

Interactions of Hydrophobically Modified Polyelectrolytes with Surfactants of the Same Charge

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Polymer–surfactant interactions in aqueous solutions of a hydrophobically modified polymer, poly-(maleic acid/octyl vinyl ether) (PMAOVE), with sodium dodecyl sulfate (SDS) were studied using surface tension, viscosity, electron paramagnetic resonance spectroscopy, and fluorescence spectroscopic techniques. When the anionic surfactant SDS was added to the aqueous solutions of the similarly charged polymer PMAOVE, the surfactant was incorporated into the hydrophobic nanodomains of PMAOVE far below the critical micelle concentration of the surfactant. Two inflection points were observed corresponding to the critical complexation concentration (formation of mixed micelles composed of SDS and the octyl chains of PMAOVE) and the saturation concentration (saturation of the polymer with SDS molecules). Above the saturation concentration, coexistence of pure SDS micelles and mixed micelles of PMAOVE and SDS was observed. At a PMAOVE concentration of 0.1% (w/w), a critical complexation concentration of 2 mM SDS and a saturation concentration of approximately 12 mM SDS were found; both the critical complexation concentration and the saturation concentration increase with increasing PMAOVE concentration.

Introduction

Hydrophobically modified polyelectrolytes (HMPs) are of growing interest because of their unique associative behavior and special rheological properties.^{1–5} Interactions of surfactants with HMPs in aqueous solutions have attracted substantial interest because of their wide applications in several industrial fields.^{6,7} These interactions are considered to be the result of complexes formed between surfactant and polymer due to electrostatic and hydrophobic forces. These complexes, besides having important practical applications in detergency, cosmetics, food, and paints, also raise some fundamental questions about the polymer–surfactant interactions that control their behavior.^{6–9}

Previous studies have been devoted mainly to systems with attractive interactions, either weak (e.g., between nonionic polymers and anionic surfactants) or strong (between oppositely charged polyelectrolytes and surfactants).^{6,7,10} Although it had been recognized a long time ago, the role of attractive hydrophobic interactions

between HMPs and surfactants has been studied systematically only during the past decade.^{11–20} In the present study, we explore the interactions between a hydrophobically modified copolymer poly(maleic acid/octyl vinyl ether) (PMAOVE; Chart 1) with a surfactant of the same charge, sodium dodecyl sulfate (SDS). To study these attractive hydrophobic interactions, we used a multi-technique approach, involving measurements of surface tension, viscosity, electron paramagnetic resonance (EPR) spectroscopy, and fluorescence spectroscopy.

Experimental Section

Materials. *Polymers.* The hydrophobically modified polymer, PMAOVE, provided by International Specialty Products, Inc., was synthesized using free-radical polymerization of a 1:1 mole ratio of maleic anhydride and octyl vinyl ether in toluene with Vazo-69 (azobisvaleryl nitrile) as the initiator. The products were purified twice by first dissolving them in acetone (5 wt %) followed by precipitation with an excess of *tert*-butyl alcohol (40 times in volume). The residual solvent was removed in a vacuum at 50 °C to a constant mass. The anhydride moiety of the polymer was then hydrolyzed in triple-distilled water to make an approximately 5 wt % solution. The solution was stirred at 500 rpm at 70 °C for about 12 h and then freeze-dried. As determined by gel permeation chromatography, the weight average molecular weight (M_w) was 160 000 Da with a polydispersity index of 1.23.

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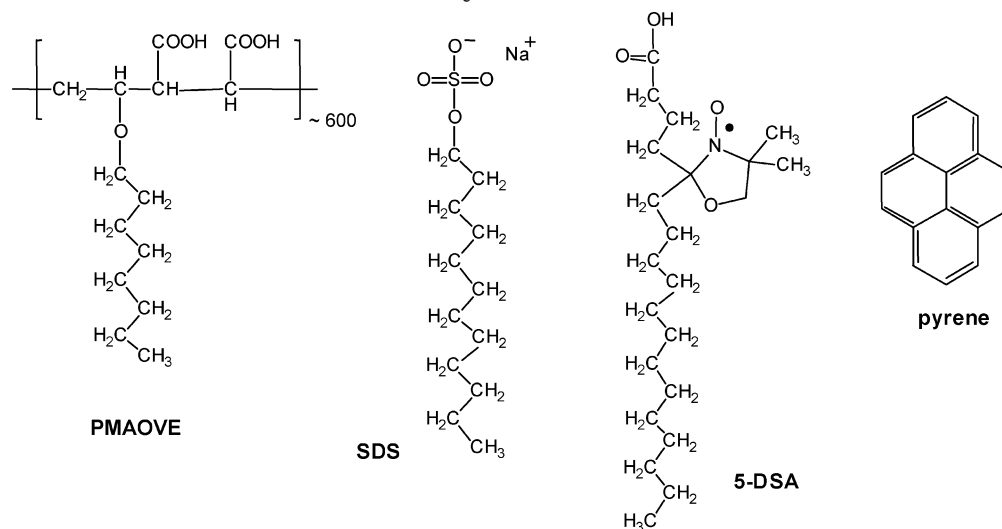
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Chart 1. Structures of the Polymer, Surfactant, and Probe Molecules

