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Fluorescence Probing of Microdomains in Aqueous Solutions of Polysoaps. 1. Use of Pyrene To Study the Conformational State of Polysoaps and Their Comicellization with Cationic Surfactants

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ABSTRACT: Pyrene can be used as a fluorescence probe to study the conformational state of copolymers of maleic acid with alkyl vinyl ethers and with styrene that form microdomains upon neutralization. The pyrene fluorescence spectra and lifetimes in the decyl and hexadecyl vinyl ether copolymers reveal that microdomains exist over the whole range of neutralization degree (α) of the maleic acid moieties and that pyrene can form excimers when solubilized in these microdomains. The pyrene fluorescence intensity and lifetime in the maleic acid/styrene and maleic acid/butyl vinyl ether (PS4) copolymers reveal a transition from a microdomain-containing conformation at low α to an open, hydrated conformation at high α. The addition of cationic surfactants to a solution of fully neutralized PS4 causes the formation of mixed micelles containing units of PS4 and cationic surfactants. The mixed micelles are either electrically neutral or negatively charged.

Introduction

In recent years there has been a large number of studies of polymers that form hydrophobic microdomains in water solution.[1] The repeat unit of these polymers resembles a surfactant, and the microdomains have properties similar to those of surfactant micelles. Thus these polymers can solubilize water-insoluble compounds such as arenes and alkanes. Polysoaps are a particular class of microdomain-forming polymers.[2-8] The term polysoap denotes an alternating copolymer of maleic acid/alkyl vinyl ether. With increasing neutralization degree α, polysoaps with an alkyl chain shorter than *n*-decyl undergo a sudden conformational transition from a compact, microdomain-containing conformation to an expanded, hydrated conformation similar to that of other strong polyelectrolytes.[6,8] Copolymers of decyl vinyl ether and longer chain homologues retain the compact conformation over the entire range of α.[8]

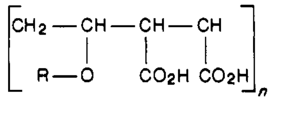
There have been few investigations of the number of repeat units in a microdomain.[3] This information is difficult to obtain by classical techniques owing to the high local concentration of microdomains in polysoap solutions and the resultant large interactions between these microdomains. Moreover, there has been no investigation of the rate at which these microdomains form and disappear, as has been done for micelles in aqueous solutions. The studies reported thus far have dealt with the rate of expansion/contraction of the microdomains brought about by pH changes.[9-11] Such processes should not have the same kinetics as the spontaneous fluctuations of the microdomains.

We have undertaken a study of aqueous polysoap solutions with recently developed fluorescence probing methods.[12-15] These methods have been used to determine the aggregation number of surfactant micelles under a variety of conditions, having the advantage over classical methods of being insensitive to intermicellar interactions. Fluorescence methods are also useful for studying the dynamics of micellar aggregates.[16,17]

In this paper we report preliminary results on the use of pyrene as a fluorescence probe to study (i) changes in the conformation of polysoaps, (ii) the dynamics of the microdomains, and (iii) the effect of cationic surfactants on the conformation of polysoaps.

Experimental Section

Materials. The polysoaps investigated have the general structure



$$\left[\mathrm{CH_2{-}CH(OR){-}CH(CO_2H){-}CH(CO_2H)}\right]_n$$

I

where n is the degree of polymerization and R = CH_3 (PS1), *n*-C_4H_9 (PS4), *n*-$C_{10}H_{21}$ (PS10), or *n*-$C_{16}H_{33}$ (PS16). We have also investigated an alternating copolymer of maleic acid and styrene (I in which OR is replaced by C_6H_5), referred to as PSS. Poly(methacrylic acid) (PMA) was also investigated for comparison with the polysoaps and because its compact coil–expanded conformational transition has been extensively investigated.[9,11,18,19] PS1 and PSS were purchased from Monomer–Polymer Lab (USA) and Aldrich-Europe, respectively. PS4, PS10, and PS16 were gifts from Drs. R. Varoqui and E. Pfefferkorn (ICS-CRM, Strasbourg).[8]

The copolymers were purified by repeated precipitation. The anhydride moieties were fully hydrolyzed by boiling the copolymer with a stoichiometric amount of NaOH. The resulting solution of the sodium salt of PS16 was used without further purification; it was viscoelastic at a concentration of 0.012 (mol repeat unit)/L. The solutions of the sodium salts of PS1, PS4, PS10, and PSS were further purified by successive passages through columns of cationic and anionic ion-exchange resins (Merck types I and III). The concentration of the polyacid solutions was determined by potentiometric titration and is expressed in moles of repeat unit per liter. Measurements of dry weight content confirmed that all anhydride moieties had been hydrolyzed, within experimental accuracy (±4%). These solutions were used to study the effect of neutralization degree on polysoap conformation. The molecular weights of the polymers were not known but are believed to be above 50 000 Da.

