Interaction of Pyrene-Labeled Poly(ethylene imine) with Sodium Dodecyl Sulfate in Aqueous Solution

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ABSTRACT: The interaction between pyrene-labeled poly(ethylene imine) (PEI−Py), a hyperbranched polymer, and the anionic surfactant sodium dodecyl sulfate (SDS) in aqueous solution was studied using steady-state fluorescence measurements. Fluorescence experiments were carried out with PEI−Py containing approximately one Py group per 900 monomer polymer units (PEI−Py/900) at two different pH and at two polymer concentrations. When SDS was added to the PEI−Py/900, at both pH 6.6 and pH 10, the monomer fluorescence I_M increased significantly, with a much less pronounced change in the excimer emission (I_E). In the absence of SDS, the monomer intensity is substantially reduced due to quenching of Py* by secondary and tertiary amino groups of the polymer, whereas the excimer emission is less affected. The increase in I_M with increasing SDS concentration indicates that SDS molecules protect Py* from quenching, through formation of polymer-bound micelles formed at the sites of the Py groups. In contrast, I_E remains practically unchanged (0.3 wt % PEI, pH 6.6) or decreases. The decrease in I_E is attributed to disruption of Py aggregates upon their binding to SDS.

Introduction

Polymer-surfactant aqueous systems have been intensively studied over the past 2 decades.[1−3] A steadily growing interest in these systems is driven by their wide range of technical applications. For example, water-soluble polymer−surfactant mixtures are used in various technological formulations, such as paints, coating fluids, inks, drug delivery systems, and foodstuffs. The polymer−surfactant association depends on many factors including Coulombic interactions, the hydrophobicity of the polymer−surfactant pair, and conformational features of the polymer.[4]

The current view that has emerged from these studies of polymer−surfactant complexation is that surfactants often interact cooperatively with polymers at a critical aggregation concentration, CAC, forming micellelike aggregates along the polymer.[5] This is the case for almost all systems consisting of uncharged polymers and ionic surfactants.[6,7] For polyelectrolytes interacting with oppositely charged surfactants,[4,8] the situation is more complex. Polymer-bound micelles form, and the CAC values are often several orders of magnitude smaller than the critical micelle concentration (cmc) of the surfactant.[4] In these systems, at even lower concentration, individual surfactant molecules can bind to the polymer through ion-pairing interactions. In these various polymer−surfactant systems, the position of the CAC depends on different types of forces which play a role. These include pure electrostatic forces, structural features of the different types of charged groups, and other factors such as the presence of hydrophobic moieties on the polyelectrolyte, the flexibility of the polymer backbone and its architecture, and the type of the counterions present.

Many experimental techniques have been used to study polymer−surfactant interactions.[3] Fluorescence spectroscopy is often particularly useful for elucidation of detailed structural aspects of the process of polymer−surfactant interaction.[9] Fluorophores can be used in two ways for the study of polymer−surfactant complexation. First, one can add a luminescent dye as a probe to the system. These dyes associate with hydrophobic domains in the system. By using fluorescent probes it is possible to determine the CAC, the aggregation number (N_{agg}) of the polymer−surfactant systems, and, also, the microenvironment (polarity and viscosity) within the complexes. In the second approach, the fluorophore is covalently attached to the polymer, and serves as a polymer-bound label. Of the various dyes that have been employed for the study of polymer−surfactant interactions, pyrene (Py) has often been used both as a probe and as a label. The features of pyrene that make it an attractive chromophore include its well-characterized long-lived excited state, the sensitivity of its fluorescence to quenching, the sensitivity of its vibrational fine structure shifts (I_1/I_3) to microenvironment polarity, and its propensity for forming excimers. These various fluorescence properties of pyrene have been used to study a variety of different kinds of polymer−surfactant systems.

Features of the interaction of polyelectrolytes with oppositely charged surfactants revealed by fluorescence spectroscopy have been described in a number of publications.[10−15] Guillemet and Piculell [15] investigated the interaction between SDS and a hydrophobically modified polyelectrolyte, a cellulose derivative substituted with cationic hydrophobic side chains. Abuin and Scaiano[11] determined the aggregation number of poly(styrene sulfonate)-(PSS-) bound dodecyltrimethylammonium bromide (DTAB) micelles. Recently, Fundin et

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al.[10] showed through time-resolved fluorescence quenching experiments in the poly(acrylic acid) (PAA)−cetyltrimethylammonium bromide (C_{16} TAB) system that the N_{agg} of the polymer-bound micelles is much smaller than that of normal C_{16}TAB micelles. Note that for other systems consisting of anionic polyelectrolytes, such as the polysaccharide hyaluronan (Hy), sodium polyacrylate (NaPA), poly(vinyl sulfate) (NaPVS), and sodium dextranesulfate (NaDxS), studies of the interaction of these polymers with a series of cationic surfactants C_nTAB leads to the finding that N_{agg} values are equal to, or even higher, than the N_{agg} for the corresponding normal surfactant micelles.[12−14]

Although a large number of studies have examined linear polymers, much less attention has been paid to branched and hyperbranched polymers. We have reported recently the synthesis and fluorescent properties of pyrene-labeled poly(ethylene imine) (PEI−Py).[16] Commercial PEI is a hyperbranched polymer containing three different types of amino groups: secondary and tertiary amino groups in the main chain, and secondary and primary amino groups in the side-chain.[17] The ratio of primary-to-secondary-to-tertiary amino groups is 1:2:1.[18] PEI is also a weak polybase. A major feature of the fluorescent labeled polymer is quenching of the Py fluorescence by amino groups of PEI. This quenching depends on the degree of protonation of these groups. Therefore, we expected that fluorescence properties of the PEI−Py would be changed upon association with surfactants, and these changes could help to elucidate the mechanism of interaction of PEI and hydrophobically modified PEI with surfactants.

We examine here the interaction between PEI−Py and the anionic surfactant sodium dodecyl sulfate (SDS) in aqueous solution. The pyrene-labeled PEI used in this study contains one pyrene moiety per 906 polymer monomeric units and is referred to as PEI−Py/900. We describe the steady-state fluorescence properties of this PEI−Py sample upon its association with SDS in unbuffered water (at pH ≈ 10) and at pH 6.6. At pH 10, PEI is practically an uncharged polymer (the degree of protonation $\alpha^* \approx 0.01$), and at pH 6.6, PEI is a strong polyelectrolyte in which approximately 20−40% of the PEI amino groups are protonated. The degree of protonation for these polymer solutions depends on PEI concentration.[16,19−21] The fluorescence measurements under these different conditions allow us to study the interaction of the surfactant with two polymers of the same structure, an essentially neutral polymer at high pH and a strong polyelectrolyte at near-neutral pH.

Experimental Section

Materials. A poly(ethylene imine) (PEI) solution (50 wt % in water, commercial name Polymin P) was obtained from BASF and was used as received. The polymer has a nominal molecular weight of 70 000 (M_w = 750 000). NaCl and NaOH were purchased from BDH, Inc. HCl and NaOH standard solutions were obtained from Aldrich and were used without further purification. Aqueous solutions were made up using distilled water which was deionized in a Millipore Milli-Q water system. The solution concentrations of PEI are given either as weight percents (grams per 100 mL) or as the molar concentration on a monomer basis (moles of monomer per liter of solution). SDS concentrations are given in moles per liter.