Probes and Additives. The spin probe 5-doxyl stearic acid (5-DSA; Aldrich, 99+% pure; Chart 1), pyrene (Aldrich), SDS (Aldrich, 99+% pure), and NaCl (Fluka, 99.5% pure) solutions of 0.1 N hydrochloric acid (Fisher Scientific) and 0.1 N NaOH (Fisher Scientific) were used as received. Triple-distilled water was used in all experiments.

Methods. Surface Tension Measurements. The surface tension of the surfactants and the polymer–surfactant solutions was measured with the Wilhelmy plate technique using a sandblasted platinum plate as the sensor. The pull exerted on the sensor was determined using a Beckman microbalance (model LM 600). The entire assembly was kept in a draft-free plastic cage at a temperature of 25 ± 0.05 °C. For each measurement, the sensor was in contact with the solutions for 30 min to allow equilibration.

Viscosity Measurements. A calibrated capillary viscometer (Canon Instruments) was used for measuring the relative viscosity on the basis of that of the triple-distilled water at 25 ± 0.05 °C. The viscometer was cleaned with chromic acid and triple-distilled water and thoroughly dried with acetone before the measurements. The efflux time for triple-distilled water was checked before every measurement for reproducibility of the results.

EPR Measurements. EPR spectra were recorded using a Bruker EMX spectrometer operating at the X band (9.5 GHz). All EPR spectra were recorded at 22 ± 1 °C. The concentration of the probe molecule (5-DSA) used in all the studies was 10^{-4} M. For the EPR measurements, the desired portions of 10^{-4} M 5-DSA in chloroform were added to a glass vial, and the solvent was evaporated. Then the aqueous polymer and polymer–surfactant solutions of desired concentrations and volumes were added to the vials under stirring. EPR spectra of these solutions were recorded 24 h after sample preparation using Pyrex capillary tubes (~1 mm inner diameter) as the sample container. The EPR spectra were analyzed by computer simulation of the spectral line shape by means of the well-established procedure by Freed et al.^{21,22}

Fluorescence Measurements. Fluorescence spectra were recorded on a SPEX FluoroMax 2 spectrofluorometer (Jobin Yvon, Inc.) using pyrene (0.05 mM) as the fluorescence probe at an excitation wavelength of 335 nm. For micropolarity measurements, fluorescence intensities at the peak maxima 373 nm (I_1) and 383 nm (I_2) were recorded using sample cells of 10-mm path length.

All the experiments were done at pH = 4–4.5.

Results and Discussions

Surface tension measurements are frequently used to study surfactant micellization. Figure 1b shows the surface

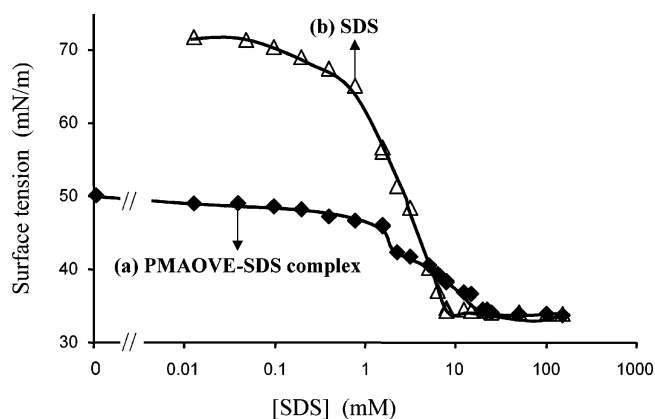


Figure 1. Surface tension of aqueous solutions in the absence (b) and in the presence (a) of 0.1% (w/w) PMAOVE as a function of the SDS concentration. Standard deviation (SD) = $\pm 2\%$.

tension of aqueous SDS solutions as a function of the SDS concentration. In agreement with published values,²³ a critical micelle concentration (cmc) of 8 mM is observed. As expected, the surface tension of an aqueous solution of 0.1% PMAOVE is lower than that of water (Figure 1a). The addition of SDS to the PMAOVE solution causes a change of the surface tension in two stages. At 2 mM SDS, a sharp decrease of the surface tension occurred (indicating the formation of mixed micelles of SDS and hydrophobic groups of PMAOVE) followed by a gradual decrease with SDS concentrations. At approximately 20 mM SDS, the surface tension reached a value similar to that of SDS micelle solutions and remained constant with further increase in the SDS concentration, suggesting the coexistence of mixed micelles and pure SDS micelles in the solution at that concentration.

