J. Chem. Eng. Data **2006,** *51,* 1576−1581

Investigation on the Interaction between Sodium Dodecyl Sulfate and Polyethylene Glycol by Electron Spin Resonance, Ultraviolet Spectrum, and Viscosity

Ming Cao and Mingtan Hai*

School of Material Science and Engineering, University of Science and Technology Beijing, Beijing 100083, PR China

The hydrophobically modified nitroxide radical molecule 2,4-dinitrophenylhydrazone of 2,2,6,6-tetramethyl-4-piperidind-1-oxyl (DNPHTEMPO) was synthesized and used as electron spin resonance (ESR) and a UV probe to investigate the interaction between sodium dodecyl sulfate (SDS) and poly(ethylene glycol) (PEG). The ESR results showed that the headgroups of SDS adsorbed on PEG were more tightly packed than those of the unperturbed micelles and a more compact structure was formed at the binding site of the polymer−micelle aggregate due to a strong decrease of the viscosity at the micelle−polymer interface. The nitroxide group of DNPHTEMPO consisted of ∼55 % water and ∼45 % hydrocarbon. The two breakpoints of the SDS + PEG system critical aggregation concentration (cac) and polymer saturation point (PSP) were obtained from the maximum absorption bands $\lambda_{\max}$ at room temperature and the viscosity measurement at different temperatures. The average location of 2,4-dinitrophenylhydrazone in the micelle consisted of an environment containing approximately 90 % water and 10 % hydrocarbon. The η/C_p (viscosity/PEG concentration) decreased with the increase of PEG concentration and temperature and exhibited a polyelectrolyte character. The electroviscosity effect increased with increasing SDS concentration. The PEG concentration had little effect on the cac of the SDS + PEG system.

Introduction

The interaction between polymers and surfactant in aqueous solutions has become a very interesting topic for widespread applications as well as theoretical studies and has been investigated for several decades and extensively documented.[1] Surfactants may bind cooperatively to nonionic water-soluble polymers to form micelle−polymer complexes,[2−4] and these interactions are largely confined to anionic surfactants. Goddard[3] gave an excellent review of the interaction between nonionic polymers and charged surfactants. Among the experimental methods used for the investigation of polymer−surfactant complex formation, viscosity measurements and fluorescence probing are the most popular.[5−6] Although various techniques have been used to probe the nature of interaction between surfactant and polymer,[7−10] the structure and morphology of the polymer−surfactant complexes as well as the nature of the interaction involved in the complex have not been well established yet. The electron spin resonance (ESR) technique has been applied for investigating the interaction between polymer and surfactant in recent years. ESR has been used to investigate the microenvironment of nitroxide spin probes in micelles by measuring the nitrogen coupling constant and ESR spectra line widths. The coupling constant is affected by the local polarity of the nitroxide. A more polar environment gives larger values of coupling constant because of greater electron density in nitrogen. The line widths are controlled by rotation of the spin probes, which in turn is affected by microviscosity at the local environment in the micelles. Witte et al.[11] confirmed that the use of a sufficiently hydrophobic spin probe is a prerequisite for the usefulness of the ESR method, and it can enhance partition coefficients between the micelles and aqueous medium, so we synthesized a sufficiently hydrophobic molecule 2,4-dintrophenylhydrazone of 2,2,6,6-tetramethyl-4-piperidind-1-oxyl (DNPHTEMPO) and used it as a spin probe.

An increase in the viscosity of many nonionic polymers, such as polyacrylamide,[12] has been reported by the addition of SDS. This increase has been attributed to surfactant adsorption on the polymer chain and to conformational changes of the macromolecular coil reduced by electric charge. Moreover, a minimum in reduced viscosity of the polymer has been observed during the first steps of addition of surfactant in some polymer surfactant system.[12] This minimum, observed just before reduced viscosity starts to increase with increasing surfactant concentration, has been attributed to the shrinking of the polymer coil due to intramolecular attraction through hydrophobic interactions with the hydrophobic tails of the surfactant molecules adsorbed on the polymer chain.

The UV spectrum is based on the use of a chromophore as the probe, which provides information about the environment of the surfactant and polymer−probe interface and gives the absorption band position. Viscometry is based on the behavior of a polymer in the presence of a surfactant on the properties of the micelle−water interface and the UV spectrum on the property of the micelle−water interface in the presence of a polymer. These two methods are complementary for the investigation of polymer−surfactant interaction.

