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An ESR Spin Probe Study of the Interaction between Poly(ethylene oxide) and Dodecyl Sulfate Surfactants with Different Monovalent Metal Counterions

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Received: November 8, 1996; In Final Form: March 10, 1997

The interaction of lithium dodecyl sulfate (LiDS), sodium dodecyl sulfate (SDS), and cesium dodecyl sulfate (CsDS) with the water-soluble polymer poly(ethylene oxide) (PEO) has been studied in aqueous solutions by the electron spin resonance (ESR) technique using 2,2,6,6-tetramethylpiperidine-*N*-oxide (TEMPO) as a spin probe. The rotational correlation time of TEMPO has been obtained and there are substantial differences in τ_c among LiDS, SDS, and CsDS with and without PEO. The results show that the microenvironment of the spin probe in the polymer−surfactant aqueous solutions depends strongly on the hydrated radius of the counterion. The headgroups of LiDS and SDS adsorbed on PEO are more tightly packed than those of the unperturbed micelles, which leads to a much more compact structure of the polymer−micelle complex. The headgroup packing of CsDS is less influenced by PEO.

Introduction

Polymer−surfactant systems have widespread applications in a variety of fields such as medicine, detergency, mineral processing, and enhanced oil recovery.[1−3] Understanding of such systems is also important in studying many biological processes and systems, including biomembranes, vesicles, and lipid−protein interactions.[4,5] As a result, research on the interaction between surfactant and polymer has increased rapidly in recent years.[6−14] There have been several important reviews[15−20] which made some significant progress toward a further recognition of polymer−surfactant interaction.

The polymer−surfactant interaction results from a relatively weak dipolar interaction and is governed by a subtle balance of hydrophilic, hydrophobic, and ionic interactions. It is not surprising, then, that aqueous solutions containing both surfactants and polymers exhibit complex interaction patterns. Despite the enormous number of articles devoted to the polymer−surfactant interactions, little is known about the details of the interaction mechanism. Chemists are still puzzled by the relationship between the chemical structure of surfactant and polymer and their propensity for mutual interaction, and also puzzled by the dominant driving force for the interaction. The structure and morphology of the polymer−surfactant complexes as well as the nature of the interaction involved in the complexation have not yet been well established.

The most investigated systems are the aqueous solutions of nonionic water-soluble polymers and anionic surfactants. The properties of ionic surfactants are affected by their counterions because the substitution of one counterion by another alters the interaction between counterion and surfactant.[21] It is obvious that the counterion of ionic surfactant is one of the main factors governing the interaction between polymers and ionic surfactants. However, few systematic studies of this effect have appeared in the literature[22−24] and most of them paid much attention to the electrolytes in the interaction.[25,26] The effect of electrolytes added to the polymer−surfactant systems is obviously unequal to that of surfactant counterion itself, because

the addition of electrolytes will increase the ionic strength of the systems (to be exact, this is the salt effect) and not only the counterion effect. Treiner and co-workers have investigated the interaction of copper dodecyl sulfate[22] or cadmium dodecyl sulfate[23] with poly(vinylpyrrolidone) (PVP) or poly(ethylene oxide) (PEO) using essentially ion-selective electrodes. The interactions of PVP with sodium, copper, nickel, and cadmium dodecyl sulfates have also been studied by a calorimetric technique. The results indicated that the extent of polymer coverage by ionic surfactant depends upon the nature of the counterion. Dubin et al.[26] reported the effect of various salts (NaCl, LiCl, NH$_4$Cl) on the interaction of PEO with dodecyl sulfate micelles and confirmed that the cations of the salts play a direct role in the stabilization of the complex formed by polymer and surfactant.

In our previous work,[27] the interactions between poly(ethylene oxide) and dodecyl sulfate surfactants with different monovalent metal counterions (MDS, M = Li, Na, Cs) have been studied by flow microcalorimetry. It can be concluded that the interaction strength of PEO with MDS depends strongly on the size of the hydrated radius of the counterion. However, we can only obtain the macroscopic information from calorimetry; the effect of counterion on the morphology of the polymer−surfactant complexes and the details of the interaction mechanism cannot be obtained.