Figure 2 shows the dependence of the viscosity on the concentration of SDS in the presence and absence of PMAOVE. As expected, in the absence of PMAOVE the viscosity increases slightly above the cmc (8mM) because of the formation of micelles (Figure 2b). In the presence of 0.1% PMAOVE, the viscosity increased at a SDS concentration of about 2 mM (Figure 2a), indicating a change in the conformation of the polymer structure or aggregation. Upon further increase in the SDS concentration, the viscosity continued to increase, suggesting

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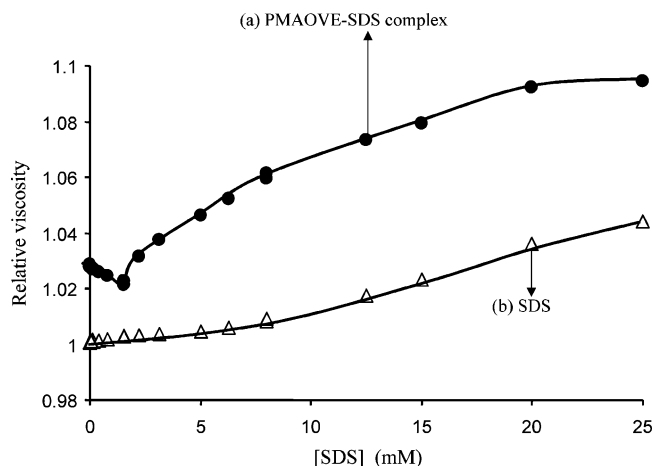


Figure 2. Relative viscosity of aqueous solutions in the absence (b) and in the presence (a) of 0.1% (w/w) PMAOVE as a function of the SDS concentration. SD = $\pm 2\%$.

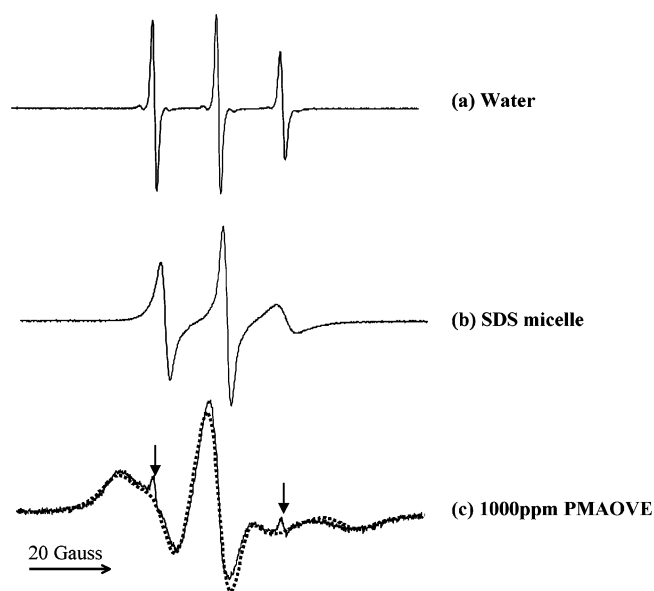


Figure 3. EPR spectra of 5-DSA (0.1 mM) in (a) triple-distilled water, (b) SDS micelles ([SDS] = 20 mM), and (c) 0.1% (w/w) PMAOVE; solid lines are experimental spectra, and dashed lines are simulated spectra.

gradual polymer restructuring and formation of mixed micelles of PMAOVE and SDS. These results are in accord with that expected from an increase in the effective volume occupied by PMAOVE–SDS mixed micelles, compared to that of the pure PMAOVE (coiled structure).

