FT-PGSE NMR Study of Mixed Micellization of an Anionic and a Sugar-Based Nonionic Surfactant

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The interaction of a sugar-based nonionic surfactant (dodecylmalonobis(*N*-methylglucamide)) with an anionic surfactant of similar tail length (sodium dodecyl sulfate) has been studied by CORE PGSE NMR. The results show that the two surfactants mix ideally and noncooperatively and that the composition of the micelle is thus given by the initial concentrations of the two surfactants.

Introduction

In nature and many industrial and technological formulations, surfactants are often present as mixtures involving more than one type of surfactant. The surfactants in such a mixture may have distinct roles, as in, for example, cleaning and conditioning in shampoos, or may have a synergistic function. Owing to the prevalence of surfactant mixtures, such systems have been extensively studied, and some excellent review articles exist.[1,2]

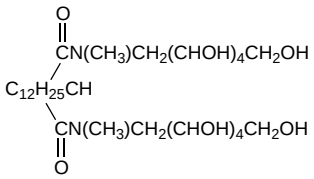
Many models for describing mixed micellization are based on equilibrium thermodynamics. The "pseudophase separation approach" treats the mixed micelle as a separate phase.[3] Although this is clearly not the case, the mixed micelle can behave like a separate phase in that it can both accept and donate unimer species. This model is widely used and incorporates the "ideal mixing model" which has been successful in describing the cmc behavior of mixed ionic and mixed nonionic surfactants.[4] In these ideal mixing situations, there is no significant interaction between the surfactant headgroups—it is merely the hydrophobic effect that determines micellization behavior. Interactions between the various surfactant headgroups lead to nonideality, and the most common model invoked in the discussion of these types of systems is that introduced by Rubingh.[5]

Generally, the onset of micellization is a cooperative process since it is more favorable for a surfactant unimer to join an existing micelle than for the same unimer to initiate the formation of a further micelle. Several surfactant unimers therefore "cooperate" in the micellization process. Noncooperative micellization is observed when the free energy of micellization is constant for all surfactant unimers present in the system.

Recently, Das *et al.*[6] have compared Rubingh's approach with the thermodynamic models proposed by Motomura *et al.*,[7] Sarmoria *et al.*,[8] and Puvvada and Blankschtein.[9] The cmc's were measured for a series of binary mixtures comprising anionic, cationic, and nonionic surfactants. The various models were successfully applied to the type of system under consideration here—a binary mixture of a nonionic and an anionic surfactant. Significant deviations from the predicted behavior were observed for the other binary mixtures, however.

Micellar systems can be studied by a variety of techniques including surface tension, light scattering, conductivity, dye solubilization, and calorimetry, to name but a few. Most of these techniques involve the measurement of the onset of micellization or the size of the micelle. There are fewer experimental measurements of the unimer concentration or micelle composition in mixed surfactant systems.

In this communication, self-diffusion results are presented for binary mixtures of sodium dodecyl sulfate (SDS) and the nonionic surfactant dodecylmalonobis(*N*-methylglucamide) (DB-NMG) shown below.



Using pulsed-field gradient NMR (PGSE NMR) data, we shown how the concentrations of both surfactants in the mixed micelle can easily be measured.

Experimental Section

Materials. Sodium dodecyl sulfate was obtained from BDH Laboratory Supplies. All solutions were made up in D_2O (Isotech, Ltd.). The nonionic surfactant obtained from Kodak European Research was used as supplied; its preparation is described in U.S. Patent 5,298,191.

NMR Experiments. The self-diffusion measurements were performed principally on a Bruker AMX300 spectrometer, but some samples were repeated on a Bruker MSL200. The experiment has been described in detail elsewhere;[10] essentially, the attenuation of the spin−echo amplitude after Fourier transformation was sampled as a function of the duration, δ, of the applied gradient pulses ($0.2 \leq \delta \leq 6.5$ ms). On both

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spectrometers, stimulated echo sequences were used in order to minimize the effects of spin−spin relaxation on the echo amplitude. Both spectrometers are equipped with Woodward gradient amplifiers[11] designed to eliminate problems associated with mismatches between successive pairs of gradient pulses.

Data Analysis. The normal procedure for measuring the self-diffusion coefficient of a species in a complex PGSE NMR data set is to isolate a peak unambiguously assignable to one component, extract the peak integral (intensity) or height, and fit the resultant exponential time decay. In some cases, the peaks are not resolvable and contain contributions from more than one component, and one must resort to fitting a double exponential to the observed time dependence. In all cases, the inherent noise in the spectra leads to a distribution of acceptable results. Given sufficient resolution or *a priori* knowledge of the systems, this is often more than adequate. However, in many cases, sufficient spectral overlap is present that the parameters resulting from fitting double exponentials to noisy data can often bear little resemblance to the "correct" solution.

