Mixed Micelles of SDS/$C_{12}E_6$ and DTAC/$C_{12}E_6$ Surfactants

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Abstract: Electron spin echo modulation (ESEM) of *x*-doxylstearic acid spin probes (*x*-DSA, *x* = 5, 7, 10, 12, and 16) in mixed micellar solutions of ionic and nonionic surfactants has been studied as a function of the doxyl position along the alkyl chain of the stearic acid spin probe and of the mixed micellar composition. The mixed micellar systems investigated were sodium dodecyl sulfate (SDS) or dodecyltrimethylammonium chloride (DTAC) with hexakis(ethylene glycol) monododecyl ether ($C_{12}E_6$), selectively deuterated along the poly(ethylene glycol) group ($C_{12}D_6$) or along the alkyl chain ($(CD)_{12}E_6$) in H_2O and D_2O. The average probe conformation and probe location in the pure surfactants and in the mixed micelles are reported as a function of the doxyl position, *x*. Modulation effects due to the interactions of the probe unpaired electron with deuterium in D_2O give direct evidence that the hydration is maximized for an equimolar mixture of SDS/$C_{12}E_6$ mixed micelles. It is also found that the polar head groups of SDS and DTAC surfactants are located in the ethylene oxide region of the $C_{12}E_6$ surfactant. A comparative analysis of the deuterium modulation depth, arising from deuteriums located in the alkyl chain or in the ethylene oxide groups of the nonionic surfactant, shows that SDS polar head groups are located at the surface of the mixed micelle, close to the second ethylene oxide group of $C_{12}E_6$, while DTAC polar head groups are located deeper inside the mixed micelle, at the 5th–6th ethylene oxide group of the nonionic surfactant. These results provide an explanation at the molecular level of the different thermodynamical behavior found for mixed micelles of anionic–nonionic and cationic–nonionic surfactants.

Introduction

Mixed micellar aggregates are composed of two of more different surfactants in equilibrium with the surfactant monomers. These systems are of theoretical interest and of considerable industrial importance since mixtures of surfactants often exhibit synergism in their physicochemical properties allowing particular applications.[1-9] Thermodynamical models for treating mixed micellization in ideal mixed micellar solutions of ionic or nonionic surfactants[1-5] have been developed for ideal and nonideal mixed micellar solutions of ionic and nonionic surfactants.[1-7,10-13] However, some properties of these systems are still unexplained. For example, mixed micellar systems composed of cationic–nonionic and anionic–nonionic surfactants show different properties.[3,7,10-18] In mixed micelles of ionic [sodium dodecyl sulfate (SDS) and dodecyltrimethylammonium chloride (DTAC)] and nonionic ethylene glycol alkyl ether surfactants (C_nE_m), the ethylene oxide groups of the nonionic surfactant do not contribute to the hydrophobic interactions in mixed micelle formation in the presence of a cationic surfactant, while in mixed micelles with an anionic surfactant the ethylene oxide groups impart a contribution to the hydrophobic interactions.[17] Another typical example is the different mean molar volumes of mixing in mixed micelles of anionic or cationic and ethylene oxide surfactants.[18] The current thermodynamic description fails to explain this behavior since the theory, based on a simple electrostatic model, predicts independence of the micellar properties on the sign of the micellar charge.

In previous studies, we showed that very detailed information at a molecular level about the micellar interface (water penetration, site of interaction of alcohol solubilized molecules and of urea molecules or crown ethers which can complex the counterions, distribution of toluene, butanol, and water in the interfacial film of sodium dodecyl sulfate of a five-component microemulsion, microviscosity, and polarity of the micellar interface) can be obtained by application of electron spin echo modulation (ESEM)[19-25] and electron spin resonance (ESR)[26-29] via nitroxide spin probes.