The cationic surfactants were hexyl-, octyl-, decyl-, dodecyl-, tetradecyl-, and hexadecyltrimethylammonium chlorides, and decyltrimethylammonium bromide and iodide. The chloride surfactants were prepared from the corresponding bromides[20] by ion exchange (anionic-exchange resin Merck type III). The iodide surfactant was prepared by quaternization of trimethylamine with decyl iodide and was purified by recrystallization from ethyl acetate/ethanol.

The sample of pyrene was the same used in previous investigations.[16,17]

Fluorescence Probing. Pyrene was selected as the fluorescence probe because of its ability to form excimers, its very low solubility in water (6×10^{-7} M) and its long lifetime (about 200 ns in water and 400 ns in organic solvents[14]). The solubility of pyrene in water is greatly increased in the presence of micelles or microdomain-forming polymers.[9,14] The fluorescence spectrum and lifetime of the pyrene molecule yield information about the polarity sensed by pyrene in its solubilization site (micropolarity) and on the change in polarity when the medium is modified.[14-16] The emission spectrum of the pyrene molecule shows vibronic peaks, and the ratio I_1/I_3 of the intensities of the first and third

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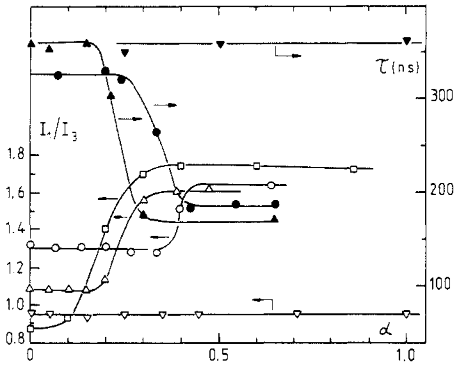

Figure 1. Variations of I_1/I_3 (□, ○, △, ▽) and τ (●, ▼, ▲) with the neutralization degree α for PMA (□); PSS (○, ●); PS4 (△, ▲); and PS10 (▽, ▼) at 25 °C. Concentrations: 0.05 M for PMA, PS4, and PS10 and 0.025 M for PSS.

vibronic peaks is a sensitive indicator of the polarity of the pyrene microenvironment.[14-16]

Fluorescence emission spectra were recorded with an absolute differential spectrofluorimeter Fica 55 over the range 350–650 nm, which includes the emission range of molecular pyrene and pyrene excimer. The fluorescence time–decay curves were determined with the same single-photon-counting apparatus used in previous investigations.[16,17] The excitation and emission wavelengths were respectively 335 and 382 nm, the latter corresponding to an emission band of molecular pyrene. At very low pyrene concentrations ($\sim 10^{-6}$ M), the decay curves were singly exponential and fit the equation

$$I(t) = I(0)\exp(-t/\tau) \qquad (1)$$

where $I(t)$ and $I(0)$ are the fluorescence intensities at time t and time 0 and τ is the fluorescence lifetime of pyrene at its solubilization site.

At higher pyrene concentrations, the decay curves deviated from the single-exponential behavior owing to excimer formation. As with micellar solutions,[12,13,21] the decay curves could then be fitted to the equation

$$I(t) = I(0)\exp(-A_2t - A_3[1 - \exp(-A_4t)]) \qquad (2)$$

where A_2, A_3, and A_4 are constants independent of time. This equation holds very well for micellar solutions. It involves two main assumptions:[12,13]

(i) There is no limit to the number of probes that can be solubilized in a given micelle or microdomain. In practice one has to use a molar concentration ratio [probe]/[microdomain] about 3 times lower than the value corresponding to the solubility of the probe in the system. The microdomain concentration is usually not known but it suffices to use a pyrene concentration 3 times lower than the pyrene solubility in the investigated system.

(ii) The probe distribution in the microdomains is random and obeys Poisson statistics. This assumption has been validated for micellar solutions[22] and for solutions of PMA,[23] which can form microdomains.[9,11,18,19]

The fitting of the decay curves to eq 1 and 2 was performed by a nonlinear least-squares procedure that involved a convolution of the calculated decay curve by the lamp signal.

