

# Cloud Point of Aqueous Solutions of Tetrabutylammonium Dodecyl Sulfate Is a Function of the Concentration of Counterions in the Aqueous Phase

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The cloud point of the surfactant tetrabutylammonium dodecyl sulfate is shown to be a function of the tetrabutylammonium counterion concentration in the aqueous phase whether the counterions are provided by the surfactant or both the surfactant and added tetrabutylammonium bromide. The micellized surfactant dissociates 17% of its counterions to aqueous phase.

## Introduction

Clouding is a phenomenon familiar in nonionic surfactants; upon raising the temperature, the system becomes cloudy and phase-separates at a well-defined temperature,  $T_{cp}$ .<sup>1</sup> For charged micelles, the phenomenon rarely occurs, presumably because electrostatic repulsion prevents phase separation in most cases (see, however, refs 2–4 and references therein). In a recent series of papers Kumar et al.<sup>5–9</sup> have reported that adding salts with large hydrophobic cations to anionic surfactants can lead to clouding when such behavior is absent in the pure surfactants. In particular, those workers<sup>5–9</sup> have attempted to understand the fact that adding various quaternary ammonium bromides larger than tetrapropylammonium bromide to aqueous solutions of sodium dodecyl sulfate (SDS) produces the clouding phenomenon, while pure SDS shows no such behavior. Those authors succeeded in showing<sup>9</sup> that the minimum concentration of salt needed to produce a given value of  $T_{cp}$  is correlated with the concentration of SDS. One problem with the experimental design of Kumar et al.<sup>5–9</sup> is that  $Na^+$  counterions are always present in the solutions, complicating the interpretation of the dependence of  $T_{cp}$  on surfactant versus salt concentrations. The purpose of the present work is to clarify the dependence of  $T_{cp}$  on these two variables by beginning with pure tetrabutylammonium dodecyl sulfate (TBADS). We find that  $T_{cp}$  is a function of the concentration of  $TBA^+$  cations in the aqueous phase, whether the counterions are provided by

the surfactant alone or by both the surfactant and added salt, tetrabutylammonium bromide (TBABr).

## Materials and Methods

TBABr, purchased from Fluka was dried overnight in a vacuum oven at 50 °C. TBADS was prepared from a sample of purified SDS by ion exchange, on a strong cation ion-exchange resin (Merck type I). A solution of SDS [Touzart Matignon (France), crystallized twice from ethanol] at a concentration of about 5 wt % was passed through a column of resin that had been treated as follows. The resin was first washed with a solution of SDS in order to eliminate impurities soluble in the surfactant solution. Then the resin was put in the acid form by using a large excess of 7% aqueous hydrochloric acid, and rinsed until complete elimination of the excess acid. It was neutralized by tetrabutylammonium hydroxide (Fluka, purum) and rinsed with deionized water until complete removal of any remaining excess base. The capacity of the resin was at least double the amount of sodium ion (from SDS) to be exchanged. The surfactant was obtained by freeze-drying of the ion-exchanged solutions. TBADS, which is a colorless, viscous liquid at room temperature, was stored in a flask protected from ambient moisture. It remained in the same state even after several weeks at 4 °C. The TBADS surfactant did not produce ashes when calcined at high temperature, contrary to SDS, which yields sodium oxide, indicating that the exchange was quantitative; 99% given the sensitivity of the scale used to weigh the amount of TBADS to be calcined and the eventually produced ashes.<sup>10</sup>

To determine  $T_{cp}$ , clear solutions of TBADS with and without TBABr were prepared in Millipore water at ambient temperature. These solutions were placed in a thermal bath, which was slowly heated until clouding was observed visually. The relative values of  $T_{cp}$  are estimated to be reproducible to  $\pm 0.2$  °C.

