decreases in intensity by 21%. Subsequent reimmersion in the dye solution results in increased absorbance by the dye (Figure 2d). This process of absorption and

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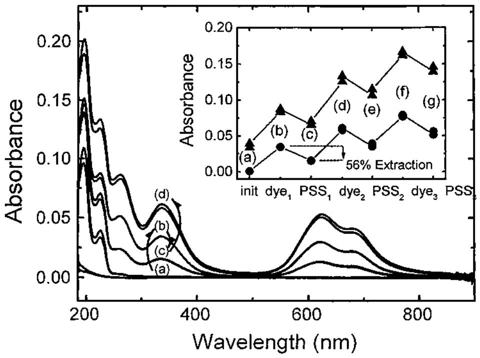

Figure 2. Ultraviolet−visible absorption spectra of a quartz substrate sequentially dipped in (a) 0.1 M poly(ethylenimine) (PEI) (30 min) followed by 0.2 M poly(styrenesulfonate), 2 M NaCl (20 min), (b) 1 mM dye (Ingrain Blue 1), (20 min), (c) 0.2 M poly(styrenesulfonate), 2 M NaCl (20 min), and (d) 1 mM dye (Ingrain Blue 1) (20 min). The inset shows the absorbances at 335 nm (circles) and 225 nm (triangles) after dipping sequentially into dye and polymer solutions. The spectra and data in this figure are shown for two experiments as obtained from the UV−vis transmission experiment where a film on each side of the substrate is sampled. The 225 nm peaks after spectrum a contain contributions from the dye and the polymer.

extraction continues with repeated immersions in polyanion and dye solutions with overall net multilayer growth (see the inset to Figure 2). The supernatant polymer solution slowly takes on the color of the dye as this process continues, additionally proving dye extraction.

For selected cases we measured by absorption with the supernatant solution that (a) all dye lost is found in solution and (b) extraction is due to polymer−dye association. The latter results from the observation that extraction does not occur with polyelctrolyte-free solution and that the absorption spectra of Ingrain Blue 1 in the polyelectrolyte solution ($\lambda_{\max} = 631$ nm) differs from that in water ($\lambda_{\max} = 610$ nm). For the polyelectrolyte solution one also observes an aggregate peak at 687 nm which is not observed for the dye in the film.

We quantified the number of monomer units and dye molecules in the films using solutions of known concentration. We find that the first poly(styrenesulfonate) layer contains 1.6×10^{15} monomer units/cm^2 (the numbers presented here are for one film, not both as measured by the transmission UV−vis experiment). We calculate the number of Ingrain Blue 1 molecules to be approximately (see Figure 2) 1.2×10^{14}/cm^2 (dye$_1$), 0.5×10^{14}/cm^2 (PSS$_1$), 2.1×10^{14}/cm^2 (dye$_2$), 1.3×10^{14}/cm^2 (PSS$_2$), 2.7×10^{14}/cm^2 (dye$_3$), and 1.9×10^{14}/cm^2 (PSS$_3$). Thus, approximately 1 dye molecule adsorbs for every 10 monomer units in the first polymer layer, where each dye molecule in the first film occupies an average area of 83 Å.^{2} We should mention that quantification of data is easy in this case because we do not observe dye aggregation, nor line broadening, the dyes are stable, and judging from some polarized studies they are isotropically oriented.

We also observed small shifts in the dye peak positions that typically suggest changes in the polarity of the surrounding matrix. For example, the dye peak at approximately 620 nm in the multilayer spectra (the Q-band) appears at 612 nm in the more polar aqueous solution (1.1 μM). As the number of multilayers increases, this peak red shifts by a small amount. When the dye is the topmost layer in the array, the peak shifts as 621 nm (dye$_1$), 623 nm (dye$_2$), and 624 nm (dye$_3$), and when the polymer is the topmost layer, the peak shifts as 620 nm (PSS$_1$), 620 nm (PSS$_2$), and 622 nm (PSS$_3$) (refer to Figure 2).

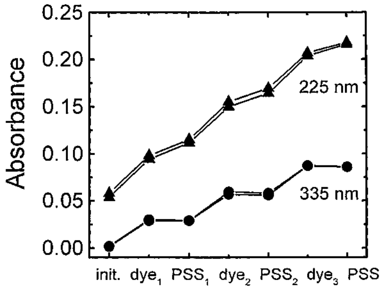

Figure 3. Absorbance at 335 nm (circles) and 225 nm (triangles) of a quartz surface that was dipped into 0.1 M poly(ethylenimine) for 30 min and 0.2 M poly(styrenesulfonate) (no salt) for 20 min (initial point) and then sequentially dipped into 1 mM Ingrain Blue 1 (dye) for 20 min and 0.2 M poly(styrenesulfonate) (PSS) (no salt) for 20 min.

