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Binding of Sulfonated Fluorophors by Metal–Poly(ethylenimine) Complexes

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ABSTRACT: The binding of 1-pyrenesulfonate (PySA), 1,3,6,8-pyrenetetrasulfonate (PySA4), and 1,8-anilinonaphthalenesulfonate (ANS) to the Cu(II), Zn(II), and Ag(I) complexes for poly(ethylenimine) (PEI) has been studied by measuring fluorescence intensities and excitation and emission spectra at various metal-to-pyrene ratios in the presence of PEI. Significant findings are as follows: (1) PySA reacts to form ground-state dimers when bound to Cu(II)- and Zn(II)-PEI; (2) on Cu(II)- and Zn(II)-PEI and to a lesser extent on Ag(I)-PEI the amounts of bound PySA exceed that required for electroneutrality under certain conditions; (3) PySA4 binds more strongly to Ag(I)-PEI than to Cu(II)-PEI; (4) PySA forms excimers to only a very small extent when bound to protonated PEI; and (5) ANS emits at shorter wavelength when bound to Zn(II)-PEI than when bound to protonated PEI. The results are interpreted as indicating that binding to Cu(II)- and Zn(II)-PEI is predominantly hydrophobic and territorial because the PEI shields the bound counterion from the charge on the metal ion. On Ag(I)-PEI and particularly on protonated PEI the charge on the polyelectrolyte is more accessible to bound counterions, causing electrostatic interactions to be more important and binding to be more site specific.

Introduction

Polyelectrolytes bind organic reagents carrying the opposite charge.[1] The driving force for binding includes both the electrostatic attraction between opposite charges and the increase in solvent interaction energy that accompanies lipophilic interaction between hydrophobic regions of the polymer and the organic ions. Binding to a polyelectrolyte modifies the local environment and can cause large increases in the rates of reactions involving the bound ion.[2] The majority of studies to date have involved anionic polyelectrolytes. The cationic polyelectrolyte that has received the most attention is poly(ethylenimine) (PEI) and derivatives thereof.[3,4]

We report here a study of the binding of anions to cationic metal–poly(ethylenimine) complexes. The goal of this study was to demonstrate that the structure of the metal center influences the relative extent of electrostatic and hydrophobic interactions between polyelectrolyte and counterion. Thus, by appropriate choice of metal ion, it is possible to vary the environment of the counterion and study how changes in environment affect reactivity.

Luminescence has been used to characterize the binding of 1-pyrenesulfonate and 1,3,6,8-pyrenetetrasulfonate to Cu(II)-, Zn(II)-, and Ag(I)-PEI complexes. Both quenching by metal ions and pyrene excimer formation have been observed. Concentration quenching and excimer formation have previously been used to demonstrate counterion clustering on anionic polyelectrolytes.[5-7] Excimer formation has also been used to study the hydrophobic binding ability of PEI quaternized with lauryl adducts.[3] Ground-state pyrene dimers have been obseved when pyrene is covalently bound to a polymer.[4] Association of ionic pyrene derivatives with polyelectrolytes has been shown to modify pyrene absorption spectra.[4]

Experimental Section

Reagents. Tetraethylenepentamine and poly(ethylenimine) were obtained from Aldrich. PEI, nominal molecular weight 40 000, was received as a 50% aqueous solution. The actual concentration determined by elemental analysis was 49.3%. The PEI is prepared by free radical polymerization and includes approximately 25% primary, 50% secondary, and 25% tertiary amine groups.[8]

1-Pyrenesulfonic acid sodium salt (PySA) and 1,3,6,8-pyrenetetrasulfonic acid tetrasodium salt (PySA4) were obtained from Molecular Probes, Inc. 8-Anilino-1-naphthalenesulfonic acid (ANS) was obtained from Aldrich as the magnesium salt. Inorganic salts, Tris buffer, and standard metal solutions were obtained from Fisher. The salts used to prepare metal standard solutions were copper nitrate, silver nitrate, and zinc chloride. All chemicals were used without further purification. Water was double-deionized and glass-distilled.

