Fluorescence Probe Studies of Aqueous Solution Interaction between Sodium Dodecyl Sulfate and Anionic Polyelectrolytes

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ABSTRACT: Fluorescence probe techniques have been employed to study interactions between sodium dodecyl sulfate (SDS) and three water-soluble anionic polyelectrolytes, poly(ethylene-*co*-maleic acid) (PEMA), poly(1-decene-*co*-maleic acid) (PDMA), and poly(1-octadecene-*co*-maleic acid) (POMA), in aqueous solution at pH 8. Interaction between SDS and POMA is confirmed by surface tension measurements. The fluorescence results indicate that PDMA and POMA are capable of solubilzing water-insoluble probes in the absence of SDS. The fluorescence data, as a function of SDS concentration, are interpreted in terms of interactions between SDS and the anionic polyelectrolytes, PDMA and POMA. Either an expansion of the polyelectrolyte coil, leading to the expulsion of the fluorescence probe, or solubilization of the fluorescent probe within SDS/polyelectrolyte mixed micelle is postulated. SDS does not appear to alter the polarity or fluidity of the environment of fluorescent probes within the polyelectrolyte at SDS concentrations less than the critical micelle concentration (cmc).

Introduction

Interactions between polymers and surfactants are important for both fundamental and practical reasons. A fundamental understanding of polymer/surfactant interactions requires detailed knowledge of the chemical and physical properties of both polymer and surfactant. An understanding of the dynamics involved in the interaction process may be applied to practical problems, for example, in the formulation of polymer/surfactant systems for enhanced oil recovery[1,2] and antiredeposition agents in the laundry industry,[3,4] among others.

Polymer/surfactant interactions have been reviewed.[5] The evidence for interactions between uncharged polymers, such as poly(vinylpyrrolidone) (PVP) and an anionic surfactant, such as SDS, supports the proposal that SDS aggregates and polymer molecules associate at a surfactant concentration slightly lower than the cmc of SDS, rather than surfactant monomer adsorbing onto the polymer.[5] For the case of charged polymers interacting with surfactants of opposite charge, surfactant binding is primarily electrostatic, starting at free surfactant concentrations often orders of magnitude less than the cmc of the surfactant.[6,7] To our knowledge, no comprehensive studies have been reported for interactions between anionic polyelectrolytes and anionic surfactants.

In this report we examine the interactions between anionic polyelectrolytes, of varying side chain length, and SDS using fluorometric techniques. Fluorescence methods have been used extensively to study surfactant and polymer systems. Turro et al.[8] have demonstrated the utility of using fluorescence probes to study interactions between water-soluble neutral polymers and SDS. α-Olefin/maleic acid copolymers are unique among polyelectrolytes in that the repeat unit consists of a highly polar carboxylate group under alkaline conditions and, in some cases, a long hydrophobic side chain. Copolymers of alkyl vinyl ethers/maleic acid and substituted α-olefins/maleic acid have been studied extensively by potentiometric titration and have been shown to undergo conformational transitions from compact to expanded coil as the degree of ionization of the copolymer increases.[9,10] To our knowledge, a distinctive conformational transition, as a function of the degree of ionization, has not been demonstrated for copolymers of C_{10} or C_{18} with maleic acid. Fluorescence probes embedded in hydrophobic domains of PDMA and POMA should provide, therefore, an understanding as to the nature of the microenvironments of these polyelectrolytes at alkaline pH. Furthermore, it may be possible to detect interactions between SDS and the polyelectrolyte if the interactions result in a change in the microenvironmental properties of the fluorescent probe.

Materials and Methods

Materials. The copolymer of maleic anhydride with ethylene (M_w = 2750, M_w/M_n = 2.5) was obtained from Monsanto. The copolymers of maleic anhydride with 1-decene (M_w = 19 030, M_w/M_n = 2.67) and 1-octadecene (M_w = 21 420, M_w/M_n = 3.03) were obtained from Gulf Oil Chemical Co. The comonomers are present in a 1:1 molar ratio. Molecular weights were determined by gel permeation chromotography (GPC). Sodium dodecyl sulfate was obtained from Fluka AG as 99% pure and was used without further purification.