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In this study, we investigated the interface of mixed micelles of cationic–nonionic and anionic–nonionic surfactants as a function of the mixed micelle composition. The results are analyzed in terms of the deuterium modulation depth from ESEM, which is a direct measure of the strength of the electron–deuterium interaction.[30] We followed an approach similar to that of previous studies[19-25] where deuterium atoms were located in specific regions of the mixed micelle: (i) micelle deuterated in the core region, (ii) micelle deuterated in the polar head group of the nonionic surfactant, and (iii) nondeuterated micelle in deuterated water. This allows determination of the location of the doxy (i.e. nitroxide) moiety in *x*-doxylstearic acids, used as probes of the mixed micellar interface, and of the hydration of the micellar interface as a function of the mixed micelle composition. It is also shown that the polar head groups of SDS and DTAC are located in different regions of the poly(ethylene oxide) mantle in ionic–nonionic mixed micelles. This provides an explanation at a molecular level of the different thermodynamical behavior of the SDS–nonionic and DTAC–nonionic mixed micellar systems.

Experimental Section

Sodium dodecyl sulfate and dodecyltrimethylammonium chloride were purchased from Eastman Kodak. SDS was recrystallized three times from ethyl alcohol, washed with ethyl ether, and dried under moderate vacuum. DTAC was recrystallized three times from acetone and dried under moderate vacuum. Hexakis(ethylene glycol) monododecyl ether ($C_{12}E_6$), hexakis(ethylene-d_4 glycol)monododecyl ether ($C_{12}D_6$) and hexakis(ethylene glycol) monododecyl-d_{25} ether ($(CD)_{12}E_6$) were gifts from Eniricerche, Milan, Italy. *x*-Doxylstearic acid spin probes (*x*-DSA) with $x = 5$, 7, 10, 12, and 16 were obtained from Molecular Probes, Eugene, OR, and were used as recieved. Stock solutions of 0.05 M surfactants were prepared in triply distilled water and in deuterated water (purity >99.8%, Aldrich) and were deoxygenated by nitrogen bubbling. A stock solution of *x*-DSA was prepared in chloroform. Films of the probes generated in vials by evaporating the chloroform were dissolved in the surfactant solutions in a nitrogen atmosphere. The following systems were investigated as a function of the doxyl position, *x*, along the alkyl chain of the stearic acid spin probe and of the mole ratio between the pure surfactants: SDS/$C_{12}E_6$/D_2O, SDS/$C_{12}D_6$/H_2O, SDS/$(CD)_{12}E_6$/H_2O, DTAC/$C_{12}E_6$/D_2O, DTAC/$C_{12}D_6$/H_2O, and DTAC/$(CD)_{12}E_6$/H_2O. Mixed micelles were obtained by mixing in the appropriate mole ratio the surfactant stock solutions. Only freshly prepared solutions were used. The concentrations were 1×10^{-4} M for *x*-DSA and 0.05 M for the total surfactant. The samples were sealed in 2 mm i.d. Suprasil quartz tubes and frozen rapidly by plunging the tubes into liquid nitrogen. Two–pulse electron spin echo signals were recorded at 4.2 K on a home built spectrometer by using 40-ns exciting pulses.

Results and Discussion

The results reported in this study are analyzed in terms of the deuterium modulation depth that is related to the strength of the electron–deuterium dipolar interaction. This interaction is detectable at X-band up to a distance of about 6 Å from the unpaired electron. Dipolar interactions are averaged out by rapid molecular tumbling in liquid solutions and consequently nuclear modulation can only be observed in solid or sufficiently viscous solutions. Several specific experiments, such as freeze-fracture electron microscopy, direct imaging, small-angle neutron scattering, and luminescence quenching, demonstrate that micellar and microemulsion structure is retained upon fast freezing.[31-36] In liquid solutions a spin probe samples many parts of a micelle on the ESR time scale, while in frozen solutions one spin probe samples only one environment but many spin probes sample a distribution of environments. While formally different these two situations appear to sample the same overall structural picture, as shown by similar results in frozen and liquid micellar[35] and vesicular[36] solutions.

In our experience "fast" freezing of aqueous solutions operationally refers to plunging 2 mm i.d. tubes into liquid nitrogen. This has given consistent, reproducible results in many systems. If the i.d. is increased to 3 mm or greater increasing variability occurs.

