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Salt Effects on Solute Exchange in Sodium Dodecyl Sulfate Micelles

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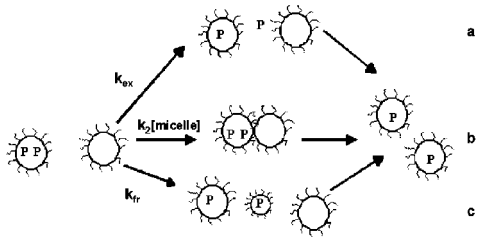
Sodium dodecyl sulfate (SDS) is one of the most important surfactants in common use. When one talks about surfactants in general or teaches students about micelle formation, SDS is almost always the first example that comes to mind. SDS self-assembles to form micelles when its concentration in water exceeds its critical micelle concentration (CMC) of 8.3 mM. Since it is an ionic surfactant, many of its micelle properties change when salts are added to its aqueous solutions. For example, the CMC decreases in the presence of salt, and the micelle size (N_{agg}) increases.[1] Chemical relaxation experiments[2−4] have shown that these micelles exhibit two relaxation times (τ_{fast}, τ_{slow}). The most important unresolved question about SDS micelles concerns the influence of salt on the slow relaxation process. The fast process involves association and dissociation of individual surfactant monomers to and from the micelles. This process can lead to a change in micelle size, while the number of micelles remains constant. Aniansson and Wall[3] attributed the slow process to relaxation of the micelle distribution through a sequence of association and dissociation events involving surfactant monomers and aggregates of surfactant molecules, including the formation and breakdown of entire micelles.

This model was modified by Kahlweit and co-workers[4] to explain the decrease of the slow relaxation rate ($1/\tau_{slow}$) with increasing sodium ion concentration up to 60 mM [Na^+]. At higher levels of salt, these authors found that a new process took over, with a rate that increased strongly with salt concentration ($1/\tau_{slow} \sim [Na^+]^y$ with $y = 6$). They attributed this new process to micelle−micelle interactions involving fusion of two micelles followed by fragmentation. The collision of two ionic micelles is opposed by the electrostatic repulsion between their surface charges. At high ionic strength, screening of the charges will reduce the Debye length. DLVO theory predicts the rate of collision between these micelles to increase as a power law, but with a much weaker exponent ($y = 2.2$). Zana et al.[2] proposed an alternative explanation, involving fragmentation of the micelles. It has not been possible to discriminate between these mechanisms.

In this paper we describe experiments that allow us to distinguish micelle fusion and micelle fragmentation events in SDS micelles. We show that under the conditions of the Kahlweit experiments, the slow rate involves not fusion but fragmentation of SDS micelles into two "submicelles" that grow back to normal micelles via condensation of free surfactant monomers. We propose a model for the spontaneous fragmentation of surfactant micelles.

Our experiments are based on fluorescence studies of solute exchange in which the solute is a water-insoluble pyrene derivative **1**, glycerol-1,2-distearate-3-pyrenebutyrate.[5] Chart 1 shows the three possible mechanisms for exchange of solutes that are solubilized by surfactant micelles. Here P refers to both a generic solute and a pyrene derivative that will give excimer fluorescence from micelles containing two P molecules. Exit−re-entry (k_{ex}) is the dominant process for exchange of most solutes.[6] In our experiments, triglyceride **1** is so insoluble that this path is suppressed. The middle path (collision−fusion−fragmentation) will exhibit kinetics second order in micelle concentration, and the lower path (fragmentation−growth, k_{fr}) will exhibit first-order kinetics. Solute exchange among micelles is itself a topic of broad importance. Hilczer et al.[7] have recently published an impressive theoretical analysis of exchange kinetics by these competing mechanisms. In our experiments, we monitor exchange by the increase in pyrene monomer intensity (I_M) at 375 nm and the decrease in excimer intensity (I_E) at 480 nm.

Chart 1. (a) Exchange via Water Mechanism, (b) Collision−Exchange−Separation Mechanism, and (c) Fragmentation−Growth Mechanism



It is not possible to dissolve **1** directly in aqueous solutions of SDS. We developed an indirect approach based on Dubin's studies[8] of SDS mixed micelles. Solutions of **1** in Triton-X 100 (TX100, 0.64 mM) were prepared containing an average of 0.44 molecule of **1** per micelle. We have previously shown that **1** behaves as a normal solute (like 1-ethylpyrene, EtPy) in these micelles.[5a] These solutions were treated with an excess of SDS (TX100/SDS < 0.005), to yield stock solutions in which there was at most one TX100 molecule per 5 SDS micelles. Upon mixing SDS with TX100, both I_E and I_M undergo rapid change (ca. 2 s) and then remain constant. Even after adding SDS, the fluorescence spectra show significant excimer emission, characteristic of a system containing micelles with two molecules of **1**. Although the micelles containing **1** coexist with excess empty SDS micelles, very little decrease in I_E is detected over a period of days to weeks, depending upon the SDS concentration. Extensive single photon timing experiments showed that, upon mixing TX100 with SDS, the environment of **1** changed from that of TX100 micelles to that characteristic of SDS micelles. When these solutions are mixed with aqueous solutions of NaCl, I_M increases at the expense of I_E (Figure 1). Both the growth of I_M and the decrease of I_E are exponential with similar rates, k_{obs}. The magnitude of k_{obs} increases from nearly 0 in the absence of salt to 10^{-1} s^{-1} at [NaCl] = 0.14 M.