The conductivity of aqueous solutions of TBADS in the absence of salt was measured as a function of concentration to determine the value of the critical micelle concentration (cmc) in the absence of salt. From these same measurements, the degree of ionization of the micelles,  $\alpha$ , was estimated by the method of Evans.<sup>11</sup> The results are given in Table 1. The aggregation numbers at the cmc,  $N^0$ , needed in Evans' method<sup>11</sup> were determined by extrapolating to the cmc the aggregation numbers obtained from time-resolved fluorescence quenching.<sup>12–16</sup> These are tabulated

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**Table 1. Values of cmc,  $\alpha$ , and  $N^0$  for TBADS Micelles**

temp, °C	$\alpha$	cmc, mM	$N^0$
10	0.19	1.3	61
25	0.17	1.1	57
40	0.17	1.15	54

in Table 1. A detailed account of these measurements and others to characterize TBADS micelles as reaction media will be reported elsewhere.<sup>17</sup>

### Theory

In a micellar solution, the concentration of counterions in the aqueous phase,  $C_{aq}$ , may be expressed as follows:

$$C_{aq} = F(C_t) \{ \alpha C_t + (1 - \alpha) C_f + C_{ad} \} \quad (1)$$

where  $C_t$  and  $C_f$  are the total and monomeric surfactant concentrations, respectively;  $C_{ad}$  is the concentration of added common counterion in the form of salt; and  $\alpha$  is the fraction of counterions dissociated from the micelles. All concentrations in this paper are given in moles per liter. The factor  $F(C_t)$ <sup>18,19</sup>

$$F(C_t) = \frac{1}{1 - VC_t} \quad (2)$$

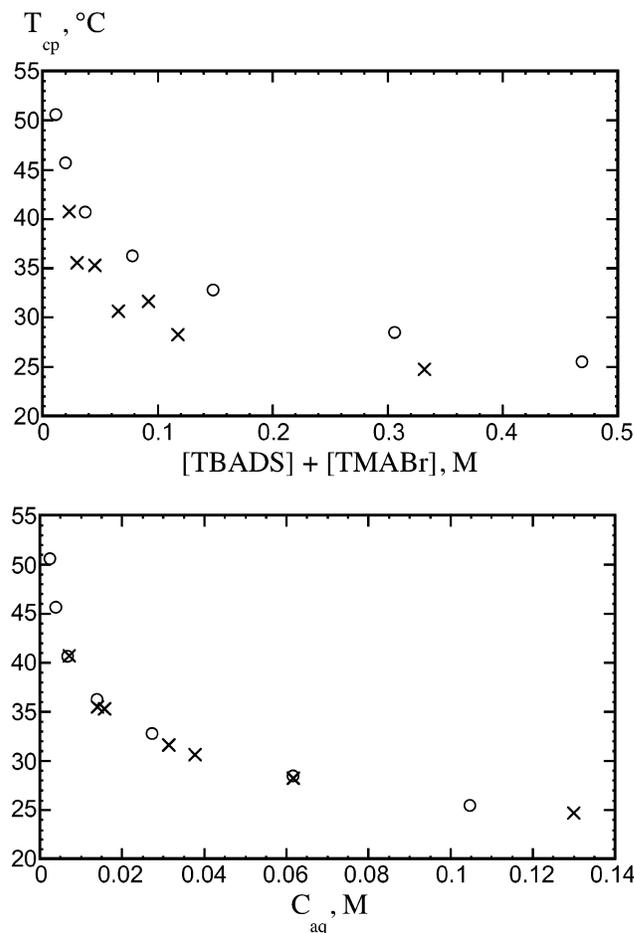
corrects the counterion concentration for the fact that they are excluded from the volume of the micelles.  $V$  is the molar volume of the anhydrous surfactant in liters per mole, with the assumption that the density of the surfactant is approximately 1.0 g/mL.<sup>18</sup> For tetrabutylammonium dodecyl sulfate (TBADS),  $V = 0.507 \text{ L mol}^{-1}$ . See recent papers<sup>19–21</sup> for detailed discussions of eqs 1 and 2. The physical content of eq 1 is that any property dependent upon  $C_{aq}$  may be varied by changing either surfactant or salt concentrations. Many combinations of  $C_t$  and  $C_{ad}$  lead to the same value of  $C_{aq}$ ; thus any property that is a function of  $C_{aq}$  will attain the same value for all of these combinations.

