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A Spin-Probe Study of the Modification of the Hydration of SDS Micelles by Insertion of Sugar-Based Nonionic Surfactant Molecules

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The spin-probe detected polarity index H(25 °C) of SDS micelles decreases linearly with the number of inserted sugar-based nonionic surfactant molecules. This decrease is interpreted as being due to the expulsion of water molecules by the sugar groups from the polar shell surrounding the hydrocarbon core of the dodecyl micelle. Employing the geometrical model described in the companion paper immediately preceding this work, the effective volume of water expulsion is found to be similar to the volume of the sugar groups after taking into account that the OH bonds of the sugar groups also contribute to the polarity index H(25 °C). The estimate of the hydration of pure SDS micelles as a function of their aggregation number from these studies with the spin probe 16 doxylstearic acid methyl ester is similar to that with 5 doxylstearic acid methyl ester. This confirms that both spin probes are located similarly in the polar shell.

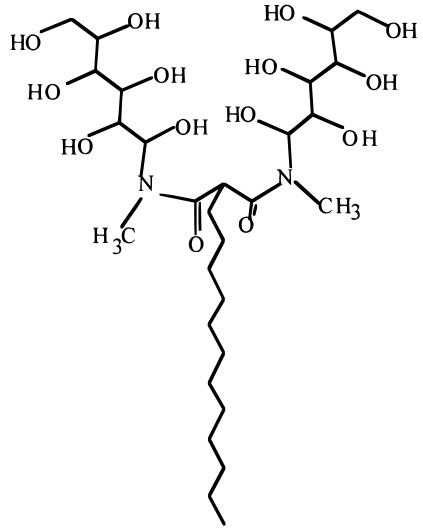
Introduction

Mixed surfactant systems find widespread use in many domestic and technical applications. Such combinations of surfactants are often preferable to single component systems since the solution properties may be tuned via the concentration ratio of two suitable surfactants and mixtures inherently obviate many worries regarding purity. For an overview, see refs 1 and 2.

Several groups are currently investigating mixed surfactant systems. For example, ionic/ionic mixtures of the same or opposite charge,[3−6] ionic/nonionic mixtures,[7,8] and nonionic/nonionic mixtures.[9] One of our groups has been investigating[10,11] mixed micelles of sodium dodecyl sulfate SDS and dodecylmalono-bis-*N*-methylglucamide DBNMG using a variety of techniques. DBNMG is an interesting nonionic surfactant because its forms small micelles with about the same aggregation number[10] as pure salt-free SDS.

Mixtures of SDS and DBNMG are particularly suitable for model studies of nonionic/anionic micelles because small-angle neutron scattering (SANS) and NMR results showed that the size of the mixed micelle, for all compositions, was largely invariant with mole fraction, not surprising perhaps given the similarity in size of the two pure micelles.

The use of EPR to study the hydration of the surfaces of micelles was discussed in detail recently for the case of SDS micelles[12] and in the companion paper[13] immediately preceding this paper, for the case of lithium dodecyl sulfate (LiDS) micelles. In those cases, the hydration was modified by varying the aggregation number of the micelles. Excellent agreement between experiment and theory was achieved using a surprisingly simple model. The method is based on the fact that the hyperfine coupling constants of nitroxide spin probes vary linearly with a nonempirical polarity index,[14] H(25 °C), defined to be the ratio of molar concentration of OH dipoles in a solvent or solvent mixture to that in water. Previously, the micelles investigated[12,13] involved solvent mixtures of water and molecules possessing no OH bonds, thus H(25 °C) was simply the volume fraction occupied by water. Here, the situation is more interesting since the sugar groups possess OH bonds.



DBNMG

The purpose of the present work is to apply a quite different test of the validity of the technique to study micelle hydration by EPR. Here we modify the hydration of SDS micelles by inserting bulky nonionic headgroups, which if the simple hydration model is valid would be expected to expel water molecules from the polar shell and lead to spin-probe detected polarities that decrease with increasing DBNMG concentration. To study SDS-type micelles, we limit our study to small DBNMG molar fractions, $X = 0-0.3$, where

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$$X = \frac{[\text{DBNMG}]}{[\text{DBNMG}] + [\text{SDS}]} \quad (1)$$

is the stoichiometric mole fraction of DBNMG. Recent work shows (see Figure 1 of ref 10) that the mixed cmc falls rapidly with X. For example, at $X = 0.05$, cmc = 3 mM and at $X = 0.1$, cmc = 1.3 mM, these values being dominated by monomeric SDS. Above $X = 0.1$, the cmc is less than 1 mM for all values of X.[10]