Apparatus. All fluorescence measurements were performed in 1.00-cm quartz cells on a Perkin-Elmer MPF44E spectrofluorometer. Conventional 90° sample geometry was used for all measurements. Wavelengths are indicated in the Results.

Cu(II) activity and pH were measured with an Orion Digital Ionanalyzer/501 meter. A combination glass electrode was used to measure pH. Cu(II) was measured by using an Orion solid-state (CuS) electrode with a calomel reference electrode. Ag(I) activity was measured using a silver wire indicator electrode and a calomel reference electrode with a Keithley digital multimeter.

Procedures. Potentiometric titrations were performed by adding known volumes of standard metal solution to a PEI solution. Both solutions were buffered with Tris to pH 7.42 in 0.10 M $NaNO_3$, which was used to maintain constant ionic strength.

Fluorescence titrations were performed at a constant PEI concentration corresponding to 0.10 mM monomer units and at a constant fluorophor concentration of 0.010 mM. Appropriate volumes of either metal standard or blank were added to achieve the desired metal-to-nitrogen ratio. All solutions contained 0.10 M $NaNO_3$ and were buffered to pH 7.42 with Tris. To get reproducible results it is critical to maintain constant ionic strength as well as to keep the order of reagent addition constant.

Results and Discussion

Potentiometric Titrations. Figures 1 and 2 show curves for potentiometric titration of PEI with Cu(II) and Ag(I), respectively. The Cu(II) curve shows a moderately sharp end point (taken as the point of maximum slope) corresponding to one Cu(II) ion per 5.6 monomer units. Since Cu(II) tends to bond strongly to four nitrogens, it is most likely that the metal site is a Cu(II)–triethylenetetramine complex. If this is the case, then at the end point of the titration, there is an average of 1.6 monomer units between adjacent Cu(II) sites. As the metal ion-to-monomer ratio increases, electrostatic repulsion between adjacent sites becomes more significant and counteracts the tendency of the metal ion to bind to nitrogen. Cu(II) complexes with PEI have been studied previously,[9-11] and it has been observed that the capacity for Cu(II) depends on the degree of cross-linking.

The curve for Ag(I) shows a change in slope at a point corresponding to 4.3 monomer units per Ag(I) ion. Since Ag(I) bonds strongly to two nitrogens, it is likely that the metal site is a Ag(I)–ethylenediamine complex. If this is

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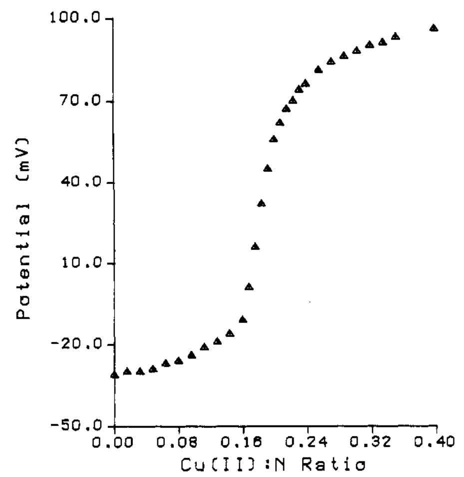

Figure 1. Potentiometric titration of PEI with 1.00 mM Cu(II).

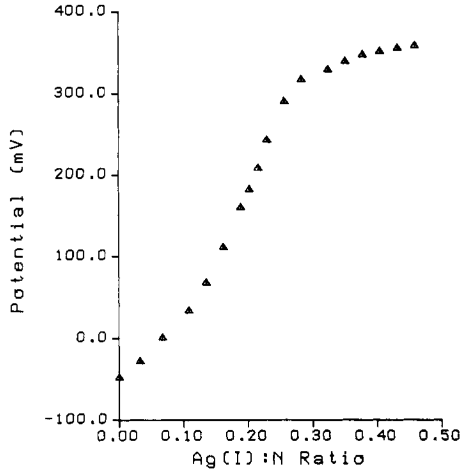

Figure 2. Potentiometric titration of PEI with 10.0 mM Ag(I).

the case, then there is an average of 2.3 monomer units between adjacent metal sites at the point of the slope change.