In our present study, we reported the use of 2,4-dinitrophenylhydrazone of 2,2,6,6-tetramethyl-4-piperidind-1-oxyl (DNPHTEMPO) as the ESR and UV chromophore probe in aqueous solutions of SDS and SDS + 0.1 % mass fraction PEG aqueous solution. The maximum absorption band $\lambda_{\max}$ of the UV absorption band can give information concerning the environment of the 2,4-dinitrophenylhydrazone group. In other words, the $\lambda_{\max}$ is a parameter for the dynamic behavior of the probe at the micelle binding sites. At the same time, the viscosity of the above-studied aqueous solutions at different temperatures was measured. The structure and morphology of the surfactant−

---

* Corresponding author. E-mail: mingtanhai@mater.ustb.edu.cn

10.1021/je060067n CCC: $30.25

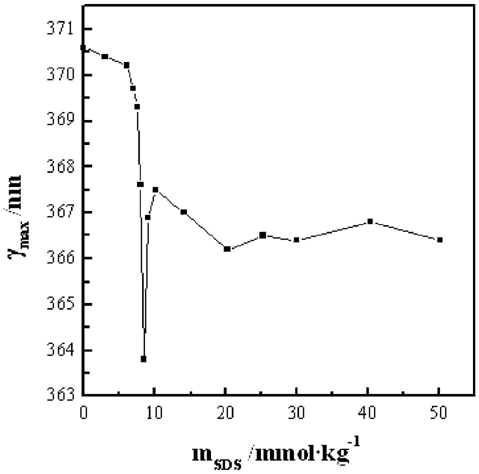

Figure 1. UV maximum absorption band γ_{max} of SDS aqueous solutions at room temperature.

polymer system was studied. The thermodynamic property and interaction strength between surfactant and polymer was discussed.

Experimental Section

Sodium dodecyl sulfate (BRL, 99.5 % SDS) was used as received. Both polymer poly(ethylene glycol) (PEG) and 2,2,6,6-tetramethyl-4-piperidine-1-oxyl (OTEMPO) were purchased from Aldrich and used without further purification. The average molecular weight of PEG is 100 000. The probe DNPHTEMPO was synthesized by the Rozantzev and Neiman method from 2,4-dinitrophenylhydrazine and OTEMPO.[13] All solutions were prepared by weight in twice-distilled water. The concentration of DNPHTEMPO was kept at 5.0×10^{-6} mol·kg^{-1}. The probe concentration was small enough to be considered as a negligible perturbation to the studied system.

The ESR spectra have been recorded at room temperature on a Brucker ESP 300E spectrometer operating at X-band with 100 kHz magnetic field modulation at 1 K and 3.19 mW microwave power to avoid power saturation. All spectra experiments were run using a quartz capillary tube with a diameter of 1.5 mm. The average relative uncertainty for the rotational correlation time was about ±1 %.

The UV spectra were measured by a TU-1221 spectrometer at room temperature. The wavelength can be measured up to 0.01 nm. The wavelength uncertainty was within ±0.2 % of the full scale range, and the repeatability of the measured viscosity was above 99.8 %.

The viscosity of the surfactant−polymer aqueous solutions was measured by an Ostwald viscometer at 298.15 K, 308.15 K, and 318.15 K. We used 0.01 mol·L^{-1} and 0.1 mol·L^{-1} NaCl solutions to calibrate the viscometer. The viscosity uncertainty was within ±0.5 % of the full scale range, and the repeatability of the measured viscosity was above 99.5 %.

Results and Discussion

The position of the probe DNPHTEMPO was determined by the measurement of the electronic spectra of the probe in each aqueous solution (SDS and SDS + PEG). The probe has several absorption bands from the UV to the visible region. The band at $\lambda_{max} = 343$ nm in *n*-dodecane is mainly solvent sensitive. Table 1 and Figures 1 and 2 show the variation of λ_{max} as a function of SDS concentration in aqueous solutions of SDS and SDS + 0.1 % mass fraction PEG at room temperature. For the SDS system, a blue shift of λ_{max} took place with the increase of the SDS concentration at the beginning because of the interaction between the chromophore of the probe and SDS, and a minimum value of λ_{max} at $m_{SDS} = 8.5$ mmol·kg^{-1} was observed, which corresponded to the critical micelle concentration (cmc) of the surfactant SDS. For SDS + 0.1 % mass fraction PEG aqueous solutions, when the concentration of SDS was below the cac of the surfactant, a blue shift of λ_{max} also took place with the increase of SDS concentration due to the interaction between the chromophore of the probe and the SDS−PEG complex, and a minimum value of λ_{max} at $m_{SDS} = 4.1$ mmol·kg^{-1} was observed, which corresponded to the cac, where the micelles bound to the PEG chain began to form in solution. A red shift of λ_{max} took place when the SDS concentration was higher than the PSP, where the polymer chains were saturated by SDS micelles and the free micelles began to form in solution, because the number of free micelles in solution increased with surfactant concentration. The minimum value of λ_{max} at m_{SDS} = 17.6 mmol·kg^{-1} corresponded to the PSP in the SDS + 0.1 % mass fraction PEG aqueous solutions. The values of cac and