It has been demonstrated that EPR spectroscopy is a powerful technique to probe microenvironments of supramolecular structures involving surfactants and macromolecules.^{24,25} We selected 5-DSA as the spin probe because of its structural similarity with SDS (Chart 1). It has been shown that 5-DSA forms mixed micelles with SDS and does not disrupt the micelle structure significantly, if used in small concentrations.²⁶

Figure 3 shows the EPR spectra of 5-DSA in water, in SDS micelles, and in PMAOVE. The EPR spectrum of 5-DSA in water solution consists of a sharp three-peak

signal characteristic of free probe molecules in the fast-motion condition in a polar environment (Figure 3a). In the presence of the SDS micelles, a broadened EPR spectrum is observed (Figure 3b), which is consistent with partial hindered rotational mobility of the probe molecule because of the incorporation of 5-DSA molecules into the SDS micelles.²⁶ In the presence of PMAOVE, a significantly different EPR spectrum was observed (Figure 3c). The spectrum is consistent with the probe in the slow-motion condition, causing a partial resolution of the anisotropic components of the magnetic tensors (g , for the coupling between the electron spin and the magnetic field, and A , for the coupling between the electron spin and the nuclear spins). Because of the significant differences in spectrum a and c, it can be concluded that 5-DSA interacts strongly with PMAOVE. Only a negligible fraction (~ 1 – 2%) of 5-DSA remains in the bulk solution in the fast-motion condition, as demonstrated by the small sharp peaks indicated by the arrows (Figure 3c). An increase in the PMAOVE concentration decreases the fraction of free 5-DSA.

Addition of SDS to PMAOVE solutions containing the spin probe 5-DSA causes significant changes in the experimental EPR spectra (Figure 4). Addition of SDS up to 1.6 mM showed experimentally indistinguishable EPR spectra (Figures 3c and 4a). At a concentration of 2.2 mM SDS, a significant change in the EPR spectrum was observed (Figure 4b). Further changes in the EPR spectra were observed at a SDS concentration between 8 and 20 mM (Figure 4c–e).

The mobility parameter, the rotational correlation time, of the spin probe was determined by spectral simulation of the experimental EPR spectra using the program of Freed et al.^{21,22} Figure 5a illustrates the changes in the rotational correlation time of 5-DSA in 0.1% PMAOVE at different concentrations of SDS. Two inflection points are observed, one at a SDS concentration of 2 mM and the other one at 12 mM (Figure 5). The first inflection point (2 mM) was also observed using other techniques, such as surface tension measurements (Figure 1a) and viscosity measurements (Figure 2a). This SDS concentration (2 mM) was assigned to the critical complexation concentration, where mixed micelles of hydrophobic chains of PMAOVE and SDS molecules are formed. For complexation with SDS to occur, a restructuring of the coiled PMAOVE is necessary. The critical complexation concentration should depend on the PMAOVE concentration. Figure 6 shows that if the PMAOVE concentration is increased from 0.1% (Figure 5) to 0.5% (Figure 6), the critical complexation concentration of SDS increases from 2 to 5 mM.

Figure 5a shows a second transition of the rotational correlation time ($8 < [\text{SDS}] < 20\text{mM}$) corresponding to a second inflection point at approximately 12 mM SDS. This SDS concentration is assigned to the saturation level of PMAOVE with SDS. Upon further addition of SDS, the rotational mobility of the spin probe remains constant, implying the coexistence of pure SDS micelles and mixed micelles of PMAOVE with SDS. The saturation level (second inflection point) is expected to depend on the PMAOVE concentration. Figure 6 shows that if the PMAOVE concentration is increased from 0.1% (Figure 5) to 0.5% (Figure 6), the second inflection point of SDS increases from 12 to 20 mM.

The hyperfine-coupling (A_N) constant, which is sensitive to the polarity of the medium in which the radical resides, is given by^{27–31}

$$A_N = \frac{1}{3}(A_{\parallel} + 2A_{\perp})$$

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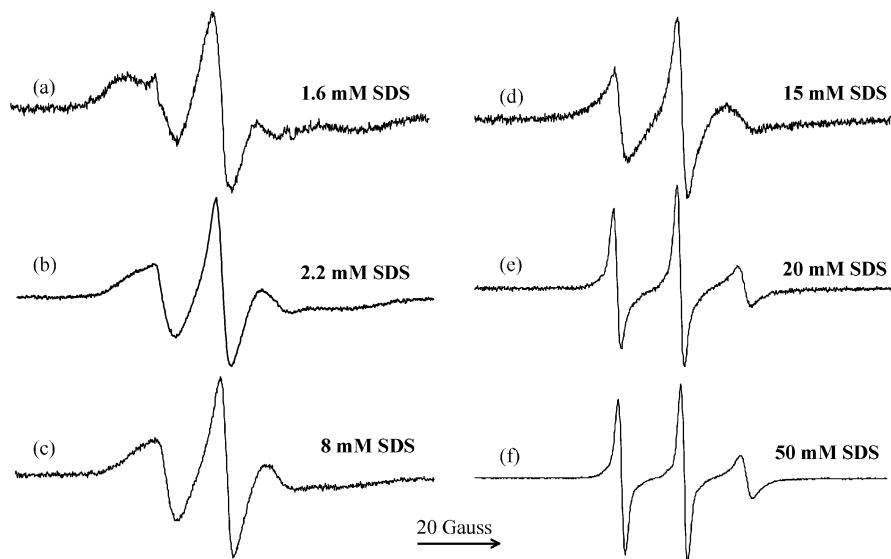