The Ag(I) titration curve is far from ideal. The slope of the curve in the region before the "end point" is considerably greater than predicted for a polymer with multiple equivalent binding sites for Ag(I). Instead the tendency to bind additional silver ions decreases as the ratio of Ag(I) to monomer increases. As a consequence it is difficult to define an end point in the conventional manner. The slope change probably overestimates the true end point, accounting for the apparent difference in the average number of monomers between adjacent metal sites for the Ag(I) and Cu(II) polymers.

PEI was not titrated with Zn(II) because there is no suitable Zn(II) electrode available. From the known solution chemistry of Zn(II), however, it is expected that the Zn(II) is bound to six monomer units. Zn(II) complexes with nitrogen ligands are weaker than the corresponding Cu(II) complexes but stronger than the Ag(I) complexes.

It is important to keep in mind that the picture of the polymer presented above is an oversimplification, particularly in view of the fact that PEI is highly branched. It also should be noted that only 70% of the nitrogens are available to accept protons when PEI is titrated with acid.[12]

Spectra. Figure 3 shows emission and excitation spectra for PySA in the presence of PEI with and without added Zn(II). The addition of Zn(II) causes the appearance of a broad emission band peaking around 470 nm. This band is normally attributed to the formation of an excited-state dimer or "excimer".[13] However, in this system the appearance of the band is accompanied by a drastic change in the excitation spectrum, implying that the interaction is occurring in the ground state rather than the excited state. It has been previously shown that PySA excimer formation in aqueous solution is not accompanied by a change in absorption or excitation spectrum.[13]

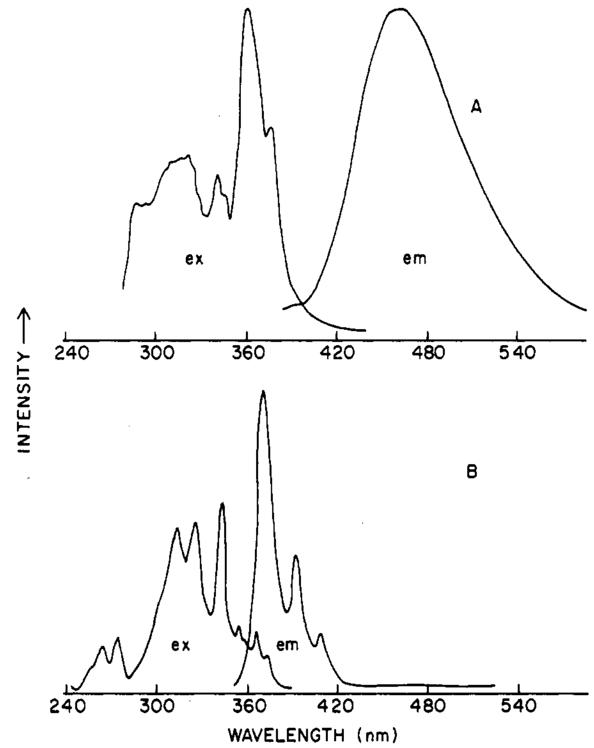

Figure 3. Excitation and emission spectra of PySA in the presence of PEI with (A) and without (B) added Zn(II). The excitation wavelength is 363 nm for the emission spectrum with added Zn(II) and 345 nm with no added Zn(II). The emission wavelength is 470 nm for the excitation spectrum with added Zn(II) and 374 nm with no added Zn(II).

The addition of Cu(II) quenches emission from PySA and PySA4 in the presence of PEI. In the case of PySA, the addition of Cu(II) causes changes in the PySA absorption spectrum, indicating that ground-state dimerization of PySA is occurring on Cu(II)–PEI.