Electron spin resonance (ESR) has been widely applied to investigate the microenvironmental properties and dynamics of surfactant micelles using persistent nitroxide spin probes[28−33] for several decades, but this technique has been rarely used for studying polymer−surfactant interaction. Recently, some important studies about the microenvironment of nitroxide spin probes in micelles with polymer have been reported.[34−40] The ESR spin probe technique has several advantages. The sensitivity and selectivity of the spin probe to changes in its microenvironment provide the possibility to detect local differences of the polymer−surfactant systems. The technique with a high time resolution of better than a few nanoseconds can give some information on the rapid fluctuation of aggregates with the nature of the surfactant and with the properties of its microenvironment.
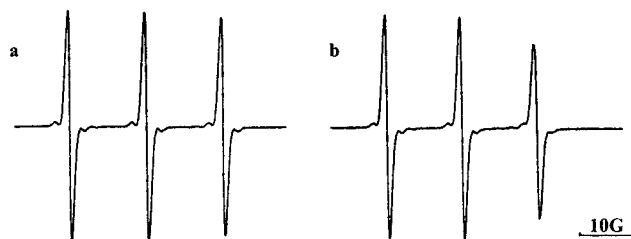

Figure 1. Representative ESR spectra of TEMPO in LiDS−PEO systems containing 0.1 wt % PEO at 25 °C: (a) 2.256 mmol kg⁻¹ LiDS (below cac); (b) 20.261 mmol kg⁻¹ LiDS (above cac).

The present paper reports an ESR spin probe study of the nitroxide radical 2,2,6,6-tetramethylpiperidine-*N*-oxide (TEMPO) in MDS solutions with and without water-soluble polymer PEO. The main objective is to make clear the counterion effect on the solution state of the polymer−surfactant mixtures and on the morphology of the polymer−surfactant complexes.

Experimental Section

Sodium dodecyl sulfate SDS (BRL, 99.5%) was used as received. Lithium and cesium dodecyl sulfate (LiDS, CsDS) were the same as described previously.[21] Poly(ethylene oxide) (PEO) from Aldrich was used without further purification. The average molecular weight of PEO is 100 000. The spin probe 2,2,6,6-tetramethylpiperidine-*N*-oxide (TEMPO) was purchased from Sigma Chemical Co. and was used as received. All solutions were prepared by weight in twice-distilled water. The concentrations of TEMPO and PEO were 1.5×10^{-4} mol kg⁻¹ and 0.1 wt %, respectively. The probe concentration was small enough to be considered as a negligible perturbation. The ESR samples were equilibrated for 2 days at 10 °C and then stabilized for 3 h at 25 °C before ESR spectroscopy.

The electron spin resonance spectra were recorded at 25 °C on a Brucker ESP300 spectrometer operating at X-band with 100 kHz magnetic field modulation at 1 K and 1.28 mW microwave power to avoid power saturation. All spectra were run using a flat cell. The average relative error for the rotational correlation time was about 10%.

Results and Discussion

The ESR results show that the ESR spectrum of TEMPO in water exhibits the usual three-line pattern ($A_N = 17.2$ G) and is closely identical with those in the LiDS, SDS, and CsDS solutions with and without PEO below cmc or below cac. Above the values of cmc and cac, TEMPO is solubilized in the micelles as evidenced by broadening of the high-field line. Representative ESR spectra in various types of surfactants with and without PEO at 25 °C are presented in Figure 1. Both the line width ratio and the height ratio are related to the surfactant concentrations.