Pyrene and 1,6-diphenyl-1,3,5-hexatriene (DPH) were obtained from Aldrich. Pyrene was recrystallized 3 times from absolute ethanol and DPH was recrystallized 3 times from acetone. Stock solutions of pyrene (4×10^{-5} M) and DPH (9×10^{-4} M) were prepared in acetone and refrigerated until used.

Cyclohexane, 1-butanol, and glycerol were obtained from Aldrich as Gold Label and used without further purification. Methanol and acetonitrile were obtained from Burdick & Jackson as distilled in glass solvents and used without further purification. Deionized water was used to prepare stock solutions of polyelectrolytes and SDS.

The polyelectrolyte PEMA was prepared by hydrolysis of the anhydride using aqueous sodium hydroxide. After hydrolysis the pH was adjusted to 8.0 by addition of dilute HCl. The disodium salts of PDMA and POMA were prepared by hydrolysis of the anhydride with a concentrated solution of NaOH followed by precipitation into methanol. The polymer was collected by filtration and washed extensively with methanol. Stock solutions of polyelectrolyte were prepared at 0.5 wt % tris(hydroxymethyl)aminomethane hydrochloride pH 8 buffer (Trizma 8.0, Sigma Chemical Co.). Stock solutions of SDS were made up at 0.3 M in pH 8.0 buffer.

Solutions for fluorescence measurements were prepared by first pipetting 100 μL of pyrene stock solution or 50 μL of DPH stock solution into a 10-ml volumetric flask. The acetone was evaporated off by passing a gentle stream of nitrogen gas over the surrface of the solvent. One milliliter of polyelectrolyte stock solution was then added to the flask, swirled, and left to stand in the dark in contact with the fluorescent probe for 1 day. Aliquots of stock SDS solution were then added to the polyelectrolyte/probe solutions, swirled to mix, and finally diluted to volume with pH 8 buffer. The solutions were allowed to equilibrate after mixing for 2–3 days, in the dark, before fluorescence measurements were made. The final concentration of polyelectrolyte was 5×10^{-4} g/mL.

Methods and Calculations. Surface tension measurements were carried out with a ring surface tensiometer.

Fluorescence Measurements. An SLM 4800S spectrofluorometer (SLM-Aminco, Urbana, IL) was used for all measure-

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ments except for fluorescence lifetimes measured by the time-correlated single-photon-counting (TCSPC) technique, in which case a PRA System 3000 instrument (Photochemical Research Associates, London, Ontario) was used. The time-dependent fluorescence decay by TCSPC was fitted to a biexponential given by

$$I(t) = a_1 e^{-t/\tau_1} + a_2 e^{-t/\tau_2} \quad (1)$$

Lifetime measurements using the SLM 4800S were by the phase-shift and demodulation method using *p*-bis[2-(5-phenyloxazolyl)]benzene (POPOP)/ethanol as the reference, 1.35 ns.[11] The modulation frequency was 30 MHz.

The fluorescence lifetimes τ_p and τ_m are related to the measured phase shift and demodulation by

$$\tau_p = \frac{1}{\omega} \tan \phi \quad (2)$$

and

$$\tau_m = \frac{1}{\omega}\left(\frac{1}{M^2} - 1\right)^{1/2} \quad (3)$$

The phase angle ϕ and demodulation factor M corrected for the reference fluorophore lifetime are given by

$$\phi = \phi_s - \phi_r + \arctan(\omega\tau) \quad (4)$$

and

$$M = M_s/[M_r/((\omega\tau)^2 + 1)^{1/2}] \quad (5)$$

where $\omega = 2\pi f$, f being the modulation frequency, s and r indicate sample and reference, respectively, and τ is the reference fluorophores lifetime. Computation of the fluorescence lifetime was performed on line with data acquisition.