The addition of Ag(I) quenches fluorescence from PySA and PySA4 in the presence of PEI. Weak (i.e., <10% of total emission) PySA excimer emission is observed upon addition of Ag(I).

The addition of acid bringing the pH to 2.5 leads to very weak PySA excimer emission (less than 4% of total emission when the H:N ratio is 5). Herkstroeter et al. have observed that association of ionic pyrene derivatives with oppositely charged polyelectrolytes does not lead to excimer emission.[4]

The addition of both protonated PEI and Zn(II)–PEI cause ANS to become fluorescent. This indicates that ANS is associating with the polymer because ANS does not fluoresce in water. In the presence of excess polymer, the wavelengths of maximum ANS emission are 484 nm for protonated PEI and 475 nm for Zn(II)–PEI. Since ANS emits at shorter wavelengths in less polar media,[14] these results indicate that ANS is in a more hydrophobic environment on Zn(II)–PEI than on protonated PEI.

Fluorescence Titrations. Figure 4 shows the effect of added Cu(II) on PySA emission intensity in the presence of PEI and tetraethylenepentamine. Cu(II) quenches strongly when PEI is present and only very weakly with tetraethylenepentamine. Since the Cu(II)–tetraethylenepentamine complex simulates the metal site on the polymer, this experiment shows that the polymer is required

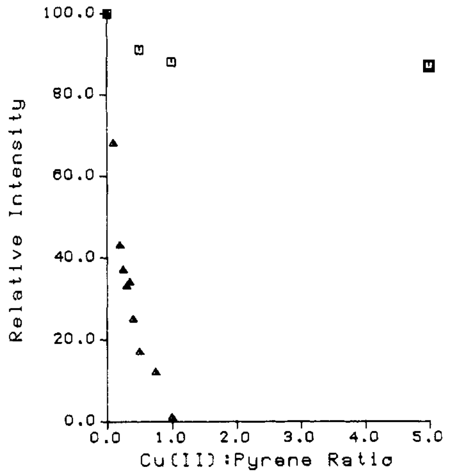

Figure 4. Effect of added Cu(II) on PySA emission intensity in the presence of PEI (△) and triethylenepentamine (□). Fluorescence was excited at 345 nm and observed at 374 nm.

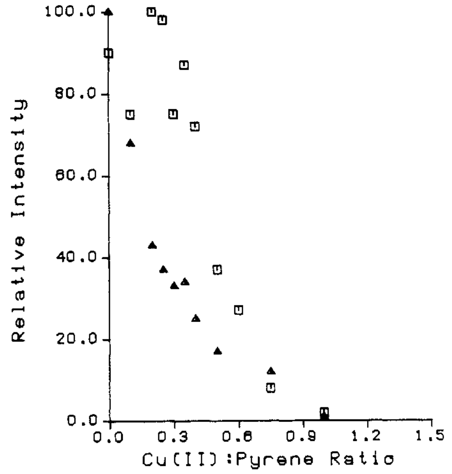

Figure 5. Intensity of emission from PySA (△) and PySA4 (□) in the presence of PEI as a function of the ratio of Cu(II) to pyrene derivative. Fluorescence from PySA was excited at 345 nm and observed at 374 nm. Fluorescence from PySA4 was excited at 368 nm and observed at 403 nm.

to bind PySA. This in turn indicates that lipophilic interaction between pyrene and the polymer is an important component of the binding since the electrostatic component of binding should be the same for Cu(II)–PEI and Cu(II)–tetraethylenepentamine.

This experiment also indicates that at the concentration levels used in this study, Cu(II) does not significantly quench PySA emission if both are free in solution.