The new data analysis[12] used here exploits the unique intrinsic property of PGSE NMR data sets in that **all** signals arising from the same molecule must decay with the same diffusion coefficient within their own signal-to-noise levels: a weak signal decays with the same time constant as an intense signal. Hence, there is some advantage to be gained if the two decays can be fitted simultaneously in such a way that the solution to one must also fit the other. In this work, we use the CORE analysis technique which involves consideration of **all** of the significant data (defined as those points in the spectrum with an intensity greater than some cut-off, typically chosen as 3% of the maximum peak intensity). Consequently, the number of channels to be fitted is then 1-2K for a typical 4K spectrum. Given overlapping peaks from two different molecules, the data in these 2K channels will contain to some extent the diffusion characteristics of both species. Two diffusion coefficients are therefore measured from 2K exponentials, compared to 2 exponentials in the conventional analysis. By using all of the spectral information in this manner, the error in the two diffusion coefficients can be substantially reduced. Furthermore, the 1D spectrum of each individual component can be extracted. A more detailed discussion of the CORE approach is given elsewhere.[12]

Results

Single-Surfactant Systems. The simplest model to use as a basis for understanding diffusion in micellar systems is a two-state model in which free unimer is in equilibrium with surfactant micelles.[10] Below the cmc, the free unimer diffusion coefficient is assumed to be independent of concentration. The unimer diffusion coefficient used, therefore, is generally a measured value from a system well below the cmc. The micellar species, on the other hand, are much larger and have a correspondingly lower self-diffusion coefficient.

Under these conditions, the observed surfactant self-diffusion coefficient, D_s^{obs}, is a concentration-weighted average of unimer and micellar diffusion; that is, the self-diffusion coefficient is given by

$$D_s^{obs} = \frac{D_s^{u} C_u + D_s^{m} C_m}{C_t} \qquad (1)$$

In this equation, C_u, C_m, and $C_t = C_u + C_m$ are the concentrations of surfactant in unimer form (u), in micellar form (m), and in total (t), while D_s^u and D_s^m are self-diffusion coefficients.

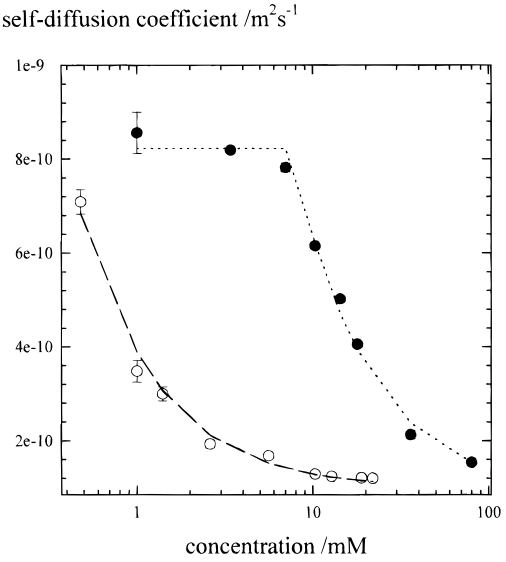

Figure 1. Concentration behavior of the surfactant self-diffusion coefficient for the single-component surfactant solutions at 44 °C: (●) SDS, (○) DBNMG.

Figure 1 shows the single-component concentration behavior of the measured self-diffusion coefficients for the two surfactants used in this study: SDS and DBNMG. Also included are the fits to the two-state mobility model. The sudden drop in the SDS self-diffusion coefficient around 7−8 mM corresponds to the cmc. The cmc for the nonionic surfactant is considerably lower (0.44 mM) and is below the range studied in these PGSE NMR experiments. From the extracted micellar diffusion coefficient, it is possible to estimate the radius of hydration, R_h, of the micelle assuming Stokes−Einstein behavior:

$$D_s = \frac{kT}{6\pi\eta R_h} \qquad (2)$$

Values of $R_h^{micelle} = 3.1(\pm 0.4)$ nm for SDS and $3.5(\pm 0.2)$ nm for DBNMG were obtained. The nonionic micelle is slightly larger than the anionic micelle, probably due to the bulky nature of the headgroup. It should be remembered that this approach ignores any nonidealities arising from inter-micelle interactions, although it is expected that these are minimal at these concentrations.

Mixed Micelle Systems. Where possible, the self-diffusion coefficients of SDS and DBNMG have been extracted by both CORE and conventional processing of the PGSE NMR data. Good agreement was found between the two data analysis methods. This agreement was less good if the weaker peaks were used in the conventional analysis to calculate the diffusion coefficients. These represent the strength of the CORE approach.