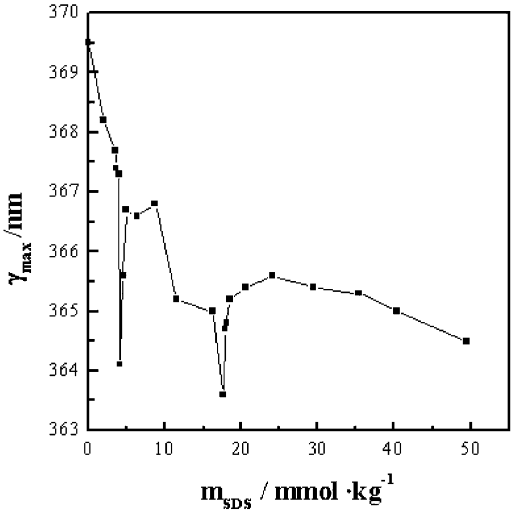

Figure 2. UV maximum absorption band γ_{max} of SDS + 0.1 % mass fraction PEG aqueous solutions at room temperature.

Table 1. UV Maximum Absorption Band (λ_{max}) for Aqueous Solutions of Sodium Dodecyl Sulfate (SDS) + Probe (DNPHTEMPO) and SDS + 0.1 % Mass Fraction Polyethylene Glycol (PEG) + DNPHTEMPO at Room Temperature

SDS + probe		SDS + 0.1 % mass fraction + probe	
m_{SDS} mmol·kg^{-1}	λ_{max} nm	m_{SDS} mmol·kg^{-1}	λ_{max} nm
0.0	370.6	0.0	369.5
3.0	370.4	2.0	368.2
6.0	370.2	3.5	367.7
7.0	369.7	3.6	367.4
7.6	369.3	4.0	367.3
8.0.	367.6	4.1	364.1
8.5	363.8	4.5	365.6
9.0	366.9	4.9	366.7
10.1	367.5	6.3	366.6
14.1	367.0	8.7	366.8
20.2	366.2	11.5	365.2
25.2	366.5	16.2	365.0
29.9	366.4	17.6	363.6
40.4	366.8	17.9	364.7
50.1	366.4	18.0	364.8
		18.5	365.2
		20.5	365.4
		24.1	365.6
		29.4	365.4
		35.4	365.3
		40.3	365.0
		49.5	364.5

Table 2. UV Maximum Absorption Band (λ_{max}) for Water + DNPHTEMPO Solution and *n*-Dodecane + DNPHTEMPO Solution at Room Temperature

solvent	band position nm		
water	225	370.5	
n-dodecane	227	343	409

Table 3. Viscosity/PEG Concentration (η/C_P) for SDS + PEG Solutions in different SDS concentrations from T = 298.15 K to 318.15 K

m_{SDS}	C_P	η/C_P		
$mmol \cdot mg^{-1}$	$g \cdot kg^{-1}$	mPa·s		
		298.15 K	308.15 K	318.15 K
0.0	0.05	1.874	1.511	1.245
0.0	0.1	0.997	0.799	0.657
0.0	0.3	0.411	0.323	0.261
0.0	0.5	0.285	0.227	0.182
4.0	0.05	1.869	1.510	1.254
4.0	0.1	0.988	0.789	0.657
4.0	0.3	0.416	0.327	0.264
4.0	0.5	0.288	0.226	0.182
8.0	0.05	2.068	1.667	1.352
8.0	0.1	1.102	0.923	0.725
8.0	0.3	0.434	0.349	0.283
8.0	0.5	0.298	0.235	0.188
16.0	0.05	2.146	1.734	1.437
16.0	0.1	1.266	1.003	0.812
16.0	0.3	0.549	0.442	0.355
16.0	0.5	0.3451	0.277	0.225
20.0	0.05	2.190	1.756	1.446
20.0	0.1	1.276	1.102	0.819
20.0	0.3	0.612	0.490	0.387
20.0	0.5	0.379	0.303	0.246
40.0	0.05	2.296	1.842	1.516
40.0	0.1	1.352	1.174	0.876
40.0	0.3	0.815	0.632	0.499
40.0	0.5	0.469	0.376	0.305