The purpose of this work is to show that for TBADS  $C_t$  and  $C_{ad}$  are correlated with one another by eq 1; i.e., that  $T_{cp}$  is a function of  $C_{aq}$ .

### Results and Discussion

Values of  $T_{cp}$  for TBADS in the absence and presence of TBABr are given in Table 2. Figure 1a shows these values as a function of the total concentration of TBA<sup>+</sup> for samples with and without added TBABr.  $T_{cp}$  is observed to decrease upon increasing the concentration of either TBADS or TBABr, in line with the observations of Kumar et al.<sup>5–9</sup> in the presence of Na<sup>+</sup>.

Figure 1b shows the same data as a function of  $C_{aq}$  where  $\alpha = 0.17$ , assumed to be constant, is taken from conductivity measurements, Table 1. Values of  $C_t$  in eq 1 are computed from eq 5 of ref 22 with  $\alpha = 0.17$ ; however, values of  $C_t$  are dominated by the value of cmc<sub>0</sub>, depending negligibly on the value assumed for  $\alpha$ . Figure 1b shows that the concentration of TBA<sup>+</sup> in the aqueous phase predicts the value of  $T_{cp}$ .



**Figure 1.** (Top) Cloud point as a function of the total concentration of TBA<sup>+</sup> without (○) and with (×) added TBABr. (Bottom) Same data versus the concentration of TBA<sup>+</sup> in the aqueous phase, with the assumption of 17% dissociation of counterions from the micellized surfactant.

**Table 2. Cloud Point Temperatures for TBADS**

[TBADS], mM	[TBABr], mM	$T_{cp}$ , °C
469.0	0.000	25.5
306.0	0.000	28.5
148.3	0.000	32.8
77.80	0.000	36.3
37.03	0.000	40.7
19.96	0.000	45.7
11.37	0.000	50.6
264.6	67.60	24.7
19.82	3.573	40.7
19.54	10.41	35.5
36.34	9.245	35.3
34.72	31.20	30.6
75.10	17.34	31.6
70.41	47.47	28.2

Figure 1b shows that holding  $\alpha$  constant gives a satisfactory account of the data. Assuming  $\alpha$  to be constant requires that it does not vary significantly with either concentration or temperature. Table 1 shows that  $\alpha$  determined at the cmc is indeed constant from 25 to 40 °C; i.e., the range over which values of  $T_{cp}$  for samples with and without added TBABr are made to be coincident in Figure 1. The constancy of  $\alpha$  with concentration has not yet been proved in the case of TBADS; however, for a similar surfactant, tetrabutylammonium dodecanoate, NMR self-diffusion measurements have shown that  $\alpha$  is constant, within experimental error, over a wide concen-

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tration range.<sup>23</sup> In many other cases<sup>19,21,24–27</sup> it has been found experimentally that  $\alpha$  remains nearly constant as electrolyte or surfactant concentrations are varied. In fact, to the best of our knowledge, the only well-documented cases in which  $\alpha$  varies are provoked by a severe change in shape; for example, in fluorocarbon micelles<sup>28</sup> (disklike) and in cetyltrimethylammonium bromide micelles<sup>29</sup> (rodlike). Theories based on a simple electrostatic view of the micelle surface as an example of a highly charged surface<sup>30–33</sup> have enjoyed some success because the constancy of  $\alpha$  approximately emerges naturally.<sup>30–33</sup> Thus, while it cannot be proved yet, it is a reasonable first approximation to assume a constant value of  $\alpha$  in preparing Figure 1.

It would be interesting to compare the results of Kumar et al.<sup>9</sup> with Figure 1b, but it is not yet clear how to do so. The experimental design of those workers<sup>9</sup> is such that  $\text{Na}^+$  counterions are always present in the system and the concentration of these counterions necessarily varies as the surfactant concentration is varied. One would need detailed understanding of the competition between  $\text{TBA}^+$  and  $\text{Na}^+$  for the micelle surface in order to proceed.