Three concentrations of nonionic surfactant have been studied, each over a range of SDS concentrations. It is assumed that the two surfactants form mixed micelles and that only one type of micelle is present. The validity of these assumptions will become apparent below. The central aim of this work is to probe the composition of the mixed micelles. A further assumption is that since the cmc of the nonionic surfactant is low, cmc = 0.44 mM, the mixed micelles will form at a comparable concentration; *i.e.*, the concentration of unimeric, nonionic surfactant is effectively zero, and the anionic surfactant merely partitions between its mixed micellar and unimeric states. At the DBNMG concentrations (9.1−25 mM) used to study the surfactant mixtures, the contribution from the unimeric DBNMG

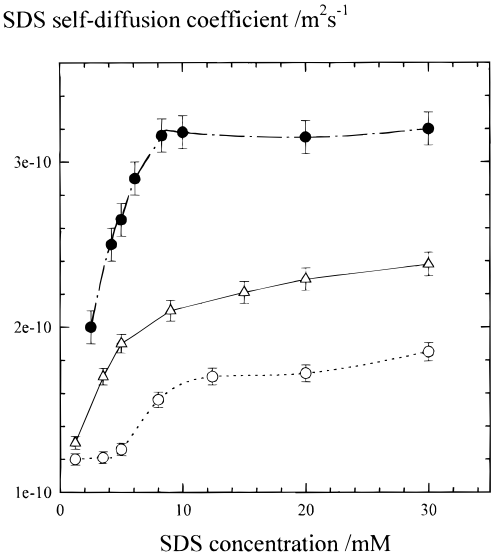

Figure 2. Behavior of the SDS self-diffusion coefficient as a function of SDS concentration at 44 °C for three DBNMG concentrations: (●) 9.1, (△) 15.0, and (○) 25.0 mM.

is negligible. Thus, the diffusion coefficient of the mixed micelle is taken to be that of DBNMG, D_s^{DBNMG}.

From the two-state mobility model (eq 1), the free SDS unimer concentration can be extracted from

$$C_u^{SDS} = \frac{D_s^{SDS} - D_s^{DBNMG}}{D_s^{u} - D_s^{DBNMG}} C_t \qquad (3)$$

where D_s^{SDS} and D_s^{DBNMG} are the measured SDS and DBNMG self-diffusion coefficients, respectively.

For all the DBNMG and SDS mixtures, the DBNMG self-diffusion coefficient is the same as that measured in the absence of SDS. Furthermore, the DBNMG self-diffusion coefficient is invariant with SDS concentration, suggesting that the inclusion of SDS into the mixed micelles does not significantly alter the size and shape of the micelles. For the higher two DBNMG concentrations, 15.0 and 25.0 mM, the DBNMG self-diffusion coefficient is slightly lower than that at 9.1 mM, consistent with the data in the absence of SDS. This suggests that the hydrodynamic size of the mixed micelle is no different from that of the larger surfactant.

Figure 2 shows the self-diffusion behavior of SDS in the same systems. There is a significant change in behavior which confirms that SDS and DBNMG are interacting. In stark contrast to the SDS-only data shown in Figure 1 where an increase in surfactant concentration caused a decrease in the SDS self-diffusion coefficient, the inclusion of DBNMG leads to an *increase* in the SDS self-diffusion coefficient with increasing SDS concentration; *i.e.*, C_u^{SDS} increases with C_t^{SDS}. This increase in C_u^{SDS} is more pronounced at lower DBNMG concentrations. Furthermore, the SDS self-diffusion coefficient when extrapolated to zero SDS concentration gives the self-diffusion coefficient of the DBNMG micelle at the respective DBNMG concentration.

With increasing DBNMG concentration, the measured SDS self-diffusion coefficient decreases because more SDS is being absorbed into the mixed micelles which have a significantly slower self-diffusion coefficient. The free SDS unimer concentration, C_u^{SDS}, extracted from the two-state mobility model is shown in Figure 3 as a function of total SDS concentration for the three nonionic surfactant concentrations. With increasing nonionic surfactant concentration, the amount of unimeric SDS