Two pyrene-labeled PEI's containing different amounts of pyrene (Py) were synthesized as described in our previous report.[16] The degree of pyrene substitution was determined by UV absorption measurements using $\epsilon_{344} = 39\,800\ L^{-1}\,cm^{-1}$ taken from the value of pyrenemethylamine in THF.[22] We describe the polymer with a notation that indicates the approximate number of EI units per pyrene (n) in the polymer (PEI−Py/n); Thus PEI−Py/900 and PEI−Py/6000 have one pyrene per 906 ethylene imine (EI) units and one pyrene per 6170 EI units, respectively.

Fluorescence Measurements. The fluorescence spectra were recorded at room temperature on a SPEX Fluorolog 2 spectrometer equipped with a DM3000F data system. The emission spectra were not corrected. The excimer-to-monomer intensity ratio (I_E/I_M) was calculated dividing the integrated fluorescence intensity between 450 and 600 nm (I_E) by the integrated fluorescence intensity between 368 and 395 nm (I_M). The excitation wavelength was 343 nm in all experiments.

Polymer solutions examined here were prepared by dilution from an aqueous stock polymer solution (3 wt %) in water. To aqueous solutions of pyrene-labeled PEI (2.5 mL) in a 1 cm quartz cell were added microliter aliquots of a stock SDS aqueous solution with stirring. Emission and excitation spectra of the solutions were recorded using front face detection. The total volume of SDS added did not exceed 0.1 mL. Polymer solutions at different pH were obtained by adding concentrated aqueous solutions of HCl or NaOH to the aqueous solutions of the polymers.

Results and Discussion

We are interested in how SDS interacts with PEI as detected by the fluorescence properties of a Py group bound to the polymer. Here we report experiments in unbuffered aqueous solution at an initial pH of ca. 10 and for partially neutralized polymer, with an initial pH of ca. 6.6. According to the literature[19−21] and our data,[16] the degree of protonation α^* of PEI varies with PEI concentration at fixed pH. We found, for example, that $\alpha^* \approx 0.01$ at pH 10, and at pH 6.6 $\alpha^* = 0.43$ for 0.3 wt % PEI, and $\alpha^* = 0.22$ for 0.03 wt % PEI. At pH 10, the PEI is essentially an uncharged polymer, and for the sake of simplicity, we refer to these solutions as high pH solutions or $\alpha^* = 0$ solutions.

Effect of SDS on the Solution Turbidity. Addition of SDS to partially neutralized solutions of pyrene-labeled PEI (PEI−Py) in water exhibits a different behavior than that for the solutions of PEI−Py at high pH. Upon addition of increasing amounts of SDS to the solution of the PEI−Py at an initial pH 6.6, we observed an increase in the turbidity of the solutions above very low SDS concentrations. For example, at an initial pH 6.6, the onset of turbidity was observed for 0.03 wt % PEI at approximately 1 mM SDS and for 0.3 wt % PEI, at 2.2 mM. Further addition of SDS to the partially neutralized pyrene-labeled PEI (PEI−Py/900) results in the formation of precipitates. This type of behavior is well-known for addition of an oppositely charged surfactant to an aqueous solution of a polyelectrolyte.[23,24]

All results presented here were obtained from samples in which incremental amounts of a stock micellar SDS solution were added to a solution of PEI−Py/900 and the fluorescence of the sample was measured. The details of sample preparation would not be very important if the surfactant added to the sample reached its equilibrium distribution over a reasonable period of time. A reviewer of our original manuscript asked us to test whether the system reached equilibrium quickly, particularly when the PEI was partially protonated. In response, we carried out a number of experiments to test whether the interaction of SDS and PEI−Py is irreversible. First we examined the turbidity of PEI−Py solutions at pH 6.6 as SDS was added, and compared these solutions to ones in which the SDS and PEI−Py were mixed at high pH followed by the slow addition of

HCl to pH 6.6. The turbidity of the solutions was evaluated by measuring their optical density at 450 nm where the contribution of Py absorbance is negligible. Here we found an earlier onset of turbidity and precipitation when SDS was added to the partially neutralized PEI−Py.

In a second set of experiments, we examined how the turbidity of solutions of PEI−Py at pH 6.6 varied with the mode of SDS addition. Here we found a significantly lower turbidity if the SDS solution was added all at once to the PEI−Py solution than if it were added dropwise with vigorous stirring. For example, the optical density of 0.03 wt % PEI−Py/900 at pH_0 6.6, containing 4.4 mM SDS added all at once was 0.21, and that for the same solution obtained by dropwise addition of SDS was 2.65. From these experiments we conclude that the interaction of SDS with protonated PEI is sufficiently strong that the system does not equilibrate on a time scale of hours. These results are consistent with the observation that the precipitate formed by protonated PEI + SDS does not redissolve in the presence of a vast excess of SDS.

A more detailed description of the effect of SDS on phase separation of PEI−SDS mixtures will be presented elsewhere. [25] In the experiments reported here on mixtures of SDS + PEI−Py at pH 6.6, all fluorescence measurements were carried out on solutions containing sufficiently low SDS concentrations such that no turbidity or precipitation of the PEI−Py/900−SDS mixture could be detected.

Fluorescence Spectra of PEI−Py in the Presence of SDS. The influence of SDS on the fluorescence of pyrene groups bound to PEI is complex and depends on polymer concentration, surfactant concentration, and pH. One feature of the system that makes the fluorescence behavior so complicated is the susceptibility of the pyrene groups to quenching by secondary and tertiary amino groups in the polymer. In Figure 1a, we present emission spectra for a 0.3 wt % solution of PEI−Py/900 at $\alpha^* = 0.43$ (initial pH 6.6) and various concentrations of SDS. As can be seen in this figure, as the SDS concentration is increased, the monomer fluorescence increases while the excimer fluorescence remains practically unchanged. The emission spectra for a 0.3 wt % PEI−Py/900 in unbuffered aqueous solution are presented in Figure 1b. Here, the intensity of the monomer emission also increases with increasing SDS concentration. Unlike the case at pH 6.6, however, there is a remarkable decrease in the intensity of excimer emission above 1.1 mM SDS. From these data, we calculated the intensities of the monomer (I_M) and excimer (I_E) fluorescence, and, also, the excimer-to-monomer ratio (I_E/I_M). The results obtained, expressed as the ratio of monomer (or excimer) fluorescence at certain SDS concentrations to that with no added SDS (I_M/I_{Mo}, I_E/I_{Eo}), are plotted in Figure 2a for a 0.03 wt % polymer solution, and in Figure 2b for a 0.3 wt % polymer solution. In Figure 3 we present similar data for the polymer at these concentrations in unbuffered aqueous solution. Here the initial pH was 10 for both 0.03 and 0.3 wt % PEI−Py/900.