Fluorescence polarization measurements were made by utilizing two channel detection, T-format geometry, to measure the intensities of the parallel and perpendicular components simultaneously. Polarization measurements corrected for instrument response are given by

$$P = \frac{I_v/I_H - G}{I_v/I_H + G} \quad (6)$$

where I_v and I_H are the fluorescence intensities polarized in the vertical and horizontal directions, respectively, using vertically polarized incident light. G is the correction factor for instrument response obtained using horizontally polarized incident light. Molecular anisotropy is related to fluorescence polarization by

$$r = \frac{2P}{3 - P} \quad (7)$$

Anistropy measurements were made using DPH as the probe molecule. The excitation wavelength was 352 nm. The emission was measured at 435.8 nm using interference filters.

The pyrene fluorescence intensity ratio, I_1/I_3, was obtained by measuring the maximum intensity of the first and third highest energy vibronic bands in the pyrene fluorescence spectrum. Pyrene excitation wavelength was 335 nm. Full width at half-maximum (fwhm) of I_1 and I_3 was 3 nm.

Results

a. Surface Tension and Particle Size. Figure 1 shows the surface tension curves for SDS in pH 8 buffer and in 0.5 wt % POMA in pH 8 buffer. The surface tension curve in the absence of POMA shows a minimum at approximately 2×10^{-3} M SDS. The minimum at approximately 2×10^{-3} M in the SDS surface tension curve is caused by the presence of small amounts of lauryl alcohol. The SDS/POMA curve is similar to that observed for SDS/poly(ethylene oxide) (PEO) solution.[12] There is an increase in the surface tension of the SDS/POMA system relative to SDS in the absence of POMA for [SDS] between 1.8×10^{-4} and 4.0×10^{-3} M. The increase in the surface tension is the result of depletion of SDS at the air–water interface due to adsorption of SDS onto POMA. Unlike the SDS/PEO system,[12] the SDS/POMA system shows a lower plateau value than SDS in the absence of polymer for [SDS] > 8×10^{-3} M.

Table I
Solvent Dependence of Pyrene Monomer Fluorescence Vibronic Band Intensity Ratio I_1/I_3

solvent system	I_1/I_3	ϵ^a	D^a
acetonitrile	1.98	37.50	3.92
pH 8 buffer	1.95		
PEMA	1.57		
ethanol	1.45	24.55	1.69
SDS micelle	1.21		
PDMA	1.02		
POMA	0.98		
cyclohexane	0.64	2.02	0

[a] Data for solvent dipole moment (D) and dielectric constant (ϵ) are taken from ref 15.

Table II
Solvent Dependence of DPH Fluorescence Lifetime

solvent system	τ(ns)[a]	ϵ^b	D^b
glycerol	3.83	42.5	2.56
acetonitrile	3.92	37.50	3.92
methanol	4.25	32.70	1.70
ethanol	5.36	24.55	1.69
1-butanol	5.86	17.50	1.66
cyclohexane	8.12	2.02	0

[a] Fluorescence lifetimes measured by phase-modulation technique. [b] Data for solvent dipole moment (D) and dielectric constant (ϵ) are taken from ref 15.

Table III
Pulsed Fluorescence Lifetime Data for DPH Solubilized in pH 8 Buffered Solutions of SDS, PEMA, PDMA, and POMA at 24 °C

solvent systems	τ_1(ns)	f_1^a	τ_2(ns)	f_2	χ^2
PEMA	1.02 ± 0.19	0.09	9.3 ± 0.08	0.91	1.2
SDS micelle	2.3 ± 0.17	0.18	5.52 ± 0.06	0.82	0.99
PDMA	4.29 ± 0.26	0.28	10.62 ± 0.19	0.72	1.02
POMA	6.95 ± 0.69	0.25	11.58 ± 0.35	0.75	1.14