In stark contrast to the results shown in Figure 2, when we again prepare a multilayer from poly(styrenesulfonate) and Ingrain Blue 1 but do not add any salt to the polymer solution, almost no dye is extracted during multilayer formation. Figure 3 shows the UV−vis intensities of the peaks at 225 and 335 nm after each step of dye−multilayer formation. Less than 3% of the dye is now extracted by the polymer solution (see peak intensities at 335 nm), and each immersion into the poly(styrenesulfonate) solution results in an increase in the intensity of the peak at 225 nm. As was the case for multilayer formation at higher salt concentration (Figure 2), the position of the peak at approximately 620 nm again red shifts by a small amount in the course of multilayer formation: 622 nm (dye$_1$), 623 nm (dye$_2$), 624 nm (dye$_3$), and 621 nm (PSS$_1$), 622 nm (PSS$_2$), 624 nm (PSS$_3$). The thickness of the film with three dye−poly(styrenesulfonate) bilayers is 107 Å by X-ray reflectivity. We have noted that, as the salt concentration is lowered, the polyelectrolyte's persistence length should increase,[19] which should result in less effective complexation between the dye and the polymer.[14] We suggest that these factors may explain the suppression of dye extraction from the surface in the absence of added salt.

To better understand the role that salt plays in controlling surface dye extraction, we prepared multilayers from poly(styrenesulfonate) and Ingrain Blue 1 with four different salts over a range of salt concentrations. These salts were a 1:1 electrolyte (NaCl), two 2:1 electrolytes (Na_2SO_4 and $MgCl_2$) and a 2:2 electrolyte ($MgSO_4$). Figure 4 shows the fraction of dye as measured by UV−vis that is extracted from the surface by a poly(styrenesulfonate) solution as a function of salt concentration. Some of the important features of this plot are that the maximum for dye extraction for each salt occurs at intermediate salt concentration, with a maximum at a defined ionic strength (3 N). Since, with exception of the broad maximum for the 2:2 salt, the value agrees for the different electrolyte stoichiometries, extraction is determined by the Debye length ($3N = 2$ Å). To explain the decrease in dye extraction that occurred going from a poly(styrenesulfonate) solution with 2 M NaCl to a solution containing no salt (see Figures 2 and 3), we noted that the polymer should be less able to complex dye in solution at low salt concentration because of its greater persistence length. For each of the four salts we consider here, Figure 4 shows that dye extraction decreases with decreasing salt concentration. To explain the decrease in complexation that occurs as the salt concentration is increased, we observe that electrostatic interactions play an important role in polyelectrolyte−dye complex-

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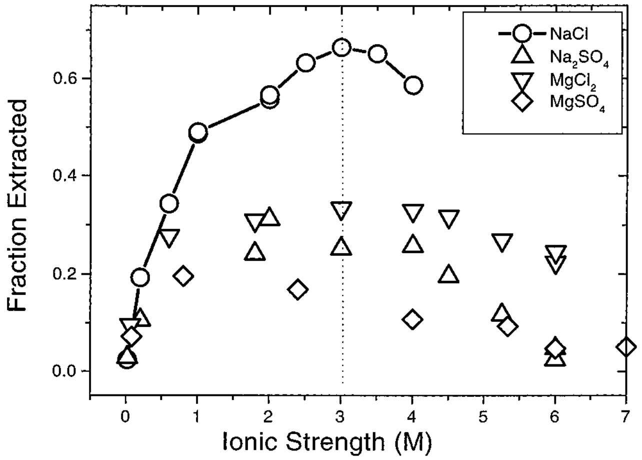

Figure 4. Fraction of dye extracted from a surface that was dipped into 0.1 M poly(ethylenimine) for 30 min, followed by immersion in a 0.2 M poly(styrenesulfonate) (as a function of ionic strength), $MgCl_2$ (downward triangles), Na_2SO_4 (upward triangles), $MgSO_4$ (diamonds)) for 20 min, followed by immersion in a 1 mM Ingrain Blue 1 (dye) for 20 min, and finally reimmersed for 20 min in the original 0.2 M poly(styrenesulfonate) solution.

