

A Reinterpretation of the Hydration of Micelles of Dodecyltrimethylammonium Bromide and Chloride in Aqueous Solution

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The hydration of dodecyltrimethylammonium (DTAB) micelles is reinterpreted in light of the results of the companion paper (immediately preceding this paper) that showed that the location of the spin probe 16-doxylstearic acid methyl ester (16DSE) changes as a function of the aggregation number, N , of anionic micelles, i.e., that it does *not* conform to the zero-order model (ZOM). The ZOM requires that the NO^{\bullet} moiety diffuse throughout the Stern layer of the micelle and nowhere else. By using the ZOM as a working hypothesis, the previous interpretation (*J. Phys. Chem. B* 2002, 106, 1926) of 16DSE data proposed that an increasing number of alkyl chain methyl groups occupied the Stern layer as N increased. In this work, the spin probe 5-doxylstearic acid methyl ester that was found to fulfill the ZOM in anionic micelles was measured as a function of N in DTAB and was found to obey the ZOM in this cationic micelle as well. Thus, a simple model of the hydration of micelles that is successful in anionic micelles is also successful in DTAB. The previous results for 16DSE are reinterpreted here as being due to small displacements of the NO^{\bullet} moiety as a function of N .

Introduction

Two of us recently proposed a model of the hydration of dodecyltrimethylammonium bromide (DTAB) micelles employing electron paramagnetic resonance (EPR) data of the spin probe 16-doxylstearic acid methyl ester (16DSE).¹ That interpretation assumed that the zero-order model (ZOM) described the average location of the nitroxide moiety (NO^{\bullet}) of 16DSE in the micelles. The ZOM, described in detail in the companion paper² immediately preceding this paper, requires that the NO^{\bullet} moiety diffuse throughout the Stern layer of the micelle and nowhere else. In the companion paper,² we showed that 16DSE does *not* conform to the ZOM in anionic micelles, prompting us to question the previous¹ assumption that the ZOM described 16DSE in DTAB. Here, we employ 5-doxylstearic acid methyl ester (5DSE) in DTAB and show that it *does* conform to the ZOM in DTAB micelles. Therefore, DTAB micelles are also described by the simple theory of hydration given in the companion paper.² Previously, we showed that DTAB and dodecyltrimethylammonium chloride (DTAC) are hydrated identically when compared at the same value of N . Apparent differences in hydration as functions of surfactant or added salt concentrations were due entirely to differences in the growth of the two micelles as functions of these concentrations.¹ Thus, we reinvestigated only DTAB here.

Experimental

The experiments and analysis were identical to those in the companion paper² employing DTAB purchased from Aldrich,

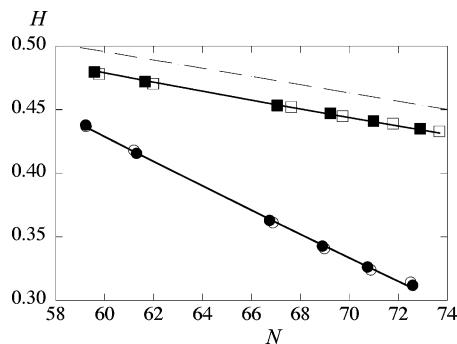


Figure 1. Volume fraction, H , of water vs aggregation number. $H_{\text{NO}^{\bullet}}$ sensed by 5DSE (\square , ■) and by 16DSE (\circ , ●) DTAB micelles, 25 °C. The solid line through the 5DSE data is H_{shell} computed from the ZOM with one parameter adjusted as described in the text. The solid line through the 16DSE data is eq 10 of the companion paper, using the solid line of Figure 2 for δ . The dashed line is the a priori estimate of $H_{\text{NO}^{\bullet}} = H_{\text{shell}}$ from SDS results, employing the same shell thickness, 5 Å, and the same $N_{\text{wet}} = 1.91$, changing only the value of $[V_{\text{hg}} + (1 - \alpha)V_{\text{ci}}]$ from 66.4 to 135 Å³ to reflect the difference in molar volumes of the constituents.

purified by recrystallization in methanol–hexane mixtures. Sodium bromide (Aldrich) was used as received. Stock 350 mM micelle solutions of DTAB containing 16DSE or 5DSE (1:350 spin probe/surfactant molar ratio) were prepared as in the companion paper.² All other samples were prepared by dilution from these stock solutions, thereby preserving the surfactant/spin probe ratio.

Results and Discussion

Figure 1 shows data taken from the previous work using 16DSE¹ (open and closed circles), and new data using a similar spin probe, 5DSE (open and closed squares). The ordinate is

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the volume fraction occupied by water, H , derived from hyperfine spacings, as detailed in the companion paper (H_{NO^*} , points) or computed from theory (lines).² See the structures of these two spin probes in the companion paper.² The open symbols correspond to zero-salt samples and closed to add-salt. Both probes report a decreasing value of H_{NO^*} versus the aggregation number, N ; however, there is a difference both in the magnitude of H_{NO^*} and the slope. Figure 1, reminiscent of Figure 4 of the companion paper,² makes clear that the ZOM cannot be correct for both 5DSE and 16DSE. We argue below, as in the companion paper,² that 5DSE does conform to the ZOM.