For polymer solutions at an initial pH of 6.6, the monomer fluorescence increases linearly with increasing SDS concentration for both 0.03 wt % PEI (Figure 2a) and 0.3 wt % (Figure 2b) PEI concentrations. In contrast, the excimer fluorescence is not changed for the 0.3 wt % PEI−Py/900 solution and decreases a little for

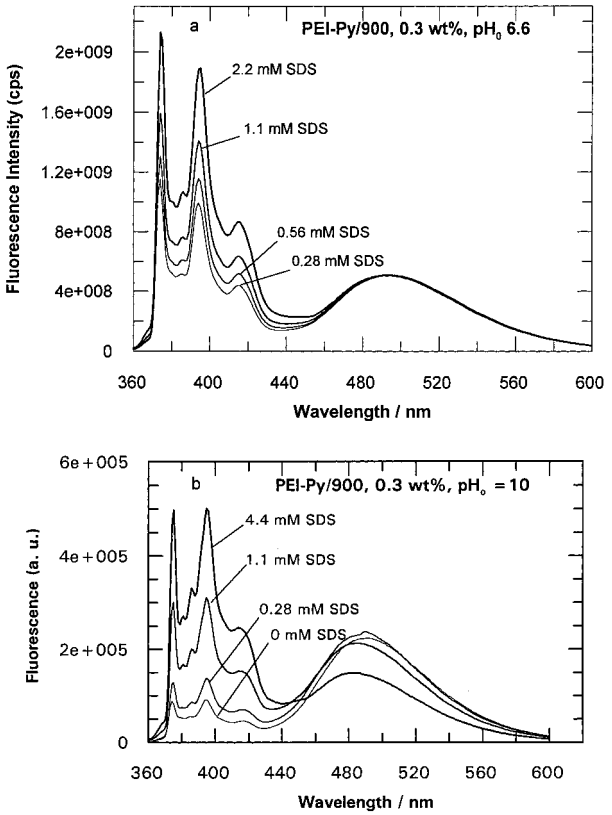


Figure 1. Fluorescence spectra of 0.3 wt % PEI−Py/900 at various concentrations of added SDS at pH 6.6 (a) and pH 10 (b). The numbers on the plot refer to the SDS concentration in each solution.

the 0.03 wt % PEI−Py/900 solution. As a result, I_E/I_M decreases for both PEI concentrations over the whole range of SDS concentrations. For PEI−Py/6000 at 0.3 wt % at pH 6.6, which exhibits a much smaller excimer emission than PEI−Py/900, the changes in I_M are very similar, and occur over the same range of SDS concentrations as the I_M changes for PEI−Py/900.

The fluorescence signal from PEI−Py derivatives at high pH is much weaker than that of the partially protonated polymer due to quenching of Py monomer emission by uncharged amino groups.[16] Nevertheless, the changes in fluorescence observed when SDS is added to these solutions parallels the behavior seen for solutions at pH 6.6. For example, when SDS is added to unbuffered solutions of PEI−Py/900, I_M increases by almost a factor of 6 for an SDS concentration of 8.8 mM, which is a little higher than the cmc value (8.1 mM [26]). Note that at high initial pH, no polymer precipitation occurs in the presence of this concentration of SDS.

As at the initial pH 6.6, the changes in monomer fluorescence intensity in unbuffered aqueous solution are much more pronounced than the changes in the excimer intensity. In Figure 3a we see that the monomer fluorescence intensity for 0.03 wt % PEI−Py/900 increases with added surfactant. There is a small drop in I_E as the SDS concentration reaches 0.001 M ($\beta = [SDS]/[EI] \approx 0.2$), whereas further addition of SDS does not affect I_E. A similar trend was observed for 0.3 wt % PEI−Py/900 (Figure 3b). In this figure we see that the monomer fluorescence for 0.3 wt % PEI−Py/900 increases until it appears to approach a plateau, whereas I_E decreases as SDS is added to about 0.002 M SDS. The behavior of the system at pH 10 appears to be more

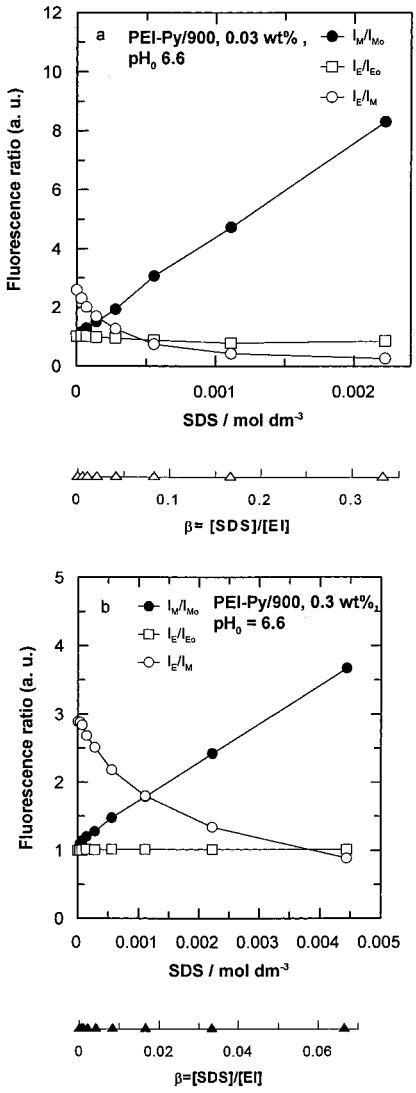


Figure 2. Relative changes in I_M, I_E, and I_E/I_M for the 0.03 wt % (a) and 0.3 wt % (b) PEI−Py/900 at an initial pH 6.6, as a function of SDS concentration. The plot also shows the corresponding ratio of SDS concentration to the molar concentration of ethylene imine units.

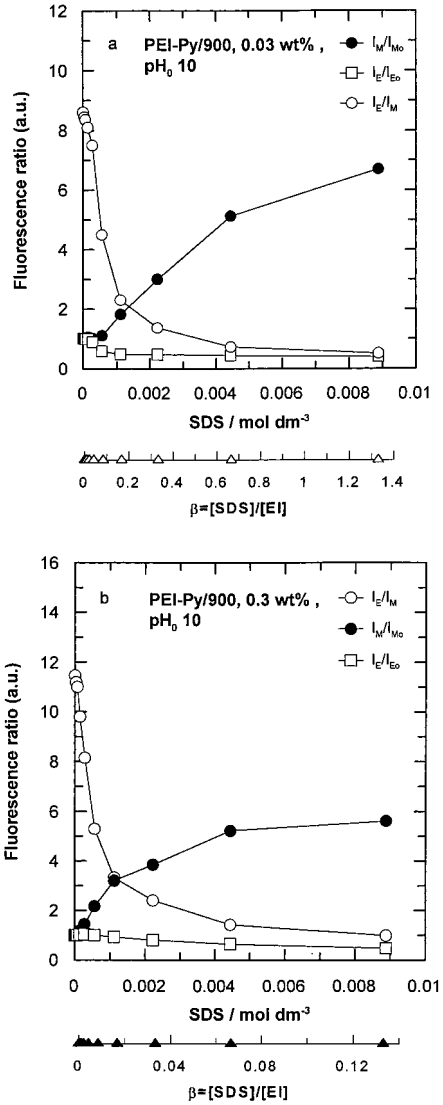


Figure 3. Relative changes in I_M and I_E and changes in I_E/I_M for the 0.03 wt % (a) and 0.3 wt % (b) PEI−Py/900 at initial pH_0 10 as a function of SDS concentration.

sensitive to the absolute concentration of SDS than the ratio β = [SDS]/[EI].