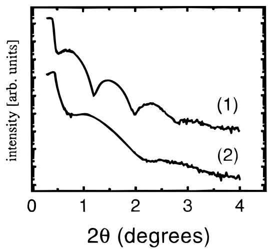

Figure 5. X-ray reflectivity for a film with one bilayer (2) of Ingrain Blue 1 and poly(styrenesulfonate) and three bilayers (1) deposited at 2 M Na_2SO_4 on a sticking layer of poly(ethylenimine) and poly(styrenesulfonate).

ation in solutions[10] so that screening these interactions, which occurs as the salt concentration increases, should decrease dye–polymer complexation.

Thickness measurements by X-ray reflectivity were performed on some of the samples shown in Figure 4 (Figure 5). For a surface with three bilayers of Ingrain Blue 1 and poly(styrenesulfonate) (2 M Na_2SO_4), on top of poly(ethylenimine) and poly(styrenesulfonate) sticking layers, we find a thickness of 110 Å by X-ray reflectivity. The film thickness by reflectivity is 65 Å for a single bilayer of the dye and polymer (at 0.0067 M Na_2SO_4) on poly(ethylenimine) and poly(styrenesulfonate) sticking layers. The observation of many Kiessig minima also proves the homogeneous film thickness.

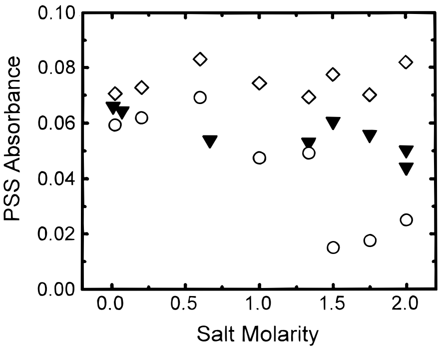

Figure 6. UV–vis absorbances at 225 nm of poly(styrenesulfonate) (0.2 M, 20 min) on a poly(ethylenimine) sticking layer as a function of salt concentration: $MgSO_4$ (diamonds), Na_2SO_4 (triangles), and $MgCl_2$ (circles).

It has been observed that the thickness of the adsorbed polyion layer can be influenced by the salt concentration of the polymer solution, with higher salt concentrations leading to more polymer adsorption.[2] Figure 6 shows preliminary UV–vis absorbance data at 225 nm from a layer of poly(styrenesulfonate) on a poly(ethylenimine) sticking layer as a function of salt concentration. While the amount of poly(styrenesulfonate) that adsorbs may increase slightly when $MgSO_4$ is used (the result for NaCl is similar to that for $MgSO_4$ except that there is more scatter in the data), the amount of poly(styrenesulfonate) that adsorbs *decreases* as the concentration of the 2:1 electrolytes (Na_2SO_4 and $MgSO_4$) increases. A possible explanation for the relatively constant amount of poly(styrenesulfonate) that adsorbs at $MgSO_4$ concentrations between 0.5 and 2 M $MgSO_4$ is that the Debye length in the solution is relatively constant, only varying from 2.1 to 1.1 Å, respectively. These distances, which are in the range of most chemical bonds, should localize the counterion in solution at its ion on the polymer or surface. To explain the decrease in polymer adsorption with increasing 2:1 salt concentration, we suggest that doubly charged ions may reverse the charge on the surface (SO_4^{2-} in Na_2SO_4) or polymer in solution (Mg^{2+} in $MgCl_2$). The much higher absorption probability of doubly charged ions can be deduced from an inspection of the Boltzmann equation. In eq 2, z is the charge

$$\frac{n_1}{n_0} = \exp\left(\frac{-ze\psi}{kT}\right) \tag{2}$$

on the ion (1 or 2), e is the electron charge, k is Boltzmann's constant, T is room temperature (298.15 K), and we assume a conservative value (−40 mV) for the surface potential (ψ). Under these conditions we find n_1/n_0 to be 4.7 for a singly charged ion and 22.5 for a doubly charged ion. The ratio of these values suggests it is roughly 5 times more likely for a doubly charged species than for a singly charged species to be adsorbed at a surface.

To determine whether the effects of ionic strength on surface extraction are unique to the poly(styrenesulfonate)/copper phthalocyanine dye system, we studied an oppositely charged system composed of a polycation (poly(diallyldimethylammonium chloride)) (0.2 M) and Direct Blue 71, an organic dye with four negative groups on it (see Figure 1). UV–vis spectroscopy was again used to follow this process. Figure 6a shows the dye absorbance maxima as a function of adsorbed layers of dye and polymer when no salt is present in the polymer solution. We observe just over 50% surface dye extraction (solid circles) after each dip in the polymer solution. When this process is repeated with a polycation solution containing 2 M NaCl (see Figure 6b), we observe that considerably more dye adsorbs onto the surface and that this dye is almost completely extracted by a subsequent immersion in a polymer solution. These results again point to a strong influence of salt concentration on dye–polymer multilayer formation.