The solutions were deoxygenated prior to decay measurements by bubbling argon through the solutions or by repeated freeze–pump–thaw cycles.

Results and Discussion

1. Effect of the Neutralization Degree of the Polymer on the Fluorescence Properties of Pyrene.

The pyrene concentration used in these experiments was very small [(1–2) × 10^{-6} M)], ensuring the absence of excimer formation in those systems where pyrene was nearly completely solubilized in the microdomains. Figure 1 shows the changes in the ratio I_1/I_3 of the intensities of the first and third vibronic peaks of the pyrene fluorescence emission with neutralization degree. The neutralization degree α is taken as equal to 1 when both carboxyl groups of the polymer repeat unit are completely neutralized. For comparison we also give our results for PMA, which are very close to those previously reported.[9] It can be seen that, with increasing α, I_1/I_3 is at first small and constant ($\sim$0.9) up to $\alpha = 0.1$ and then increases rapidly to 1.7 over the range $\alpha = 0.1$–0.3, remaining constant to $\alpha > 0.3$. The values of I_1/I_3 at low and high pH indicate respectively a hydrophobic (microdomain) environment and a nearly aqueous environment for pyrene. The α range 0.1–0.3 is where the transition from compact coil to expanded coil has been shown to take place.[9,11,18,19]

The changes in I_1/I_3 for PS4 and PSS are qualitatively similar to those for PMA but with a smaller amplitude. Here also the ranges of α where I_1/I_3 increases are the same as those for which other methods have indicated a transition for compact coil to expanded coil.[5,10] The values of α for PMA, PS4, and PSS at midtransition are 0.18, 0.24, and 0.4, respectively. The transitions in these latter polymers were accompanied by a large emission band centered at 480 nm, which corresponds to the pyrene excimer fluorescence. This band arises from the precipitation of solubilized pyrene as microcrystals during the transition; PMA can solubilize only one molecule of pyrene per macromolecule,[9] in contrast to PS10 or PS16.

In PMA the value of I_1/I_3 at $\alpha = 1$ is fairly close to that in pure water. However, in PS4 and PSS, which undergo a similar conformational change,[5,10] the values of I_1/I_3 are significantly smaller than in pure water but still high enough to indicate a strongly hydrophilic environment. This behavior probably indicates that pyrene interacts with the hydrophobic butyl or phenyl side groups in PS4 and PSS rather than remaining in the bulk water.

The pyrene fluorescence lifetime τ changes with α in PS4 and PSS in the same way as I_1/I_3. Thus τ is about 300 ns at low α (presence of microdomains) and then decreases rapidly during the transitions to <200 ns, indicating an aqueous environment for pyrene.

In PS1, I_1/I_3 remains high (about 1.50) and τ short (about 190 ns), independent of α. This behavior indicates an open conformation over the whole pH range, in agreement with other studies.[4]

In PS10, I_1/I_3 and τ are also independent of α but respectively low (about 0.97) and long (360 ns), indicating that the microdomains persist over the whole range of α. The same appears to be true for PS16, although the measurements were performed only at $\alpha = 1$ ($I_1/I_3 = 0.9$ and $\tau = 360$ ns) because PS16 is not water-soluble in the unneutralized state. Here again our conclusions are in agreement with those of other studies.[8]

Thus pyrene is a very sensitive probe for detecting conformational changes in aqueous polymer solutions through changes in its fluorescence spectrum and lifetime. Its use avoids the chemical synthesis of pyrene-labeled monomers and polymers.[24]

At elevated temperatures (T), the fluorescence spectra of pyrene solubilized in the microdomains of PS10 and PS16 at α close to 1 showed the 480-nm excimer emission band even when the pyrene concentration was low ($\sim 2 \times 10^{-6}$ M). In PS16, I_1/I_3 decreased slightly with increasing T, whereas the intensity of the pyrene vibronic peaks and the ratio I_1/I_E (I_E is the excimer emission intensity) decreased rapidly (Figure 2). The intensity of the pyrene excimer band goes through a maximum around 50 °C.