For the sake of clarity, in Figure 4, we present the data shown in Figures 2 and 3 with a logarithmic SDS concentration scale. Figure 4a compares the dependence of I_M/I_{Mo} on SDS concentration at initial low pH with that at high pH for PEI−Py/900, both at 0.03 wt % and 0.3 wt %. In Figure 4 we see that the monomer fluorescence starts to increase at very low SDS concentrations, with differences due to the degree of polymer protonation and the polymer concentration. For the 0.03 wt % PEI−Py/900 at pH 6.6, an increase in the monomer fluorescence is observed at SDS concentrations smaller than 0.1 mM. At the same polymer concentration at high pH, the monomer fluorescence begins to increase at approximately 1 mM SDS. Close inspection of the data in Figure 4a shows that at low SDS concentrations there is a range of concentrations where I_M remains essentially constant. For the 0.3 wt % PEI−Py/900 at pH 6.6, the relative changes in the monomer fluorescence are significantly smaller than those for the 0.03 wt % PEI−Py/900 at the same pH, which suggests that here the pyrene fluorescence may be sensitive to the SDS/EI ratio. At high pH the relative monomer fluorescence changes for the 0.3 wt % PEI−Py/900 are larger than those for the 0.03 wt % PEI−Py/900 below 4 mM SDS, and, approximately, the same above this point. At pH 6.6, in contrast, the monomer fluorescence changes are larger for the lower polymer concentration over the whole range of SDS concentrations.

Relative changes in excimer fluorescence also depend on the pH and polymer concentration (Figure 4b). At pH 6.6, the excimer fluorescence intensity is not changed for 0.3 wt % PEI−Py/900 and decreases a little with increasing SDS concentration for 0.03 wt % PEI−Py/900. At high pH, the relative excimer changes are more pronounced for the lower PEI−Py/900 concentration. It should be emphasized that changes in the excimer fluorescence intensity are much smaller than those of the monomer fluorescence intensity. Because I_M increases and I_E decreases with increasing SDS concentration, plots of I_E/I_M vs [SDS] accentuate the effect of SDS on the polymer fluorescence. Four such plots are presented in Figure 4c. As can be seen in this Figure, the I_E/I_M ratio with no SDS added is larger for the PEI−

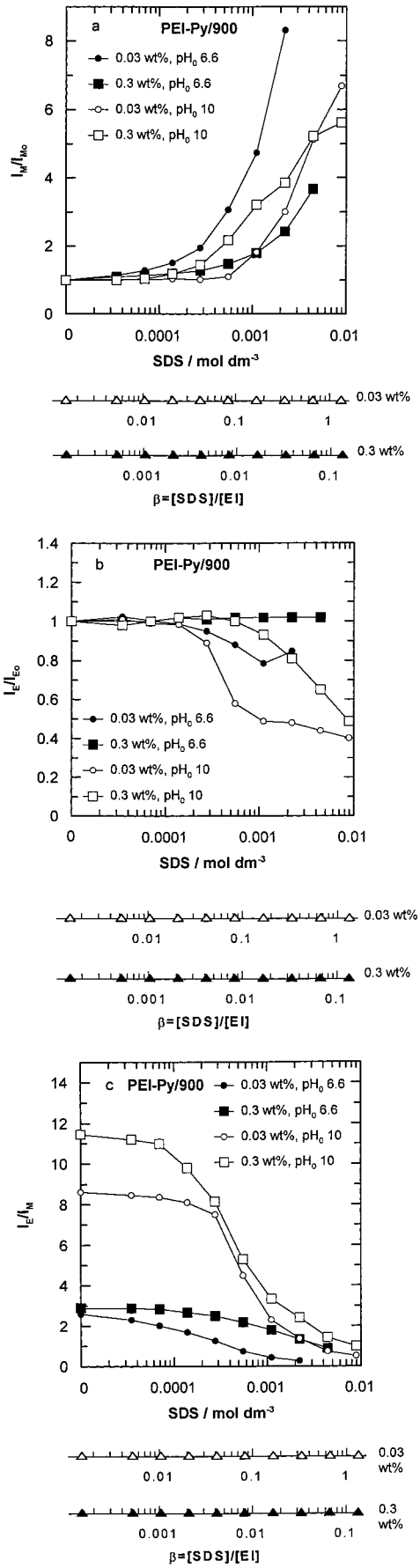


Figure 4. Plots of the relative changes in I_M (a), I_E (b), and I_E/I_M (c) vs the logarithm of the SDS concentration.

Py/900 samples at high pH than that at pH 6.6. As the concentration of SDS is increased, I_E/I_M in all samples decreases.

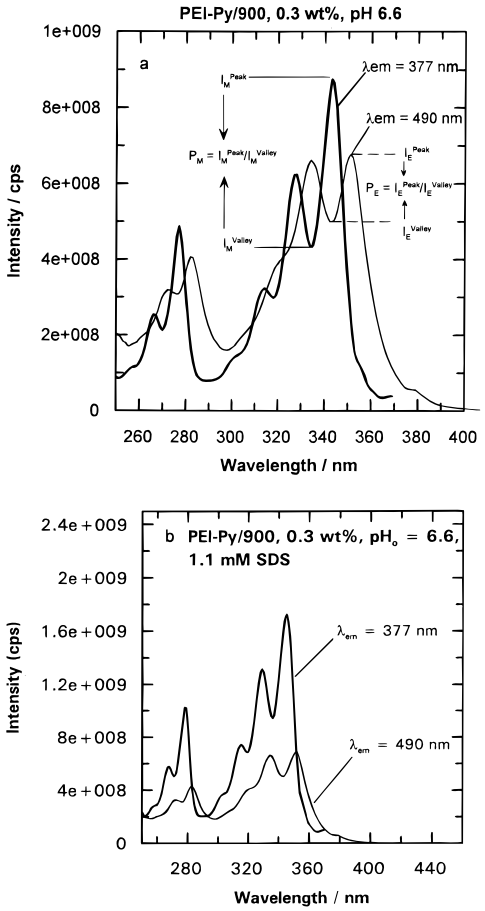


Figure 5. Excitation spectra of 0.3 wt % PEI−Py/900, monitored at 377 nm (monomer, thick line) and at 490 nm (excimer, thin line) at pH 6.6 in the absence (a) and presence (b) of 1.1 mM SDS.

SDS Effects on the Excitation Spectra of PEI−Py. Another interesting feature of the fluorescent properties of PEI−Py/900 appears in the excitation spectra. At 0.3 wt % at both $\alpha^* = 0$ (pH ≈ 10) and $\alpha^* = 0.43$ (pH = 6.6), there is a striking difference in the excitation spectra monitored at the monomer emission and that monitored at the excimer emission as shown in Figures 5a and 6a. For example, at both $\alpha^* = 0$ and $\alpha^* = 0.43$ the peak-to-valley ratios are around 2.0 for the excitation corresponding to the monomer emission and 1.4 for the excitation corresponding to the excimer emission. The excimer excitation shows a pronounced red-shift (7−8 nm) compared to that of the monomer excitation.[16] These results are attributed to direct absorption of light by ground-state preassociated pyrene aggregates, at both $\alpha^* = 0$ and $\alpha^* = 0.43$.