The relative anisotropy observed in an ESR spectrum is directly related to the rotational mobility of the probe. The rotational motion is an important feature of molecular dynamics. The rotational motion is usually described by rotational correlation time τ_c, 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:

$$\tau_c = 4\pi\eta a^3/3kT$$

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. As an approximation, from the
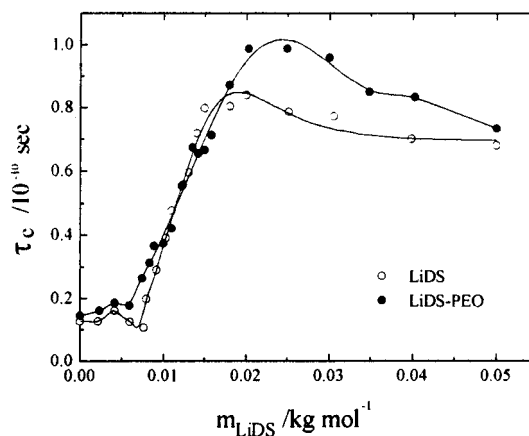

Figure 2. Variation of rotational correlation time, τ_c, of TEMPO in PEO−LiDS aqueous solutions.
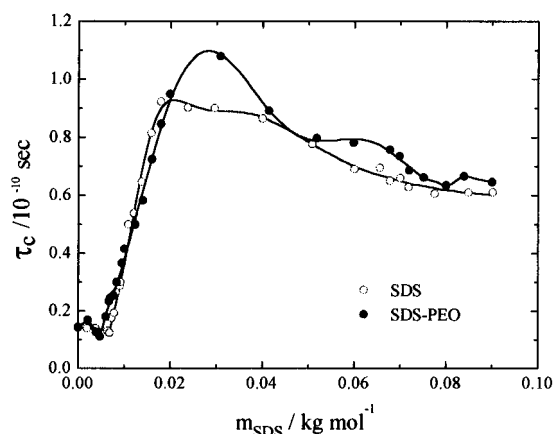

Figure 3. Variation of rotational correlation time, τ_c, of TEMPO in PEO−SDS aqueous solutions.

ESR spectra, the rotational correlation time can be calculated from the following equation [41,42]

$$\tau_c = 6.6 \times 10^{-10} W_0 \left[\left(\frac{h_0}{h_{-1}}\right)^{1/2} + \left(\frac{h_0}{h_{+1}}\right)^{1/2} - 2 \right]$$

where W_0 represents the peak-to-peak line width of the ESR mid-field line (in gauss) and h_{-1}, h_0, and h_{+1} are the peak-to-peak heights of the low-, mid-, and high-field lines, respectively. The constant 6.6×10^{-10} has been calculated for di-*tert*-butyl nitroxide,[43,44] but, to a good approximation, it can be used for other nitroxide radicals as well.

Figures 2−4 show the variation of rotational correlation time as a function of the surfactant concentration in the LiDS−PEO, SDS−PEO, and CsDS−PEO systems, respectively. In every system, there is a pronounced increase in τ_c at the onset of micelle or aggregate formation. In the absence of PEO, τ_c of TEMPO in aqueous solutions of LiDS, SDS, and CsDS increase, respectively, above 8.1 ± 0.3, 6.7 ± 0.3, and 5.6 ± 0.3 mmol kg⁻¹, which correspond to the cmc values of LiDS, SDS, and CsDS. In other words, the starting points of increase in τ_c correspond to the cmc values of surfactants. The increase of τ_c is indicative of slower molecular tumbling of the probes in the micelle than in water. On the other hand, in aqueous solutions of MDS containing PEO (0.1 wt %), the τ_c values start to increase, respectively, above 5.7 ± 0.3, 4.6 ± 0.3, and 3.5 ± 0.3 mmol kg⁻¹, which are all smaller than the cmc values and correspond to the cac values of surfactants in the presence of PEO. The values of cmc and cac decrease in the same order, LiDS > SDS > CsDS. The cmc values of LiDS and CsDS are
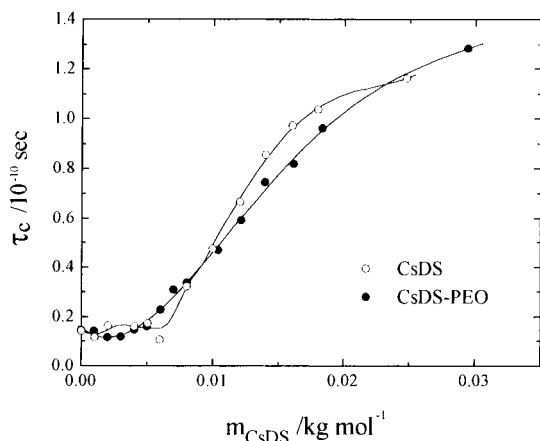
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Figure 4. Variation of rotational correlation time, τ_c, of TEMPO in PEO−CsDS aqueous solutions.
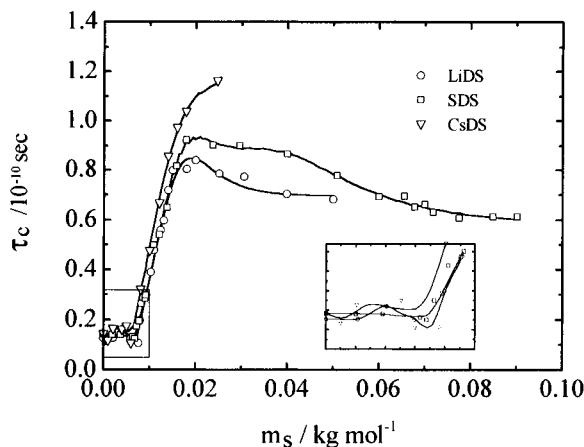