The *x*-doxylstearic acid spin probes in micellar solutions solubilize in the micelle with the acidic group at the micellar interface.[37] The probe location in a micellar system can be unambiguously determined by using specific deuteration and by comparing the strength of the normalized modulation depth arising from the differently labeled regions of the micellar system. This also allows the detection of possible artifacts due to the freezing procedure. The normalized modulation depth is defined as the depth at the first minimum relative to the echo intensity in the absence of modulation divided by the depth to the baseline. The normalized modulation depth has been found to be quantitatively comparable between different surfactant systems and is useful for revealing trends with experimental variables.[19] Because of the uncertain and probably variable structure of surfactant assembly interfaces a quantitative analysis in terms of numbers and distances of interacting deuterium nuclei is not as valuable as it is in polycrystalline materials. In general in surfactant assemblies the number of interacting deuterons is relatively large and the changes in the normalized modulation depth are mainly due to distance differences on the scale of 0.01 nm.

Figure 1 reports the deuterium contrasts used to determine the location of the *x*-DSA probes in $C_{12}E_6$, SDS, and DTAB micelles assuming micelles with a spherical or nearly spherical (as in $C_{12}E_6$ micelles) shape. In micelles with deuterated water as solvent with the probes present in an all-trans conformation, increasing *x* moves the doxyl group further away from the acidic group, i.e. from the surface of the micelle. Therefore one expects a decrease in the normalized deuterium modulation depth due to the increasing distance between the unpaired electron and water deuterium atoms. On the other hand, a decrease of the deuterium modulation depth from $x = 5$ to 10 and an increase at $x = 12$ and 16 indicate that the doxyl probe bends near $x = 10$–12, thus 12- and 16-DSA have a U-shape introduced by a few gauche links.

In previous studies[19,23,38] it was shown that the *x*-DSA probes are located in the ethylene oxide region of the $C_{12}E_6$ micelle and in the Stern layer of the SDS or DTAC micelles and that the 12-DSA and 16-DSA probes are bent. A bent conformation for the 12-DSA and 16-DSA can be easily explained since the nitroxide group is polar, hydrophilic, and far enough from the carboxyl group of the stearic acid to allow bending of the alkyl chain. Therefore, when the 12- and 16-DSA probes are at an interface with "low packing" of the alkyl chains of the host system (i.e. in micellar systems), they behave like bipolar molecules with both carboxyl and nitroxide polar groups interacting with the water. This behavior has been shown by monolayer studies,[39,40] where the doxylstearic acid probes have been studied as a function of the molecular packing at a water–air interface. Furthermore, spectroscopic studies show that 5-DSA and 16-DSA, solubilized

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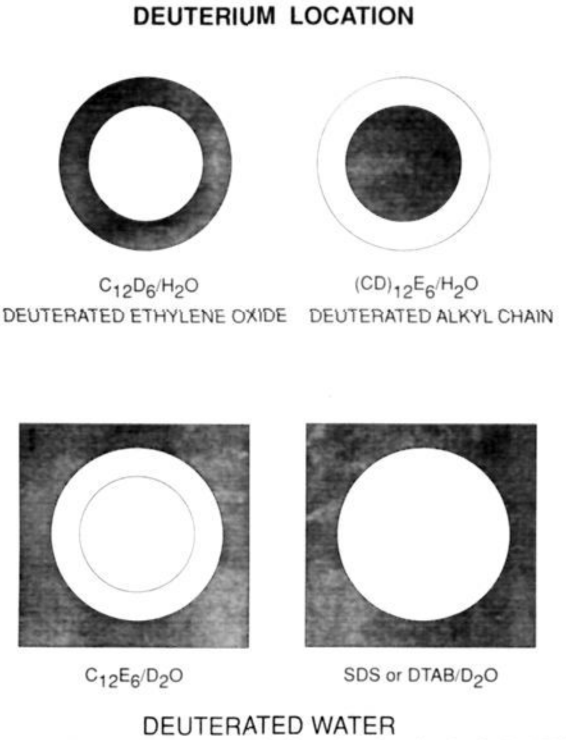

