An ESR Spin Probe Study of Micelle–Polymer Complexes. Poly(ethylene oxide)- and Poly(propylene oxide)-Complexed Sodium Dodecyl Sulfate and Cetyltrimethylammonium Bromide Micelles

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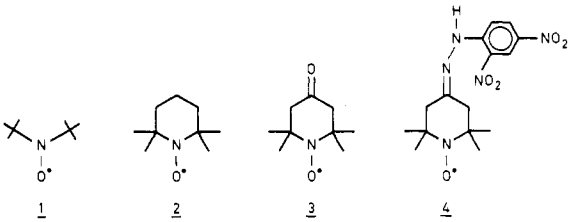
Four persistent nitroxides of varying hydrophobicity have been employed in an ESR spin probe study of polymer-complexed micelles formed by complexation of sodium dodecyl sulfate (SDS) micelles with poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) as well as cetyltrimethylammonium bromide (CTAB) micelles with PPO. Binding of the spin probes to the surfactant aggregates is revealed by a substantial increase of the apparent rotational correlation time (τ_c) and a decrease of the nitrogen hyperfine splitting constant (A_N) relative to the corresponding parameters for the free radical in bulk water. It is found that, relative to the unperturbed micelles, the spin probes experience a more polar microenvironment and rotate faster at the binding sites of micelle–polymer complexes. Presumably the head groups of the micelles sorbed on the polymer are less tightly packed, leading to a more "open" structure of the polymer-complexed micelle. The more hydrophobic PPO binds more strongly to the micelles than PEO and has a larger effect on the structure of the micellar surface.

Surfactants may bind cooperatively to nonionic, water-soluble polymers to form micelle–polymer complexes.[1-4] These interactions are largely confined to anionic surfactants, but cationic and nonionic surfactants occasionally also form polymer-complexed micelles. Apart from being industrially important, there is much interest in the morphology of the micelle–polymer complexes and in the nature of the interactions involved in the complexation process.[5-11]

Although microenvironmental properties and dynamics of surfactant aggregates have been studied extensively by using persistent nitroxide spin labels and spin probes,[12-16] these ESR techniques have been rarely applied for investigating micelle–polymer complexes.[17] In our preliminary report[18] we showed that effective rotational correlation times (τ_c) for di-*tert*-butyl nitroxide (DTBN) in polymer-complexed SDS micelles were indicative of decreased cmc's and diminished head-group packing in the micelle–polymer complexes relative to unperturbed micelles. In the present study, we report the use of the radicals DTBN (1), 2,2,6,6-tetramethylpiperidine-1-oxyl (Tempo, 2), 2,2,6,6-tetramethyl-4-piperidone-1-oxyl (Tempone, 3), and the 2,4-dinitrophenylhydrazone of 3 (Tempone-DNPH, 4) as molecular spin probes in aqueous solutions in the presence of SDS and CTAB micelles com-



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plexed to poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO). In the analysis of the ESR spectra, emphasis will be placed on the nitrogen hyperfine splitting constant (A_N) as a useful micropolarity reporter and on line widths as parameters for the dynamical behavior of the spin probes at the micellar binding sites.

Results and Discussion

The line widths and line shapes of ESR spin probes in aqueous surfactant solutions are determined by several factors.[15] The most important are the (effective) rotational correlation time of the spin probe, unresolved proton hyperfine splittings, intermolecular spin–spin interactions, and the rotational correlation time of the aggregate. The last two factors constitute no problems in the present study in view of the low concentrations of the spin probes ($<5 \times 10^{-4}$ M) and the much faster rotation of the spin probes (τ_c ca. 10^{-11}–10^{-10} s) relative to that of the SDS or CTAB micelle in water (ca. 10^{-8} s, calculated from Stokes' law[12a]). The spectra considered in this study are indicative for fast isotropic motion. Therefore, effective rotational correlation times can be calculated, to a good approximation, from the equation[19-21]

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

where W_0 is 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 DTBN[21,22] but, to a good approximation, can be used

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Table I. Nitrogen Hyperfine Splitting Constants and Effective Rotational Correlation Times for 1–4 in Water and SDS Solutions

	A_N, G			$\tau_c \times 10^{11}$,[e] s	
probe[a]	H_2O	SDS[b]	ΔA_N,[c] G	H_2O	SDS[b]
1	17.16	16.84	0.32	1.7	19.0
1[d]	17.19	16.75	0.44	1.4	27.1
2	17.35	17.00	0.35	1.0	5.0
3	16.13	15.96	0.17	2.2	17.7
4	16.25	15.88	0.37	6.9	50.0