[a] Fractional intensity $f_i = a_i\tau_i/\sum a_i\tau_i$.

b. Polarity. The intensity of the fine structure in the pyrene monomer fluorescence spectrum shows strong solvent dependency.[13,14] The ratio of the first and third highest energy vibronic bands (I_1/I_3) has been used as a microenvironmental polarity indicator for micelles[13] and surfactant/polymer aggregates.[8]

The existence of hydrophobic domains within PDMA and POMA in aqueous solution at pH 8 is evident from the I_1/I_3 values listed in Table I. Both PDMA and POMA are capable of solubilizing water insoluble probes such as pyrene and DPH. The magnitude of the I_1/I_3 values indicates that the polarity of the microenvironment for PDMA and POMA is less than that of pyrene in SDS micelles.

I_1/I_3 is a measure of the polarity averaged over all solubilization sites and as a result does not provide site specific information unless the location of the pyrene molecule is known. Site specific polarity information can be obtained from fluorescence lifetime measurements. The trend in DPH fluorescence lifetime as a function of solvent dielectric constant is shown in Table II. The fluorescence lifetime of DPH increases with decreasing solvent dielectric constant.

Pulse fluorescence lifetime data for DPH in SDS micelles, PEMA, PDMA, and POMA are listed in Table III. The fluorescence decay function gave a reasonably good

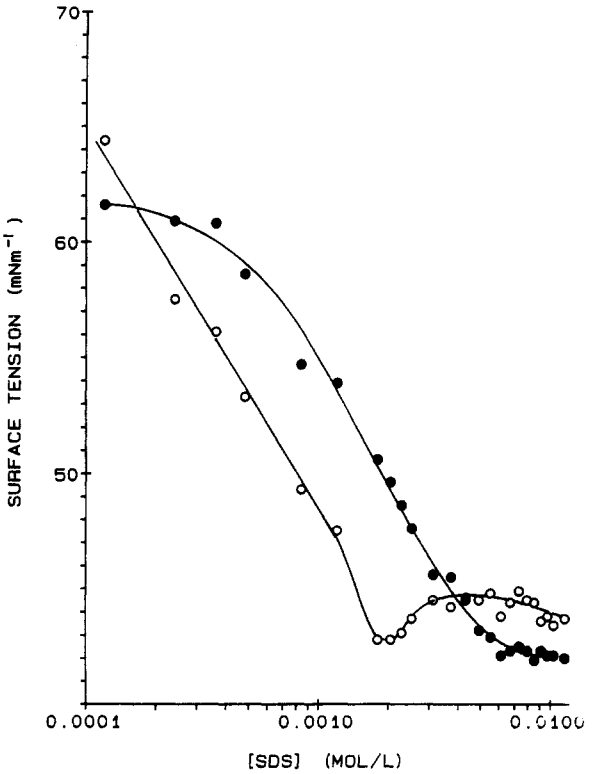

Figure 1. Surface tension values as a function of SDS concentration for pH 8.0 buffer (○) and 0.5 wt % POMA/pH 8.0 buffer systems (●).