The cmc behavior as a function of X is characteristic of a "synergistic" interaction; that is, the mixed surfactant cmc is lower than would be expected based on a simple ideal mixing argument.[15] Such synergy is common in many anionic−nonionic mixtures and arises due to a favorable interaction between the headgroups of the two surfactants. The regular solution theory proposed by Rubingh[16] permits the calculation of the micelle composition for any given value of total surfactant concentration and solution mole fraction from a knowledge of the values of the cmc of the two pure surfactants and the mixture. At low total surfactant concentrations, the composition of the micelle is heavily weighted toward the hydrophobic component so the nonionic micellar mole fraction is substantially greater than the solution composition. However, at 50 mM total surfactant concentration employed in this study, this segregation or preferable solubilization is minimal due to the large number of micelles present. Accordingly, the micellar and stoichiometric compositions are the same to within a few percent. For further discussion of this point, see for example ref 17. Thus, we may use the simplified notation of eq 1 to denote the micelle composition.

Methods and Materials

Surfactants. The nonionic surfactant DBNMG (U.S. patent 5 298 191) was purified by HPLC using a reverse phase column. The stationary phase consisted of silica-g-C18 alkyl chains, while the mobile phase was 80% methanol (HPLC grade) and 20% doubly distilled water. Elution times were typically 1 h with a flow rate of 3 mL per min. Four fractions were collected from the column which were analyzed by mass spectrometry and ^{1}H/^{13}C NMR. The first two fractions consisted of unreacted starting material, while the last two were the single-headed sugar analogue (RMM = 405) and the desired double-headed sugar surfactant (RMM = 626). After purification, the critical micelle concentration of DBNMG was found using surface tension measurements as described before[10] to be 0.60 ± 0.05 mM. The desired fraction was collected in a preweighed round-bottomed flask, and the solvent was removed with a rotary evaporator. The mass of the material was determined by weight and the appropriate amount of distilled water was added to produce a 50 mM solution. Eight runs were required to collect enough material for this experiment, each run requiring about 3 h. SDS was purchased from Sigma and purified by recrystallization from ethanol.

EPR. In preliminary experiments, we observed that fatty acid ester spin probes show longer rotational correlation times in DBNMG micelles than in SDS micelles. Thus, the spin probe 16-doxylstearic acid methyl ester (16DSE) was chosen for this study rather than the previously employed 5-doxylstearic acid methyl ester (5DSE) because it has a higher intrinsic flexibility[18] leading to shorter rotational correlation times and narrower line widths. The spin probe 16DSE was purchased from Sigma and used as received. A stock solution was prepared in ethanol by weight and the appropriate amount weighed into two vials. The ethanol was evaporated in an oven at 50 °C for 4 h. SDS plus water were added to one vial, and the 50 mM solution of DBNMG was added to the other to form two 50 mM stock solutions with 16DSE/surfactant molar ratios of 1:400. At this concentration, spin exchange reduces the apparent value of the nitrogen hyperfine coupling constant by about 5 mG;[12] however, this correction was not applied since it is negligible in this context. Furthermore, the correction would be very nearly the same for all of the samples since the 16DSE/surfactant molar ratio was the same in all of the samples. These mother solutions were mixed by weight to prepare solutions with mole fractions of DBNMG varying from 0 to 0.3. The EPR spectra were obtained over the following 2 days.

The samples, not degassed, were sealed with a gas-oxygen torch into melting point capillaries which were housed within a quartz EPR tube for the measurements. All of the measurements were carried out at 44 ± 0.5 °C as measured with a thermocouple before and after the spectra were taken.

The spectra were taken at X-band with a Bruker ESP-300 spectrometer. A macro within Bruker's software tuned the bridge, obtained a spectrum, and wrote it to the hard disk, repeating the process five times in a row for each sample. The microwave power was 2 mW, sweep width 50 G, time constant 10 ms, and sweep time 41 s. At low modulation amplitudes, the central line of 16DSE in SDS micelles was found to have a Gaussian line width $\Delta H_{pp}^{G} = 0.851 \pm 0.004$ G in good agreement with NMR data.[19] A large modulation amplitude of 1.03 G was employed, taking advantage of the fact[20] that only the inhomogeneous (Gaussian) component is broadened. This broadens the Gaussian component of the Voigt line to $\Delta H_{pp}^{G} = 0.947 \pm 0.002$ G as expected.[21] A series of measurements were made varying the modulation amplitude to confirm the expectation[20,21] that the modulation would broaden only the Gaussian component. The spectra were transferred to a PC and fit with the program LOWFIT, coded in C, which fits the experimental lines to approximate Voigt line shapes.[22,23] This separates the Gaussian and Lorentzian components of the spectral lines and locates the resonance fields of the three EPR lines to a precision of a few milligauss. The sweep width was measured with the Bruker NMR Gaussmeter operating in the 1 mG resolution mode. A mean value of the sweep for the five spectra corresponding to a given sample was used to calibrate the field. These mean values were reproducible to within ±2 mG; thus, the random error in determining a hyperfine coupling constant of about 15 G is less than 1 mG. We define the spacings between hyperfine lines as $A_+ = H_0 - H_{+1}$ and $A_0 = (H_{-1} - H_{+1})/2$, where H_{MI} denotes the resonance fields of the three lines $M_I = +1$, 0, and −1 corresponding to the low-, center-, and high-field lines, respectively. See Figure 1. Small second-order shifts due to motional effects[24−26] were previously found[12] to affect the apparent hyperfine coupling constant A_0 more than A_+. Thus, for the purposes of studying polarity, A_+ is the more appropriate.