[a] Probe concentrations were 5×10^{-4} M except for 4 ($\sim 5 \times 10^{-6}$ M). [b] [SDS] = 70 mM. [c] Difference in A_N between water and the micellar pseudophase. [d] In the presence of 0.4 M NaBr. [e] τ_c values calculated by using eq 1.

for other nitroxide radicals as well. However, the contribution of unresolved proton hyperfine coupling to the line width is neglected (vide infra). A still more serious problem is associated with the situation that the spin probe exchanges between bulk water and the micellar pseudophase.[23] This results either in a splitting of the high-field line in the spectrum[24] or in an extra contribution to the line width, dependent on the exchange rate. In such cases no accurate value for τ_c can be obtained by using eq 1. This problem can be circumvented by employing a spin probe that is sufficiently hydrophobic to be incorporated to a large extent in the micellar pseudophase. Thus, it is important that the distribution of the spin probe between the two pseudophases can be measured. For aqueous solutions of phospholipids, Polnaszek et al.[25] and Wu and McConnell[26] have described methods to calculate this distribution, but these are not reliable for our system. As shown below, we have determined the distribution of the probe by using computer simulations. Values of τ_c were then calculated at only those surfactant concentrations where more than 80% of the probe molecules reside in the (polymer-complexed) micelle. In those cases no splitting of the ESR high-field line was observed.

Table I lists A_N and τ_c values for the spin probes 1–4 in water and at a relatively high concentration of SDS (ca. 9 × cmc). In pure water the ESR spectra show the usual three-line pattern. Above the cmc of SDS, the high-field line is broadened as a result of solubilization of the probe in the micelle. The increase of τ_c is indicative of slower molecular tumbling of the probes in the micelle than in water. Concomitantly, the A_N values are smaller as a result of a reduced micropolarity at the binding sites of the probes in the micelle. Two *distinct* high-field lines are observed only for spin probe 4. This is illustrated in Figure 1, which shows ESR spectra of 4 in aqueous solutions containing 0.5 g·dL^{-1} of PPO and varying concentrations of CTAB. Clearly, two superimposed spectra are observed, the broader signal of the micelle-solubilized spin probe increasing with increasing CTAB concentration. Further evidence for this interpretation was obtained from experiments using solutions of 4 in SDS micelles in the presence of 10^{-4} M of paramagnetic Mn^{2+} ions. The Mn^{2+} ions bind to the negatively charged head groups of SDS in the micelle and the ESR spectrum of the spin probe in the micellar pseudophase is broadened beyond detection.[13] Thus, the ESR spectrum of 4 in a solution containing 10 mM SDS (A_N = 16.13 G, $\tau_c = 46.4 \times 10^{-11}$ s) changes upon addition of Mn^{2+} into the normal water spectrum (A_N = 16.25 G, $\tau_c = 13.7 \times 10^{-11}$ s).

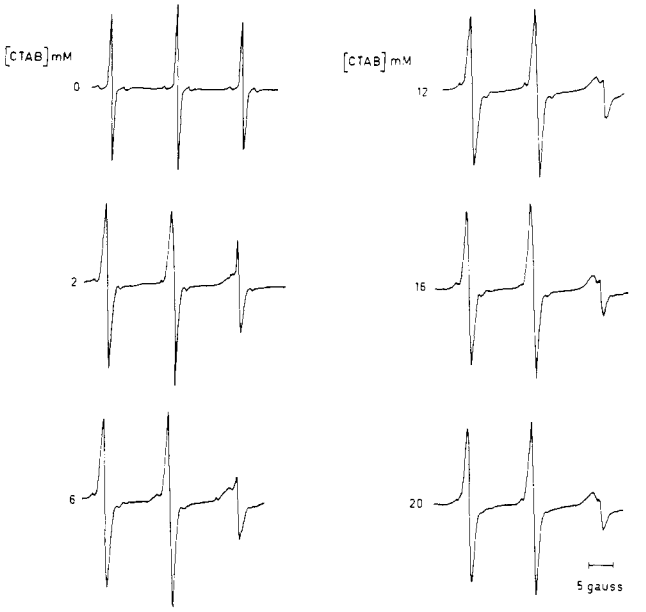

Figure 1. ESR spectra of Tempone-DNPH in aqueous solutions containing 0.5 g·dL^{-1} of PPO and varying concentrations of CTAB.

