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Photoluminescence Probes for the Investigation of Interactions between Sodium Dodecyl Sulfate and Water-Soluble Polymers

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ABSTRACT: Fluorescence probe techniques have been employed to monitor interactions between sodium dodecyl sulfate (SDS) and two water-soluble polymers, poly(*N*-vinylpyrrolidone) and poly(ethylene oxide). The results are analogous to those found by conventional methods and lead to the conclusion that SDS micelles bind to the polymers. The fluorescence probe method also provides information on the solubilization mechanism, since the site of solubilization of the probe can be inferred.

Introduction

Polymer/Surfactant Interactions in Aqueous Solution. Investigations of the interactions of polymers and surfactants in aqueous solution are of interest from the fundamental standpoint of obtaining an understanding of the structure and dynamics of polymer/surfactant associates and from the practical standpoint of employing fundamental understanding to assist in formulations for polymer/surfactant systems that can be used in the process of enhanced oil recovery.[1] The ability of surfactants to aggregate and form micelles[2] adds a particularly intriguing dimension to their interactions with polymers. An extensive body of evidence has accumulated that supports the proposal that anionic surfactants such as sodium dodecyl sulfate (SDS) and water-soluble polymers such as poly(*N*-vinylpyrrolidone) or poly(ethylene oxide) (PVP and PEO, respectively) form associates between surfactant aggregates and polymer rather than surfactant monomers and polymer.[3]

The following picture has emerged to describe the polymer/surfactant interactions that occur when SDS is added to a dilute aqueous solution of water-soluble PVP or PEO.[2-4] In the absence of polymer, SDS forms well-defined micelles above the critical micelle concentration (cmc) of 8×10^{-3} (termed x_0). When SDS is added to a dilute ($\lesssim 1\%$) solution of PVP (or PEO), there is no association between polymer and surfactant until a concentration x_1 is reached. Above x_1 (which is a lower concentration than the cmc, x_0) the polymer /surfactant association process starts abruptly and then saturates abruptly at a concentration x_2 (which is a higher concentration than the cmc, x_0). Thus, three well-defined regions are suggested by available information: region I, for which [SDS] ranges from 0 to x_1; region II, for which [SDS] ranges from x_1 to x_2; and region III, for which [SDS] is greater than x_2. In region I, there is no significant polymer/surfactant interaction. In region II, clusters of SDS molecules (termed premicelles) cooperatively associate with the polymers. In region III, free micelles of SDS form and exist in equilibrium with the polymer/surfactant associates. These situations are summarized schematically in Figure 1.

Pyrene and 11-(3-Hexyl-1-indolyl)undecyl Sulfate as Fluorescence Probes of Surfactant Association. Pyrene is a strongly hydrophobic probe with low solubility (ca. 3×10^{-7} M) in water. The fluorescence spectrum of pyrene at low concentration ($<1 \times 10^{-6}$ M) in homogeneous solutions possesses considerable fine structure whose relative peak intensities undergo significant perturbation upon going from polar to nonpolar solvents.[5] The ratio of the fluorescence intensity of the highest energy vibrational band (I_I) to the fluorescence intensity of the third highest energy vibrational band (I_{III}) has been shown to correlate with solvent polarity for a range of solvent structures. For example,[5] in hydrocarbon solvents I_I/I_{III} is ca. 0.6, in ethanol I_I/I_{III} is ca. 1.1, and in water I_I/I_{II} is ca. 1.6.

This distinct dependence of fluorescence vibrational fine structure has been utilized to investigate the formation of SDS micelles.[6] In the presence of SDS micelles, pyrene is preferentially solubilized in or near the interior hydrophobic region of the micelle. The value of I_I/I_{III} is ca. 1.1 when pyrene is solubilized in SDS micelles (Figure 2). Since the value of I_I/I_{III} for pyrene is a convenient, readily measured quantity and since pyrene is poorly water soluble and is preferentially solubilized in the hydrophobic regions of aqueous systems that are microheterogeneous, it seemed apparent that polymer/surfactant associations could be investigated by employing the I_I/I_{III} parameters.