Theory

Figure 1 shows schematically the three-line nitroxide spectra for two SDS micelles with n (Figure 1a) and $n + 1$ (Figure 1b) molecules of DBNMG inserted, respectively, where we have drawn the figure anticipating the result that $A_+(n+1) - A_+(n) = \delta a < 0$. Figure 1 is vastly exaggerated; $|\delta a|/A_+ \approx 10^{-3}$. A decrease in the hyperfine coupling constant of a nitroxide free is accompanied by an increase in the g value.[27] The same mechanism of spin delocalization due to electric fields[28] which alters the hyperfine coupling constant also alters the g value.[27] This means that a spectrum with smaller line spacings moves to lower fields by $\delta H_g < 0$ as shown in Figure

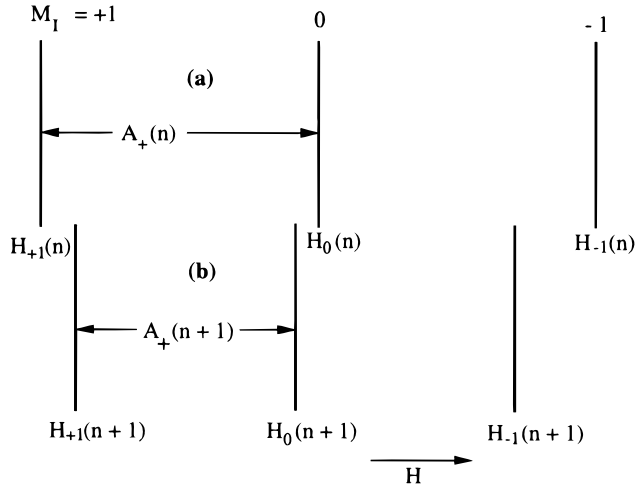

Figure 1. Schematic representation of three-line nitroxide EPR spectra corresponding to (a) n molecules of DBNMG and (b) $n + 1$ molecules of DBNMG inserted into the SDS micelle. The shifts are greatly exaggerated.

1. Therefore, the center line moves downfield by $\delta H_0 = |\delta H_g|$, the low-field line moves upfield by $\delta H_{+1} = |\delta a| - |\delta H_g|$, and the high-field line moves downfield by $\delta H_{-1} = |\delta a| + |\delta H_g|$. It is clear from Figure 1 that a superposition of spectra due to many values of n would be inhomogeneously broadened, the high-field line being affected the most.

The resonance fields may be summarized by

$$H_{MI}(n+1) = H_{MI}(n) - M_I\delta a + \delta H_g \tag{2}$$

Taking δa to be independent of n, we have

$$H_{MI}(n) = H_{MI}(0) + n(-M_I\delta a + \delta H_g) \tag{3}$$

where $H_{MI}(0)$ are the resonance fields in pure SDS; i.e., $X = 0$.

At a given value of X, the observed spectrum, S_{obs}, is given by

$$S_{obs}(X) = \sum_{n=0}^{N} S_n(X)P_n \tag{4}$$

where $S_n(X)$ is a three-line spectrum of Voigt line shapes imposed on the "stick" diagram in Figure 1a, P_n is the probability of obtaining n, and N is the aggregation number of the mixed micelle. In principle, N could depend on both X and n; however, we show below that the analysis of these data are insensitive to the value assumed for N. Thus, for simplicity, we proceed by assuming a constant value of N. Inherent in this assumption is a neglect of the size dispersity in these micelles. This is probably a sound assumption, but in any case, we show in the Appendix that such dispersity is not detectable with currently available spin probes. $S_n(X)$ is a slowly changing function of n; thus, to a good approximation, the resonance fields of the superposition in eq 4 are the mean values of the resonance fields of the stick diagrams.