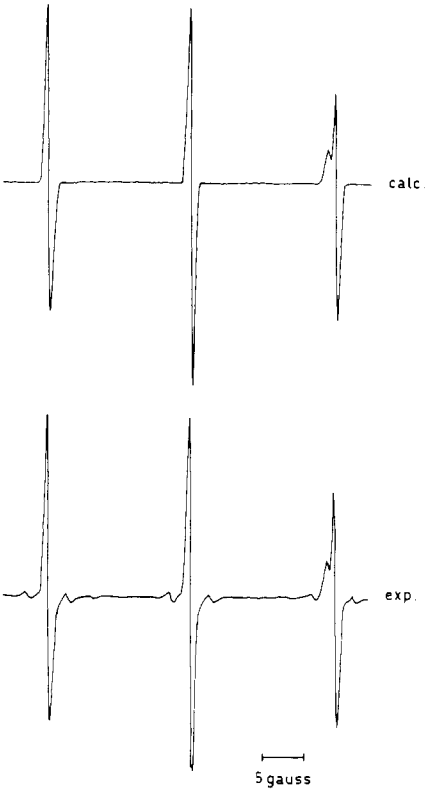

Figure 2. Fit of the experimental and simulated ESR spectrum of DTBN in water containing 20 mM SDS and 0.4 M NaBr.

In view of the large differences in counterion binding between unperturbed micelles and micelle–polymer complexes,[27] ESR spectra were also run in SDS solutions containing 0.4 M NaBr. In these cases, the spin probe 1 also exhibits a splitting of the high-field line in SDS solutions. The slow (on the ESR time scale) exchange of the probe between water and the micelle is presumably the result of the larger aggregation number and more compact

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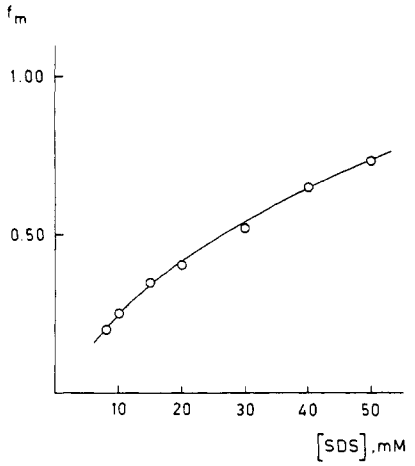

Figure 3. Fraction of spin probe DTBN bound to the micellar pseudophase (f_m) as a function of the SDS concentration.

Table II. Nitrogen Hyperfine Splitting Constants and Effective Rotational Correlation Times for Tempone-DNPH in Aqueous Solutions in the Presence of Micelles and Micelle–Polymer[a] Complexes

medium	[surfactant], mM	A_N, G	ΔA_N,[b] G	$\tau_c \times 10^{11}$,[e] s
H_2O	0.00	16.25		6.9
SDS	70.0[c]	15.88	0.37	50.0
SDS–PEO	40.0[c,d]	15.94	0.31	44.3
SDS–PPO	30.0[c,d]	16.00	0.25	39.6
CTAB	20.0[c]	15.75	0.50	160
CTAB–PPO	20.0[c]	16.06	0.19	120

[a] [Polymer] = 0.5 g·dL^{-1}; [Tempone-DNPH] = ~5 × 10^{-6} M. [b] Difference in A_N between water and the (polymer-complexed) micelle. [c] Complete binding of the spin probe to the micelles. [d] Polymer saturated with micelles. [e] τ_c values calculated by using eq 1.

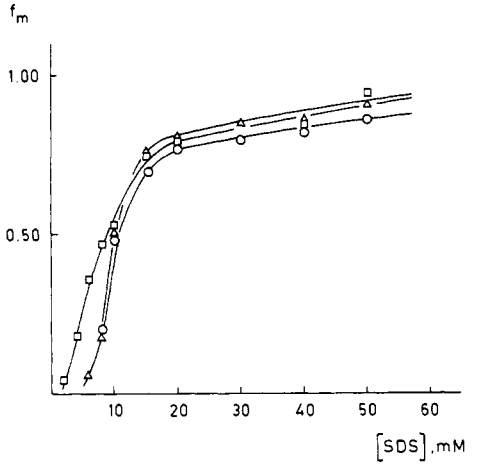

Figure 4. Fraction of spin probe Tempone-DNPH bound to the micellar pseudophase (f_m) as a function of the SDS concentration ((○) SDS; (△) SDS–PEO; (□) SDS–PPO; polymer concentration 0.5 g·dL^{-1}).