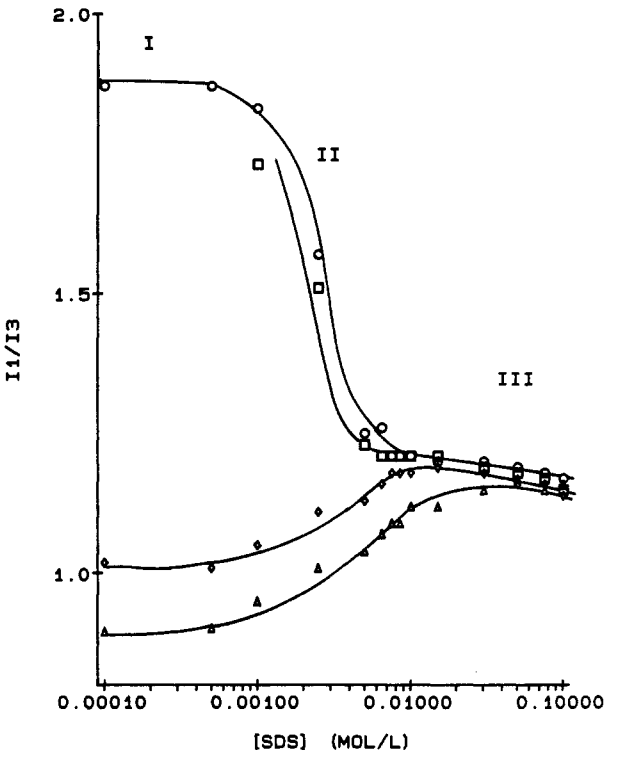

Figure 2. Values of I_1/I_3 as a function of SDS concentration for pH 8.0 buffer (○), PEMA (□), PDMA (◇), and POMA (△) systems. All polymer concentrations are 0.05 wt % in pH 8.0 buffer.

fit to a biexponential decay, as judged by the magnitude of the χ^2 values. The biexponential decay is interpreted in terms of two distinct solubilization sites for DPH. It is reasonable to assume that the overwhelming contribution to the total fluorescence comes from DPH solubilized in SDS or polyelectrolyte since the fluorescence quantum yield for DPH in the aqueous phase is essentially zero. This was evident from the observation that it required 4 times the amount of time to acquire one-fifth the number of counts for equal amounts of DPH added to 0.15 wt % PEMA as that for 0.05 wt % POMA solutions. The fluorescence intensity of DPH increased in the order PEMA (0.15 wt %) < PDMA (0.05 wt %) < POMA (0.05 wt %) = SDS (0.1 M).

The fluorescence lifetimes for DPH in PDMA and POMA listed in Table III are similar to those observed for DPH in dipalmitoylphosphatidylcholine (DPPC) vesicles (9.35 and 3.03 ns),[16] in that both cases yielded biexponential decays, suggesting partitioning of DPH into two domains. The longer fluorescence lifetime values are assigned to more nonpolar regions. From the magnitude of the fluorescence lifetimes of DPH in SDS micelles, it is concluded that the solubilization sites for DPH are relatively polar. From I_1/I_3 measurements of pyrene in SDS micelles, it is concluded that the solubilization site is predominantly within a region which is more polar than that which would be expected for solubilization of the probe within a purely hydrocarbon core. The fluorescence lifetime for DPH in SDS micelles would also indicate that DPH is solubilized in a manner similar to that of pyrene.

I_1/I_3 values for pyrene in pH 8 buffer, PEMA, PDMA, and POMA as a function of [SDS] are plotted in Figure 2. The trend in I_1/I_3 for pyrene in the three SDS/polyelectrolyte solutions is shown relative to SDS in the absence of polyelectrolyte. The I_1/I_3 vs. [SDS] for the pH 8 buffer solution curve can be characterized by three distinct concentration regions. In region I, [SDS] < cmc, pyrene is localized in the aqueous phase. Region II is the transition region, through the cmc of SDS, as pyrene becomes solubilized by SDS micelles. In region III, [SDS] > cmc, pyrene is solubilized by SDS micelles, and a further increase in [SDS] has only a slight effect on I_1/I_3. A comparison of the PEMA curve with the pH 8 buffer curve reveals that the presence of 0.05 wt % PEMA has little effect on the shape of the curve other than a shift of the transition to lower [SDS]. The curves for PDMA and POMA are markedly different than those for pH 8 buffer or PEMA. For the PDMA and POMA curves, pyrene is preferentially solubilized within the polyelectrolyte at [SDS] < cmc. The transition to I_1/I_3 values comparable for pyrene in SDS micelles is much broader in the presence of PDMA and POMA. The transition is broadest for the POMA system. The broad nature of the transition is similar to that recently observed by Turro et al.[17] for pyrene in mixed systems of ionic and nonionic surfactants.