$$\langle H_{M_I}\rangle = \sum_{n=0}^{N} H_{M_I}(n)P_n = H_{M_I}(0) + \langle n\rangle(-M_I\delta a + \delta H_g) \tag{5}$$

where $\langle n\rangle$ is the average value of n. There will be a dispersion in this resonance field about the mean field given by

$$\sigma(M_I) = \sqrt{\langle(n - \langle n\rangle)\rangle^2}(-M_I\delta a + \delta H_g) \tag{6}$$

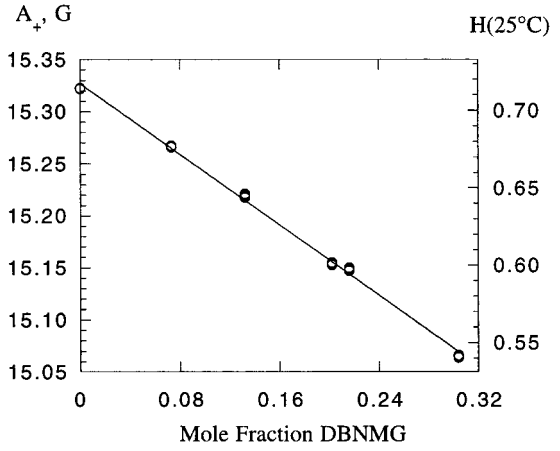

Figure 2. Hyperfine spacing A_+ of the spin probe 16DSE versus the mole fraction of added DBNMG molecules. The right-hand ordinate is the polarity index H(25 °C), eq 12. The straight line is a linear least-squares fit to the data, eq 10.

In principle, the second moment $\sigma(M_I)$ could yield valuable information about the detailed distribution of DBNMG molecules in SDS micelles; however, we show in the Appendix that it is too small to measure using spin probes currently available.

The observed hyperfine spacing

$$\begin{aligned} A_+(X) &= \langle H_0\rangle - \langle H_{+1}\rangle \\ &= H_0(0) - H_{+1}(0) + \langle n\rangle\delta a \\ &= A_+(0) + \langle n\rangle\delta a \end{aligned} \tag{7}$$

The average number of DBNMG molecules in an ensemble of micelles of aggregation number N is determined by the molar fraction of DBNMG molecules in the micellar phase as follows:

$$\frac{\langle n\rangle}{N} = \frac{[\text{DBNMG}]_m}{[\text{DBNMG}]_m + [\text{SDS}]_m} = X \tag{8}$$

using the arguments following eq 1. Therefore, combining eqs 7 and 8,

$$A_+(X) = A_+(0) + X\delta aN \tag{9}$$

Results

Figure 2 shows the variation of A_+ with X at 44 °C. Since A_+ is directly related to the polarity index H(25 °C) (eq 12), the results show a decreasing polarity with increasing X. In Figure 2, each point is in fact five overlapping symbols from each of the five measurements on the same sample illustrating that the reproducibility of A_+ is smaller that the size of the plotting symbols for a given sample preparation. The two points near $X = 0.2$ were derived from samples prepared on different days, but from the same mother samples. The solid line is a fit to eq 9 yielding $\delta aN = -(0.845 \pm 0.007)G$ and $A_+(0) = (15.327 \pm 0.001)G$; i.e.,

$$A_+(X) = 15.327 - 0.845X \tag{10}$$

with $A_+(X)$ in gauss.

Figure 3 shows data from pure SDS micelles using the spin probe 16DSE. These data are at 25 °C in order to compare the results derived from 16DSE with our previous work derived from 5DSE.[21,29−32] Previously, we found[33] that A_+ only varies by about 0.2 mG/°C in water/methanol mixtures, so the intrinsic

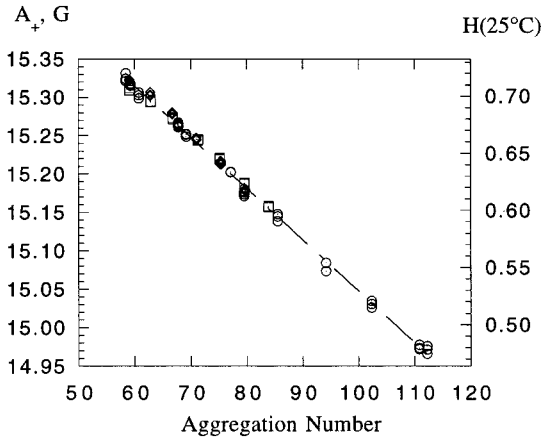

Figure 3. Hyperfine spacing A_+ of the spin probe 16DSE versus the aggregation number of pure SDS micelles. The aggregation number is varied by varying [NaCl] (○) or by varying [SDS] (△, □). The abscissa is computed from eq 3 of the companion paper[13] using values appropriate to SDS,[34] $\kappa_2 = 164$, $\gamma = 0.25$. The straight line is a linear least-squares fit of all of the data, eq 11.