Table III. Calculated[a] Rotational Correlation Times for Tempone-DNPH in Aqueous Solutions in the Presence of SDS Micelles and Micelle–Polymer[b] Complexes

medium	[SDS], mM	$\tau_c \times 10^{11}$, s
H_2O	0.00	4.6 (6.9)
H_2O–PEO	0.00	3.9 (8.1)
H_2O–PPO	0.00	2.6 (9.5)
SDS	70.0	34.2 (50.0)
SDS–PEO	40.0[c]	31.6 (44.3)
SDS–PEO	70.0	33.9 (46.4)
SDS–PPO	30.0[c]	27.0 (39.6)
SDS–PPO	70.0	29.0 (43.5)

[a] See text. The τ_c values obtained by using eq 1 are given in parentheses. [b] [Polymer] = 0.5 g·dL^{-1}; [Tempone-DNPH] = ~5 × 10^{-6} M. [c] Polymer saturated with micelles.

packing of the surfactant molecules in the micelle in the presence of the electrolyte.[28,29]

As shown in Table I, both τ_c and ΔA_N are increased in the presence of added salt, indicative of binding of the probe to a more structured micellar aggregate with less polar binding sites. These NaBr-induced effects are depressed upon addition of the polymers,[27] and no splitting of the high-field line is observed for these solutions. The strongly decreased counterion binding in the presence of the polymers accounts for these observations.

The experimental ESR spectra could be reproduced by computer simulations (Figure 2). From simulated spectra of **1** in SDS solutions with added salt it was deduced that even at 50 mM SDS only 75% of the spin probe is solubilized in the micellar pseudophase (Figure 3). Similar simulations for **4** revealed much stronger binding (Figure 4), and 80% of the probe is bound to the aggregates at 20 mM SDS. Therefore spin probe **4** is preferable. Table II lists A_N and τ_c values for solutions of the micelles and polymer-complexed micelles. Interpretation of these data is greatly facilitated by the fact that the polymers alone exert only very small effects on τ_c (Table III). The most important observation is that for both SDS and CTAB, the τ_c values are smaller for the micelle–polymer complexes than for the unperturbed micelles. Thus the spin probe rotates faster in the polymer-complexed micelles. This is indicative of a more "open" structure of the aggregate. The τ_c values were also calculated by using an iterative computer program (see Experimental Section), taking into account unresolved long-range proton hyperfine interactions. As anticipated, these calculated τ_c values (Table III) are definitely smaller than the approximate values obtained by using eq 1, but the trends are similar. The calculated τ_c values at the saturation concentration of the polymers also point to more "open" polymer-complexed micelles although the difference between SDS and SDS–PEO is relatively small.

Generally A_N values are lower for the spin probe in the micelle than in bulk water, which reflects the reduced micropolarity at the micellar binding sites.[30] However, spin probe **4** must be located near the micellar surface since the A_N value is much higher than that expected for a hydrocarbon-like microenvironment (A_N = 14.30 G for **4** in *n*-dodecane).

The ΔA_N values (Table II) are clearly smaller for the polymer-complexed micelles than for unperturbed micelles, the effect being most pronounced for CTAB vs CTAB/PPO. One concludes that the micropolarity at the spin probe binding sites is higher for the micelle–polymer complexes, which is again consistent with a more "open" structure of these aggregates.[31] The lower τ_c and ΔA_N values for SDS–PPO as compared with SDS–PEO suggest

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(31) Alternatively, the smaller A_N value could be the result of an alteration in the local dipole environment of the spin probe caused by the (high) local polymer concentration at the micellar surface. However, this explanation is less likely since A_N values measured in PEO solutions at concentrations as high as 10 g·dL^{-1} vary only by 0.05 G.

a stronger perturbation of the SDS micelles by the more hydrophobic PPO. The additional stabilization of the micelles upon complexation to the polymers can be calculated from $\Delta\Delta G^{\ominus} = RT \ln (cmc_{pol}/cmc)$, in which cmc_{pol} and cmc are the critical micellar concentrations with and without polymer as measured previously.[27] The values of $\Delta\Delta G^{\ominus}$ for SDS–PEO (–1.0 kJ·mol^{-1}) and SDS–PPO (–1.8 kJ·mol^{-1}) demonstrate the stronger stabilization by PPO then by PEO and indicate the stronger binding of SDS micelles to the more hydrophobic polymer.