In principle, either the fusion−fragmentation or the fragmentation−growth process could lead to exchange of **1** in the presence of salt. To distinguish between these mechanisms we carried out experiments in which we varied the concentration of empty SDS micelles and kept constant the concentration of added salt (Figure 1 insert, [NaCl] = 140 mM). This plot shows a strong first-order contribution to the exchange rate and a weak dependence on micelle

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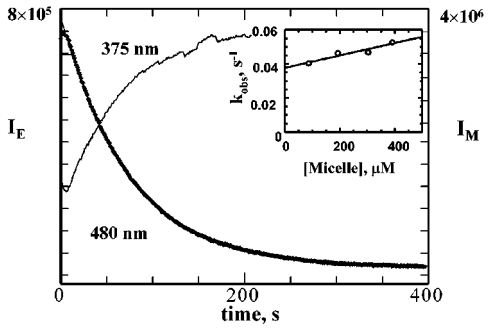

Figure 1. Time-scan experiments monitoring the increase in the monomer emission I_M (λ_{em} = 375 nm) and the decrease in the excimer emission I_E (λ_{em} = 480 nm) after mixing a solution of **1** in SDS micelles ([**1**] = 1.1 μM, [SDS] = 80 mM) with an equal volume of NaCl solution ([NaCl]] = 0.2 M) at 23 °C. Insert: The relaxation rates k_{obs} for **1** calculated from the fits of the data from individual time-scan experiments plotted vs the concentration of SDS micelles. In this experiment the concentration of NaCl is 0.14 M.

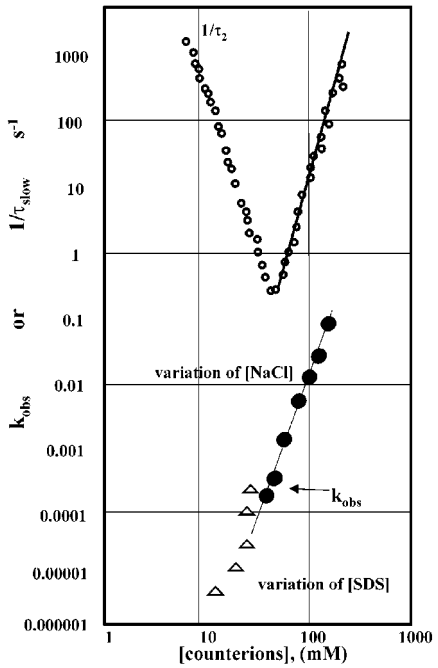

Figure 2. Log−log plot of the exchange rate of **1** in SDS against the counterion concentration, compared to the slow rate from the chemical relaxation experiment reported by Kahlweit et al. in ref 11.

concentration. This result shows that fragmentation−growth is the dominant mechanism for exchange of **1** for [NaCl] ≤ 100 mM.

We next consider the small positive slope seen in the insert of Figure 1. In this range of salt concentrations, SDS makes a significant contribution to the ionic strength of the solution. While there may be a second-order exchange process competing with fragmentation, the increase in k_{obs} may also be due to the increase in [Na^+]. In Figure 2 we plot the variation of k_{obs} with [Na^+], combining data from experiments in which SDS is the sole source of Na^+ with those in which NaCl is also present. We find a strong powerlaw dependence ($k_{obs} \sim [Na^+]^y$), with y ≈ 4. The common line for all experiments indicates that the increase in k_{obs} seen in Figure 1 is due to the increase in ionic strength and not due to micelle fusion. For comparison, we plot the data for $1/\tau_{slow}$ taken from ref 4. The $1/\tau_{slow}$ values obtained by the Kahlweit group are more than 2 orders of magnitude faster than the exchange rate monitored with **1** as a probe. Since fusion has been ruled out for the process described by k_{obs}, it is unlikely to play a role in the much faster $1/\tau_{slow}$ process.

The rate of the fragmentation process can be affected in several ways by the presence of **1**. First, a micelle bearing a strongly hydrophobic probe may fragment at an intrinsically slower rate than a normal micelle. This argument provides one explanation for the slower rates observed in our experiments than those found in the relaxation experiments. Second, the fluorescence experiment samples only a fraction of all of the fragmentation processes taking place in the system. Even if all micelles fragment at similar rates, only a fraction of the fragmentation events involving micelles carrying two probes will be successful at creating new micelles with one probe each. If one of the daughter submicelles in a fragmentation event is too small, it will be unable to transport a probe molecule. The other larger fragment will be left with both probe molecules, and this event will not be detected by a change in fluorescence. While we cannot distinguish which of these two reasons is more important, both are consistent with our finding a slower exchange rate than $1/\tau_{slow}$.

To explain how the fragmentation rate can be so sensitive to counterion concentration, we propose a mechanism for this process induced by surface fluctuations of the micelle core.[9] When the amplitude of these fluctuations is large enough, the probability of "pinching off" a subunit becomes significant. Surface fluctuations that lead to fragmentation bring headgroups into close contact. These deep fluctuations are opposed by electrostatic repulsions between adjacent headgroups. Increased counterion concentration helps to screen these interactions and thus increase the amplitude of the fluctuations and the frequency of fragmentation.

We conclude with a final word about the exit−re-entry mechanism shown in the top of Chart 1. For very slow exchange, molecules with tiny but finite water solubility can exchange via this pathway. Since salt decreases the water solubility of these probes, a signature of this pathway is a slower exchange rate at elevated salt concentrations. Corresponding experiments with 1-dodecylpyrene (C_{12}Py) exhibit faster exchange than with **1**, and with rates that decrease as [NaCl] is increased.[10] For SDS micelles, the water solubility of C_{12}Py is too large for it to serve as a probe to distinguish fusion−fragmentation from fragmentation−growth as the dominant slow micelle relaxation process.

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