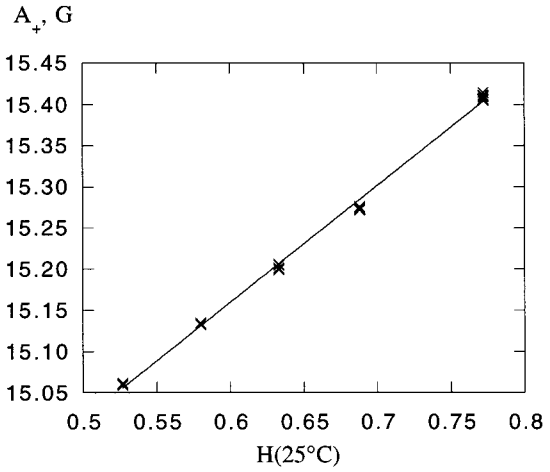

Figure 4. Calibration of the hyperfine spacing A_+ for 16DSE in a series of MeOH/H_2O mixtures following the procedure detailed previously[12] for 5DSE. The straight line is a linear least-squares fit, eq 12.

variation of A_+ is only about 5 mG over the range 25−45 °C. The values of the aggregation numbers are computed from eq 3 of the companion paper[13] with values appropriate to SDS[34] $\kappa_2 = 164$, $\gamma = 0.25$. The experiments involved varying [NaCl] (circles) or varying [SDS] (diamonds and squares). The solid line is a linear least-squares fit to all of the data yielding

$$A_+ = (15.716 \pm 0.003) - (0.00669 \pm 0.00004)N \quad (11)$$

See the companion paper[13] and ref 12 for a discussion of the results in Figure 3. As predicted,[12] the results using 16DSE are very similar to those previously found[12] using 5DSE. This is because all of the YDSE spin probes, where Y is the position of the doxyl label, are expected to probe the same polar layer and report similar results. See ref 12 for a discussion of this point. To compare the results in Figure 3 for 50 mM SDS with those in Figure 2 ($X = 0$), we note that for 50 mM SDS micelles at 25 °C, $N = 59.3$ which, employing eq 11, yields $A_+ = 15.319$ G. This value of A_+ for 50 mM SDS at 25 °C is very similar to that at 44 °C of 15.327 at 44 °C (eq 10). Thus, the temperature dependence of A_+ is rather small in pure SDS micelles.

In other experiments (not shown), extending to higher values of N than those shown in Figure 3, the sphere−rod transition is detected by 16DSE as a leveling of the value of A_+ near $N =$ 130, identical to the behavior reported by 5DSE.[12]

Figure 4 shows the variation of A_+ with the polarity index H(25 °C) for the spin probe 16DSE following the same procedures as before.[12] The solid line is a linear least-squares fit yielding

$$A_+ = (14.309 \pm 0.009) + (1.418 \pm 0.013)H(25\ °C) \quad (12)$$

Thus, measurements of A_+ may be converted into values of H(25 °C). Combining eqs 10 and 12,

$$H(25\ °C) = -(0.596 \pm 0.007)X + (0.718 \pm 0.018) \quad (13)$$

where the uncertainties are found by propagating those in eqs 10 and 12. Values of H(25 °C) are shown as the right-hand ordinates of Figures 2 and 3.

For the pure SDS micelles, Figure 3, the right-hand ordinate, H(25 °C), is the volume fraction in the polar shell occupied by water since only water and molecules not possessing an OH bond comprise the sample. In the SDS micelles modified by the addition of DBNMG molecules the situation is more interesting.

Model of the Surface Hydration of Mixed Micelles. We employ the same geometrical model of the hydration of the surface of mixed micelles that we recently employed[12] to discuss pure SDS micelles and in the companion paper[13] to discuss LiDS micelles. See ref 12 for a detailed discussion of the assumptions in the model and the rationale for the selection of the parameters to describe the micelle geometry. Briefly, the nitroxide moiety of 16DSE is assumed to sample, randomly and rapidly, all portions of the polar layer surrounding the hydrocarbon core reporting the average value of H(25 °C).