Pyrene in PS10 also showed a slight decrease in I_1/I_3 and large decreases in I_1 and I_3 with increasing T. However, in this system the ratio I_1/I_3 goes through a shallow minimum around 50 °C (Figure 3). A similar minimum in I_1/I_3 has been reported[25] for the fluorescence of pyrene

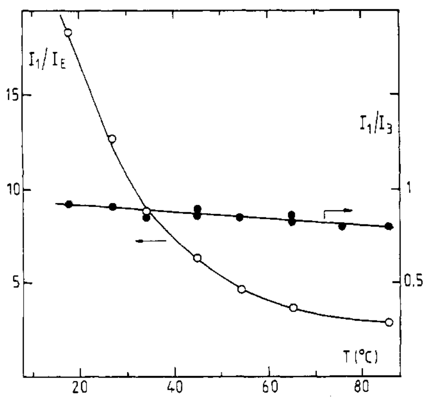

Figure 2. Effect of temperature on the fluorescence intensity ratio I_1/I_3 (●) and I_1/I_E (○) of pyrene solubilized in PS16 solutions ([pyrene] = 2.76 × 10^{-5} M; [PS16] = 0.01 M).

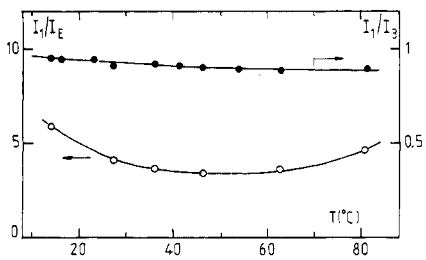

Figure 3. Effect of temperature on the fluorescence intensity ratio I_1/I_3 (●) and I_1/I_E (○) of pyrene solubilized in PS10 solutions ([pyrene] = 3.01 × 10^{-5} M; [PS10] = 0.01 M).

solubilized in alkylbenzenesulfonate micelles and interpreted by the scheme for monomer–excimer equilibrium proposed by Birks et al.[26] We did not attempt such an analysis because of our low pyrene concentration and the relatively small changes in I_1/I_3.

We determined that the 480-nm excimer emission band observed at high T or higher pyrene concentration is not due to the formation of pyrene microcrystals in the polymer solutions. First, UV illumination[27] of a 10^{-2} M PS16 solution containing 2.4 × 10^{-4} M pyrene did not reveal any microcrystals. Microcrystals could be clearly seen as bright points in an aqueous suspension of pyrene at a concentration as low as 10^{-5} M. We then examined the effect of some fluorescence quenchers, molecular oxygen, iodide ion,[28] and dodecylpyridinium ion (DP^+),[23] on the fluorescence emission spectra of pyrene solubilized in 10^{-2} M PS16 solutions and of the pyrene microcrystals in the 10^{-5} M aqueous pyrene suspension. Addition of 3 × 10^{-4} M I^- or DP^+ to the aqueous suspension of pyrene reduced the intensity of the pyrene emission band but had little effect on the intensity of the pyrene excimer band. Addition of the same amount of I^- to the pyrene-containing PS16 solution had no effect on either the pyrene or the excimer intensities, presumably because I^- cannot approach the pyrene solubilized in negatively charged microdomains. On the other hand, DP^+ induced a large decrease in both monomer and excimer intensities, the latter being reduced more than the former. The DP^+ quencher should be completely bound to the anionic polysoaps through both electrostatic and hydrophobic interactions. Had pyrene microcrystals been present in the PS16 solution, the excimer fluorescence should have been unaffected by DP^+ and the monomer fluorescence strongly quenched. Finally, deoxygenation of the aqueous suspension of pyrene microcrystals had only a very small effect on either part of pyrene emission spectrum. On the contrary, deoxygenation of the PS16 solution resulted in a large increase (5- to 10-fold) in the pyrene and excimer fluorescence intensities, but the ratio of the two intensities remained unchanged to within 5%, even at the highest pyrene concentration (2.4 × 10^{-4} M). Such behavior was to be expected if all of the pyrene were solubilized in the microdomains because oxygen would be solubilized in both the aqueous and micellar phases. If part of the pyrene in the PS16 solution had been in the form of microcrystals, the excimer fluorescence from these crystals would not have been enhanced by deoxygenation and the ratio of monomer/excimer intensities would have increased upon deoxygenation. In view of these results, it can be concluded that pyrene is indeed solubilized in the microdomains. The increase in the intensity of the excimer band with T up to 50 °C in PS16 solutions is noteworthy because it is opposite to the decrease usually observed in micellar solutions of ionic surfactants.[29] In such solutions the decrease of I_E is due to the decrease in micelle size and the consequent more complete dispersion of pyrene among the more numerous micelles. The more likely explanation for the increase of I_E in polysoap solutions may be an increase in the microdomain size, although other effects may also contribute. The maximum in I_E around 50 °C occurs at about the same temperature where excimer dissociation in micelles of ionic surfactants becomes significant.[29]