Figure 4. EPR spectra of 5-DSA (0.1 mM) in the aqueous solutions of the complex of PMAOVE (0.1% w/w) with SDS at SDS concentrations of 1.6 (a), 2.2 (b), 8 (c), 15 (d), 20 (e), and 50 mM (f).

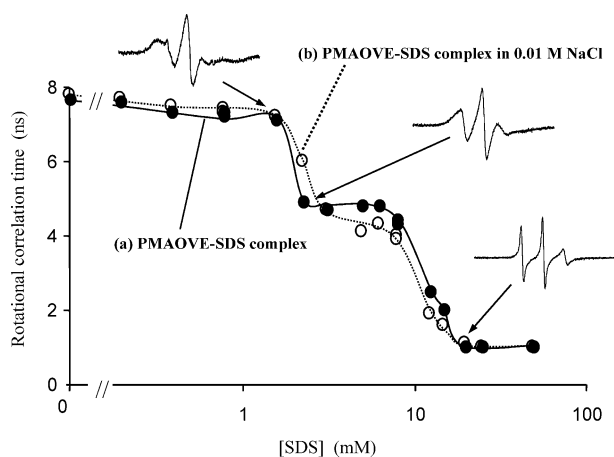


Figure 5. Rotational correlation time of the spin probe (5-DSA; 0.1 mM) as a function of the SDS concentration of aqueous PMAOVE (0.1% w/w) solutions in the absence (a) and in the presence (b) of NaCl (0.01 M). SD = $\pm 2\%$.

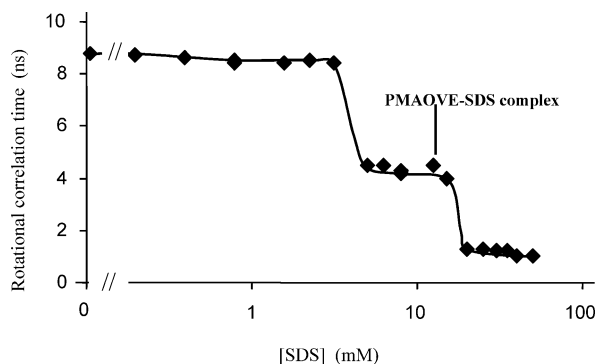


Figure 6. Rotational correlation time of the spin probe (5-DSA; 0.1 mM) as a function of the SDS concentration of aqueous PMAOVE (0.5% w/w) solutions. SD = $\pm 2\%$.

where A_{\parallel} is the time-averaged electron-nuclear hyperfine tensor (parallel) and $2A_{\perp}$ is the time-averaged electron-nuclear hyperfine tensor (perpendicular).

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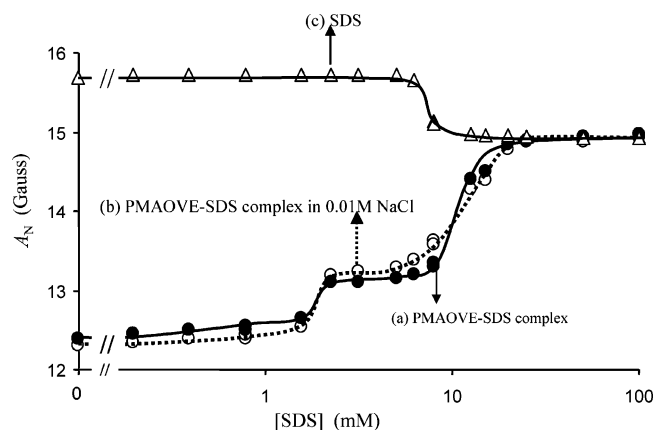


Figure 7. Hyperfine splitting constant (A_N) of 5-DSA (0.1 mM) as a function of the SDS concentration of aqueous solutions in the presence of PMAOVE (0.1% w/w); a, in the presence of PMAOVE (0.1% w/w) and NaCl (0.01 M); b, and in the absence of both (c). SD = $\pm 2\%$.

