Fluorescence Probe Investigation of Anionic Polymer–Cationic Surfactant Interactions

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ABSTRACT: Pyrene and pyrene-labeled poly(acrylic acid) were used as fluorescence probes to investigate the interactions between poly(acrylic acid) and dodecyltrimethylammonium bromide. The polarity dependence of the vibrational structure of the pyrene emission spectrum indicated the formation of micelle-like surfactant aggregates at concentrations that are significantly below the critical micelle concentration (cmc). The extent of excimer formation of the polymeric probe was found to depend significantly upon the surfactant concentration. These results were interpreted in terms of polymer conformational changes induced by surfactant as well as the static versus dynamic nature of excimer formation.

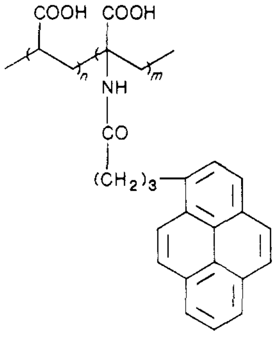
Introduction

When polymers and surfactants are present together either inherently or by design, there can be significant interactions between them that can be important in long-established areas such as mineral and materials processing, enhanced oil recovery, detergency, and paint formulation.[1] More recent interest also stems from the potential for utilizing the microstructural environment of polymer–surfactant complexes in applications such as control of chemical reactivity, drug delivery, solar energy conversion, and isotope separation.[2] Oppositely charged polymers and long-chain surfactants can interact strongly owing to electrostatic factors and the self-aggregation tendency of the surfactant. Thus polymer can induce micelle-type aggregation of the surfactant at concentrations well below the surfactant critical micelle concentration (cmc).[3] Such aggregation has been studied by viscometric, surface tension, dialysis, conductivity, and potentiometric techniques.[4]

The microstructural characteristics of polymer–surfactant complexes are only beginning to be understood with the advent of molecular probing techniques involving phenomena such as fluorescence.[5] In most of these studies the fluorescent species is used to probe the surfactant microenvironment in terms of molecular properties such as micropolarity,[5c] aggregation numbers,[5b] etc. Almost no information is available on the conformational aspects of the polymer upon interaction with surfactants although it is recognized that this factor can play an important role in polymer–surfactant complexation. A priori, polymer conformations in polymer–surfactant complexes could be studied by using labeled polymers. Indeed labeled polymers have been used to study chain conformation and flexibility for a number of polymer systems as well as to study interpolymer complexation.[6] In this paper we report the use of pyrene-labeled poly(acrylic acid) as a probe for studying the interactions in polyacrylic acid–dodecyltrimethylammonium bromide (DTAB) system. Specifically, the extent of excimer formation was used as a measure of polymer strand coiling. Also, particular attention was paid to the influence of the pyrene label on the native polymer by comparing the results obtained by using the polymeric probe versus that obtained by using unlabeled polymer and "free" pyrene probe.

Experimental Section

Dodecyltrimethylammonium bromide, DTAB (Aldrich Chemicals), was recrystallized from ethanol. Sodium polyacrylate, PAA (40K MW monodispersed, molecular weight standard, Polysciences) was used as received. Pyrene-labeled poly(acrylic acid), py-PAA (~40K MW, 1.5 mol % pyrene), shown below was synthesized as described elsewhere.[6a]



n = 0.985; *m* = 0.015; DP = 510; MW = 40 000

Methods. Micropolarity Tests. An aqueous solution of PAA (1 g/L) containing 6 × 10^{-7} M pyrene and 0.03 M NaCl was adjusted to the desired pH value and titrated with DTAB. After each titration, a pyrene emission spectrum was obtained (320-nm excitation) and the third (384 nm) to first (374 nm) vibrational peak ratio, I_3/I_1, was measured. This ratio is known to be a monitor of environment polarity.[7]

Excimer Formation of Pyrene-Labeled Polymer. The titration experiments were repeated with the solution containing 2.5 mg/L of py-PAA instead of free pyrene. The ratio of excimer to monomer, I_e/I_m, was determined at each titration point from the emission spectrum (excitation at 332 nm, monomer 376 nm, excimer 490–486 nm). Single photon counting was used to obtain fluorescence decay profiles of the excimer for each sample (320-nm excitation, 480-nm emission).