It should be noted that the solubility of pyrene in PS16 solutions is several times greater than that of pyrene in aqueous micellar solutions of alkali metal soaps at the same concentration. Apparently the pyrene solubility is enhanced by the ether oxygen of the polysoap; the solubility of pyrene in solutions of nonionic surfactants that contain ether groups is also much greater than in soap solutions.[17b,30]

The formation of pyrene excimer in the microdomains of PS10 and PS16 offers the interesting possibility of measuring the number of alkyl chains constituting a microdomain and of studying the migration of pyrene from microdomain to microdomain on the fluorescence time scale.[12,13,21] The former problem is under investigation.

2. Fluorescence Decay of Pyrene Solubilized in Polysoap Microdomains. We determined the change in the pyrene fluorescence lifetime τ with temperature in solutions of PMA, PS4, and PSS at $\alpha = 0$, PS10 at $\alpha = 0$ and 1, and PS16 at $\alpha \sim 1$. The fluorescence decay curves at very low pyrene concentration ($\sim 10^{-6}$ M, no excimer present) and temperatures up to 60 °C were all singly exponential. Plots of log τ vs. $1/T$ were all linear in the range 10–60 °C and yielded activation energies E_M^* of 0.9 ± 0.2 kcal/mol for the decay of the fluorescence lifetime. This value is very close to those found for pyrene solubilized in surfactant micelles[17b,29] and in cyclohexane.[26]

At higher pyrene concentration the decay curves for PS10 and PS16 solutions became increasingly nonexponential, and a 480-nm excimer emission band appeared. Since the decay curves were obtained at the pyrene emission wavelength of 382 nm, we attribute the departure from single–exponential behavior to the contribution of excimer formation to the pyrene fluorescence decay; this effect has also been observed in simple micellar systems.[12,13] The decay curve for a 0.01 M PS16 solution containing 10^{-5} M pyrene at room temperature was clearly nonexponential, suggesting that the number of repeat units in these microdomains is >100.

The changes in the decay curves with temperature at given concentrations of pyrene and of a surfactant or polysoap differentiates the behavior of these two types of systems. In micellar solutions the departure from single-exponential decay due to excimer formation becomes less with increasing T because the rate of dissociation of pyrene

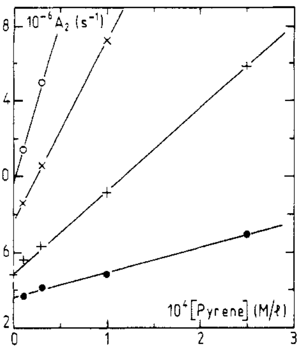

Figure 4. Variation of the fitting parameter A_2 of eq 2 with pyrene concentration at (●) 10 °C; (+) 25 °C; (×) 43.6 °C; (○) 60.5 °C in a 0.01 M PS16 solution.

excimers increases and micelle size decreases with increasing T.[29] The latter effect results in a lower average [pyrene]/[micelle] ratio and thus in a lower probability that micelles will contain two or more pyrene molecules. On the contrary, in polysoap solutions the departure from single-exponential decay increases with T. We are attempting to determine whether this effect reflects an increase in microdomain size.

The decay curves for 0.01 M fully neutralized PS16 solutions containing various amounts of pyrene, determined in the T range 10–60 °C, were fitted to eq 2. The parameter A_2 was found to be larger than τ^{-1}, the reciprocal of the pyrene fluorescence lifetime determined at very low [pyrene] and to increase linearly with [pyrene] (Figure 4). This interesting results suggests that pyrene can migrate from one microdomain to another within the lifetime of its excited state. It is known that pyrene migrates among micelles in solutions of nonionic surfactants[17b] and that other probes migrate in water-in-oil microemulsions.[31] If we assume that pyrene migration in PS16 solutions takes place through microdomain collisions and temporary merging, the slope of the A_2 vs. [pyrene] plot gives the quantity k_e[M], where [M] is the microdomain concentration and k_e the bimolecular rate constant for microdomain collision with exchange.[17b,32] The plot of log k_e[M] vs. 1/T was almost linear and yielded an activation energy of about 10 kcal/mol. Additional experiments are required to determine [M] and thus k_e.