The variation of the hyperfine-coupling constant (A_N) of 5-DSA in PMAOVE-SDS complexes as a function of the SDS concentration is illustrated in Figure 7. Free 5-DSA in water shows a high hyperfine-coupling constant ($A_N = 15.8$ G), because of the highly polar environment.³² Addition of SDS (Figure 7c) does not change A_N up to a SDS concentration of 8 mM, the cmc. Above 8 mM SDS, micelles are formed and 5-DSA is incorporated into the SDS micelles. This causes a decrease in the hyperfine-coupling constant ($A_N = 15.1$ G), because of the decreased polarity of the micelles. A much lower hyperfine-coupling constant ($A_N = 12.3$ G) was observed for 5-DSA located in hydrophobic domains of PMAOVE, indicating a more nonpolar environment.³³⁻³⁵ Addition of SDS to 5-DSA/PMAOVE systems causes a change in A_N , and two inflection points are observed, at 2 and 12 mM (Figure 7a). The two inflection points are consistent with the

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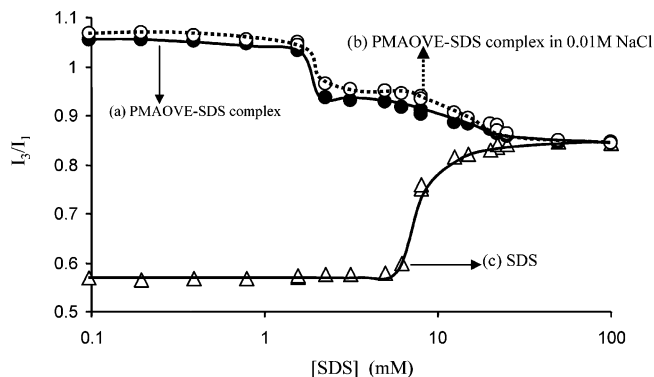


Figure 8. Vibrational fine structure (I_3/I_1) of pyrene fluorescence as a function of the SDS concentration of aqueous solutions in the presence of PMAOVE (0.1% w/w; a), in the presence of PMAOVE (0.1% w/w) and NaCl (0.01 M; b), and in the absence of both (c). SD = $\pm 2\%$.

results from the rotational correlation time (Figure 5a), surface tension (Figure 1a), and viscosity measurements (Figure 2a). The first inflection point (2 mM SDS) was assigned to the critical complexation concentration. At a SDS concentration of 2.2–10 mM, a hyperfine-coupling constant of $A_N = 13.1$ G was observed (Figure 7a), indicating the transfer of 5-DSA from a nonpolar environment (hydrophobic domains of PMAOVE) to an environment with increased polarity, such as mixed micelles of hydrophobic chains of PMAOVE and SDS. After saturation of PMAOVE with SDS (second inflection point, approximately 12 mM, Figure 7a) A_N reaches a value similar to that of SDS micelles (Figure 7c), suggesting the formation of SDS micelles without any PMAOVE.

An increase in the PMAOVE concentration from 0.1% (w/w; Figure 7) to 0.5% (w/w) shifts the inflection points toward higher SDS concentrations (experimental results not shown), which is consistent with the results for the rotational correlation time (Figures 5a and 6). This is attributed to the increase in the available binding sites for SDS with an increase in the PMAOVE concentration, leading to a higher critical complexation concentration and saturation concentration.

Another useful technique to study the micropolarity of surfactant-containing systems is fluorescence spectroscopy using pyrene as the probe.^{36–39} The vibrational fine structure of the pyrene fluorescence depends strongly on the polarity of the environment. The ratio between the intensities of the third (I_3) and the first (I_1) fluorescence peaks of pyrene is commonly used as the polarity probe.^{36,37} For SDS systems only (Figure 8c), below the cmc a low I_3/I_1 value was observed ($I_3/I_1 = 0.56$), which is in agreement with the location of the pyrene molecules in the polar water solution. A sharp increase in the I_3/I_1 value was observed at the cmc of SDS (8 mM), and above it, the I_3/I_1 value remained constant within the tested SDS concentration range.³⁹ Pyrene (0.05 mM) in PMAOVE solutions (without SDS) showed an I_3/I_1 value of 1.07, which is characteristic for a nonpolar environment similar to that of *iso*-propyl ether and *p*-xylene ($I_3/I_1 = 1.07$ and 1.05, respectively).⁴⁰ This indicates that the water insoluble pyrene is located in the hydrophobic microdomains