Figure 3 shows the results of the I_1/I_3 measurements for POMA as a function of surfactant concentration when SDS is replaced with sodium decyl sulfate (SDeS). The transition shifts to a higher surfactant concentration as a result of the larger cmc value for SDeS.

Microviscosity. The viscosity of the environment within a micelle or polymer aggregate, termed microviscosity, can in principle be determined by measuring the molecular anisotropy or degree of depolarization as a result of molecular rotational diffusion. For a rotating fluorescent sphere, the observed anisotropy obeys the well-known Perrin equation

$$\frac{r_0}{r} = 1 + \frac{\tau}{\phi} \tag{8}$$

where r_0 is the limiting fluorescence anisotropy in the absence of motion of the probe, τ is the fluorescence lifetime, and ϕ is the rotational correlation time. If the fluorescence lifetime and the anisotropy are known, it should be possible to calculate the rotational correlation

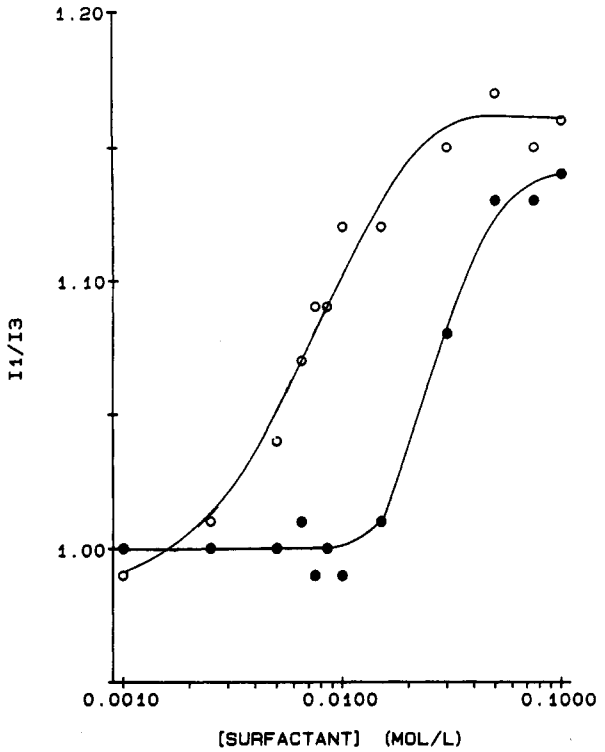

Figure 3. Values of I_1/I_3 for POMA in pH 8.0 buffer as a function of SDS concentration (○) and sodium decyl sulfate concentration (●).