In Figure 5b, we see that at pH 6.6 ($\alpha^* = 0.43$), when 1 mM SDS is added to the solution, small changes in the excitation spectra of the PEI−Py/900 occur. For example, the red-shift of excimer excitation compared to that of the monomer excitation equals 6 nm. In contrast, at $\alpha^* = 0$, the difference between excitation spectra monitored at the monomer emission and that monitored at the excimer emission is diminished with increasing the SDS concentration. The excitation spectra for the monomer and the excimer emissions at $\alpha^* = 0$ in the presence of 1 mM SDS are shown in Figure 6b. As can be seen in this figure, the red-shift between these spectra is only about 1 nm.

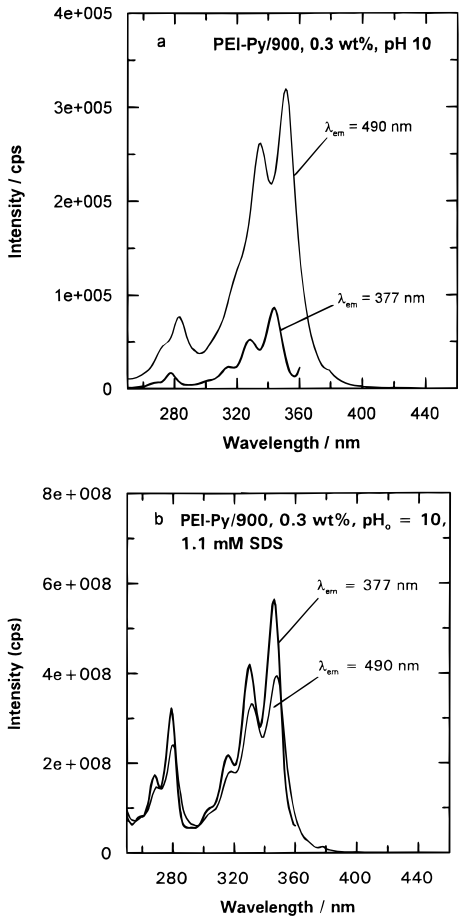


Figure 6. Excitation spectra of 0.3 wt % PEI−Py/900, monitored at 377 nm (monomer, thick line) and at 490 nm (excimer, thin line) at initial pH_0 in the absence (a) and presence (b) of 1.1 mM SDS.

This type of change in the excitation spectra for the monomer and excimer emissions as surfactant is added to a polymer solution was described in ref 27 for the case of pyrene-labeled hydroxypropylcellulose (HPC−Py) at high surfactant concentrations. F. Winnik et al.[27] showed that the excitation spectra of HPC−Py for the monomer and the excimer emissions are similar in shape, with the former blue-shifted by about 4 nm in the absence of SDS. At high SDS concentrations, the excitation spectra of the monomer and excimer emissions become very similar. From our point of view, this effect is explained by changes in the packing of pyrene caused by the presence of surfactant. Mixed micelles form in the region of the aggregates. Pyrene pairs in the same micelle can move apart from one another and still remain close enough to form an excimer following excitation of either pyrene.

The fact that the monomer and excimer excitation spectra of PEI−Py/900 at initial pH 6.6 remain different in the presence of SDS is a striking result. At this pH a significant fraction of the amino groups are protonated. The high local ionic strength inside the polymer coil at pH 6.6 should enhance the strength of hydrophobic interactions and make it more difficult to break up the associated pyrenes. Coulombic interactions of DS^- anions with the protonated amino groups of the polymer at pH 6.6 are much stronger than the interaction of the surfactant with the neutral polymer at high pH. Indeed, the Coulombic interactions are so strong that the system does not readily reach equilibrium over a time scale of hours, and the locus of the sulfate headgroups may affect the interaction of the $C_{12}H_{25}^-$ chains with the pyrene aggregates. As a consequence, pyrene groups remain in physical contact even in the presence of SDS and thus have a very different excitation spectrum than isolated pyrenes.

A Model for the Interaction of PEI with SDS. Other Polymers. Before proposing a mechanism for the effect of SDS on PEI−Py/900 fluorescence, we consider several examples in the literature which describe the interaction between surfactants and pyrene-labeled polymers in water. Changes in conformation of pyrene end-labeled poly(ethylene oxide) (PEO−Py), and PEO containing Py groups at both ends (Py−PEO−Py) upon association with SDS were reported by Quina et al.[28] for PEO−Py and Hu et al.[29] for Py−PEO−Py. In these systems, addition of increasing amount of SDS initially causes an increase in Py excimer emission (I_E) and in the excimer-to-monomer intensity ratio (I_E/I_M). Further addition of SDS results in a decrease in I_E and in I_E/I_M. The authors [28,29] of both papers interpreted this behavior of the polymer in terms of the Py end groups becoming incorporated into micellar aggregates. At lower SDS concentration, the probability of finding two groups per micelle was high. When more SDS was added, dilution of the polymer molecules into an increasing number of micelles led to a decrease in excimer emission. In both reports, the authors detected a lower CAC, compared to that of SDS with unlabeled polymer. They concluded that the hydrophobic Py groups on the polymer promote interaction with surfactant.

F. Winnik et al.[27] reported the interaction of hydroxypropylcellulose (HPC) with anionic and cationic surfactants as studied by fluorescence probe and fluorescence label experiments. In pure water, HPC labeled with Py exhibits both monomer and excimer emission. The latter is shown to originate from pairs or aggregates of preassociated pyrene molecules. The authors[27] showed that addition of surfactant causes a large decrease in the intensity of the excimer emission and a considerable increase in intensity of the monomer fluorescence. As a consequence, the solutions exhibit a sharp decrease in the I_E/I_M ratio for surfactant concentrations above 1×10^{-4} M. These results were interpreted in terms of a mechanism in which the surfactant disrupts the polymer aggregates or promotes changes in the local conformation of the polymer. Either phenomenon would result in a separation of preassociated pyrenes, leading to a decrease in I_E, while I_M should increase at the expense of the excimer emission.