Figure 1. Schematic drawing of the deuterium location in $C_{12}E_6$, SDS, and DTAC micelles. The different deuterium locations are used to determine the *x*-DSA probe locations in the pure and mixed micelles. In the $C_{12}E_6$ micelle three different deuterium locations were used: (i) deuteriums located in the alkyl chain of the surfactant, (ii) deuteriums located in the ethylene oxide chain, or (iii) deuteriums located in the water solvent (D_2O). In the SDS and DTAC micellar systems deuteriums were located in the water solvent.

in SDS micellar solutions, have the same λ_{max} in the visible spectra, demonstrating that the nitroxides are in the same polar microenvironment[37] at the micellar interface.

From a comparative analysis of the deuterium modulation depth arising from deuterium atoms located in different regions of the $C_{12}E_6$ micellar system (micelle core, micelle polar head groups, water), it was shown that the ethylene oxide segments form a region around the hydrophobic core that does not allow much water penetration. Only the outer one of two ethylene oxide groups experience significant contacts with water molecules.[38] Furthermore, the deuterium modulation depth as a function of the doxyl position shows symmetrically inverse shapes for deuterated alkyl versus deuterated ethylene oxide curves. This is consistent with the different deuterated portions of the surfactant molecules being separated (no interdigitation between the ethylene oxide and the alkyl chains) as expected from small-angle neutron scattering (SANS) experiments.[41,42] Figure 2 shows a schematic drawing of a cross section of $C_{12}E_6$, SDS, and DTAC micelles showing a probable conformation of an *x*-doxylstearic acid molecule and its average location within the micelle. It should be stressed that this is an overall average probe location and conformation.

As noted above, the normalized deuterium modulation depth depends on the number and distance of deuterium nuclei from the unpaired electron. This modulation can be detected up to 5–6 Å from the site of the unpaired electron for physically reasonable deuterium densities.[30,43] Figures 3 and 4 show the trends of the normalized deuterium modulation depth for SDS/$C_{12}E_6$ and DTAC/$C_{12}E_6$ mixed micelles with a mole ratio of unity between the surfactants, and for different deuterium locations in the $C_{12}E_6$ micelle. The shape of these curves indicates that the *x*-doxylstearic acid spin probes are bent in these mixed micelles as they are in the ionic SDS DTAC, and nonionic $C_{12}E_6$ micelles.[19,38] The symmetrically inverse shapes for the deuterated alkyl versus the deuterated ethylene oxide groups are also consistent with the different deuterated portions of the surfactant molecules in the mixed micelle being separated as found for the pure nonionic micelles.[41]

An analysis of the trends of the deuterium modulation depths allows determination of the average probe locations in the equimolar mixed micelle. We first consider the modulation arising from deuterium located in the alkyl and ethylene oxide regions of the nonionic surfactant. If the probes have the same location in the mixed micelle as they have in the pure nonionic micelle, we expect a lower modulation depth (due to the decreased local density of deuterium atoms) and the same modulation trend as a function of the doxyl position along the stearic acid chain, i.e. the modulation curve is simply shifted toward lower values of the normalized deuterium modulation depth.

The normalized deuterium modulation depth in the mixed micelle is lower than the normalized modulation found for the pure nonionic surfactant, as expected from the substitution in the mixed micelle of a molecule of deuterated nonionic surfactant with a molecule of SDS or DTAC (see Figures 3 and 4). In mixed SDS/$C_{12}E_6$ micelles (Figure 3), the 7-DSA probe shows a slightly greater modulation in $C_{12}D_6$ than in $(CD)_{12}E_6$, indicating that the probe is located, as in pure $C_{12}E_6$ micelles, in the ethylene oxide region of the mixed micelle about 1–2 Å from the micellar core. Furthermore, for mixed micelles of SDS/$C_{12}E_6$ the changes of the normalized modulation depth in going from the 7-DSA to 10- and 12-DSA are the same as in pure $C_{12}E_6$ micelles, indicating that 10- and 12-DSA probes are located in the mixed micelle in the same region as they are in the pure $C_{12}E_6$ micelle.