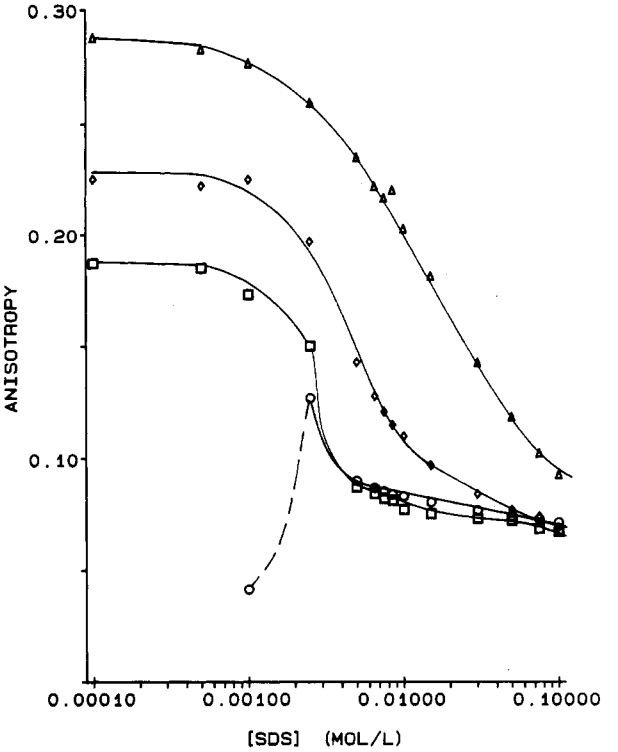

Figure 4. DPH anisotropy as a function of SDS concentration in pH 8.0 buffer (○), PEMA (□), PDMA (◇), and POMA (△) systems. All polymer concentrations arre 0.05 wt % in pH 8.0 buffer.

time. The relationship between the rotational correlation time and the effective viscosity of the solvent which opposes the probes rotational diffusion is given by the Stokes–Einstein equation

$$\phi = \frac{\eta V}{RT} \tag{9}$$

where η is the viscosity, V is the volume of the rotating unit, R is the gas constant, and T is absolute temperature. The Stokes–Einstein equation is more accurately applied to systems where the rotating molecule is spherical and rotating in an isotropic medium where the solvent molecules are significantly smaller than the probe.

Shinitzky et al.[18] used fluorescence depolarization to measure the microviscosity of the hydrocarbon region of micelles and membranes. Methods for analysis of fluorescence depolarization data using both pulse and phase fluorometry have been reviewed.[19]

In light of the complexities involved in extracting microviscosity information from depolarization of a fluorescence probe embedded in micelles and membranes,[19] the molecular anisotropy values reported herein are used only as an observation to express changes within the microenvironment of the polyelectrolyte solubilized probe as a function of [SDS].

Anisotropy values measured for DPH in SDS micelles, PEMA, PDMA, and POMA are 0.073, 0.187, 0.225, and 0.273, respectively. The anisotropy values indicate that there is a distinct difference in the microenvironments of the four systems, while I_1/I_3 values of some of the microenvironments, PDMA and POMA, are very nearly equal. The r values also indicate a marked difference between the microenvironment of DPH in POMA, r = 0.273, and that of DPH in SDS micelles, r = 0.073.

Figure 4 shows the dependence of DPH anisotropy as a function of [SDS] for pH 8 buffer, PEMA, PDMA, and POMA. The microenvironment of DPH in PEMA and PDMA shows the greatest change in the region around the cmc of SDS in pH 8 buffer. For the case of DPH in POMA, the change in the microenvironment is more gradual. The sharp decrease in r for PEMA and, to some extent, in PDMA can be explained by an increase in the amount of solubilized DPH as a result of SDS micelle formation. Observation of the relative fluorescence intensity of DPH for these systems indicates that not all of the DPH added to the PEMA and PDMA solutions is solubilized by the polymer. POMA is capable of solubilizing all of the added DPH.

The sharp increase in r for the SDS/DPH system at [SDS] = 2.5×10^{-3} is reproducible. The same trend is observed[20] when the phase shift or demodulation of DPH fluorescence is plotted vs. [SDS]. The increase in r may be attributed to the formation of a dye-rich-induced micelle in the premicellar region. Sato et al.[21] reported evidence for dye-rich-induced micelle in the premicellar region based on fluorescence lifetime and energy-transfer studies of acridine orange/SDS and rhodamine 6G/SDS systems.

Discussion

The fluorescence data for PDMA and POMA, I_1/I_3 and r as a function of [SDS], show a transition from microenvironments of lower polarity and fluidity observed for the probe solubilized in the polyelectrolyte at [SDS] < cmc to microenvironments of higher polarity and fluidity observed for the probe solubilized in the SDS micelle. The transition can be interpreted in terms of either an expulsion of the probe from the polyelectrolyte as a result of coil expansion followed by SDS micelle solubilization or a modification of the probe's environment as a result of SDS interaction with the polyelectrolyte. Examples are present in the literature for probe molecules staying within poly(methacrylic acid) (PMA) in the presence of 0.5 M SDS at pH < 3[22] and also unidirectional probe molecule migration from an environment of high fluidity to one of lower fluidity for mixed membrane systems.[23] Surface

tension data for the SDS/POMA system indicate association between SDS and POMA. The discussion which follows will address the possible interpretations of the fluorescence data in terms of SDS interaction with polyelectrolytes.