Similar results are described in ref 30, where the interaction of pyrene-labeled derivatives of poly(*N*-isopropyl acrylamide) (PNIPAM) with surfactants was examined. These authors looked at two types of polymers, PNIPAM−Py in which pyrene is the only additional substituent, and PNIPAM−C_{18}Py in which the pendant substituent contains both a Py and a $C_{18}H_{37}$ chain. Aqueous solutions of all these pyrene-labeled polymers, PNIPAM−Py/200, PNIPAM−C_{18}Py/200, and PNIPAM−C_{18}Py/400 exhibited both monomer and excimer emission. The excimer emission for the PNIPAM−Py/200 originates from "static excimers", whereas excimer emission from polymers containing both C_{18} and pyrene groups originates from "dynamic excimers". Despite the different origins of the excimer emission for these two types of pyrene-labeled polymers, addition of surfactants such as SDS and hexadecyltrimethylam-

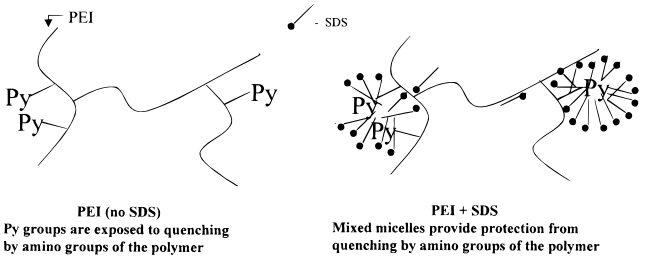
monium chloride (HTAC) affects the fluorescent properties of the samples in a similar manner. I_M increases at the expense of I_E, and as a consequence, I_E/I_M decreases with increasing surfactant concentrations. The authors[30] proposed that the surfactant molecules perturb the intrapolymeric micelles in which several pyrene molecules were in close proximity. Such a disruption, for example through the formation of mixed micelles with the added surfactant, causes the pyrenes to be separated from each other. These authors also found that surfactant binding to the PNIPAM-Py/200 has a cooperative character, whereas binding to PNIPAM-C_{18}Py/200 and PNIPAM-C_{18}Py/400 is noncooperative.

In a recent report,[31] the interaction between SDS and a pyrene-labeled hydrophobically modified cationic cellulose ether (LM-200) was described. Here it was shown that addition of SDS (concentrations above 1×10^{-5} M) to an aqueous solution of the polymer LM-200 led to an increase in I_M, but with no corresponding change in excimer emission intensity. In fact I_E remained nearly constant over the entire range of SDS concentrations. In previous studies of the interaction of other pyrene-labeled cellulose ethers with surfactants,[27] an increase in the Py monomer emission intensity occurred at the expense of the excimer emission. To our knowledge, the report in ref 31 is the first in which added surfactant affects pyrene monomer fluorescence intensity without affecting the excimer emission. The authors[31] assumed that the increase in monomer emission originates primarily from a relief of pyrene self-quenching in nonemissive aggregates in aqueous LM-200−Py solutions.

It should be noted that, in studies of the interaction of pyrene-labeled HPC with SDS,[27] the data were interpreted in terms of a model in which individual SDS molecules interact with isolated pyrene groups in a different manner from pyrene dimers and larger pyrene aggregates because of their different hydrophobicity.

Yoshida et al.[32] recently described interactions between unlabeled and pyrene-labeled poly((acrylamido)-2-methylpropanesulfonate), denoted PAMS and Py-PAMS, respectively. Mixed micelles of *n*-dodecylhexaoxyethylene glycol monoether ($C_{12}E_6$) with HTAC were studied by turbidimetry, dynamic light scattering, fluorescence quenching, and UV spectroscopy. This report focused on the effect of the pyrene label on the polymer−micelle interaction. Yoshida et al.[32] showed that there is a critical mole fraction of ionic surfactant (Y_c) which corresponds to the onset of polyelectrolyte-micelle interaction, and that this Y_c value is the same for PAMS and PyPAMS. However, PyPAMS shows an additional transition at lower surfactant concentration, which was referred to as Y_{c1}. The authors concluded that Y_{c1} and Y_c correspond to the binding of micelles to polymeric pyrene sites and AMPS sites, respectively. By analyzing UV spectra at varying values of Y, they also demonstrated that the polymer-bound pyrene penetrates inside micelles and resides at or near the hydrophobic core. These results indicate preferential binding of micelles to pyrene binding sites. Nevertheless, since Y_{c1} and Y_c show a dependence on the square root of the ionic strength, the authors draw the conclusion that electrostatic forces play a dominant role, and conjoint hydrophobic and electrostatic effects determine the interaction between PyPAMS and $C_{12}E_6$/HTAC mixed micelles. This study clearly shows that the properties of pyrene-labeled polymers in water may be different from those of unlabeled polymers.

Chart 1



PEI−Py + SDS. The PEI−Py system has some features in common with the cationic cellulose derivative LM-200 but differs in many important respects. PEI is hyperbranched and has an amino group in each repeat unit. At pH 6.6, PEI is significantly protonated and acts as a strong polyelectrolyte. When SDS is added to PEI solutions, both at pH 6.6 and in unbuffered solution, the solution pH increases.[25,33,34] Protons are consumed, perhaps by one of the process shown below

$$\text{PEI} + \text{H}^+ + \text{DS}^- \rightleftharpoons \text{PEI}-\text{H}^+/\text{DS}^- \qquad (1a)$$

or

$$\text{PEI}-\text{H}^+/\text{OH}^- + \text{DS}^- \rightleftharpoons \text{PEI}-\text{H}^+/\text{DS}^- + \text{OH}^- \qquad (1b)$$

We suggest that SDS can affect Py fluorescence intensity in three ways. First, it can affect the extent of amine group protonation as described by eq 1. Second, SDS can lead to dimer dissociation through the formation of polymer-bound micelles. Third, it can form polymer-bound micelles at the point of pyrene substitution and thereby protect that Py from quenching by nearby amino groups. The fluorescence of isolated pyrenes on PEI−Py is quenched by secondary and tertiary amino groups on the polymer, whereas these groups are less effective at quenching pyrene excimer fluorescence.[35,36] Thus any feature of the binding of DS^- to PEI which suppresses quenching will have a bigger effect on the Py monomer fluorescence than on the excimer intensity.

Our analysis of potentiometric titrations of PEI indicates that the enhanced protonation of amino groups according to eq 1 is too small to have a significant effect on quenching. [33,25] Thus the first mechanism is not important from the point of view of its influence on pyrene fluorescence. The second mechanism couples an increase in I_M to the disruption of Py aggregates, which would be accompanied by a decrease in I_E. As can be seen in Figure 4b, a decrease in I_E occurs for 0.03 wt % PEI−Py/900 for solutions initially at pH 6.6, and for both the 0.03 and 0.3 wt % solutions of PEI−Py/900 at high initial pH. However, the changes in I_E are much smaller than those in I_M, and the contribution of SDS to the disruption of Py aggregates should have only a small effect on the increase in I_M. We conclude that the major mechanism of interaction between SDS and PEI−Py that affects pyrene fluorescence involves polymer-bound micelles that protect the pyrene groups from quenching.

The drawing in Chart 1 indicates how this interaction may occur: SDS molecules and SDS micelles interact with the polymer. At high pH, the preferred site of interaction is the locus of the pyrene groups, either isolated pyrene chromophores or aggregated pyrenes.

When the pyrenes are incorporated in the micelles, they become further removed from the amino groups responsible for quenching. At lower pH, the interaction is different. At pH 6 to 7, PEI is a strong polyelectrolyte. In this pH range, the dominant interaction between SDS and the polymer is likely to be Coulombic.