PSP of aqueous solutions of SDS and SDS + 0.1 % mass fraction PEG solutions were obtained from the UV spectrum shown in Figures 1 and 2 and agreed well with those obtained from the viscosity measurement. If the band positions in *n*-dodecane and water (Table 2)[14] are taken as values for hydrocarbon and aqueous environments, then the UV results indicated that the average location of 2,4-dinitrophenylhydrazone in the micelle consisted of an environment containing approximately 90 % water and 10 % hydrocarbon, respectively.

The viscosity of aqueous solutions of SDS, SDS + 0.05 % mass fraction PEG, SDS + 0.1 % mass fraction PEG, SDS + 0.3 % mass fraction PEG, and SDS + 0.5 % mass fraction PEG were measured at 298.15 K, 308.15 K, and 318.15 K.The values of η/C_P (viscosity/polymer concentration) vs polymer PEG concentration in different SDS concentrations at different temperatures were listed in Table 3 and shown in Figures 3−5. The η/C_P value decreased sharply with the increasing PEO concentration at all studied temperatures. The viscosity decreased with increasing temperature. At a certain temperature, the viscosity was first decreased and then increased, showing the minimum values which corresponded to the cmc of SDS or the cac of the SDS + PEG solutions. The polymer−micelle aggregate formed a more compact structure at the binding site, yielding a decrease in the viscosity. The values of cmc and cac of the studied solutions at 298.15 K were listed in Table 4. The η/C_P value increased with increasing SDS concentration, which means the adsorption of SDS on PEG molecule chains and leads to the increase of fluid resistance of the solutions, so the electroviscosity effect was increased.

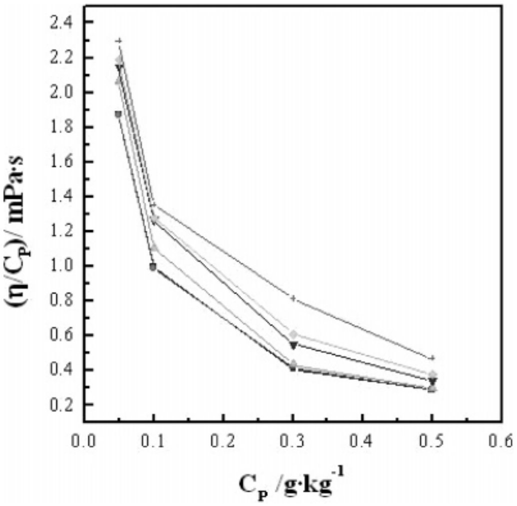

Figure 3. η/C_P of PEG + SDS aqueous solutions at 298 K containing m_{SDS}: ■, 0; ●, 4.0; ▲, 8.0; ▼, 16.0; ◆, 20.0; +, 40.0 $mmol \cdot kg^{-1}$.

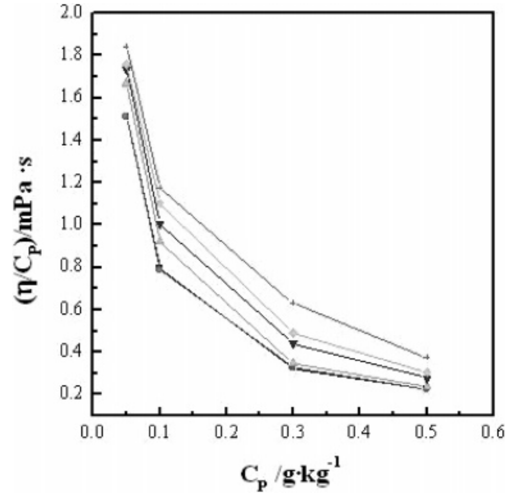

Figure 4. η/C_P of PEG + SDS aqueous solutions at 308 K containing m_{SDS}: ■, 0; ●, 4.0; ▲, 8.0; ▼, 16.0; ◆, 20.0; +, 40.0 $mmol \cdot kg^{-1}$.