Results and Discussion

Micropolarity Studies Using Pyrene. Figure 1 shows typical results for the change in the pyrene fluorescence parameter, I_3/I_1 in 1 g/L PAA as a function of DTAB concentration obtained at pH 6.4, 0.03 M NaCl. The sharp decrease in micropolarity (increase in I_3/I_1) in the presence of the polymer and at DTAB concentration well below the cmc (1.3 × 10^{-2} M, indicated by the arrows, suggests the association of polymer-bound surfactant.[6a] The onset of this polymer-induced association, referred to here as the critical aggregate concentration (CAC), was determined at various pH and NaCl levels and these results are shown in Figure 2. It is noted that the addition of salt as expected leads to an increase in the CAC as a result of the suppression of the electrostatic binding of the surfactant.[3a]

The data in Figure 2 also show that the CAC is relatively independent of pH with no NaCl. At 0.03 M NaCl, CAC increases from 0.4 to 0.9 mM when the pH is increased from 5 to 8 and remains relatively constant above pH 8. This variation of CAC with pH is somewhat surprising since as the degree of ionization, α, increases with pH, an increase in the extent of electrostatic binding consequently

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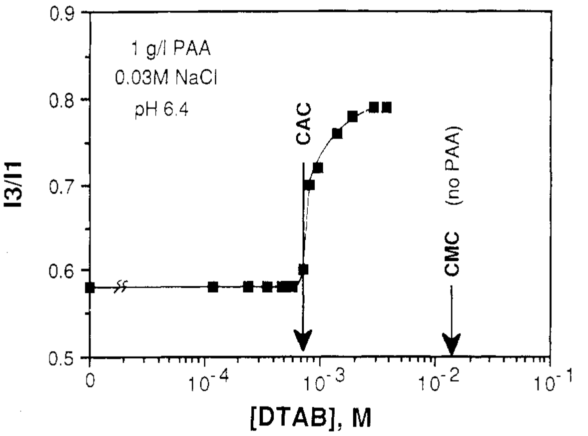

Figure 1. Ratio of third to first vibrational peak of pyrene emission spectrum as a function DTAB concentrations in the presence of 1 g/L sodium polyacrylate.

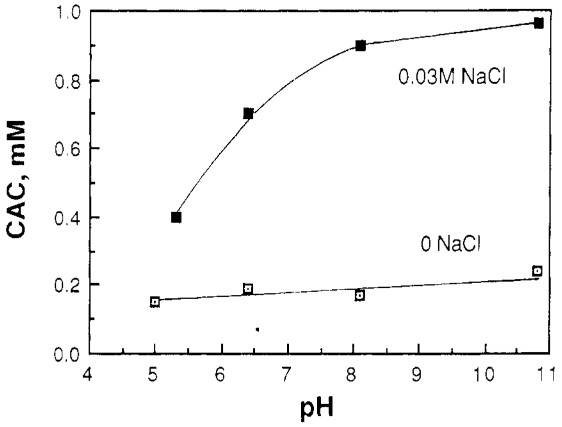

Figure 2. Critical aggregate concentration, CAC, of DTAB in 1 g/L sodium polyacrylate in 0 and 0.03 M added NaCl.

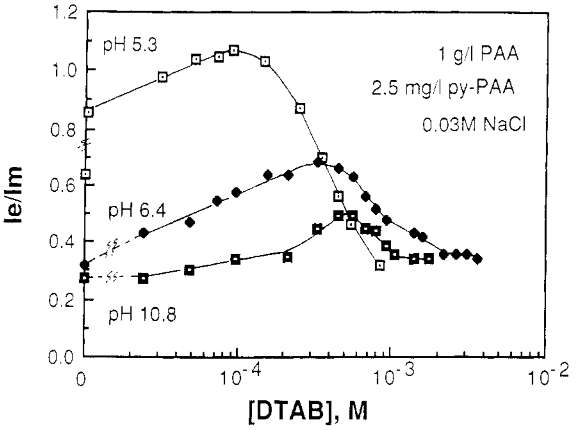

Figure 3. Excimer to monomer ratio, I_e/I_m, of pyrene-labeled poly(acrylic acid), py-PAA, as a function of DTAB concentration in 1 g/L sodium polyacrylate and 0.03 M NaCl.

and a decrease in CAC would have been expected a priori. It should be noted, however, that CAC, in addition to being a measure of the extent of electrostatic binding, is a measure of the efficiency of association of the surfactant with the latter depending upon the conformational flexibility of the polymer which in turn depends upon α. That is, when the polymer is highly charged (large α), the association of alkyl chains of the surfactant and accompanying collapse of the polymer will be opposed by segment–segment repulsive forces. As α decreases, the polymer adopts a more coiled conformation and the association becomes easier to achieve.