The value of H(25 °C) prior to the insertion of one DBNMG molecule is

$$H(25\ °C) = \frac{30N(H_2O)}{V_p} \quad (14)$$

where V_p is the volume (Å^3) and $N(H_2O)$ is the number of water molecules (volume, 30 Å^3) housed in the polar shell per surfactant molecule. Equation 14 implies that there is a volume inaccessible to water per surfactant molecule, V_{dry}, such that

$$H(25\ °C) = (V_p - V_{dry})/V_p \quad (15)$$

We suppose that inclusion of one DBNMG molecule renders a volume inaccessible to water, denoted by V_{DBNMG}. At the same time, one molecule of DBNMG carries a number, N_{OH}, of OH bonds into the polar shell that could form hydrogen bonds with 16DSE and therefore increase the value of H(25 °C). Since we take the aggregation number N to be independent of mole fraction of DBNMG, upon adding one molecule of DBNMG to the micelle, one molecule of SDS exits the polar shell. For the purpose of computing the new value of H(25 °C), an *effective* total volume $V_{DBNMG} - V_{dry} - 30N_{OH}$ is excluded which is $(V_{DBNMG} - V_{dry} - 30N_{OH})/N$ per surfactant molecule. The term $30N_{OH}$ adjusts the excluded volume by the amount that N_{OH} water molecules would occupy. The value of H(25 °C) after the insertion of n molecules of DBNMG becomes

$$H'(25\ °C) = \frac{V_p - \{V_{dry} + n(V_{DBNMG} - V_{dry} - 30N_{OH})/N\}}{V_p} \quad (16)$$

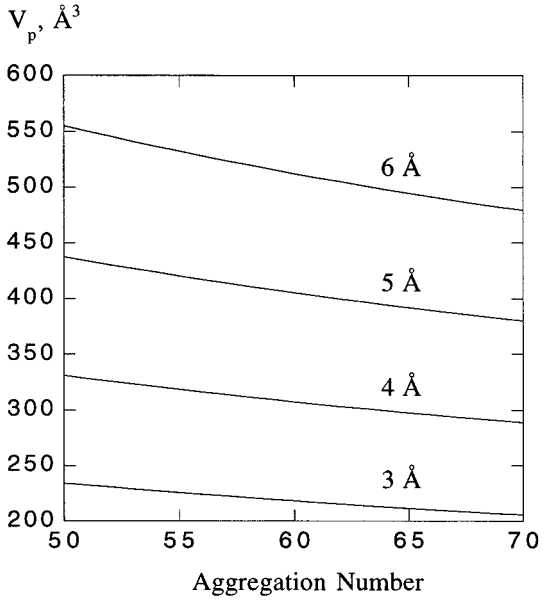

Figure 5. Volume per surfactant molecule in the polar shell versus the aggregation number. The numbers near each line indicate the thickness of the polar shell. The value of V_p is dominated by thickness of the shell and is relatively insensitive to the value of N.

where the prime indicates the altered value of $H(25\ ^\circ C)$ upon the addition of n molecules of DBNMG.

Therefore, the change in $H(25\ ^\circ C)$ per added molecule of DNBMG is

$$\frac{\partial H(25^\circ)}{\partial n} = -\frac{V_{DBNMG} - V_{dry} - 30N_{OH}}{NV_p} \qquad (17)$$

From the experimental data, we may evaluate the average value of eq 17

$$\frac{\partial H(25\ ^\circ C)}{\partial \langle n\rangle} = \frac{\partial H(25\ ^\circ C)}{\partial X}\frac{\partial X}{\partial \langle n\rangle} = -0.596/N \qquad (18)$$

Using $\partial H(25\ ^\circ C)/\partial X = -0.596$, eq 13 and $\partial X/\partial\langle n\rangle = 1/N$, eq 12. Setting the average value of eq 17 equal to eq 18 yields

$$V_{DBNMG} - V_{dry} - 30N_{OH} = 0.596V_p \qquad (19)$$

The factor N cancels in eqs 17 and 18; thus, the value of V_{DBNMG} depends on the assumed value of N only weakly, through the dependence of V_p on N. From eq 13 evaluated at $X = 0$ and eq 15, $V_{dry} = 0.282V_p$; thus, eq 19 becomes

$$V_{DBNMG} = 0.878V_p + 30N_{OH} \qquad (20)$$

To compute V_p, we employ eqs 15−17 of the companion paper[13] using $N_c = 12$ as the number of carbon atoms per chain that are embedded in the micelle core. We have previously used 5 Å as the thickness of the polar shell for pure dodecyl sulfate micelles[12,13] based on the SANS data of Cabane.[35] SANS has not been carried out for mixed micelles with [SDS] + [DBNMG] = 50 mM; however, a few measurements have been made at other total surfactant concentrations. See Table 2 of ref 10, where the thickness varies from 3 to 6 ± 1 Å. One measurement at [SDS] + [DBNMG] = 45 mM and $X = 0.33$ yielded 4 ± 1 Å. Another at [SDS] + [DBNMG] = 75 mM and $X = 0.33$ yielded 6 ± 1 Å. Figure 5 shows the values of V_p computed from assumed values of the thickness of the polar shell for values of N from $N = 50$ to 70. The values of V_p are weakly dependent on the assumed value of N, but strongly dependent on the value of the shell thickness. At this point, at least for the SDS-rich compositions, it appears that assuming a constant thickness of ∼5 ± 1 Å is reasonable, yielding from Figure 5, $V_p = 400 \pm 100$ Å^3, using a nominal value of $N = 60$.[10] For the purpose of estimating V_{DBNMG}, the assumed value of N is irrelevant since the uncertainty is dominated by the uncertainty in the thickness. Substituting $V_p = 400 \pm 100$ Å^3 into eq 20 yields

$$V_{DBNMG} = 30N_{OH} + (350 \pm 80) \qquad (21)$$

with V_{DBNMG} in units Å^3.