There is no essential difference in the hydration of anionic and cationic micelles according to the simple theory outlined in the companion paper;² thus, DTAB and sodium dodecyl sulfate (SDS) micelles, both having 12-carbon alkyl chains, differ only in the values of V_{dry} and, perhaps, the shell thickness. To emphasize the similarity, the dashed line in Figure 1 is an a priori estimate of the values of H_{shell} employing the results used to fit SDS in the companion paper.² For simplicity, we use the same shell thickness (5 Å) and the same value of $N_{wet} = 1.91$. Then we use $[V_{hg} + (1 - \alpha)V_{ci}] = 135 \text{ \AA}^3$, appropriate for DTAB¹ instead of the value 66.4 \AA^3 appropriate for SDS.² Thus, there are no further adjustable parameters in deriving the dashed line. The slope of the experimental values derived from 5DSE in DTAB is predicted by the dashed line to high precision and is only about 4% too large in absolute magnitude. A minor change in either N_{wet} or the shell thickness brings theory and experiment into agreement. Thus, the only significant difference in the hydration of SDS and DTAB is due to the different molar volumes of the headgroups and counterions; the larger constituents in DTAB force more water from the polar shell. For example, at the same aggregation number, $N = 60$, 68% and 48% of the polar shells of SDS and DTAB, respectively, are occupied by water. The solid line through the 5DSE data is the prediction from the ZOM (eqs 3–7, of companion paper²), i.e., one adjustable parameter brings the theory and experiment into agreement, no further parameters are needed to match the slope. If we take the shell thickness of the polar shell to be the same as in SDS, 5 Å, and adjust one parameter in $V_{dry} = N[V_{hg} + (1 - \alpha)V_{ci} + N_{wet}V_{CH_2}]$, we obtain $N_{wet} = 2.08$. This value is computed by taking $[V_{hg} + (1 - \alpha)V_{ci}] = 135 \text{ \AA}^3$ from estimated molar volumes¹ and the experimental value of $\alpha = 0.257$.¹ Alternatively, fixing $N_{wet} = 0$ results in $[V_{hg} + (1 - \alpha)V_{ci}] = 211 \text{ \AA}^3$. Either of these choices yields the solid line through the points for 5DSE in Figure 1; the slope of the line is not adjustable. It is interesting that, for DTAB, as was the case with the anionic micelles in the companion paper,² fixing the molar volumes to reasonable values leads to about two methylene groups (or one terminal methyl group) in the polar shell. We take the excellent agreement between theoretical prediction of H_{shell} , either the dashed or the solid line, and experiment (H_{NO^*}) for 5DSE in Figure 1 to be evidence that it satisfies the ZOM. Obviously, we do not yet have as solid a case here as in the companion paper² because other chain lengths have not yet been studied.

To account for the observed value of the slope of H_{NO^*} versus N employing 16DSE, we erroneously proposed¹ that N_{wet} increased with N in DTAB, displacing water leading to smaller

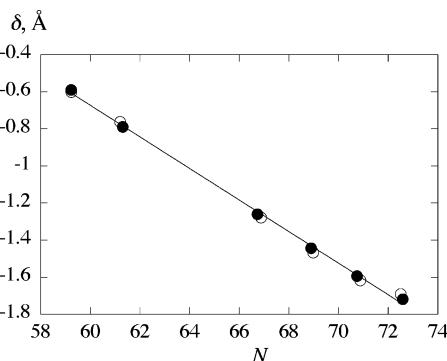


Figure 2. Displacements of the zone through which NO^* diffuses from the polar shell for 16DSE vs aggregation number for DTAB micelles, 25 °C. The solid line is a linear least-squares fit. Note that the diffusion zone for NO^* for 16DSE is always displaced toward the interior of the micelle in contrast to SDS. See Figure 4 of the companion paper.²

values of H_{NO^*} . The new 5DSE data makes it clear that the previous interpretation is in error. A simpler and more persuasive interpretation is that NO^* departs from the ZOM for 16DSE in the same manner as in the anionic SDS.² This displacement is modeled as probe I in Figure 2 of the companion paper.²

Values of δ were computed by using eqs 9 and 10 of the companion paper,² and these are presented in Figure 2. The solid and open symbols represent salt-added and zero-salt samples, respectively. The solid line is a linear least-squares fit yielding $\delta = -(0.22 \pm 0.02) - (0.085 \pm 0.001)(N - N^0)$ with units in Å, where $N^0 = 54.7$ is the aggregation number of DTAB at the cmc without added salt.¹ Figure 2 is qualitatively similar to Figures 4b and 6 of the companion paper² with the quantitative difference that NO^* for 16DSE is always displaced toward the inside the polar shell in DTAB, while it moved from outside the polar shell to inside as the anionic micelles grew. We emphasize that, even though the difference in 5DSE and 16DSE appears to be dramatic in Figure 1, they both largely occupy the polar shell, 5DSE entirely and 16DSE with 67% probability averaged from $N = 59$ to 73.

Conclusions

The hydration of cationic micelles DTAC and DTAB is described by the same simple continuum model that characterizes anionic micelles, the only difference being due to larger volumes of the headgroups and counterions. The volume fraction of water detected by 16DSE decreases faster with increasing N because NO^* is displaced approximately 1.2 Å toward the inside of the core as the micelle grows over the range $N = 59$ to 73. Over this range, NO^* resides, on average, 67% of the time inside the polar shell.

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References and Notes

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