of PMAOVE, which is in agreement with the low hyperfine-coupling constant ($A_N = 12.3$ G) of the 5-DSA probe. Addition of small amounts of SDS (<2 mM) did not change the I_3/I_1 value (Figure 8a). At a SDS concentration of 2 mM (critical complexation concentration), a sharp decrease in the I_3/I_1 value was observed, which is consistent with the formation of mixed micelles of PMAOVE and SDS. Because the I_3/I_1 value (0.95) is higher for PMAOVE–SDS complexes than for pure SDS micelles ($I_3/I_1 = 0.84$), it is concluded that the mixed micelles of PMAOVE and SDS are less polar than the SDS micelles, which is in agreement with the results from the EPR probe technique shown previously. The second inflection point, which was found by means of other techniques (see previous text) is also found from the fluorescence measurements. Because the change in the I_3/I_1 value is too small (from 0.95 to 0.84), the inflection point could not be assigned correctly (Figure 8a).

The effects of the ionic strength on PMAOVE–SDS complexation was investigated by performing surface tension, viscosity, EPR, and fluorescence measurements in the presence of NaCl (0.01 M). Figures 5b and 7b show the variations of the rotational correlation time and the hyperfine-coupling constant of 5-DSA in the presence of NaCl and PMAOVE as a function of the SDS concentration. Only minor differences were observed for the systems in the presence of NaCl compared to the systems in the absence of NaCl (Figures 5a and 7a). In addition, the I_3/I_1 values of the pyrene fluorescence in PMAOVE–SDS complexation studies were almost identical in the presence and absence of NaCl (Figure 8b,a, respectively). Surface tension and viscosity measurement results (not shown) also did not show any significant difference due to NaCl, indicating that the ionic strength (0.01 M) does not influence the PMAOVE–SDS complexation. This is expected because only a single surfactant molecule is entering an existing micelle and, hence, no condensed counterions are required at the onset of complexation.

Discussion

On the basis of the surface tension, viscosity, EPR, and fluorescence spectroscopy results, we have proposed a model for PMAOVE–SDS interactions, which is illustrated in Scheme 1. PMAOVE in aqueous solutions forms a coiled structure, with the nonpolar chains forming hydrophobic nanodomains.¹ EPR experiments using 5-DSA as the spin probe reveal that the packing of the hydrophobic chains is tight (low rotational mobility of the spin probe) and the polarity of the microdomains is low compared to that of the SDS micelles (low A_N). Fluorescence spectroscopy using pyrene as the probe confirmed the low polarity of the microdomains.

When small amounts of SDS were added ($[SDS] < 2$ mM) to PMAOVE solutions (0.1%), only negligible changes in the properties (surface tension, viscosity, and spin and fluorescence probe techniques) were observed. At approximately 2 mM SDS, a significant change in properties was observed by surface tension, viscosity, EPR, and fluorescence measurements. Because the surface tension decreased (Figure 1a), the viscosity increased (Figure 2a), the rotational correlation time of the spin probe decreased (Figure 5a), and the polarity of the microdomains increased (Figures 7a and 8a), it is concluded that SDS is incorporated into the hydrophobic microdomains of PMAOVE at a SDS concentration of 2 mM. The SDS concentration of 2 mM was, therefore, assigned as the critical complexation concentration (formation of mixed micelles of SDS and the hydrophobic *n*-octyl chains of PMAOVE). A concentration of 0.1% PMAOVE corresponds to a concentration