In a recent paper, Zana et al.[11] discussed the difference between the effect of 1-pentanol and PEO on SDS micelles. The added alcohol reduced the cmc and the aggregation number of SDS, just as the polymer does, but it was proposed that the alcohol is able to fill the space between the SDS chains and thus prevents water penetration into the micellar interior. The polymer, however, will be bound at the surface of the micelle and cannot penetrate more deeply into the micellar interior. Recently, however, Baglioni and Kevan[32] reported contradictory views. These authors suggested that the addition of 1-pentanol to SDS micelles leads to increased penetration of water molecules into the micellar interface region. However, we contend that intercalation of the polymer in the head-group region leads to a perturbation of the interfacial area in the sense that a more "open" micelle is formed with increased head-group hydration.

Apart from Nagarajan's model[5] for surfactant aggregation in the presence of polymers, which places emphasis on the area per surfactant molecule in the micellar interface shielded by the polymer, another approach has been proposed by Ruckenstein et al.[33] The latter model considers the change in interfacial tension between the micelle and water caused by interaction with the polymer. Both models provide a rationalization for the observation that surfactants with relatively large head groups bind polymers only weakly or not at all. Thus, SDS with a relatively small sulfate head group readily interacts with PEO whereas CTAB does not. We note that both models do not readily explain our finding that the micelles bind more strongly to PPO than to PEO. By contrast, it could be anticipated on the basis of the models that the more flexible PEO, having hydrophilic/lipophilic characteristics that are more compatible with the micellar surface, would show stronger polymer–micelle complexation. Therefore it seems that the higher hydrophobicity of PPO compared to that of PEO plays a major role in the complexation process. Finally we note that the effect of the relatively high electrolyte concentration in the Stern region of the micelle on the conformational distribution of the polymer may be a factor in micelle–polymer interactions in view of similar effects operating on vesicle–polymer complexation.[34]

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Conclusion

The main results of the present study can be summarized as follows: (a) the ESR spin probe technique can be employed to monitor the changes in the micellar aggregate upon interaction with a polymer. The use of a sufficiently hydrophobic spin probe is a prerequisite for the usefulness of the method; (b) the more hydrophobic PPO perturbs SDS (and CTAB) micelles more than PEO and induces a more "open" structure of the polymer-complexed micelle.

Experimental Section

Materials. SDS (BDH, specially pure) was used as received. The purity of this sample has been discussed previously.[27] CTAB (Merck) was purified as described by Duynstee and Grunwald.[35] PEO (Fluka, weight-average molecular weight 10000) was purified as described previously.[18] PPO (Janssen, weight-average molecular weight 1000) was used as received. In all experiments the polymer concentration was 0.5 g·dL^{-1}. DTBN was prepared from *tert*-butyl chloride by the method of Rozantsev and Sholle.[36] Tempo was purchased from Janssen. Tempone was synthesized by oxidation[36] of 2,2,6,6-tetramethyl-4-piperidone.[37] Tempone-DNPH was obtained from Tempone as described by Rozantsev and Neiman.[38]

ESR Measurements. The ESR spectra were measured at room temperature on a Varian E-4 spectrometer. The aqueous solutions were purged with nitrogen for 3 min to remove dissolved oxygen. The spin probe concentrations were 5×10^{-4} M, except for the hydrophobic spin probe **4** ($\sim 5 \times 10^{-6}$ M). ESR spectra were simulated by using standard computer programs.[39] The variable line width of the peaks in the ESR spectra was introduced in the computer program by using the expression $\Delta H_m = A + Bm + Cm^2$, where B and C are dependent on the correlation time τ_c. Spectra at intermediate surfactant concentrations were reproduced by a summation (in the appropriate ratio) of the simulated spectrum in water and the spectrum pertaining to 100% binding of the probe to the surfactant aggregate (70 mM SDS). This ratio is expressed in the fraction of the probe in the micelle (f_m; Figures 3 and 4). The τ_c values listed in Table III were calculated from the B values, determined by means of the simulations, according to the equation of Polnaszek et al.[25] The proton hyperfine coupling constants and the other parameters for this approach were taken from the literature.[40]

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Registry No. **1**, 2406-25-9; **2**, 2564-83-2; **3**, 2896-70-0; **4**, 13012-06-1; PEO, 25322-68-3; PPO, 25322-69-4; SDS, 151-21-3; CTAB, 57-09-0.

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