The first case to be considered is probe migration from solubilization sites within PDMA and POMA to SDS micelles. The transitions in the fluorescence data, as a function of [SDS], occur within a region which bounds the cmc of SDS. The transitions converge from values of I_1/I_3 and r measured for the probes in the polyelectrolytes in the absence of SDS to values measured for the probes in SDS micelles. When SDS is replaced by SDeS, the transition shifts to higher surfactant concentration in accordance with the higher cmc value for SDeS. Copolymers of short chain alkyl vinyl ethers ($\leq C_8$) with hydrolyzed maleic anhydride have been described as consisting of uniformly sized intramolecular micelles formed from adjacent chain elements.[24] It has been proposed[25] that in the presence of a denaturant solution, the affinity of the hydrophobes for the aqueous phase is enhanced and the alkyl vinyl ether/maleic acid copolymer undergoes a conformation transition from a hypercoiled to extended state. Such a mechanism can be used to explain the fluorescence results observed for PDMA and POMA. A destabilization of the polyelectrolyte coil by SDS, leading to coil expansion, may result in the expulsion of the fluorescence probe into the aqueous phase where it can readily be solubilized by free SDS micelles. In this case, I_1/I_3 and r would be the sum of the contributions from the probe in SDS micelles and the hydrophobic domains of the polyelectrolyte. The difference in transitions for the PDMA and POMA polyelectrolyte systems then would be indicative of the relative difference in hydrophobic effect of the n-alkyl side chains of the two polyelectrolytes in the presence of SDS.

A second interpretation of the transition in the fluorescence data is based upon a change in the probe's environment as a result of the formation of an SDS/polyelectrolyte mixed micelle with no migration of the probe molecule. In this case, adsorption of SDS onto polyelectrolyte hydrophobic sites would change the environment of the probe molecule to be more similar, in terms of polarity and fluidity, to that of an SDS micelle. Considering the ratio of SDS monomer to polyelectrolyte repeat unit, approximately 7 at [SDS] = 0.01 M and 70 at [SDS] = 0.1 M, it seems reasonable to assume that the probe molecule sees more of an SDS environment than a polyelectrolyte environment. Therefore, the I_1/I_3 and r values should be similar to that found for the probe in an SDS micelle, assuming that the ratio of SDS molecules to polyelectrolyte repeat unit is large at 0.1 M SDS.

Conclusion

Interactions between anionic, hydrophobically modified, water-soluble polyelectrolytes and SDS were studied by using extrinsic fluorescence probe techniques. The fluorescence data indicate that PDMA and POMA are capable of solubilizing water-insoluble hydrocarbons and that the solubilization sites are less polar and less fluid relative to SDS micelles. The pulsed fluorescence lifetime data for DPH suggest two distinct solubilization sites within SDS micelles, PDMA, and POMA, one site being more hydrocarbon-like than the other. The fluorescence data, as a function of SDS concentration, are interpreted in terms of interactions between SDS and the anionic polyelectrolytes, PDMA and POMA. Either an expansion of the polyelectrolyte coil, leading to the expulsion of the fluorescence probe, or solubilization of the fluorescent probe within SDS/polyelectrolyte mixed micelle is postulated. Surfactant adsorption at hydrophobic sites at the polyelectrolyte–water interface for SDS concentrations less than the cmc does not appear to modify the environment of the fluorescence probe.

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Registry No. PDMA, 59447-44-8; POMA, 108919-65-9; DPH, 1720-32-7; SDS, 151-21-3; pyrene, 129-00-0.

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