3. Effect of Cationic Surfactants on the Fluorescence Properties of Pyrene Solubilized in Solutions of Fully Neutralized PS4. We wished to determine the effect of cationic surfactants on the conformation of PS4. It is known that the addition of a cationic surfactant to a polymeric anion often results in the precipitation of a polymer–surfactant complex, which may redissolve upon further surfactant additions.[32]

However, addition of alkyltrimethylammonium halides with alkyl chains from *n*-hexyl to *n*-hexadecyl to a 0.05 M fully neutralized PS4 solution gave no precipitate. Precipitates did form under similar conditions from sodium poly(acrylate), sodium salts of (carboxymethyl)celluloses, Na–PMA, and PMA ($\alpha = 0$). As will be seen below, no precipitation occurred with the PS4 solution because of the formation of mixed micelles between the surfactant and the PS4 repeat units. It thus appears that microdomain-forming polymers are capable of delaying or suppressing the precipitation of complexes of surfactants and polyelectrolytes of opposite charge.

The effects of surfactant additions on the fluorescence of pyrene present at a concentration of about 10^{-6} M in the 0.05 M fully neutralized PS4 solution are shown in Figure 5–7. The ratio I_1/I_3 is not affected by the addition of surfactant as long as the surfactant concentration C remains below a certain value, which depends on the length of the alkyl chain. In this range, the values of I_1/I_3 (1.6–1.7) are about that of pyrene in a hydrophilic environment but still smaller than that of pyrene in pure water. As C is further increased, I_1/I_3 decreases rapidly to about 1.2, irrespective of the surfactant chain length. This value is intermediate between that for PS4 in the compact state (1.1) and for the alkyltrimethylammonium chloride surfactants (1.28 for decyl- and tetradecyltrimethylammonium chlorides, measured as part of this work). Figure 5 shows that the decrease of log C at the midchange of I_1/I_3 is not a linear function of surfactant chain length, contrary to what is most often found in the micellization of pure surfactants or in interactions between surfactants and other compounds.[33,34] Finally, the sharpness of the change in I_1/I_3 with C indicates a cooperative process.

We determined the effects of changing the surfactant counterion (decyltrimethylammonium chloride, bromide, and iodide, Figure 5), the ionic strength by adding NaCl (Figure 6), and the PS4 concentration (0.05, 0.025, and 0.005 M, Figure 7). The concentration at midchange of I_1/I_3 decreases with increasing ionic strength or decreasing PS4 concentration and increases as the surfactant counterion is changed from Cl^- to Br^- to I^-. In all instances the surfactant concentration at midchange of I_1/I_3 is below the critical micelle concentration of the surfactant in the absence of polysoap by a factor of 5–20.

All these results suggest the formation of mixed micelles, comprising butyl chains of PS4 and alkyl chains of the added surfactant, in which pyrene is solubilized. These mixed micelles appear to be electrically neutral or negatively charged, as indicated by the results of fluorescence

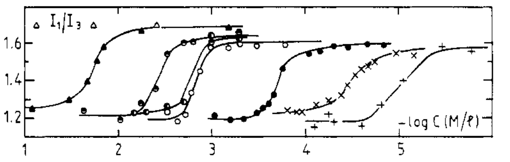

Figure 5. Effect of the chain length and nature of the counterion of the added alkyltrimethylammonium halide on the variation of I_1/I_3 with surfactant concentration: (+) hexadecyl-, (×) tetradecyl-, (●) dodecyl-, (○) decyl-, (▲) octyl, and (△) hexyltrimethylammonium chlorides; (◒) and (◐) decyltrimethylammonium iodide and bromide. Our results for the hexyl surfactant extended to 0.4 M and showed no change of I_1/I_3. [pyrene] ~ 10^{-6} M; concentration of fully neutralized PS4 was 0.05 M; T = 25 °C.

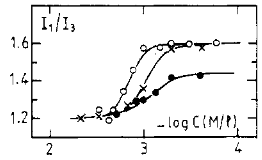

Figure 6. Effect of decyltrimethylammonium chloride additions on the value of I_1/I_3 for pyrene solubilized in 0.05 M fully neutralized PS4 solutions in the absence of NaCl (○) and in the presence of (×) 0.1 M NaCl and (●) 0.5 M NaCl at 25 °C. [pyrene] ~ 10^{-6} M.