Considering these factors, we suggest the following explanation for the pH dependence of CAC: At low NaCl levels, the electrostatic binding efficiency and the segment–segment repulsive contribution offset each other so that the net driving force for association is the hydrophobic chain interaction which can be considered to be independent of pH. On the other hand, at high salt levels the electrostatic binding of the surfactant is suppressed so that the pH dependence of the CAC observed is essentially due to the conformational differences of the polymer.

The above results suggested that the chain flexibility/conformation of the polymer plays a key role in governing the surfactant aggregation process as well. We therefore attempted to get information on the conformational aspects of the polymer–surfactant interaction process using a pyrene-labeled poly(acrylic acid) as a probe, and these results are discussed in the next section.

Excimer Formation of Pyrene-Labeled Poly(acrylic acid). The variation in excimer to monomer ratio of the polymeric probe, py-PAA, as a function of DTAB concentration (1 g/L PAA, 0.0025 g/L py-PAA) in 0.03 M NaCl and 3 pH values is shown in Figure 3. I_e/I_m first increases and reaches a maximum and then decreases. This general trend was observed at all pH values above 5 and at both NaCl levels tested (0 and 0.03 M). The interpretation of this behavior requires an understanding of the nature of the excimer formation process. Two cases may be distinguished:[6c,d] "Dynamic" excimer formation occurs through the excitation of isolated pyrene groups and subsequent diffusional encounter with ground-state pyrene. On the other hand "static" excimer formation can occur if the pyrene groups on the polymer are in juxtaposition either due to the statistical conformation of the chain or due to ground-state aggregation of pyrene groups. Static and dynamic excimer formation can be distinguished by examination of the fluorescence spectra as well as time-resolved behavior as discussed below.[6d,8]

The emission and excitation spectra and the excimer fluorescence decay profiles obtained at the DTAB concentrations before the maximum in I_e/I_m and after the maximum showed the following features:

1. In water as well as at premaximum DTAB concentrations, the excimer emission was centered around 490 nm. Above the maximum, the emission wavelength shifts gradually to about 486 nm.

2. The premaximum excimer excitation spectra (emission at 490 nm) were red-shifted by about 4 nm compared to the monomer excitation spectra (emission at 376 nm) as shown in Figure 4a. In the postmaximum region, the red shift was progressively less with addition of DTAB (compare Figure 4b).

3. Whereas the fluorescence decay profiles of the excimer in the premaximum region showed no initial growth (rise time) those in the postmaximum region showed an initial growth characteristic of a diffusion-controlled excimer formation process (nanosecond timescale) (compare Figure 5, curves A and B).

The above observations are consistent with the existence of ground-state pyrene dimers or aggregates at the premaximum DTAB concentrations (as well as in water) so that the excimer formation is a "static" process. With addition of DTAB beyond the maximum the ground-state aggregates dissociate and the absorbing species are the isolated pyrene groups. Thus at high DTAB concentrations, the excimer formation is dynamic in nature with a characteristic rise time. It is noteworthy that similar findings were reported by Winnik et al.[6d] for the interaction of a polymeric pyrene-labeled probe, (hydroxypropyl)cellulose, with SDS and HTAC. These authors also concluded that at low surfactant concentrations, excimer

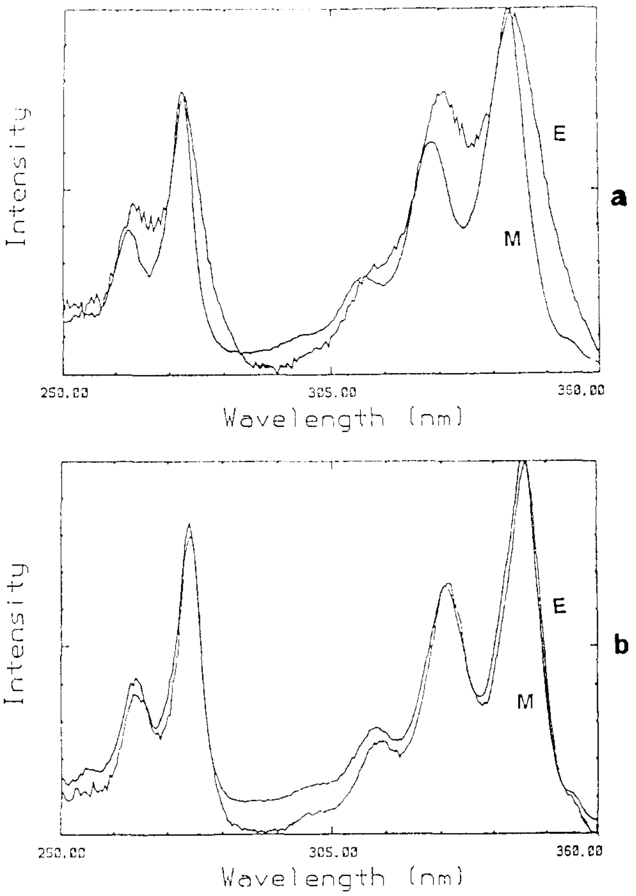

Figure 4. Excitation spectra of monomer, M (376 nm), and excimer, E (480 nm), in (a) no DTAB (premaximum) and (b) 0.001 M DTAB (postmaximum); points correspond to pH 6.4 in Figure 3.