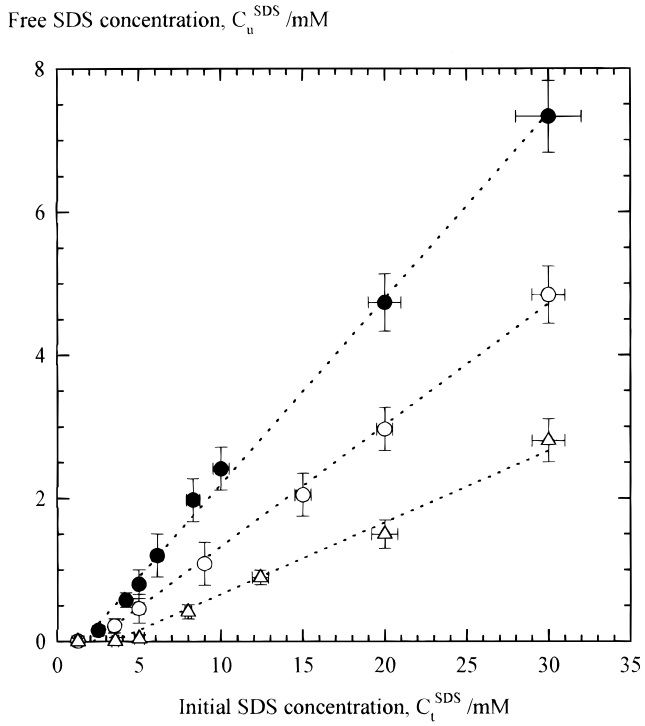

Figure 3. Free unimer SDS concentration as a function of initial SDS concentration for three different nonionic surfactant concentrations: (●) 9.1, (○) 15.0, and (△) 25.0 mM.

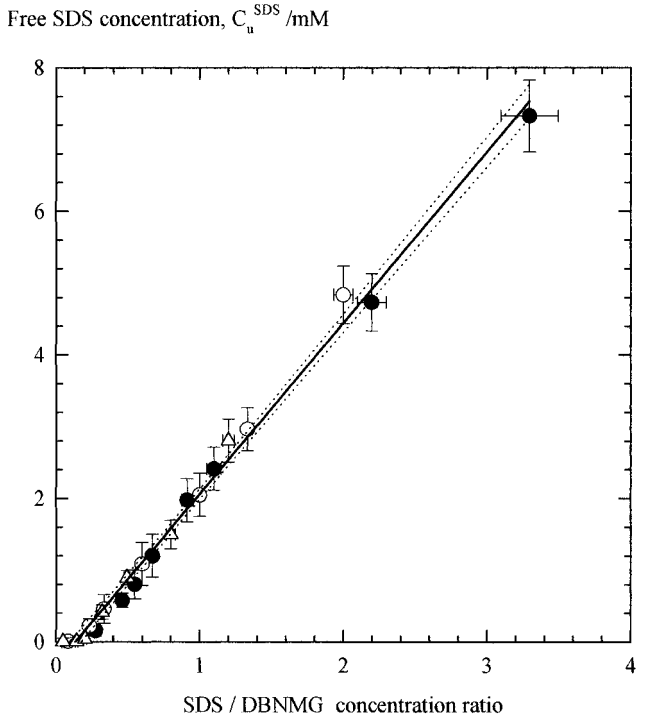

Figure 4. Free unimer SDS concentration as a function of surfactant molar concentration ratio for three different nonionic surfactant concentrations: (●) 9.1, (○) 15.0, and (△) 25.0 mM. Solid line is a linear fit to the data with a 95% confidence level (dotted lines).

decreases as expected, since it is incorporated into the mixed micelles. The linear behavior in these three sets of data suggest a simple partitioning of the SDS between the two environments.

In Figure 4, the same data have been replotted as a a function of the SDS/DBNMG molar concentration ratio and it may be seen that the data fall onto a common line. The broken line corresponds to a 95% confidence linear fit to the data (solid line). The fact that these three data sets can be normalized in

this manner confirms that the composition of the mixed micelle is determined only by the initial concentration of the two surfactants—noncooperative, ideal mixing must prevail.

Interestingly, the data do not pass exactly through the origin, as would be expected. This might be due to the fact that the initial SDS added to the system cannot be detected in the diffusion experiment due to the stronger DBNMG signal or that all the SDS is actually incorporated into the mixed micelle and, therefore, $C_u^{SDS} \approx 0$. Implicit in the CORE analysis are the nonoverlapping SDS peaks, and thus, it would appear that that latter reason is more probable; *i.e.*, $C_u^{SDS} \approx 0$. The initial mixing of SDS and DBNMG might be, therefore, cooperative—the initial SDS added is more tightly bound into the mixed micelle compared to higher SDS concentration systems. Similar behavior is observed in some hydrophobically modified polymer–surfactant systems.[13] This aspect is being pursued further.

Conclusions

SDS and DBNMG mix noncooperatively and ideally with the composition of the mixed micelle depending only on the relative magnitudes of the initial concentrations of the two surfactants. At very low molar concentration ratios of SDS/DBNMG, some cooperative binding may be occurring. Furthermore, the CORE-processed PGSE NMR data presented here show that this technique is a powerful method for probing the composition of mixed micelles.

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