Figure 5. Variation of rotational correlation time, τ_c, of TEMPO in surfactant aqueous solutions.
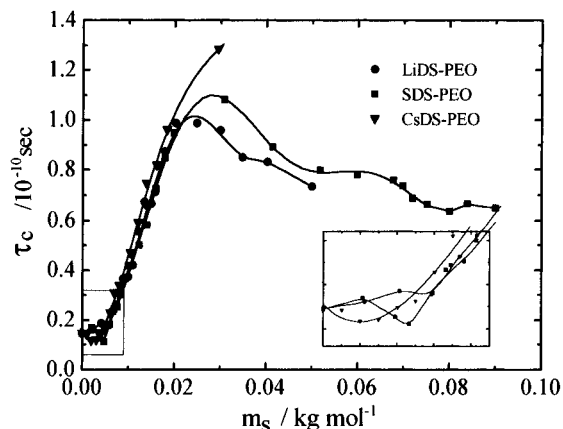

Figure 6. Variation of rotational correlation time, τ_c, of TEMPO in PEO−surfactant aqueous solutions.

in agreement with those reported by Mukerjee.[45,46] Although the cmc of SDS is not identical to the literature values, the values from several τ_c curves are reasonably close and the cmc of SDS is identical to that in ref 47.

Figures 5 and 6 compare the curves of the rotational correlation times against the surfactant concentrations in three different surfactant solutions without and with PEO, respectively. In the absence of PEO (see Figure 5), for the surfactant concentrations m_s below cmc, τ_c shows no significant variation and the spin probe experiences low rotational friction just like in water. When the surfactant concentrations reach the cmc, τ_c begins to increase. Then, with the increase of surfactant

concentration, a marked increase in τ_c is found, about $10-130$ ps, which is readily attributed to the motional restriction of the probe within the micelle.[48] At about 19 mmol kg^{-1} of LiDS, 21 mmol kg^{-1} of SDS, and 25 mmol kg^{-1} of CsDS, the τ_c values do not increase any more, where the order of τ_c values is as follows: LiDS < SDS < CsDS. Ramachandran et al.[49] reported that most of the TEMPO solubilized in the micelles is located at the micelle−water interface. So the microviscosity at the micelle−water interface increases in the same order, which is strongly dependent on the nature of the surfactant counterion. The results confirm the increase in the viscosity is produced by the gradual neutralization of the micellar surface.[50] The neutralization is caused by the binding of counterions to the micellar surface and the process depends on the hydrated radius of the counterion. Li$^+$ has the largest hydrated radius and its center of charge is further away from the surface of the negatively charged heads, and therefore, it binds least strongly with the anionic surfactant ions and screens the charge of the headgroups least effectively. Cs$^+$ has the smallest hydrated radius and interacts strongly with the oppositely charged headgroups. The different binding degree for different counterions to micellar surface produces an effect on the cmc as well as on the microviscosity at the micelle−water interface.