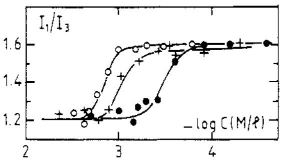

Figure 7. Effect of dodecyltrimethylammonium chloride additions on the value of I_1/I_3 for pyrene solubilized in fully neutralized PS4 solutions of increasing concentration: (●) 5 × 10^{-3} M; (+) 2.5 × 10^{-2} M; (○) 5 × 10^{-2} M at 25 °C. [pyrene] ~ 10^{-6} M.

lifetime measurements on the PS4–decyltrimethylammonium bromide (DeTAB) system. The pyrene lifetime was 340–360 ns, in contrast to the lower value of 170 ns for pure DeTAB micelles, due to the quenching effect of the bromide ions.[35] This result shows that there is no bromide ion from the DeTAB surfactant in the Stern layer of the microdomains of the PS4/DeTAB/pyrene system. Therefore the charge of the surfactant ions must be exceeded by that of the carboxylate groups of PS4 in order to prevent the approach of the bromide ions.

The decrease in concentration at the midchange of I_1/I_3 with increasing ionic strength indicates that micelle formation is enhanced by an increase in ionic strength (Figure 6). On the contrary, this concentration increases on substituting Cl^- with Br^- or I^- because the halide ions and PS4 units compete for complexation with the surfactant ions and the tendency for complexation increases in the lyotropic order $Cl^- < Br^- < I^-$. Furthermore, the increase the concentration at midchange of I_1/I_3 is less than proportional to the increase in PS4 concentration (Figure 7). This result also indicates a process more complex than a simple complexation of monomeric surfactant by the charged PS4 groups.

Finally, we note that a large increase in fluorescence intensity occurred in the same C range where I_1/I_3 decreased. This result, together with those discussed previously, indicates that the onset of mixed micelle formation occurs at a value of C where I_1/I_3 starts decreasing. The nonlinear decrease in the logarithm of this concentration is not unexpected for a process of mixed micellization at a constant concentration of PS4 and increasing concentration of the surfactant. Herkstroeter et al.[24] have also concluded that mixed micelles are formed upon addition of anionic surfactants to a pyrene-labeled cationic polyelectrolyte.

Conclusions

The nearly water-insoluble compound pyrene can be used as a fluorescence probe to reveal the conformational transitions of polysoaps in aqueous solutions. The microdomains in polysoap solutions are large enough to accommodate two pyrene molecules, which can form an excimer upon excitation. This excimer formation opens the possibility of determining the number of monomeric units in a microdomain by time-resolved fluorescence. We have obtained evidence for the formation of mixed micelles between the repeat units of fully neutralized PS4 and cationic alkyltrimethylammonium halide surfactants.

While this paper was being reviewed, Chu and Thomas reported results very similar to ours for PMA–cationic surfactant systems.[36] The addition of the same cationic surfactants we used to PMA solutions induced the transition of the expanded conformation to a compact coil just as in our PS4 solutions.

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Registry No. $H_3C(CH_2)_5N(CH_3)_3{}^+Cl^-$, 29801-86-3; $H_3C(CH_2)_7N(CH_3)_3{}^+Cl^-$, 10108-86-8; $H_3C(CH_2)_9N(CH_3)_3{}^+Cl^-$, 10108-87-9; $H_3C(CH_2)_{11}N(CH_3)_3{}^+Cl^-$, 112-00-5; $H_3C(CH_2)_{13}N(CH_3)_3{}^+Cl^-$, 4574-04-3; $H_3C(CH_2)_{15}N(CH_3)_3{}^+Cl^-$, 112-02-7; $H_3C(CH_2)_9N(CH_3)_3{}^+Br^-$, 2082-84-0; $H_3C(CH_2)_9N(CH_3)_3{}^+I^-$, 7447-24-7; pyrene, 129-00-0; (methyl vinyl ether)(maleic anhydride) (copolymer) (sodium salt), 28133-65-5; (butyl vinyl ether)(maleic anhydride) (copolymer) (sodium salt), 36350-26-2; (decyl vinyl ether)(maleic anhydride) (copolymer) (sodium salt), 80508-30-1; (hexadecyl vinyl ether)(maleic anhydride) (copolymer) (sodium salt), 80508-29-8; (sytrene)(maleic anhydride) (copolymer) (sodium salt), 25736-61-2.

References and Notes

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