We do not believe that the mechanism for clouding in TBADS (or SDS + TBA) has been satisfactorily established. Kumar et al.<sup>9</sup> are of the opinion that reducing the water hydrating the micelle is responsible, but the details are not clear. That hypothesis is supported by the fact that alkylammonium counterions are quite bulky and ought to expel water from the palisade layer in the same way that bulky headgroups do.<sup>34</sup> Measurements of the water content of the palisade layer will be needed to confirm this expectation.<sup>35</sup> If indeed clouding is induced somehow by dehydrating the micelle surface, then the interpretation of the data of Kumar et al.<sup>9</sup> will be further complicated by presence of  $\text{Na}^+$  because increasing the aggregation number of a globular micelle leads to less water per surfactant.<sup>21,35</sup> This is a consequence of the fact that the surface area of a micelle grows more slowly than its volume, leading to a smaller volume per surfactant in which to fit the water.<sup>21,35</sup> Adding  $\text{Na}^+$  increases the aggregation number of SDS. Therefore, there would be two competing mechanisms to dehydrate: one by displacement of water by the counterions and another by the geometric constrictions due to micelle growth. Therefore, one would need to know the details of the micelle aggregation numbers in the presence of both  $\text{TBA}^+$  and  $\text{Na}^+$  to gain a clear understanding.

Figure 1b suggests that 17% of the counterions from the micellized surfactant are dissociated into the aqueous

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phase, meaning that the micelle remains charged by this percentage. Apparently the micelles are able to overcome electrostatic repulsion sufficiently for them to coalesce, leading to phase separation.

Note that clouding is not dependent on the concentration of micelles. For example, the two nearly coincident data points at  $T_{cp} = 35.5$  and  $35.3$  °C differ in surfactant concentrations by a factor of approximately 1.9. Interpolating between measured values of the aggregation numbers gives  $N = 70$  and  $75$  for these two samples, from which the micelle concentrations may be calculated to be 0.28 and 0.49 mM, respectively. Similarly, the surfactant concentration difference for the two nearly coincident points at  $T_{cp} = 28.5$  and  $28.2$  °C differ in surfactant concentrations by a factor of approximately 4. It may be important that  $\text{TBA}^+$  cations themselves tend to self-associate in water into ill-defined clusters with multiple charge.<sup>36–40</sup> Thus, the counterions themselves are capable of overcoming electrostatic repulsion in order to aggregate into clusters.

Kaler and co-workers<sup>4</sup> suggest that the presence of hydrophobic counterions might render the still slightly charged micelles pseudo-nonionic. See ref 4 for a good summary of thinking on the subject up until 2002. Note, however, that in the present study the micelles remain substantially charged, as indicated by the values of  $\alpha$  in Table 1.

Yu and Xu<sup>2</sup> propose a mechanism for clouding in tetrabutyl tetradecyl sulfate. They postulate that butyl chains belonging to  $\text{TBA}^+$  associated with one micelle could cross-link to another micelle helping overcome the effects of electrostatic repulsion and an energetic barrier due to oriented water near the surfaces of the two micelles. To be operative geometrically, it appears that the two micelles would have to approach one another intimately due to the limited extent of the short butyl chains.

To the previously suggested mechanisms for clouding in ionic micelles, we offer the following tentative observation. We have recently suggested<sup>10</sup> that a second layer of  $\text{TBA}^+$  is loosely attached outside the polar shell of the TBADS micelle because steric restrictions did not appear to allow enough available volume to house a sufficient number of counterions to yield the values of  $\alpha$  found in Table 1. If this second layer is in fact available, the cross-linking between micelles could take place between butyl groups of the  $\text{TBA}^+$  ions in the second layer. This possibility is supported by the tendency of  $\text{TBA}^+$  ions to self-associate.<sup>36–40</sup>

The value of  $\alpha$  determined by conductivity and used to codify the cloud points in Figure 1b could be very different from the value as defined by the aggregation number<sup>19,27</sup> through eq 1 because of the clustering mentioned above. For the present, we consider eq 1 to be a sound way to predict  $T_{cp}$  and a basis upon which to pursue studies of the phenomenon under the influence of various additives, as have been pursued by Kumar et al.<sup>9</sup> To avoid the complication of the competing  $\text{Na}^+$  counterions, these investigations should begin with pure TBADS.

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