A different trend of the normalized deuterium modulation depth is found for 5-DSA and 16-DSA in mixed micelles. 5-DSA shows weaker changes of the modulation depth as compared to that of pure $C_{12}E_6$ micelles. In fact, the change of the modulation depth in going from the 7-DSA to 5-DSA for deuterium atoms located in the alkyl chain ($(CD)_{12}E_6$) is 0.04 and 0.08 for the mixed micelle and the pure $C_{12}E_6$ micelle, respectively, and 0.05 and 0.1 for deuterium atoms located in the ethylene oxide region ($C_{12}D_6$). The reverse occurs for 16-DSA where the change of the modulation depth, for deuteriums located in the alkyl chain ($(CD)_{12}E_6$), is 0.08 and 0.05 for the mixed micelle and pure $C_{12}E6$ micelle, respectively, and 0.09 and 0.04 for deuterium atoms located in the ethylene oxide region ($C_{12}D_6$).

These results show that SDS changes only the deuterium density of the micellar region monitored by 5-DSA and 16-DSA. Since these probes are located in the ethylene oxide mantle, close to the second to third ethylene oxide, and considering that modulation can be detected only up to 5–6 Å and that the 7-DSA modulation is unaffected by SDS addition, one must conclude that the SDS in the SDS/$C_{12}E_6$ mixed micelle is located at the micellar surface close to the second ethylene oxide group of the nonionic surfactant.

The location of the DTAC polar head group in the mixed micelle can be obtained by similar considerations from an analysis of the trend of the deuterium modulation depths of *x*-DSA in the equimolar DTAC/$C_{12}E_6$ mixed micelle (Figure 4). In this system the shape for deuterated alkyl versus deuterated ethylene oxide curves is the same as for the SDS/$C_{12}E_6$ mixed micelle and the $C_{12}E_6$ micelle. However, a comparative analysis of the trend of the deuterium modulation depths for the mixed micelle and for the $C_{12}E_6$ micelle shows that only 10-DSA is unaffected by the presence of the DTAC surfactant. Furthermore, the deuterium modulation depth of 10-DSA in mixed micelles with deuterium located in the alkyl chain of the nonionic surfactant ($(CD)_{12}E_6$/DTAC) is about half of the deuterium modulation depth in pure

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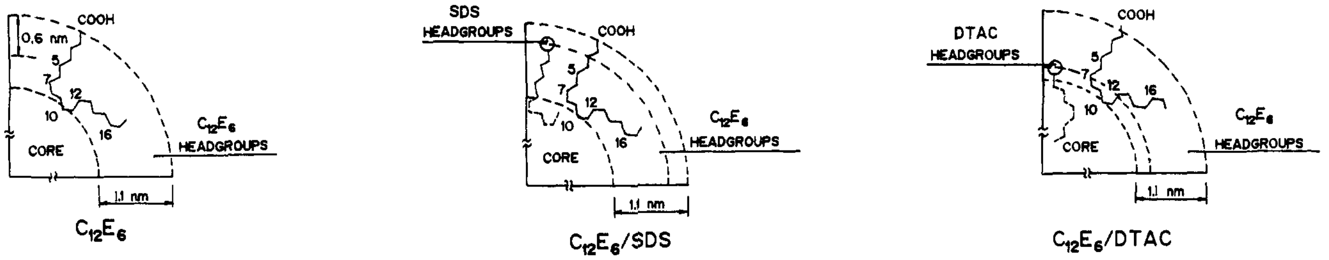

Figure 2. Schematic drawing of a cross section of SDS, DTAC, and $C_{12}E_6$ and micelles showing a probable conformation of an *x*-doxylstearic acid molecule and its average location within the micelle. The doxyl group is not shown, and its position along the stearic acid chain is indicated by the corresponding number. The 12-DSA and 16-DSA probes are bent and behave like bipolar molecules at the micellar interface.