Discussion

Adding the nonionic surfactant DBNMG to SDS micelles leads to decreasing values of the polarity, which is the qualitative prediction of the hydration model discussed previously[12] and in the companion paper.[13] As the bulky sugar groups occupy volume in the polar shell, water is expelled. The order of magnitude estimate of the expelled volume in eq 21 depends on the assumed value of N_{OH}. The maximum value of N_{OH} is 12, the total number of OH bonds in the DBNMG molecule; however, it is conceivable that N_{OH} would be less than 12 due to steric hindrance and the fact that some of the OH bonds might extend out into the aqueous region, inaccessible to the nitroxide group. If we use the maximum value of $N_{OH} = 12$, $V_{DBNMG} = 350 + 360 = 710$ Å^3. Trevor Wear has calculated the volume of the sugar groups to be 524 Å^3 using PCMODEL by Serena Software. Equation 21 gives $V_{DBNMG} = 590$ Å^3 for $N_{OH} = 8$. Obviously, the various uncertainties in the model do not allow us to draw quantitative conclusions on the number on interacting OH groups. The important point is that the molecular volume of the sugar groups and the volume of the expelled water (after adding back the effect of the sugars' OH bonds) are similar.

Rewriting eq 14, after insertion of n molecules of DBNMG, yields

$$H(25\ ^\circ C) = \frac{30[N(H_2O) + nN_{OH}/N]}{V_p}$$

which, taking the average value, becomes

$$H(25\ ^\circ C) = \frac{30[N(H_2O) + XN_{OH}]}{V_p} \qquad (22)$$

At $X = 0$, eq 13 yields $H(25\ ^\circ C) = 0.718$; thus, eq 22, using our best estimate of $V_P = 400$ Å^3, gives a value of $N(H_2O) = 9.6$ molecules of water per surfactant molecule in the pure SDS micelle. One molecule of DBNMG expels $V_{DBNMG}/30$ molecules of water, which according to eq 21 would be 12−24 molecules depending on the value assumed for N_{OH}. This is the water originally associated with 1.3−2.5 SDS molecules in the pure SDS micelle. This would mean that a mixed micelle *of the SDS-rich type that we are discussing* would become very dry somewhere in the middle range of the mixed micelle composition; however, preliminary measurements show that the linearity in Figure 2 only persists to about $X = 0.5$ at which point the values of $H(25\ ^\circ C)$ level, go through a minimum and then increase. A detailed analysis of the hydration of the SDS/DBNMG mixed micelles over this more complicated region of the compositions will have to await more careful aggregation number determinations, preferably with time-resolved fluores-

cence quenching and SANS results on the mixed micelles near the $X = 1$ composition.

Care is needed in comparing Figures 2 and 3. It seems at first sight that the water content per surfactant molecule for a mixed micelle with DBNMG mole fraction of, say, $X = 0.3$ is about the same as that for a pure SDS micelle at an aggregation number of about 97; both yield values of H(25 °C) of about 0.54. This would be so if the sugars' OH bonds contributed nothing to the value of H(25 °C); however, if we assume that they do contribute, then eq 22 shows that the mixed micelle is dryer than one might think. For example, assuming $N_{OH} = 8$ reduces the calculated number of water molecules at $X = 0.3$ by $XN_{OH} = 2.4$ molecules compared with a pure micelle with aggregation number 97.

Conclusions

SDS−DBNMG mixed micelles have been studied using the spin-probe method for SDS-rich compositions. The simple model of micelle hydration recently shown[12,13] to be successful for SDS and LiDS micelles predicts a linear decrease in the number of water molecules per surfactant molecule residing in the polar shell provided that DBNMG molecules are assumed to replace SDS molecules one for one in the SDS-type molecule. This qualitative linear behavior is observed up to the rather large DBNMG molar fraction of $X = 0.3$. Quantitatively, employing a simple geometric model, the volume of expelled water per added DBNMG molecule was found to be similar to the volume of the sugar group after taking into account the effect of the sugar's OH groups. These mixed micelles are predicted to become "dry" near the middle of the composition range; i.e., the number of water molecules per surfactant molecule would fall below that needed to hydrate the sodium counterions associated with the SDS component of the micelle.