The functionalized detergent 11-(3-hexyl-1-indoyl)undecyl sulfate (6-In-11$^-$) possesses a "built-in" fluorophore that allows this detergent to serve as a photoluminescence probe.[7] It has been shown that the fluorescence maximum (λ_F) of 6-In-11$^-$ is sensitive to solvent polarity so that λ_F (in a manner similar to I_I/I_{III}) may be employed to probe the formation of hydrophobic associates in aqueous solution.

Results

Pyrene as a Fluorescence Probe for Polymer/Surfactant Interactions for the PVP/SDS and PEO/SDS Systems. The variation of I_I/I_{III} was measured for aqueous solutions containing fixed concentrations of

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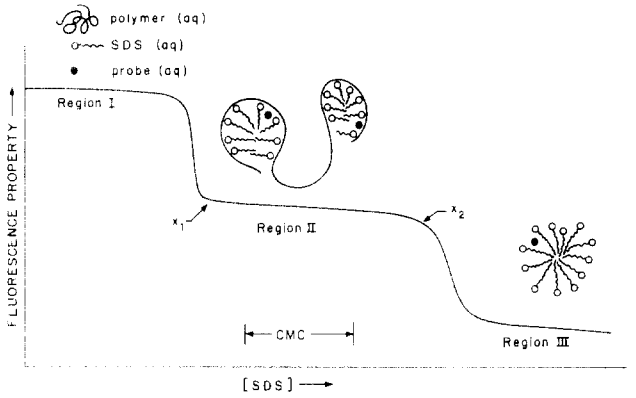

Figure 1. Idealized schematic representation of three regions of polymer/surfactant interactions as a function of surfactant concentration. In region I the water-soluble probe, SDS monomers, and probes are solubilized in the aqueous phase and are not associated. In region II, at a concentration x_1 (below the cmc of SDS), association of SDS with the polymer begins, and at a concentration x_2 (above the cmc of SDS), the association of SDS with the polymer is saturated. In region III micelles (which exist in equilibrium with polymer/SDS associates) become the predominant species.

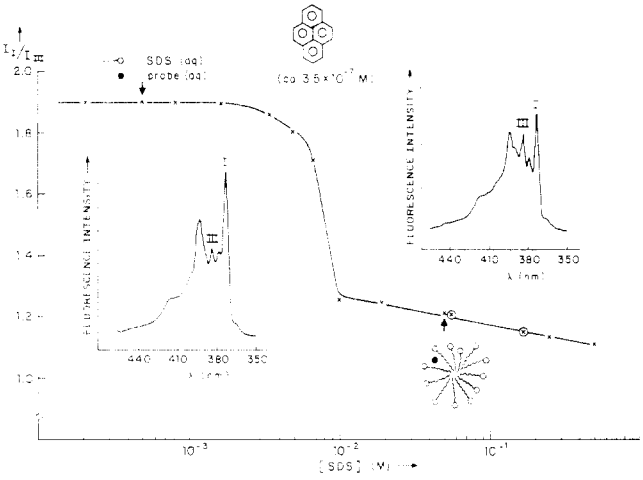

Figure 2. Demonstration of the use of pyrene as a fluorescence probe for micelle formation by SDS in aqueous solution. The points on the line correspond to the I_I/I_{III} values (see text for discussion) as a function of SDS concentration. The inserts are spectra of pyrene fluorescence below the cmc (concentration indicated by heavy arrow) and above the cmc (concentration indicated by heavy arrow).

polymer and variable concentrations of SDS. The results for PVP/SDS systems are shown in Figure 3 and the results for the PEO/SDS systems are shown in Figure 4.

For the PVP/SDS system the I_I/I_{III} vs. [SDS] profiles (Figure 3) look like "textbook" examples of regions I, II, and III.[3b] The first break (transition from region I to region II) in the value of I_I/I_{III} occurs at $x_1 \cong 2 \times 10^{-3}$ M. Literature values[8] of x_1 for PVP/SDS systems fall in the range (1–2) $\times 10^{-3}$ M SDS. The second break (transition from region II to region III) occurs at $x_2 \cong 5 \times 10^{-3}$ M and is independent of the molecular weight of PVP for 0.1% concentration of polymer. For solutions containing 1% PVP break at x_2 is not sharp, but the value of x_2 is clearly larger than that for the more dilute polymer system. The value of I_I/I_{III} at high concentration (>0.1 M) of SDS approaches that for SDS micelles in the absence of polymer.