To explain all of the features of the interaction of PEI−Py with SDS, particularly the influence of SDS concentration on the relative intensities of the pyrene monomer and excimer emission intensities at different pH, additional data are required. The most important information still not available is the fraction of added SDS which is bound to the pyrene-labeled PEI. Beyond that, one would like to know the mean number of SDS molecules per polymer-bound micelle and how the size of these micelles depends on the site of attachment on the polymer. One would like this information for the polymer both at high pH and in the partially protonated state. Even without this information, it is still possible to draw some general insights from the results of experiments on the influence of SDS concentration on the relative intensities of the locally excited monomer fluorescence I_M/I_{Mo}, the excimer fluorescence I_E/I_{Eo}, and the excimer-to-monomer ratio ($I_E/I_{Eo}/I_M/I_{Mo}$).

To help clarify the behavior of this complex system, we replot these data as a function of β = [SDS]/[EI] in Figure 7. We see in Figure 7b for the solutions at an initial pH of 6.6 that increasing SDS concentration has very little effect on the excimer fluorescence intensity. There is a decrease in I_E/I_{Eo} for the lower concentration solution in the vicinity of $\beta = 0.1$, but compared to the changes observed for the unbuffered solutions, this decrease is small. In Figure 7a we see that the relative changes in I_M are not very sensitive to polymer concentration for the low pH solutions. These values increase as β increases, but the differences between the 0.03 and 0.30 wt % solutions are not large. These observations support the idea that in the vicinity of pH 7 almost all of the SDS added is bound to the polymer, but with some preference for binding to sites where pyrenes are attached. At this pH, PEI is a polyelectrolyte with a degree of protonation $\alpha^* = 0.43$ for the 0.3 wt % PEI solution and $\alpha^* = 0.22$ for the 0.03 wt % PEI solution. Electrostatic interactions provide the major driving force for surfactant binding, but hydrophobic interactions influence the site of binding. On the basis of the turbidity experiments described above, we know that this interaction is so strong as to be virtually irreversible.

At high pH, the relative changes in excimer intensity with added SDS are virtually identical for both concentrations of PEI (Figure 7b). In contrast, the plots of I_M/I_{Mo} vs β seen in Figure 7a exhibit a much stronger increase at low values of β for the solution at 0.3 wt % PEI than for the more dilute polymer solution. If I_M/I_{Mo} is sensitive to the amount of polymer-bound SDS, one may infer that, in the range of $0.003 < \beta < 0.1$, the ratio of the polymer-bound SDS to the total PEI−Py concentration is higher for the solution of PEI−Py/900 at 0.3 wt % than at 0.03 wt %. Changes in the relative intensity of the excimer emission for these two solutions begin only at $\beta > 0.01$−0.02. These results suggest that not all of the PEI is bound to the polymer at high pH and that the driving force for binding depends on both the global and local concentrations of hydrophobic substituents on the polymer.

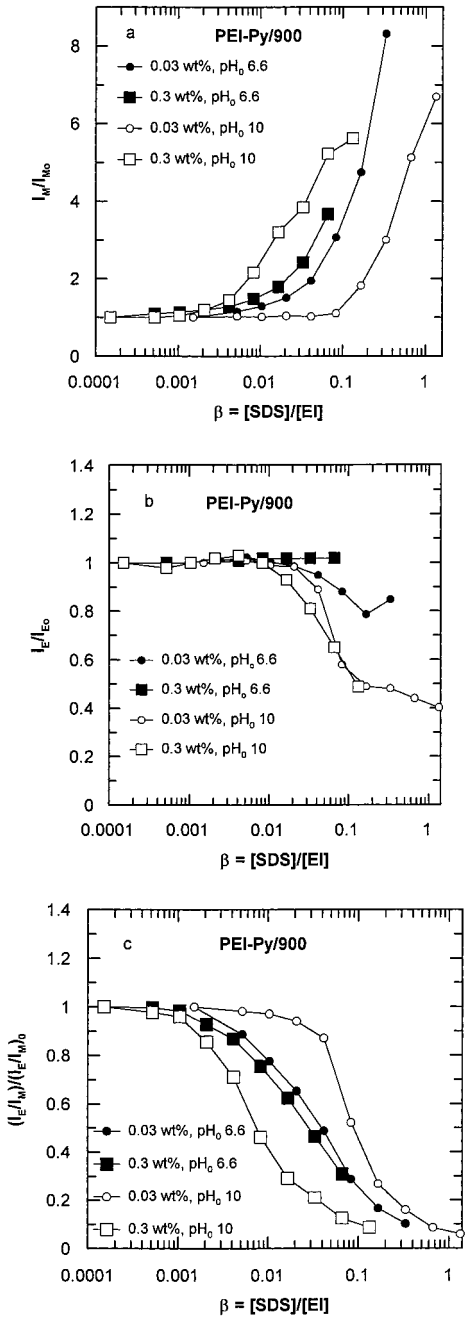


Figure 7. Relative changes in I_M (a), I_E (b), and I_E/I_M (c) obtained from Figures 2 and 3 as a function of the parameter β = [SDS]/[EI].

It is likely that hydrophobic interactions dominate the binding of SDS to the essentially uncharged polymer at high pH. Musabekov's group in Russia studied the interaction of linear PEI with SDS in unbuffered water.[37,38] Linear PEI is a crystalline polymer with limited solubility in water in the unprotonated state at ordinary temperatures. They interpreted their experiments in terms of hydrophobic interactions between SDS and the polymer being much more important than electrostatic interactions at high pH. Our results on hyperbranched PEI at high pH are consistent with their results on linear PEI.

Conclusions

In this paper we report steady-state fluorescence measurements on mixtures of pyrene-labeled poly-

(ethylene imine) (PEI) with sodium dodecyl sulfate in aqueous solution. Addition of SDS affects the intensity of both the pyrene monomer emission (I_M), originating from individual Py groups, and the excimer emission (I_E), originating from preassociated Py aggregates. The magnitude of the changes in I_M and I_E depend on the polymer concentration and the pH of the solution. We found that I_M increases significantly with increasing SDS concentration at both high pH (10) where the degree of protonation $\alpha^* \approx 0$ and at low pH (6.6) where $\alpha^* \approx 0.2$ to 0.43. The onset of the increase in I_M starts at very low SDS concentrations, much lower than the cmc of SDS in the absence of PEI. In contrast, as the SDS concentration is increased, I_E decreases, and the changes in I_E are much less pronounced than those for I_M. It is interesting that at pH 6.6, I_E for 0.3 wt % PEI−Py remains practically unchanged with increasing SDS concentration.

We considered several possible mechanisms for the increase in the monomer fluorescence intensity of pyrene-labeled PEI. The major reason for the increase in I_M with increasing SDS concentration is that quenching of pyrene fluorescence by secondary and tertiary amino groups on the polymer is suppressed through interaction of the pyrene substituents with the surfactant. SDS appears to form polymer-bound micelles that incorporate Py and shield the pyrene chromophore from quenching. Since the pyrene excimer emission is much less effectively quenched by uncharged amino groups, compared to the monomer emission, the shielding effect of SDS is more pronounced for I_M than for I_E. The small decrease in I_E is presumably caused by disruption of Py aggregates bound to SDS.