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Appendix

Dispersion in the Values of A_+. At a given value of X, there will be micelles containing $n = 0$ up to $n = N$ molecules of DBNMG which produces a dispersion in the value of A_+. To compute this dispersion the probability P_n of obtaining a micelle with n molecules of DBNMG would be required; however, this probability is not yet known. Were there to be no interactions between the SDS and DBNMG molecules as they mixed to form the mixed micelles, a binomial distribution would result. For the binomial distribution, the probability of a given molecule in the micellar phase being DBNMG is equal to X; thus, the probability of having a micelle with n DBNMG molecules and $(N - n)$ SDS molecules is

$$P_n = \frac{N!}{n!(N-n)!}(X)^n(1-X)^{(N-n)} \qquad (23)$$

A binomial distribution is not likely to hold over the entire range of X, since it predicts a statistical distribution without any interactions between the molecules. For values of X approaching unity, as one adds SDS molecules to uncharged DBNMG micelles, one might expect an electrostatic repulsion between the SDS molecules similar to the case of adding divalent cations to SDS micelles.[29−31] Physically, less energy is required to place an SDS molecule in a DBNMG micelle that does not already contain one. Even for small values of X, as we are considering in this paper, it is not hard to imagine small interactions. For the present work, the distribution is immaterial; eq 10 holds independent of the distribution. Our purpose in this Appendix is to compute the dispersion using eq 23 to provide an estimate of the order of magnitude of the effect. This estimate is likely to be an upper limit because most departures from the binomial distribution lead to narrower distributions, i.e., smaller dispersions. The distribution in eq 23 could serve as a starting point in the calculation of a more realistic distribution in the spirit of the calculations in refs 29−31.

Utilizing the fact that,[36] for the binomial probability $\langle(n - \langle n\rangle)^2 = pqN$, eq 6 becomes

$$[\sigma(M_I)]^2 = X(1-X)N(-M_I\delta a + \delta H_g)^2 \qquad (24)$$

In a series of 33 solvents, Griffith and co-workers[27] found that the g value of di-*tert*-butylnitroxide was a linear function of A_0 such that $\delta H_g = -\delta g H/g = 0.41\delta$a at X-band ($H \approx 3300$ G). Inserting $\delta H_g = 0.41\delta$a into eq 24 yields

$$[\sigma(M_I)]^2 = X(1-X)N(\delta a)^2(-M_I + 0.41)^2 \qquad (25)$$

This dispersion due to the superposition of spectra with different resonance fields will inhomogeneously broaden the resonance lines in a manner very similar to inhomogeneous broadening due to unresolved hyperfine structure[23] which will increase the Gaussian line width, ΔH^G_{pp}. Since Gaussian line widths add in quadrature,[23] the observed values will be

$$[\Delta H^G_{pp}(M_I)]^2 = [\Delta H^G_{pp}(\text{Inhom})]^2 + 4[\sigma(M_I)]^2 \qquad (26)$$

Using the value $\delta aN = -0.845$, eq 10, and the value $N = 60$, we find that

$$4[\sigma(M_I)]^2 = 4X(1-X)(0.0119)(-M_I + 0.41)^2 \qquad (27)$$

in units G^2, which reaches a maximum of 0.0237 G^2 for the high-field line ($M_I = -1$) at $X = 0.5$. Comparing this with the first term on the right-hand side of eq 26 which is $(\Delta H^G_{pp}(\text{Inhom}) = 0.851)^2 = 0.724$ G^2, shows that the additional effect of the dispersion in A_+, at its maximum point, is only about 3% of the always present first term. Most commercially available spin probes have values of ΔH^G_{pp}(Inhom) similar to 16DSE; the exceptions being small spin probes that are not useful for this type of work because they are too soluble in water. ΔH^G_{pp}(Inhom) could be reduced to ∼0.2 G by substituting deuterons for protons.[19] Then, the second term in eq 26 would reach about 50% of the first term rendering $\sigma(M_I)$ measurable.

For the most likely departures from the binomial distribution; i.e., those due to small repulsive or attractive potentials, the dispersion in A_+ would be even less than the estimate in eq 27 because these types of interactions serve to narrow the probability distribution.[31]

The dispersion in A_+ due to the variation in n in the micelles does not affect the observed EPR spectra appreciably because the entire effect is small. The line widths of the EPR spectra vary from about 1.2 to 1.6 G for $X = 0-0.3$. Note that the full extent of variation of A_+ in Figure 2 is only about 0.262 G. The effect that we are studying, the separation in the lines, is at most about 22% of the line width. The high precision in

measuring A_+ allows us to measure small effects and at the same time ignore the dispersion in A_+. For this same reason, the effect of polydispersity, here in mixed micelles and in most pure micelles, does not affect the results.

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