We performed two controls for the experiments shown in Figure 7a,b. We first absorbed dye onto a poly(diallyldimethylammonium chloride) surface made without salt (upward triangle in Figure 7a at dye$_1$) and then immersed it in a polymer solution that contained 2 M NaCl (upward triangle in Figure 7a at p-mer$_1$). In the opposite experiment we adsorbed dye onto a poly(diallyldimethylammonium chloride) surface made with 2 M salt (downward triangle in Figure 7a at dye$_1$ that is covered by solid circles) and then immersed it in a polymer solution that did not contain any salt (downward triangle in Figure 7a at

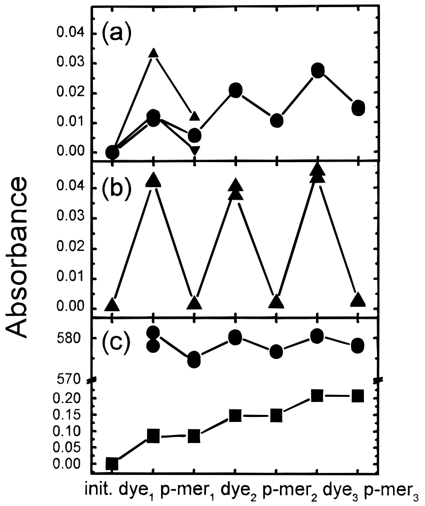

Figure 7. UV−vis absorbances from Direct Blue 71 maximum. Quartz substrates were first dipped in 0.1 M poly(ethylenimine) for 30 min, 0.2 M poly(styrenesulfonate) (2 M NaCl) for 20 min and then alternately into (a) 0.2 M poly(diallyldimethylammonium chloride) (no salt) and 1 mM Direct Blue 71, (b) 0.2 M poly(diallyldimethylammonium chloride) (2 M NaCl) and 1 mM Direct Blue 71, and (c) 0.2 M poly(allylamine hydrochloride) (2 M NaCl) and 1 mM Direct Blue 71. From a solution of known dye concentrations, we calculate that there are approximately 3.8×10^{15} dye molecules per absorbance unit per square centimeter in one film (not in both sides of the substrate as measured in the experiment and shown here).

p-mer$_1$). These results are in good agreement with those obtained from polymer solutions with constant salt concentration that are shown in Figure 7a,b and further suggest that the primary factor influencing dye extraction is the polymer solution and not the polymer layer the dye adsorbs on.

To study the effect of changing the composition of the polycation, we examined multilayer formation from Direct Blue 71 and poly(allylamine hydrochloride) with 2 M NaCl. Figure 7c shows UV−vis absorbances of the dye maximum as a function of multilayer growth. Two significant differences between parts c and b of Figure 7 are that Figure 7c shows almost no surface extraction and that the amount of dye that is adsorbed onto the poly(allylamine hydrochloride) surface is about twice as high as the amount adsorbed onto the poly(diallyldimethylammonium chloride) surface. Clearly the polymer composition strongly influences dye adsorption and extraction.

As was the case in the copper phthalocyanine/poly(styrenesulfonate) system, UV−vis spectroscopy suggests that the dye molecules (Direct Blue 71 in a poly(diallyldimethylammonium chloride) matrix) are sensitive to their environments. Figure 6c shows the dye peak maxima as a function of multilayer formation. These peak positions oscillate depending on whether the last layer is dye (higher) or polymer (lower). The oscillation decreases with increasing number of layers. These peak positions are lower than the corresponding dye peak maximum in a dilute aqueous solution (6.3 μM, 587 nm). We again attribute these shifts to changes in the polarity of the surrounding matrix.

Conclusion

We have demonstrated that dye incorporation into a polyelectrolyte matrix depends on the type of dye and polymer employed and have further shown a peculiar dependence on ionic strength. We noted that the stiffness of the polymer at low ionic strength reduces dye binding. At very high ionic strength the polymer appears to complex ions in solution and not the dye. We show that there is an optimum salt concentration or set of concentrations for most efficient dye inclusion. This optimum depends on the type of salt in a qualitatively predictable way. At this optimum the dye washed out may correspond to the fraction weakly bound in ref 8. These studies have been undertaken to better understand film formation and the incorporation of functional molecules in them and to better control the properties of this promising class of macromolecular structures.

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