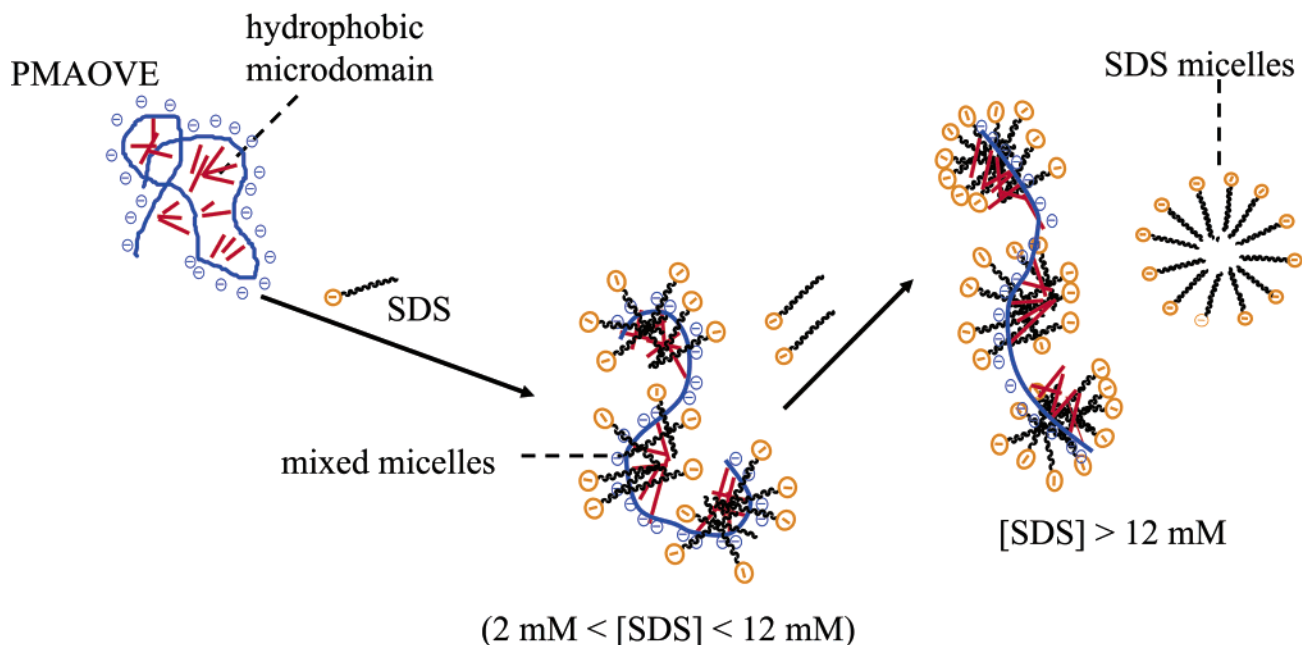
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Scheme 1. Effects of SDS on the Structural Reformation of PMAOVE (0.1% w/w)Critical complexation concentration $\sim 2\text{mM}$ Saturation concentration $\sim 12\text{mM}$ 

of 3.7 mM *n*-octyl chains, which is similar to the critical complexation concentration (2 mM).

As the SDS concentration is increased ($2 < [\text{SDS}] < 10$ mM), more SDS is incorporated into the PMAOVE–SDS complex to form mixed micelles of hydrophobic groups of PMAOVE and SDS on the PMAOVE backbone (Scheme 1). This is consistent with only minor changes in the polarity of the mixed micelles (Figure 7a) and microviscosity (Figure 5a). The macroviscosity increases gradually (Figure 2a) as the mixed micelles increase in size.

At approximately 12 mM SDS, the microviscosity (Figure 5a) and polarity (Figure 7a) experienced by the spin probe, 5-DSA, change dramatically. The SDS concentration of 12 mM corresponds to approximately 3 SDS molecules per *n*-octyl chain of the PMAOVE (mixed micelles are mixtures of SDS monomers and hydrophobic side chains of PMAOVE). The SDS concentration of 12 mM is assigned as the saturation concentration. Above 12mM SDS, in addition to the mixed micelles of SDS and PMAOVE, pure SDS micelles are formed (Scheme 1). The presence of pure SDS micelles is based on the observation that the properties, such as surface tension (Figure 1a), microviscosity (Figure 5a), and polarity (Figures 7a and 8a), at high SDS concentrations (e.g., 25 mM) are similar to those of pure SDS micelle systems without PMAOVE.

The critical complexation concentration and the saturation concentration of SDS depend on the PMAOVE concentration. If the PMAOVE concentration increases from 0.1 to 0.5%, the critical complexation concentration and the saturation concentration increase (from 2 to 5 mM and 12 to 20 mM, respectively). This is consistent with an increase in the total number of complexation sites on PMAOVE for SDS molecules with increasing PMAOVE concentration.

Conclusions

Interactions of a hydrophobically modified anionic polymer (PMAOVE) with an anionic surfactant (SDS) were

studied using surface tension, viscosity, EPR, and fluorescence spectroscopic techniques. The *n*-octyl chains of PMAOVE form hydrophobic nanodomains in aqueous solutions. If a surfactant of the same charge (SDS) is added to the PMAOVE solutions, SDS gets incorporated into the existing hydrophobic polymer nanodomains. This process involves a structural reformation of PMAOVE. Two inflection points were observed for the surface tension, viscosity, EPR (using 5-DSA as the mobility and polarity probe), and fluorescence spectroscopy (using pyrene as the polarity probe), corresponding to the critical complexation concentration (formation of mixed micelles) and the saturation concentration (saturation of the polymer with SDS molecules). Above the saturation concentration, coexistence of pure SDS micelles and mixed micelles of PMAOVE and SDS were observed. At a PMAOVE concentration of 0.1%, a critical complexation concentration of 2 mM and a saturation concentration of approximately 12 mM SDS were found; both increase with increasing PMAOVE concentration.

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