For the PEO/SDS system the I_I/I_{III} vs. [SDS] profile (Figure 4) shows only one sharp break for PEO concentrations varying from 0.4% to 0.02%. For 0.4% and 0.2% PEO, the first break allows assignment of the value of x_1

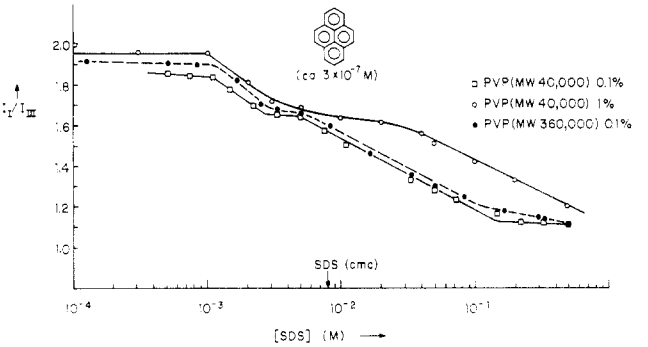

Figure 3. Values of I_{II}/I_{III} for the PVP/SDS system as a function of SDS concentration for different concentrations and molecular weights of PVP.

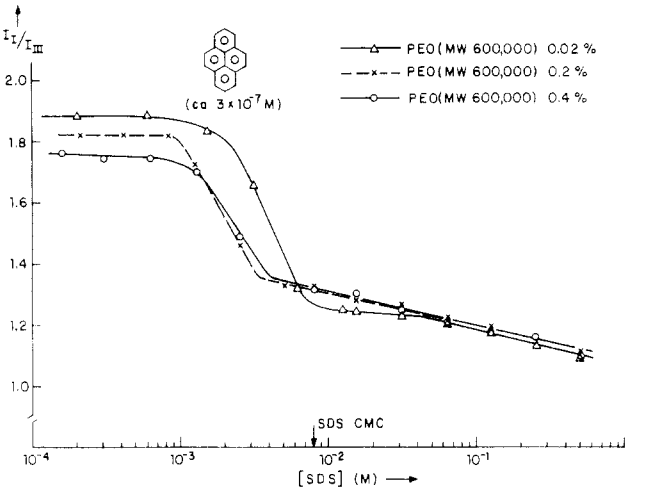

Figure 4. Values of I_I/I_{III} for the PEO/SDS system as a function of SDS concentration for different concentrations of PEO.

as ca. 3×10^{-3} M SDS; for 0.02% PEO, the value of x_1 is ca. 7×10^{-3} M SDS and a slight break assignable to x_2 occurs at ca. 5×10^{-2} M SDS. Literature values[9,10] of x_1 for PEO/SDS systems fall in the range (3–5) $\times 10^{-3}$ M SDS. For [SDS] > 5×10^{-2} M, the slope of the I_I/I_{III} vs. [SDS] plot and the limiting value of I_I/I_{III} are very similar to those for solutions of SDS (Figure 2) in the absence of polymer.

6-In-11⁻ as a Functionalized Detergent Probe for Polymer/Surfactant Interactions for the PVP/SDS and PEO/SDS Systems. The variation of λ_F for 6-In-11⁻ (ca. 1×10^{-4} M) was measured for aqueous solutions containing fixed concentrations of polymer and variable concentrations of SDS. For aqueous systems in the absence of polymer and SDS, the value of λ_F was ca. 373 nm. For the PVP/6-In-11⁻ system at 0.1% PVP (molecular weight 40 000 or 360 000) the value of λ_F is ca. 355 nm in the absence of SDS, and maintains this value (±2 nm) upon addition of up to ca. 10^{-2} M SDS, at which point the value of λ_F increases and approaches a limiting value of 363 nm, the same as the value of λ_F for SDS above its cmc in the absence of PVP. When the concentration of PVP is 1%, the value of λ_F is 363 nm in the absence of SDS, decreases slightly to a minimum value of ca. 356 nm at [SDS] $\simeq 2 \times 10^{-3}$ M, increases to a limiting value of ca. 360 nm upon addition of SDS, and remains at that value up to [SDS] $\simeq 10^{-2}$ M.