In aqueous solutions of MDS containing PEO (Figure 6), below the cac values, τ_c values show no obvious difference with that in the absence of PEO. This indicates that PEO interacts with surfactant monomers very weakly below the cac. Above the cac values, MDS aggregate on the PEO and τ_c begins to increase rapidly. When the concentrations of LiDS, SDS, and CsDS are about 24, 28, and 30 mmol kg^{-1}, respectively, τ_c stops increasing almost. These concentrations are called saturation concentrations, where the regular free micelles start to form. There is an obvious difference among three surfactants with PEO on the magnitude in τ_c. The τ_c values increase in the order of LiDS, SDS, and CsDS, i.e., the rotation of the spin probe changes to be slower in the same order. Exceeding the saturation concentration, the τ_c values decrease gradually with the increase of the surfactant concentrations, apart from the CsDS−PEO system, because of the insufficient data for the limit of the CsDS solubility in water at 25 °C. On the curve of the SDS−PEO system (Figure 3), there is an unusual change at about 68 mmol kg^{-1}, which may be produced by the conformational transition of the micelle.[51]

The τ_c values in the LiDS−PEO and SDS−PEO complexes are greater than those in the unperturbed micelles of LiDS and SDS. These results suggest that the headgroups of LiDS and SDS adsorbed on PEO are more tightly packed than those in the LiDS and SDS micelles. This implies that the microviscosity of the aggregate−polymer interface is greater than that of regular micelle−water interface of LiDS and SDS. For the CsDS−PEO system, the difference between the τ_c curves of the perturbed micelle and the unperturbed micelle is not significant. This point shows that the headgroup packings of CsDS are less influenced by PEO. The packing degree of the headgroups of the micelle-like aggregates on the polymer is probably decided by the strength of the interaction between polymer and surfactant and by the structure of polymer and surfactant. Then, from the different extent of the surfactant morphologies being influenced by PEO, it may be concluded that the interaction between MDS and PEO decrease in the order LiDS > SDS > CsDS. The results are identical with that of our previous work.[27]

The large differences between different unperturbed micelles and different micelle−polymer complexes are also introduced by the hydrated radius of the counterion. The interactions

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existing in polymer−surfactant systems are mainly electrostatic interaction and hydrophobic interaction. Schwuger suggested that a positive charge on PEO could arise from partial protonation of ether oxygens.[52] Cabane concluded from NMR measurements that there is "an electrostatic interaction of PEO with the polar groups(of SDS)".[53] The strength of hydrophobic interaction between MDS and PEO is the same for the same hydrophobic alkyl chain; thus the difference stems from electrostatic interaction. The hydrated radius of the counterions decreases with the increase of the ionic radius. The decrease in hydrated radius results in a strengthening in the counterion binding to the ionic headgroup of the micelles, which stabilizes the micelle itself but reduces the electrical potential of the micellar surface. Therefore, the electrostatic attraction between the ethylene oxide group of PEO and the ionic headgroup of MDS is weakened. The electrostatic interaction of MDS with PEO decreases in the order of LiDS > SDS > CsDS, which results that the effect of PEO on the compactness of the PEO−MDS complex decreases in the same order.

Conclusion

ESR spin probe spectroscopy is a useful tool for structural and dynamic investigation. τ_c is very sensitive to the molecular microenvironment of the spin probe, and hence it can be used to characterize local composition changes as well as the onset of the aggregate formation for the surfactant−polymer system. The main results of this study can be summarized as follows: (1) The viscosity at the micellar surface increases in the order of LiDS < SDS < CsDS, which is produced by the gradual neutralization of the micellar surface and depends on the size of the hydrated radius of the counterion. (2) The headgroups of LiDS and SDS adsorbed on PEO are more tightly packed than those of unperturbed micelles, which suggests that the microviscosity of the aggregate−polymer interface is greater than that of the unperturbed micelles; the headgroup packing of CsDS is less influenced by PEO.

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