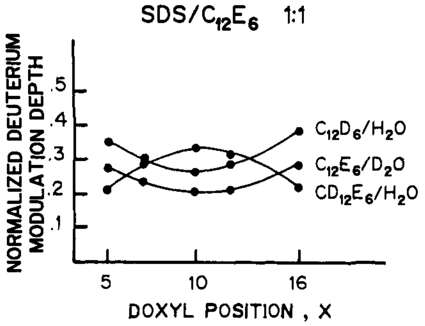

Figure 3. Dependence of the normalized deuterium modulation depths on the doxyl group position (*x*) in the stearic acid alkyl chain for SDS/$C_{12}E_6$ (1:1 mol ratio) mixed micelles. The nonionic surfactant has been selectively deuterated along the alkyl chain ($(CD)_{12}E_6$) or in the ethylene oxide groups ($C_{12}D_6$).

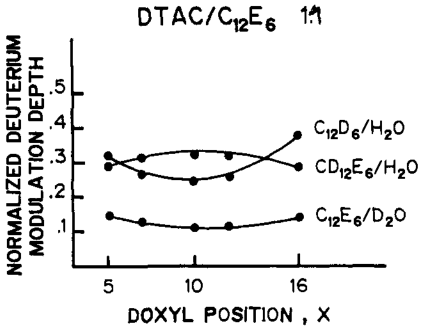

Figure 4. Dependence of the normalized deuterium modulation depths on the doxyl group position (*x*) in the stearic acid alkyl chain for DTAC/$C_{12}E_6$ (1:1 mol ratio) mixed micelles. The nonionic surfactant has been selectively deuterated along the alkyl chain ($(CD)_{12}E_6$) or in the ethylene oxide groups ($C_{12}D_6$).

$(CD)_{12}E_6$, as expected for the replacement of a deuterated with a nondeuterated C_{12} chain (see also below).

This indicates that in the DTAC/$C_{12}E_6$ mixed micelle the doxylstearic acids are bent as in the SDS/$C_{12}E_6$ mixed micelle and the $C_{12}E_6$ micelle and that 10-DSA is located in the same region as in pure nonionic micelles. Since the deuterium modulations of the 5-, 7-, 12-, and 16-DSA probes are affected by the presence of the DTAC polar head group, and changes in the deuterium modulation depth can be detected up to a distance of about 6 Å, it is concluded that the polar head group of the DTAC surfactant is located in a region of the ethylene oxide mantle that is close to the region monitored by the 7-DSA probe, which is located close to the fifth ethylene oxide of the nonionic surfactant. These results are also supported by an analysis of the deuterium modulation depth as a function of the mixed micelle composition.

It is generally accepted that, since all the surfactants have the same alkyl chain length, changes in the mixing ratios between the ionic and nonionic surfactants should be essentially considered as the replacement of one polar head group by another.[44] This is true only if the polar head groups of the ionic surfactant penetrate

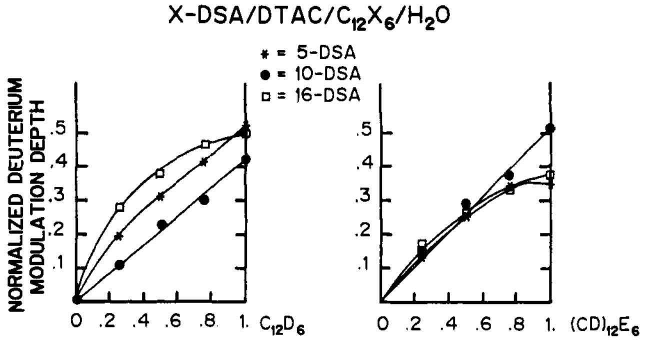

Figure 5. Dependence of the normalized deuterium modulation depths for *x*-DSA probes as a function of the composition of DTAC/$C_{12}E_6$ mixed micelles. The nonionic surfactant has been selectively deuterated along the alkyl chain ($(CD)_{12}E_6$) or in the ethylene oxide groups ($C_{12}D_6$).