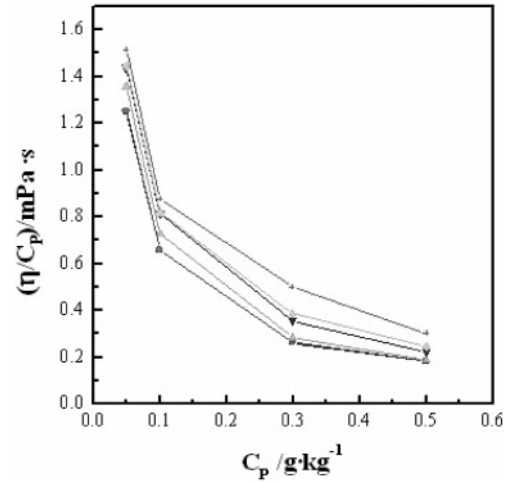

Figure 5. η/C_P PEG + SDS aqueous solutions at 318 K containing m_{SDS}: ■, 0; ●, 4.0; ▲, 8.0; ▼, 16.0; ◆, 20.0; +, 40.0 $mmol \cdot kg^{-1}$.

Unpaired electrons are not inherently present in the surfactant−polymer systems, so a spin probe DNPHTEMPO must be introduced to enable ESR studies. A spin probe was found to be located near the surface of the micelle. This molecule should provide a convenient probe for the surfactant of the micelle, because of its polar nature and nitrobenzene molecules

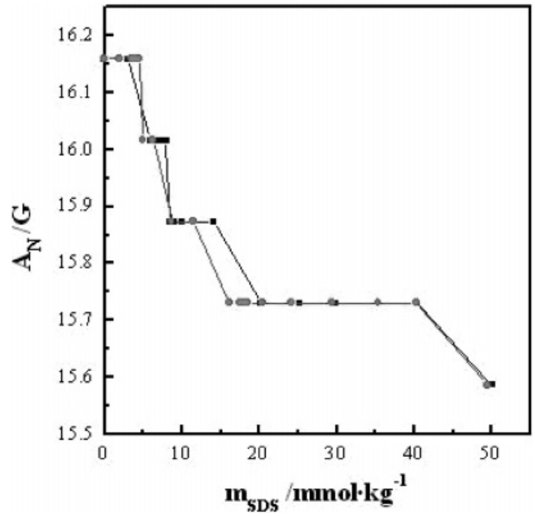

Figure 6. Hyperfine coupling constant A_N of SDS + DNHPTEMPO and SDS + 1 % mass fraction PEG + DNHPTEMPO aqueous solutions at room temperature: ■, SDS; ●, SDS + 0.1 % mass fraction PEG.

Table 4. Values of cac (mmol·kg^{-1}), PSP (mmol·kg^{-1}), and Free Energy Per Mole Surfactant (ΔG_{PS}°/kJ·mol^{-1}) for Different SDS + PEG Solutions at 298.15 K

solvent	CAC mmol·kg^{-1}	PSP mmol·kg^{-1}	ΔG_{PS}° kJ·mol^{-1}
SDS	8.5 (CMC)		
SDS + 0.1 % mass fraction PEG	4.0	17.5	−3.5
SDS+ 0.3 % mass fraction PEG	4.5	22.6	−2.9
SDS + 0.5 % mass fraction PEG	4.6	28.5	−2.8

adsorb at the surface of the micelle. The spin probe used in this study is 2,4-dinitrophenylhydrazone of 2,2,6,6-tetramethyl-4-piperidind-1-oxyl (DNPHTEMPO). By analysis of ESR spectra, the rotational correlation time (τ_C) and nitrogen hyperfine coupling constant (A_N) can be obtained.

Figure 6 showed the hyperfine coupling constant A_N as a function of the surfactant SDS concentration in aqueous solutions of SDS and SDS + 0.1 % mass fraction PEG, respectively. A more polar environment produced large values of A_N due to greater electron density at nitrogen. Below the cmc and cac of SDS, the A_N values of DNPHTEMPO were all 16.16 G and were essentially invariant with and without polymer, which means that the micropolarities of the probe microenvironments did not change in this concentration range. Above the cmc or cac, the values of A_N decreased with increasing SDS concentration. Obviously, for all the studied systems, A_N values are lower for the spin probes in the micelle and polymer−micelle aggregate than in bulk water, which reflected the reducing micropolarity at the binding sites of the probes in the micelle and the polymer−micelle aggregate. The spin probes were found to be located near the surface of the micelle. If the A_N values in *n*-dodecane and water are taken as values for hydrocarbon and aqueous environment, then ESR coupling constants suggested that the environment of the nitroxide group was consisted of ∼55 % water and ∼45 % hydrocarbon according to the calculation method of ref 12. The nitroxide group is oriented toward the center of the micelle, probably positioned at about the 3−6 carbon, penetrating a small distance into the hydrocarbon core of the micelle.