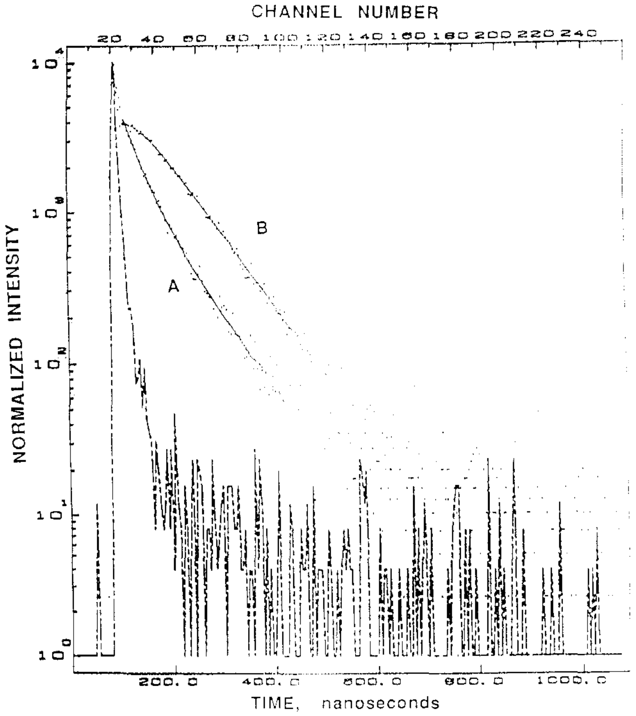

Figure 5. Fluorescence decay profile of excimer (480 nm) for no DTAB, curve A (premaximum), and 0.001 M DTAB, curve B (postmaximum), corresponding to pH 6.4 in Figure 3.

formation occured through the excitation of ground state pyrene aggregates whereas at high surfactant concentrations, excimer formation occured through the excitation of isolated pyrene groups followed by diffusion.

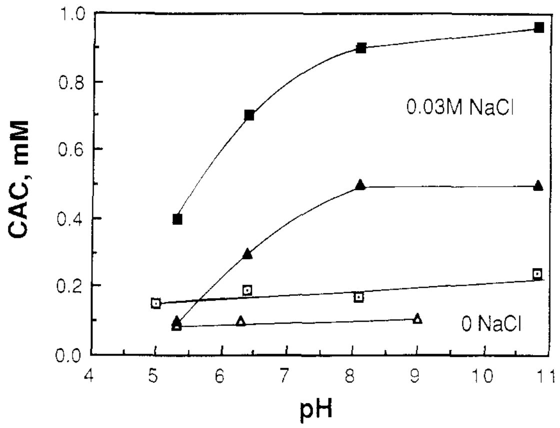

Figure 6. Comparison of critical aggregate concentration determined by excimer formation of covalently labeled polymer (△, ▲) and micropolarity response of free pyrene (□, ■).

It is important to note that since ground-state aggregation of pyrene is most likely due to hydrophobic interactions, the extent of excimer formation will depend not only upon the conformational state of the polymer but also upon the polarity of the pyrene environment. Indeed in nonpolar solvents the extent of pyrene aggregation would be less.[9] Considering these factors, we propose the following explanation to account for the trend in I_e/I_m as a function of DTAB concentration: Addition of the initial amounts of DTAB leads to coiling of the polymer which in turn results in increased excimer formation; this coiling probably results from the charge neutralization as well as the polymer becoming increasingly hydrophobic due to surfactant binding.[10] The maximum in the I_e/I_m indicates the DTAB concentration where surfactant aggregation begins, i.e., the CAC. The associated surfactant provides relatively nonpolar microenvironments in which the pyrene moieties can be "solubilized" so that ground-state aggregates dissociate. Thus the decrease in I_e/I_m at high DTAB concentrations is most likely due to a decrease in the amount of static excimers. Indeed the typical growth and decay profiles obtained for the time-resolved emission at high DTAB concentration is similar to that obtained for dynamic excimer formation in micelles.