Some further insights into the nature of the surfactant interaction with the hydrophobic sites on the polymer are provided by the influence of SDS on the excitation spectra of the pyrene groups. In the absence of SDS, polymer solutions at both low pH and high pH show a red-shifted excitation spectrum for the excimer emission compared to the monomer emission, a result indicative of pyrene association prior to light absorption. At high pH, where the polymer is essentially uncharged, in the presence of SDS, the difference in the excitation spectra is very much diminished. From this result we learn that in polymer-bound micelles containing two or more pyrenes at $\alpha^* = 0$, the pyrene groups can move apart from one another, but have enough mobility to form excimers following excitation with light. In contrast, when SDS is added to the 0.3 wt % PEI solution at pH 6.6, almost no changes in the excitation spectra occur. This effect may be explained by assuming that at $\alpha^* = 0.43$, SDS preferentially binds to charged amino groups on the polymer and is less effective at breaking up associated pyrene dimers and aggregates.

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References and Notes

(1) *Water-soluble Polymers: Synthesis, Solution Properties, and Applications*; Shalaby, S. W., McCormick, C. L., Butler, G. B., Eds.; ACS Symposium Series No. 467; American Chemical Society: Washington, DC, 1991.
(2) *Hydrophilic Polymers, Performance with Environmental Acceptance*; Glass, J. E., Ed.; Advances in Chemistry Series No. 258; American Chemical Society: Washington, DC, 1996.
(3) *Interaction of Surfactants with Polymers and Proteins*; Goddard, E. D., Ananthapadmanabhan, K. P., Eds.; CRC Press: Boca Raton, FL, 1993.
(4) Hayakawa, K.; Kwak, J. C. T. In *Cationic Surfactants*; Rubingh, D. N., Holland, P. M., Eds.; Marcel Dekker: New York, 1991; p 189.
(5) Cabane, B.; Duplessix, R. *J. Phys. (Paris).* **1982**, *43*, 1529.
(6) Saito, S. In *Nonionic Surfactants*: *Physical Chemistry*; Schick, M. J., Ed.; Surfactant Science Series; Marcel Dekker: New York, 1987, Chapter 15.
(7) Brackman, J. C.; Engberts, J. B. F. N. *Chem. Soc. Rev.* **1993**, 85.
(8) Wei, Y.-C.; Hudson, S. M. *J. Macromol. Sci.—Rev. Macromol. Chem. Phys.* **1995**, *C35*, 15.
(9) Winnik, F.; Regismond, S. *Colloids Surf. A: Physicochem. Eng. Asp.* **1996**, *118*, 1.
(10) Fundin, J.; Hansson, P.; Brown, W.; Lidegran, I. *Macromolecules* **1997**, *30*, 1118.
(11) Abuin, E. B.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6274.
(12) Thalberg, K.; van Stam, J.; Lindblad, C.; Almgren, M.; Lindman, B. *J. Phys. Chem.* **1991**, *95*, 8975.
(13) Hansson, P.; Almgren, M. *J. Phys. Chem.* **1995**, *99*, 16684.
(14) Hansson, P.; Almgren, M. *J. Phys. Chem.* **1995**, *99*, 16694.
(15) Guillemet, F.; Piculell, L. *J. Phys. Chem.* **1995**, *99*, 9201.
(16) Winnik, M. A.; Bystryak, S. M.; Liu, Z.; Siddiqui, J. *Macromolecules* **1998**, *31*, 6855.
(17) Rivas, B. L.; Geckeler, K. E. *Adv. Polym. Sci.* **1992**, *102*, 171.
(18) Dick, R. C.; Ham, G. E. *J. Macromol. Sci., Chem. A4.* **1970**, 1301.
(19) Lindquist, G. M.; Straton, R. A. *J. Colloid Interface Sci.* **1976**, *55*, 45.
(20) Kokufuta, E. *Macromolecules* **1979**, *12*, 350.
(21) van Treslong, C. J. B.; Staverman, A. J. *Recl. Trav. Chim. Pays-Bas* **1974**, *93*, 171.
(22) Nemeth, S.; Jao, T.-C.; Fendler, J. H. *Macromolecules* **1994**, *27*, 5449.
(23) Saito, S. V. *Kolloid Z.* **1955**, *143*, 66.
(24) Goddard, E. D.; Hannan, R. B. *J. Colloid Interface Sci.* **1976**, *55*, 73.
(25) Winnik, M. A.; Bystryak, S. M.; Siddiqui, J. Manuscript in preparation.
(26) Moroi, Y.; Matsuoka, K. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 2057.
(27) Winnik, F. M.; Winnik, M. A.; Tazuke, S. *J. Phys. Chem.* **1987**, *91*, 594.
(28) Quina, F.; Abuin, E.; Lissi, E. *Macromolecules* **1990**, *23*, 5173.
(29) Hu, Y.-Z.; Zhao, C.-L.; Winnik, M. A.; Sundararajan, P. R. *Langmuir* **1990**, *6*, 880.
(30) Winnik, F. M.; Ringsdorf, H.; Venzmer, J. *Langmuir* **1991**, *7*, 912.
(31) Winnik, F. M.; Regismond, S. T. A.; Goddard, E. D. *Langmuir* **1997**, *13*, 111.
(32) Yoshida, K.; Morishima, Y.; Dubin, P. L.; Mizusaki, M. *Macromolecules* **1997**, *30*, 6208.
(33) (a) Van den Berg, J. W. A.; Staverman, A. J. *Recl. Trav. Chim. Pays-Bas* **1972**, *91*, 1151. (b) The amount of protons consumed upon addition of SDS can be calculated from the measured changes in the pH of the solution. Potentiometric titrations in unbuffered solution show that the proton consumption upon addition of 8.8 mM SDS to unlabeled PEI at 0.2 wt % is 1.7×10^{-11} M and is 2.26×10^{-10} M for 0.025 wt % PEI. The amount of protons consumed upon addition of SDS is equal to the concentration of "modified" PEI amino groups, which is several orders of magnitude smaller than the concentration of the monomer EI units. The bulk solution pyrene concentration for the 0.3 wt % PEI−Py/900 sample is on the order of 10^{-4} M, and that of 0.03 wt % PEI−Py/900 sample is on the order of 10^{-5} M. Even if the SDS molecules bind only to amino groups in close proximity to pyrene moieties, it is difficult to obtain by this mechanism the 6-fold increase in the intensity of monomer fluorescence observed in our experiments.
(34) Vanlerberghe, G.; Handjani-Vila, R. M.; Poubeau, M. C. *Proceedings of the 7th International Congress on Surface Acting Agents, Moscow, 1976*; V. M. Zimina: Moscow, 1978; p 791.
(35) Hrdlovic, P.; Horinova, L.; Chmela, S. *Can. J. Chem.* **1995**, *73*, 1948.
(36) Duhamel, J.; Yekta, A.; Hu, Y.-Z.; Winnik, M. A. *Macromolecules* **1992**, *25*, 7024.
(37) Yui, T. S. T. I.; Abilov, Zh., A.; Pal'mer, V. G.; Musabekov, K. B. *Issled. Ravnovesnykh Sist.* **1982**, 78.
(38) Abilov, Zh. A.; Beisebekov, M., K.; Musabekov, K. B. In *Reakzii v zhidkoi faze;* Izd. KazGU: Alma-Ata, USSR, 1979; p 134.

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