For the PEO/6-In-11⁻ system at 0.02% PEO or at 0.2% PEO (molecular weight 600 000) the value of λ_F is ca. 362 nm in the absence of SDS and does not change significantly (±2 nm) upon addition of SDS.

Quenching of 6-In-11⁻ as a Probe of Dynamics of Polymer/Surfactant Systems. The intensity of 6-In-11⁻

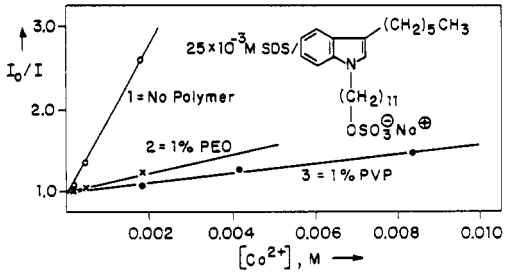

Figure 5. Stern–Volmer quenching of 6-In-11$^-$ (0.9×10^{-4} M) in SDS (25×10^{-3} M) in the presence of hydrophilic polymers: (1) no polymer, slope = $(9.1 \pm 0.5) \times 10^2$ M^{-1}; (2) 1% (w/v) PEO, slope = $(11.4 \pm 1.7) \times 10$ M^{-1}; (3) 1% (w/v) PVP, slope = $(5.9 \pm 1.4) \times 10$ M^{-1}. All error limits are to 95% confidence limit.

Table I
Quenching of 6-In-11$^-$ Fluorescence by Co(II)

system	K_{SV}, M^{-1}	$10^9\tau_F$, s	k_q, M^{-1} s^{-1}
H_2O		16	$<10^8$
SDS	912	9.9	92×10^{10}
PVP/SDS	59	9.2	6.4×10^9
PEO/SDS	114	9.5	12×10^9

fluorescence in dilute aqueous solutions of SDS (25×10^{-3} M) is quenched by Co(II) and follows Stern–Volmer kinetics[7a] (Figure 5 and Table I). However, a Stern–Volmer constant of 59 M^{-1} is found for the PVP/SDS system and 114 M^{-1} is found for the PEO/SDS system. From the 6-In-11$^-$ lifetimes of 9.2×10^{-9} s (PVP/SDS system) and of 9.5×10^{-9} s (PEO/SDS system) in the absence of Co(II), quenching constants of 6.4×10^9 M^{-1} s^{-1} and 12.0×10^9 M^{-1}, respectively, are evaluated.

The rate constant for quenching of 6-In-11$^-$ fluorescence by Co(II) in pure water has been determined[7] to be $<10^8$ M^{-1} s^{-1}.

Discussion

The data summarized in Figures 3 and 4 indicate the utility of the pyrene fluorescene I_I/I_{III} ratio as a probe of polymer/surfactant interactions in aqueous solutions. In water or for SDS concentrations such that $0 <$ [SDS] $< x_1$ (2×10^{-3} M), the value of I_I/I_{III} is ca. 1.8–1.9, independent of the percentage or molecular weight of PVP or PEO present. For the more dilute (0.1%) PVP/SDS system, a plateau region is clearly defined in the range x_1 (ca. 2×10^{-3} M)–x_2 (ca. 5×10^{-3} M) and is independent of molecular weight. For the more concentrated (1%) PVP/SDS system, the plateau region is not as sharply defined but falls in the range x_1 (ca. 3×10^{-3} M)–x_2 (ca. 4×10^{-2} M). For each PVP/SDS system a value of I_I/I_{III} of ca. 1.1 is approached at [SDS] $> 5 \times 10^{-1}$ M.

For the more dilute (0.02%) PEO/SDS system, a fairly sharp break is seen, and a plateau region occurs between ca. 7×10^{-3} and 6×10^{-2} M SDS. The value of I_I/I_{III} of ca. 1.25 in the plateau region is close to the value of I_I/I_{III} of ca. 1.15 for SDS micelles. This in itself explains the lack of sharpness for the break from region II to region III for the PEO/SDS, compared to the PVP/SDS. In the latter case the plateau region corresponds to I_I/I_{III} of ca. 1.6, a value that is considerably different from that for the probe in SDS micelles.