The CAC as determined by the maximum in I_e/I_m of the covalently labeled polymer probe is compared in Figure 6 with that from the I_3/I_1 micropolarity response presented earlier. It can be seen that the labeled polymer always reports a lower CAC than "free pyrene" which is attributed to the additional hydrophobic driving force for surfactant binding arising from the presence of the pyrene label so that the association begins at a lower DTAB concentration on the labeled polymer than on the unlabeled one. This difference in CAC for the two cases is more pronounced at high salt concentrations when the hydrophobic contribution to the overall binding is significant; at low salt concentrations the major binding force is electrostatic so that the hydrophobic contribution is less significant.

Importantly, it is noted that the pH dependence of CAC at both salt levels as determined by the polymeric probe is the same as that from the micropolarity tests. This is in agreement with the earlier suggestion that the CAC, in part, reflects the conformational flexibility of the polymer as it changes with the degree of ionization. Thus the I_e/I_m maximum at each pH serves as a measure of the conformational state of the polymer at the onset of association. Examination of I_e/I_m for the three pH values in Figure 3 agrees with the suggestion that the association occurs more efficiently (lower CAC) when the polymer is in a less expanded conformation (higher I_e/I_m).

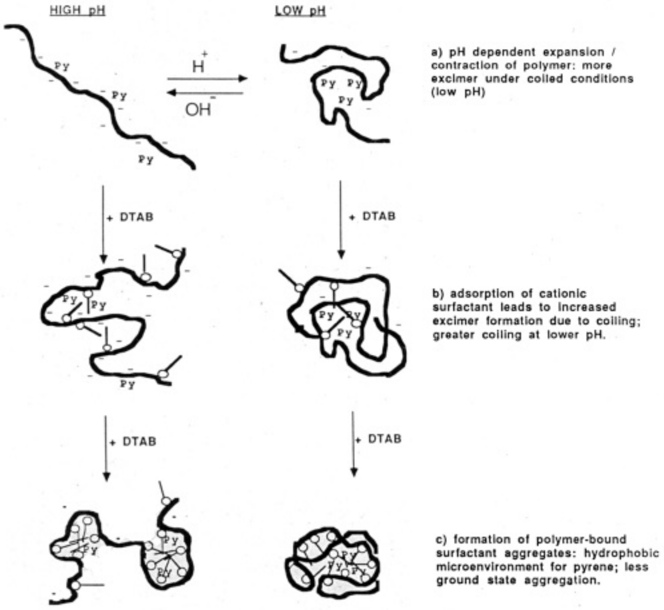

Figure 7. Schematic representation of the formation of polymer–surfactant complexes for pyrene-labeled poly(acrylic acid)–dodecyltrimethylammonium bromide system for high (high pH) and low (low pH) degrees of ionization.

Summary

Pyrene-labeled poly(acrylic acid) was used to investigate interactions between poly(acrylic acid) and dodecyltrimethylammonium bromide, and a schematic representation of these interactions is shown in Figure 7. In particular it was possible to show that binding of surfactant leads to increased excimer formation as a result of polymer coiling. A decrease in excimer formation was observed when the critical aggregate concentration was reached which was attributed to a decrease in the extent of ground-state pyrene aggregation and resulting static excimer formation as a result of solubilization of the pyrene moieties within polymer-bound surfactant aggregates. The critical aggregate concentration determined by the maximum in excimer formation was always lower than that determined by using the micropolarity response of free pyrene. This difference was attributed to the hydrophobic contribution to the binding process resulting from the presence of the pyrene label so that surfactant aggregation starts at lower DTAB concentrations for the labeled polymer then for the unlabeled one. The variation of CAC with pH indicated that the efficiency of surfactant aggregation depended significantly upon the conformational flexibility of the system. Indeed with decrease in pH, the extent of coiling of the polymer–surfactant complex was greater, as indicated by the higher excimer to monomer ratio, resulting in a lowered CAC.

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Registry No. DTAB, 1119-94-4; PAA·Na, 9003-04-7; py, 129-00-0; (acrylic acid)(2-((4-(1-pyrene)butanoyl)amino)propenoic acid) (copolymer, 103315-59-9.

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(9) The excitation spectra of the monomer and excimer in ethanol and propanol as well as dioxane coincided which is in agreement with the idea that the ground-state aggregation and resultant static excimer formation in aqueous solution are due to the hydrophobic interactions between pyrenes.
(10) We suggest that the initial coiling is not due only to charge neutralization since addition of equivalent amounts of tetramethylammonium bromide did not result in an increase in I_e/I_m; the presence of the hydrophobic chain is a requirement for the coiling to occur.