The effective rotational correction times can be calculated from the following equation[15−16]

$$\tau_C = 6.6 \times 10^{-10} W_0[(h_0/h_{-1})^{1/2} + (h_0/h_{+1})^{1/2} - 2] \quad (1)$$

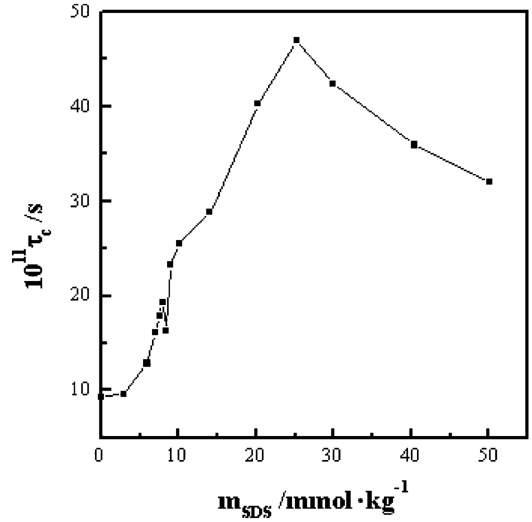

Figure 7. Rotational correlation time τ_C of SDS + DNPHTEMPO aqueous solutions at room temperature.

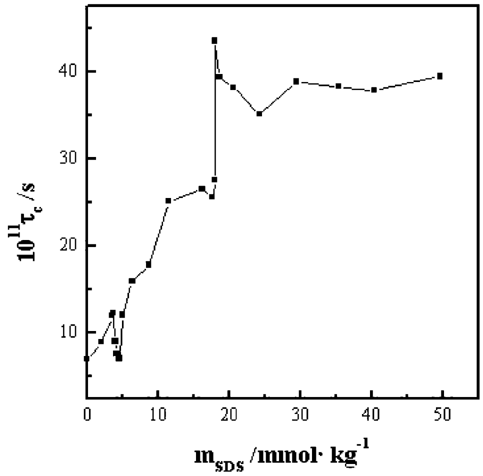

Figure 8. Rotational correlation time τ_C of SDS + 0.1 % mass fraction PEG + DNPHTEMPO aqueous solutions at room temperature.

where W_0 represents the peak-to-peak line width of the ESR mid-field line (in gauss) and h_0, h_{-1}, and h_{+1} are the peak-to-peak heights of the mid-, low-, and high-field lines, respectively. The constant 6.6 × 10^{-10} has been calculated for di-*tert*-butyl nitroxide (DTBN),[15] but to a good approximation, it can be used for other nitroxide radicals as well.

The rotational motion is usually described by rotational correction time, which may be regarded as the time needed for a molecule to rotate for an angle of π and can be correlated with the microviscosity of the probe by the following relation

$$\tau_C = 4\pi\eta a^3/3kT \quad (2)$$

where a is the hydrodynamic radius of the probe, η is the viscosity, and k and T represent the Boltzmann constant and the temperature, respectively.

Figures 7 and 8 showed the variation of rotational correlation time (τ_C) (as a function of the SDS concentration in aqueous solutions of SDS and SDS + 0.1 % mass fraction PEG, respectively. In each system, there was a pronounced decrease in τ_C at the onset of the micelle or aggregate formation, which corresponded to the cmc or cac value of SDS solution and SDS + PEG solution, respectively.

In the absence of PEG, the τ_C value of DNPHTEMPO in aqueous solutions of SDS increased first, then decreased, and further increased, the second starting point (8.45 mmol·kg^{-1}) of increase of τ_C, which corresponded to the CMC of SDS. The increase of τ_C was indicative of the slower molecular tumbling of the probes in the micelle than in water. On the other hand, in aqueous solutions of SDS + 0.1 % mass fraction PEG, the τ_C values start to increase, respectively, above 4.5 mmol·kg^{-1}, which was smaller than the cmc value of SDS and corresponds to the cac values of SDS in the presence of PEG. The cmc and cac values were in agreement with our viscosity measurement.