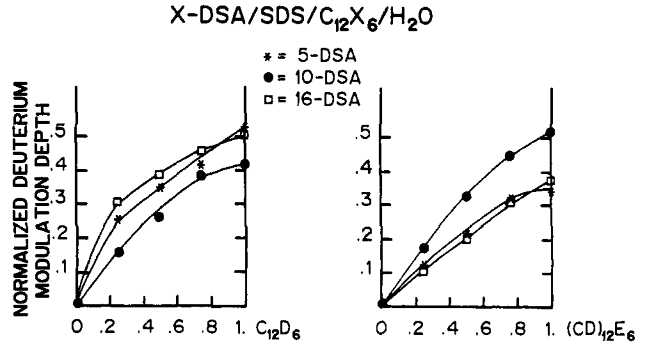

Figure 6. Dependence of the normalized deuterium modulation depths for *x*-DSA probes as a function of the composition of SDS/$C_{12}E_6$ mixed micelles. The nonionic surfactant has been selectively deuterated along the alkyl chain ($(CD)_{12}E_6$) or in the ethylene oxide groups ($C_{12}D_6$).

all of the ethylene oxide region of the micelle, which is extended about 11 Å,[41,42] and locate close to the alkyl core of the nonionic micelle. In this case the changes in the deuterium modulation depths arising from the deuterated alkyl region of the micelle must be additive. Figure 5 shows the normalized deuterium modulation depths of 5-, 10-, and 16-DSA as a function of the mixed micelle composition and for different deuterium locations in the DTAC/$C_{12}E_6$ mixed micelle (alkyl core and ethylene oxide region). The trend of the deuterium modulation depths of 10-DSA, which is the probe closest to the alkyl core region of the micelle, is linear as expected for a DTAC location at the fifth ethylene oxide of the nonionic surfactant. A positive deviation is present for the SDS/$C_{12}E_6$ system (see Figure 6). In this case the 10-DSA is located about 1 Å inside the alkyl core while the SDS polar head group is located close to the second ethylene oxide group of the nonionic surfactant, that is about 8–9 Å from the alkyl core. It follows that the substitution of one molecule of $C_{12}E_6$ by SDS produces two different effects. The first is related to the substitution of the bulkier polar head group of $C_{12}E_6$ by the smaller polar head group of SDS, and the second

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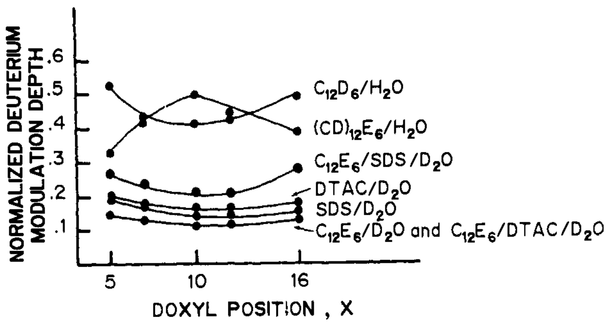

Figure 7. Dependence of the normalized deuterium modulation depths on the doxyl group position (*x*) in the stearic acid alkyl chain for micelles of SDS, DTAC, and $C_{12}E_6$ and for mixed micelles of SDS/$C_{12}E_6$ and DTAC/$C_{12}E_6$ (1:1 mol ratio). The deuterium modulation depth trends for the nonionic surfactant, selectively deuterated along the alkyl chain ($(CD)_{12}E_6$) or in the ethylene oxide groups ($C_{12}D_6$), are also reported.

is related to the fact that the alkyl core of the nonionic micelle is only partly penetrated by the alkyl chain of SDS. This means that the local deuterium density "seen" by the 10-DSA is greater than that calculated considering an additive behavior, leading to a positive deviation of the normalized deuterium modulation depth. In summary, the trends of the normalized deuterium modulation depths confirm and strengthen the previous deductions about the SDS and DTAC locations in the mixed micelle.

Figure 7 shows the deuterium modulation depth as a function of the doxyl position for the pure micellar systems and the equimolar mixture between the ionic surfactants and $C_{12}E_6$ is deuterated water. Therefore the deuterium modulation "seen" by the doxylstearic acid probes is related to the water penetration at the micellar interface.