In addition to serving as a probe of polymer/surfactant interactions, the measurement of I_I/I_{III} provides information on the time-average location of the pyrene probe in the polymer/surfactant systems. In the case of PVP/SDS, the pyrene probe experiences in region II an environment whose polarity is intermediate between that of water and SDS micelles ($I_I/I_{III} \simeq 1.6$). For comparison, the value of I_I/I_{III} is ca. 1.6 for the following homogeneous solvents: ethylene glycol (1.6), formic acid (1.6), acetone (1.5). On the other hand, in the case of PEO/SDS the pyrene probe experiences in region II an environment whose polarity is very close to that of SDS micelles (1.1). For comparison, the value of I_I/I_{III} is ca. 1.1 for the following solvents: benzene (1.1), benzyl alcohol (1.2), 1-chlorobutane (1.1).

Thus, in general, the pyrene probe in polymer/SDS associates experiences a more hydrophilic environment than that experienced in SDS micelles. This conclusion is consistent with smaller SDS micelles (bound to the polymer) with too loose aggregation of the SDS along the polymer strand. We favor the former model, which has independent support from NMR measurements and from thermodynamic calculations. For smaller micelles, water penetration is expected to be greater so that the probe "sees" more of the polar palisade layer of the micelle and the water associated with the palisade layer.

Recent results that overlap with and complement our studies come to a similar conclusion.[10] Indeed, evaluation of the "aggregation number" of the polymer-bound micelles in region II via a dynamic fluorescence probe method leads to values 30–50% smaller (25–45) than those for SDS micelles in the absence of polymer (60–70).

From the results for quenching of 6-In-11$^-$ emission by Co(II), it is concluded that although water may penetrate the interior of polymer-bound micelles, metal cations may not. Thus, probes solubilized by polymer-bound micelles are protected from quenching by cations, compared to the probe in free SDS micelles. For example, the rate constant for quenching of 6-In-11$^-$ fluorescence in region II decreases from 92×10^{10} M^{-1} s^{-1} (a "pseudo"-second-order rate constant) for SDS micelles to 12×10^9 M^{-1} s^{-1} for the PEO/SDS system to 6.4×10^9 M^{-1} s^{-1} for the PVP/SDS system. A detailed interpretation of these data is not warranted at this time because of potential special effects in expelling cations, which might be possible for PVP (cationic tautomer)[11] or for stabilizing cations (crown ether type coordination).[12]

Conclusion

The results of our investigation demonstrate that fluorescence probe methods may be used to investigate interactions in polymer/surfactant systems in a manner quite analogous to conventional methods such as measurements of surface tension, conductivity, and viscosity. Our results are consistent with the existence of SDS micelles bound to PVP and PEO polymers. The size of these polymer-bound micelles is probably smaller than that of SDS micelles in the absence of polymer. The average environmental polarity experienced by the pyrene probe is in the order H_2O > region II (PVP/SDS) > region II (PEO/SDS) $\gtrsim$ SDS micelles. In the case of the 6-In-11$^-$ probe, from the values of λ_F its average environment is in the order H_2O > region II (PEO/SDS) $\sim$ SDS micelles > region II (PVP/SDS). In summary, in addition to providing a convenient method for measuring polymer/surfactant interactions, the fluorescence probe method also provides information on the mechanism of solubilization by polymer/surfactant aggregates, since the site of solubilization can be inferred.

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On the Nature of the Poly(γ-benzyl glutamate)–Dimethylformamide "Complex Phase"

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ABSTRACT: The system poly(γ-benzyl L-glutamate)/dimethylformamide (PBLG/DMF) has been studied by small-angle X-ray scattering, polarizing optical microscopy, differential scanning calorimetry, and visual observation. The effects of a nonsolvent, water, have been assessed. We find that a small amount of water, which can be easily absorbed from the atmosphere under normal ambient conditions, even when samples are stored in capped containers, seriously alters the visual appearance, phase behavior, and morphology of the system. The various morphologies available in PBLG/DMF/H_2O are classified and discussed in terms of a pseudobinary, biphasic system, in which a polymer-rich ordered state coexists with a polymer-poor phase, which may be ordered or disordered depending on water content and temperature. We conclude that the "complex phase" reported for PBLG/DMF is a result of water contamination and is related to the phase behavior of the PBLG/DMF/H_2O ternary system.