In the absence of PEG, for the SDS concentration below the cmc, the τ_C showed no significant variation. It increased slowly, and the ESR probe experienced low rotational friction just like in water. When the SDS concentration reached the cmc, the τ_C value began to increase dramatically, which was attributed to the motional restriction of the probe within the micelle. At about 25.2 mmol·kg^{-1}, the τ_C value did not increase anymore. Oakes[14] reported that the spin probe DNPHTEMPO solubilized in the micelles was located at the micelle−water interface. The nitroxide group of DNPHTEMPO was in contact with water and formed a strong hydrogen bond with water. The hydrophobic cycle was oriented toward the hydrocarbon core of the micelle. Therefore, the τ_C order indicated that the microviscosity at the micelle−water interface increased in the same order. The results confirmed that the increase in the viscosity was produced by the gradual neutralization of the micelle surface.

In the aqueous solutions of SDS containing PEG, below the cac of SDS, τ_C values showed no obvious difference with that in the absence of PEG. This indicated that PEG interacted with SDS monomers very weakly below the cac. Above the cac value, SDS aggregated on the PEG chain and τ_C began to increase rapidly. Then, with the increase of SDS concentration, a marked increase in τ_C was found, which was readily attributed to the motional restriction of the probe within the micelle. At about 17.9 mmol·kg^{-1}, the value did not increase anymore, which corresponded to the polymer saturation point (PSP), where the regular free micelles started to form. The τ_C value in the PEG−SDS solution was greater than those in the unperturbed micelles of SDS. The result suggested that the headgroup of SDS adsorbed on PEG was more tightly packed than that in SDS micelle. This implied that the microviscosity of the aggregate−polymer interface was greater than that of the regular micelle−water interface of SDS.

The interaction between SDS and PEG was mainly electrostatic interaction and hydrophobic interaction. Cabane[3] concluded from NMR that that is "an electrostatic interaction of PEG with the polar groups (of SDS)". The strength of hydrophobic interaction between SDS and PEG was the same for the same hydrophobic alkyl chain, thus the difference stemmed from electrostatic interaction.

Interaction Strength between the Surfactant and the Polymer. The free energy of micellization ΔG_{mic} in the absence of polymer and the free energy of aggregation ΔG_{agg} in the presence of polymer can be calculated using the following equations[17]

$$\Delta G_{\text{mic}} = (1 + K)RT \ln \text{cmc} \tag{3}$$

$$\Delta G_{\text{agg}} = (1 + K)RT \ln \text{cac} \tag{4}$$

where K is the effective micellar charge fraction; for SDS, K was found to be 0.85.[17] The free energy per mole of surfactant for the reaction can be derived as

$$\Delta G_{\text{ps}} = \Delta G_{\text{agg}} - \Delta G_{\text{mic}} = (1 + K)\ RT \ln(\text{CAC/CMC}) \tag{5}$$

This quantity is a convenient measure of the interaction strength between the surfactant and the polymer. The values of cmc and cac were obtained by UV spectrum and viscosity in SDS, SDS + 0.1 % mass fraction PEG, SDS + 0.3 % mass fraction PEG, and SDS + 0.5 % mass fraction PEG solutions at room temperature, and the calculated ΔG_{ps} values according to eq 5 were listed in Table 4. The cmc value was obtained by the UV spectrum, and the viscosity agreed well with that obtained by ESR and vapor pressure and surface tension in refs 18 and 19. We can see that PEG concentration had little effect on the cac of SDS−PEG solution, so it has little effect on the interaction strength of the SDS + PEG system.

Conclusion

The interaction between SDS and PEG has been obtained by investigating the morphology and property sensed by the sufficiently hydrophobic molecule as a function of surfactant concentration by ESR, UV spectrum, and viscosity measurement. The main results can be summarized as follows: (1) the microviscosity at the micelle surface increased in the same order of τ_C, which was produced by the gradual neutralization of the micelle interface. (2) The micropolarity decreased with increasing SDS concentration. (3) The headgroup of SDS adsorbed on PEG is more tightly packed than those unperturbed micelles, which suggested that the microviscosity of the aggregate−polymer interface was smaller than that of the unperturbed micelles. (4) The nitroxide group of DNPHTEMPO consisted of ∼55 % water and ∼45 % hydrocarbon. (5) The average location of 2,4-dinitrophenylhydrazone in the micelle consisted of an environment containing approximately 90 % water and 10 % hydrocarbon. (6) The electroviscosity increased with increasing SDS concentration. (7) The PEG concentration had little effect on the SDS−PEG interaction strength.

Literature Cited

(1) Goddard, E. D. In *Interactions of Surfactants with Polymers and Proteins*; CRC Press: Boca Raton, FL, 1993.

(2) Goddard, E. D. Polymer−surfactant interaction part II. Polymer and surfactant of opposite charge. *Colloids Surf.* **1986**, *19*, 301−329.