The analysis of Figure 7 shows that the water penetration into the mixed micelle of DTAC/$C_{12}E_6$ is very similar to that of the $C_{12}E_6$ micelle. This is expected since the location of the polar head group is below the micellar surface. A different result is obtained for the SDS/$C_{12}E_6$ mixed micelle which shows a strong increase of the deuterium modulation depth. For example, the normalized deuterium modulation depth of the 5-DSA probe, which is the most exposed to water interactions, is about 0.15 and 0.19 for pure micelles of $C_{12}E_6$ and SDS, respectively, and about 0.29 for the equimolar mixed micelle. This indicates a significant increase of the water penetration into the ethylene oxide region in the mixed micelle, suggesting that SDS opens up the ethylene oxide mantle to more water penetration. Figure 8 shows the trend of the deuterium modulation depths for 5-, 10-, and 16-DSA as a function of the mixed micelle composition in D_2O. The modulation depth as a function of the DTAC/$C_{12}E_6$ mixed micelle composition follows an ideal behavior, showing that the amount of water in the ethylene oxide mantle is related to the mixed micelle composition. The SDS/$C_{12}E_6$ system shows strong positive deviations from ideal behavior for all the probes indicating, as reported above, the SDS produces a significant increase in the amount of water in the ethylene oxide region. These deviations are greater for the 5-DSA and 16-DSA probes, which are closer to the mixed micellar surface and depend on the mixed micelle composition. Furthermore, positive deviations for the 10-DSA probe show that SDS produces a consistent increase in the water amount close to the alkyl core of the mixed micelle.

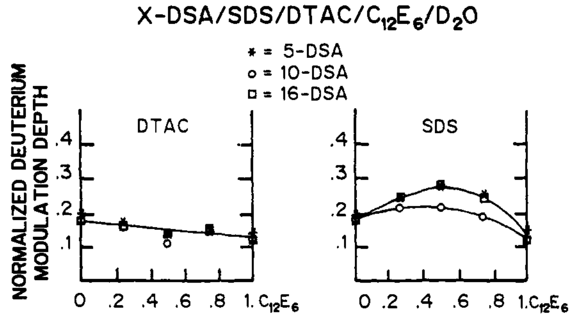

Figure 8. Dependence of the normalized deuterium modulation depths for *x*-DSA probes as a function of the composition of DTAC/$C_{12}E_6$ and SDS/$C_{12}E_6$ mixed micelles in D_2O.

Conclusions

From the analysis of the results of electron spin echo modulation of doxylstearic acids in SDS/$C_{12}E_6$ and DTAC/$C_{12}E_6$ mixed micelles the following conclusions can be drawn:

(1) The doxylstearic acid spin probes have similar conformations in all the mixed micellar systems studied to those in the pure SDS, DTAC, and $C_{12}E_6$ micellar systems.

(2) In SDS/$C_{12}E_6$ and DTAC/$C_{12}E_6$ mixed micellar systems, SDS and DTAC solubilize with their polar head groups in the ethylene oxide region of the nonionic surfactant. From the trend of the normalized deuterium modulation depths as a function of the doxyl position, and from a comparative analysis of the modulation depths in mixed micelles with the nonionic surfactant selectively deuterated in the alkyl chain or in the ethylene oxide region, it is found that the DTAC polar head groups are located closer to the core region of the mixed micelle at the fifth ethylene oxide group of the nonionic surfactant while the SDS polar head groups are located close to the mixed micellar surface in a more "hydrophilic region", close to the second ethylene oxide group of the nonionic surfactant.

(3) The analysis of the normalized deuterium modulation depths shows that the addition of SDS to $C_{12}E_6$ to form mixed micelles opens up the ethylene oxide region to more water penetration in the mixed micelle. This effect depends on the SDS/$C_{12}E_6$ mole ratio and it is maximum for the equimolar mixture. The mixtures of DTAC/$C_{12}E_6$ do not show a similar effect probably because of a deeper location of the DTAC polar head groups in the ethylene oxide region of the nonionic surfactant.

These results provide an explanation at the molecular level of the different thermodynamical behavior found for mixed micelles composed of cationic–nonionic and anionic–nonionic surfactants.

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