Figure 5 shows that added Cu(II) quenches emission intensity for both PySA and PySA4 in the presence of PEI. However, significant quenching of PySA4 emission is not observed until the Cu(II)-to-PySA4 level reaches 0.3. At this point Cu(II) sites on PEI may be close enough to each other that PySA4 can interact with two adjacent sites. If the relative decrease in intensity is assumed to be proportional to the fraction of PySA4 bound to Cu(II) sites on PEI, then a charge balance can be performed to calculate the number of PySA4 ions bound per Cu(II) and the net charge on the polymer. For example, at a Cu(II):PySA4 ratio of 0.50, there are approximately 1.3 bound PySA4 ions per Cu(II) site. This is consistent with the idea that PySA4 is interacting with adjacent sites and indicates that under these conditions the net charge on Cu(II)–PEI–PySA4 is negative.

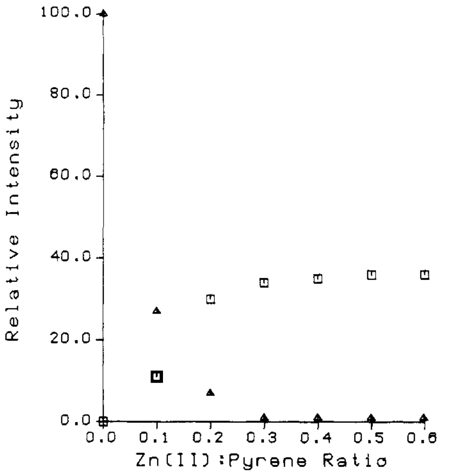

Figure 6. Monomer (△) and dimer (□) emission from PySA as a function of added Zn(II). Monomer emission was excited at 345 nm and observed at 374 nm. Dimer emission was excited at 363 nm and observed at 470 nm.

Figure 6 shows that added Zn(II) leads to a decrease in PySA monomer emission with a parallel increase in dimer emission. The amount of Zn(II) required to bring about this change is small. For example, at a Zn(II):PySA ratio of 0.1, 30% of the final excimer intensity is observed. If excimer intensity is directly proportional to the amount of PySA bound to PEI, then there are three PySA ions bound per Zn(II) at this point and there is a net negative charge on the polymer. Analysis of the decrease in PySA monomer emission with added Zn(II) or Cu(II) leads to the same conclusion.

The behavior of excimers formed upon addition of Zn(II) was found to depend on the particular lot of PEI used in the experiment. In particular, with one lot of PEI, excimer emission was observed immediately upon addition of Zn(II) but was found to disappear in 15–30 min upon standing. Since the supplier indicated the different lots of PEI should be the same, the implication is that the formation of PySA excimers on Zn(II)–PEI is highly sensitive to slight changes in PEI characteristics.

Taken together, the data for Cu(II) and Zn(II) show that the lipophilic component of anion binding is dominant and that the binding is highly "territorial" in nature. The observation that the polymer assumes a negative charge under certain conditions indicates that PySA can associate with PEI in the absence of any electrostatic interaction at all. The observation that bound PySA exists almost exclusively as a dimer indicates that the relatively weak driving force for ground-state dimer formation is still much greater than any tendency of the PySA to assume a specific orientation relative to the charged sites on the PEI. The fact that Cu(II)–PEI binds PySA more strongly than PySA4 confirms the relative importance of lipophilic interactions.

Figure 7 shows that added Ag(I) quenches emission from both PySA and PySA4 in the presence of PEI. Unlike Cu(II), quenching of PySA4 by Ag(I) does not require a threshold level of metal ion. Instead it begins immediately upon addition of Ag(I). Charge balance considerations indicate the ratio of Ag(I) to bound PySA4 is very close to 1.00 at all Ag(I) levels tested. In the case of PySA there is a slight excess of negative charge at low Ag(I) levels, but not to the same extent as in the Cu(II) and Zn(II) systems. As noted above weak excimer emission was observed upon addition of Ag(I). The intensity was nearly constant for all levels of added Ag(I) rather than showing an increase with added Ag(I).