(3) Cabane, B. Structure of some polymer-detergent aggregates in water. *J. Phys. Chem.* **1977**, *81*, 1639−1645.

(4) Fishman, M. L.; Elrich, F. R. Interactions of aqueous poly(*N*-vinylpyrrolidone) with sodium dodecyl sulfate. II. Correlation of electric conductance and viscosity measurements with equilibrium dialysis measurements. *J. Phys. Chem.* **1975**, *79*, 2740−2744.

(5) Zana, R.; Lianos, P.; Lang, J. Fluorescence probe studies of the interactions between poly(oxyethylene) and surfactant micelles and microemulsion droplets in aqueous solutions. *J. Phys. Chem.* **1985**, *89*, 41−44.

(6) Thomas, J. K. Radiation-induced reactions in organized assemblies. *Chem. Rev.* **1980**, *80*, 283−299.

(7) Guo, W.; Sun, Y. W.; Luo, G. S.; Wang, Y. J. Interaction of PEG with ionic surfactant SDS to form template for mesoporous material. *Colloids Surf., A* **2005**, *252*, 71−77.

(8) Bernazzani, L.; Borsacchi, S.; Catalano, D.; et al. On the Interaction of Sodium Dodecyl Sulfate with Oligomers of Poly(ethylene glycol) in Aqueous Solution. *J. Phys. Chem. B* **2004**, *108*, 8960−8969.

(9) Middleton, H.; English, R. J.; Williams, P. A. Interaction of sodium dodecyl sulfate with methacrylate-PEG comb copolymers. *Langmuir* **2005**, *21*, 5174−5178.

(10) Romani, A. P.; Gehelen, M. H.; Itris, R. Surfactant−polymer aggregates formed by sodium dodecyl sulfate, Poly(*n*-vinyl-2-pyrrolidone), and Poly(ethylene glycol). *Langmuir* **2005**, *21*, 127−133.

(11) Witte, F. M.; Engberts, J. B. F. N. ESR spin probe study of micelle−polymer complexes. Poly(ethylene oxide)- and poly(propylene oxide)-complexed sodium dodecyl sulfate and cetyltrimethylammonium bromide micelles. *J. Org. Chem.* **1988**, *53*, 3085−3088.

(12) Hai, M. T.; Han, B. X.; Yan, H. K. Investigation on Interaction between Sodium Dodecyl Sulfate and Polyacrylamide by Electron Spin Resonance and Ultraviolet Spectrum. *J. Phys. Chem. B* **2001**, *105* (21), 4824−4826.

(13) Rozantzev, E. G.; Neiman, M. B. Organic radical reactions involving no free valence. *Tetrahedron* **1964**, *20*, 131−137.
(14) Oakes, J. Magnetic resonance studies in aqueous systems. Part 1. Solubilization of spin probes by micellar solution. *J. Chem. Soc., Faraday Trans. 2* **1972**, *68*, 1464−1471.
(15) Martinie, S.; Michon, J.; Rassat, A. Nitroxides. LXX. Electron spin resonance study of cyclodextrin inclusion compounds. *J. Am. Chem. Soc.* **1975**, *97*, 1818−1823.
(16) Wang, Y. L.; Lu, D.; Yan, H.; Thomas, R. K. An ESR Spin Probe Study of the Interaction between Poly(ethylene oxide) and Dodecyl Sulfate Surfactants with Different Monovalent Metal Counterions. *J. Phys. Chem. B* **1997**, *101* (20), 3953−3956.
(17) Lu, J. R.; Marrocco, A.; Su, T. J.; et al. Adsorption of Dodecyl Sulfate Surfactants with Monovalent Metal Counterions at the Air−Water Interface Studied by Neutron Reflection and Surface Tension. *J. Colloid Interface Sci.* **1993**, *158*, 303−316.
(18) Hai, M. T.; Han, B. X.; Yan, H. K.; Han, Q. Vapor Pressure of Aqueous Solutions of Polyacrylamide + Sodium Dodecyl Sulfate with and without NaOH. *J. Chem. Eng. Data* **1998**, *43* (6), 1056−1058.
(19) Hai, M. T.; Han, B. X. The solublization of *n*-pentane gas in Sodium Dodecyl Sulfate-poly(ethylene glycol) solutions with and without electrolyte. *J. Colloid Interface Sci.* **2003**, *267*, 173−177.

Received for review February 15, 2006. Accepted June 9, 2006. The authors are grateful to the National Natural Science Foundation of China (No. 29725308) for financial support.

JE060067N