Introduction

Poly(γ-benzyl L-glutamate) (PBLG) was the first synthetic polymer to exhibit cholesteric liquid crystalline behavior in solution.[1,2] A cholesteric phase is known to exist in a number of solvents.[4–10] However, there is disagreement over the morphological state in dimethylformamide (DMF). In two independent X-ray investigations on the PBLG/DMF system, a "complex phase" was reported.[11,12] This state, which occurred below ca. 40 °C, was described as an opaque gel.[11] Watanabe et al. noted an opaque gel at $T < 60$ °C in 20 wt % PBLG/DMF.[8] Over the years, opaque whitish states have occasionally been seen in this laboratory. However, the vast majority of PBLG/DMF samples have been clear, with the cholesteric thumbprint pattern clearly evident in the polarizing optical microscope.[1–3] Many flame-sealed samples,[13,14] used to determine the phase boundaries in this system, have remained clear for a decade. The occasional whitish samples have been routinely discarded in the belief that a nonsolvent, such as water, caused the whitish appearance.

In this paper, we report the findings of a reexamination of both clear and whitish samples. Using small-angle X-ray scattering (SAXS), polarizing optical microscopy (POM), differential scanning calorimetry (DSC), and visual observations, we have determined the effect of a small amount of water. For comparison, the effect of a nonsolvent on the phase behavior has also been calculated. We conclude that a small amount of water drastically changes the appearance and morphology of the system in a fashion consistent with its phase behavior.

Materials and Methods

PBLG of 310 000 and 130 000 daltons (M_w) was obtained from New England Nuclear and Miles Yeda, respectively, and designated as PBLG-310000 and PBLG-130000. On the basis of the polymerization mechanism and results from other studies,[15a] M_w/M_n is considered to be 1.2–1.3. PBLG was vacuum-dried to constant weight at temperatures not exceeding 60 °C prior to use. Reagent grade DMF was dried over 4-Å molecular sieves and distilled under reduced pressure at ca. 50 °C. Solutions were prepared by weight in a dry atmosphere or as rapidly as possible in the open atmosphere. Solutions were homogenized in capped vials containing magnetic stirbars placed on a stirring hotplate in a dry nitrogen atmosphere. The temperature required for dissolution increased with water content. If necessary, the temperature was raised to as much as 80–100 °C for a short time to ensure homogeneous samples. For conversion to volume fraction (v_p), the specific volume of PBLG was taken as 0.791 cm^3/g and the density of DMF as 0.944 g/cm^3.

All X-ray studies were performed in 1-mm glass capillaries with 0.01-mm-thick walls (Charles Supper Co.). The sample was transferred into the capillary and spun to the bottom in a low-speed centrifuge, both operations taking place under a dry nitrogen atmosphere. The capillaries were removed from the dry atmosphere and immediately flame sealed. A good seal was ensured by dunking the capillary tip several times into molten beeswax. The capillaries were then weighed over a period of several days to check for leaks. The delicate capillaries were stored inside tubular holders glued to microscope slides held in a slide box. Temperature equilibration was achieved by immersing a watertight slide box into a temperature-controlled bath (±0.005 °C). The samples were transported to the X-ray camera in a capped Dewar containing some water from the bath. The sample was mounted in a brass cell holder of original design. The holder had a volume of 3 $in.^3$, through which thermostated water circulated, and was designed to fit into the standard slots of the Warhus pinhole-collimated camera used throughout these studies. Kel-F insulators prevented heat transfer to the rest of the camera, and the water inlet lines were sealed to permit vacuum operation for reduced air scatter. Since facilities for measurement of the temperature at the brass block during the measurement were not available, the temperature reported is that at the water bath, which was connected to the cell holder by well-insulated lines. All measurements were performed under vacuum. The camera had several standard film positions. The distance from the sample

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