The data for Ag(I) and the fact that only very slight excimer emission is observed for PySA on protonated

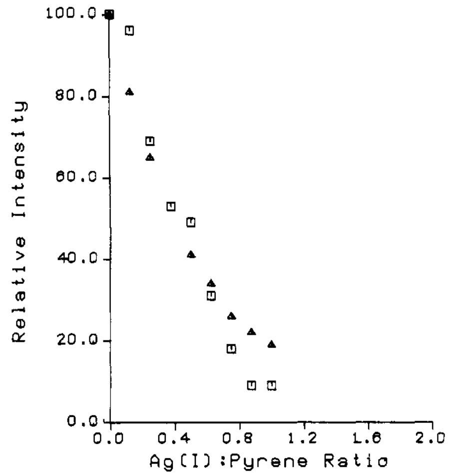

Figure 7. Intensity of emission from PySA (▲) and PySA4 (□) in the presence of PEI as a function of the ratio of Ag(I) to pyrene derivative. Wavelengths are the same as indicated in the caption of Figure 5.

polymer indicate that in these systems the electrostatic component of binding is far more important. The fact that Ag(I) quenches PySA4 emission so readily indicates that there is a direct electrostatic interaction. The weak tendency of PySA to form dimers on Ag(I)–PEI indicates that the PySA tends to be in a specific site, which limits its freedom to interact with other PySA ions. In particular, the sulfonate group bearing the negative charge must position itself very close to the positive charge on the Ag(I). This effect is even greater for the protonated polymer.

Conclusions

Lipophilic interactions are much more important in the binding of PySA and PySA4 to Zn(II)- and Cu(II)–PEI than to Ag(I)–PEI and protonated PEI. Both Zn(II) and Cu(II) form strong complexes with nitrogen ligands. The coordination numbers of the complexes with the polymer are probably 6 and 4 for Zn(II) and Cu(II). As a consequence the metal ion site is surrounded by the polymer and the charge is not directly accessible to counterions. For this reason the electrostatic interaction is weak on these polyelectrolytes, leading to binding which is territorial rather than site specific.

Electrostatic interactions are more important when PySA and PySA4 associate with Ag(I)–PEI. Because the coordination number of Ag(I) is lower than for Cu(II) and Zn(II), the charge may be less effectively shielded from counterions and thus more accessible. Alternatively, because Ag(I) forms a weaker complex with PEI, the electrostatic interaction between Ag(I) and counterion may be strong enough to displace one of the bound nitrogens.

The limited degree of excimer formation when PEI is protonated indicates that in this case electrostatic interactions are dominant and the binding is site specific.

A significant result of this work is to show how one can prepare polyelectrolytes that bind territorially due to lipophilic interactions and that bind in a site-specific manner both using PEI as the base polymer. This system can thus provide a means of studying how the type of binding influences the reactivity of bound counterions.

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Registry No. PySA, 59323-54-5; PySA4, 59572-10-0; ANS·$^1/_2$Mg, 18108-68-4.

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Physical and Spectroscopic Properties of Ternary Polymer Electrolytes Composed of Poly(vinylpyrrolidone), Poly(ethylene glycol), and Lithium Trifluoromethanesulfonate

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ABSTRACT: Poly(vinylpyrrolidone) (PVP) complexes with lithium trifluoromethanesulfonate were plasticized by poly(ethylene glycol) to give solvent-free polymer electrolytes with low glass transition temperatures (from −46 to +3 °C) and good ionic conductivities ($5 \times 10^{-5}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at 100 °C). The complexes were all determined to be amorphous, and they contained no excess salt over a wide range of polymer salt stoichiometries. The PVP-based electrolytes proved to be thermally stable, and separate phases did not form at 100 °C. Infrared spectroscopy of the plasticized polymer electrolytes demonstrated strong interaction between the lithium cation and the carbonyl of PVP.

Introduction

Polar polymers with low glass transition temperatures (T_g) form polymer–salt complexes that are good solvent-free polymer electrolytes.[1] The necessity of a low T_g excludes many potential polymer hosts.[2,3] For example, poly(vinylpyrrolidone) (PVP, 1) is known to complex many

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