Micelle and Surface Tension of Double-Chain Cationic Surfactants

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ABSTRACT: Since the early 20th century, the slightly disparate measurements of a surfactant’s critical micelle concentration, via either surface tension or electrical conductivity, have been assumed one and the same. As a consequence, the possibility that micelles can adsorb at the air/water surface has been disregarded and has led to some abnormalities in the literature that remain as yet unresolved. In this paper, we closely examined the two critical concentrations for a double-chain cationic surfactant. We confirmed that the two concentrations represent two different physical phenomena. Furthermore, the results verified the existence of surface micelles, which are different from the bulk micelles. The formation of the surface micelles can be explained by the structural changes of the adsorption layer, which was also corroborated by molecular simulations. The findings open new challenges to examine the surface adsorption, which offers new insights into the molecular levels.

INTRODUCTION

In surfactant studies, the critical micellization concentration (cmc) is an important measure for surfactant characterization. The cmc is often used as the effective concentration threshold for practical applications.1 In the literature, the cmc is often measured via either surface tension or electrical conductivity, these being the two oldest and simplest methods. Furthermore, these two methods can be done without additional chemical probes, which can interfere with the micellization process.2

The first method (surface tension) is based on the surface properties of the sample, whereas the second method (conductivity) is based on the properties in the bulk. The two values, denoted here as \( c_{cs} \) and \( c_{cc} \), respectively, are demonstrated in Figure 1. In both cases, the cmc is defined as the breakpoint in the measured variable with respect to concentration.

Changes in conductivity provided the first evidence of aggregate existence, which were originally thought of as the associated form of the surfactant.3 Subsequently, it was argued that the aggregates consist of multiple molecules and counterions and are referred to as “micelles”.4 It should be noted that there is a wide transition region between the two linear trends in the conductivity data. Consequently, complicated mathematical treatments can be applied instead of linear regression5 to improve the precision in identifying the breakpoint. With surface tension data, determination of the breakpoint remains almost the same as it was a century ago.1

After earlier reports with anionic surfactants,6 most studies in the literature assumed that the two measurements of the critical micelle concentration held the same physical meaning, attributing the variance in the values to artifacts of the measurement method. This assumption allowed surfactant studies to be significantly simplified. The main consequences can be found in the hypotheses in now-common texts:

1) Surface activity (or surface tension reduction) is governed by the monomer only, not aggregates/micelles.1
2) The saturation of the surface layer corresponds to interfacial saturation of the monomer. All excessive surfactant molecules form micelles and do not affect the surface layer.7
3) These same arguments apply equally to oil/water and solid/water interfaces.

In summary, if the two concentrations \( (c_{cs} \text{ and } c_{cc}) \) are the same, it follows that micelles have no impact on the surface layer. Yet, this assumption has not been verified. Seven decades ago, Lottermoser and Stoll proposed that micelles can quantitatively interact with the adsorbed monomer and affect the surface tension.8 Subsequently, Powney and Addison6

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argued that micelles may indirectly affect surface tension by increasing the concentration of the free counterions (as micelles are not neutrally charged and their balancing counterions remains dissociated in the bulk). Later on, Israelachvili has showed theoretically that "hemimicelles" can exist at the air/water interface.7 Recent studies on adsorbed surfactants at the air/water surface have indicated that micelles can cause a deviation between the obtained adsorption and the theoretical prediction from the Gibbs adsorption equation, occurring at as low as 80% of cmc.18 Our previous tension model also demonstrated the failure of the conventional model near the cmc.11 More recently, Rusanov looked closely at the surface tension near cmc of cationic and nonionic surfactants and concluded that the micelles can slightly reduce surface tension above cmc.12 Collectively, the available reports suggested that micelles have a certain impact on the surface tension above cmc. Yet, under what conditions will micelles start interacting with surface tension? Furthermore, is there any quantitative evidence of such an impact?

This short paper addresses the above two questions. First, we re-examine the reported data for cmc measurement of common cationic surfactants. Subsequently, we present evidence that the two values are not the same. More importantly, we confirm the measurable impact of micelles on surface tension. Finally, the consequences, in both fundamental knowledge and practical application, are discussed.

### ANALYSIS

While the last century has seen many reports in the literature of discrepancies in the cmc measured by different methods, the difference could be caused by impurities or measurement errors. Hence, we only list the studies in which both reported values were obtained from the same sample (Table 1). The two values are denoted as cc (from surface tension measurement) and cs (from conductivity measurement). Because the reported cmc for all ionic surfactant are enormous (Rosen has compiled a long table of 16 pages),7 we will restrict ourselves to the cationic surfactants with trimethyl ammonium as the head group. It should be noted that the results in Table 1 were obtained within the last 20 years and employed the latest apparatuses.

Statistically, the reported values cannot confirm the hypothesis that cc = cs. The most profound difference was reported by Menger and Shi, in which cc was 10 times higher than cs.17 The result subsequently led to the debate on the applications of the Gibbs excess adsorption and surface tension.18 It is noteworthy that this large deviation (Figure 1b) was obtained for the mixture of C12H25(CH3)3NBr and a trianionic compound, rather than a single surfactant.

In this paper, we confirm the difference with another cationic surfactant, a double-chain surfactant with dimethylammonium as the head group. This class of surfactants has two distinct breakpoints in surface tension.16,19 The synthesis and measurement of the surfactant hexadecyltrimethylammonium bromide, C16H33C12H25(CH3)2NBr, are described in the Supporting Information. In addition to the surface tension and conductivity measurements, a simulation of the surfactant at the air/water interface was also carried out. The results (Figure 2a) clearly show two critical concentrations from surface tension, consistent with previous reports.19 With conductivity results (Figure 2b), it is clear that cc1 < cc < cc2. The relative differences between these critical concentrations were more than three times. An analysis with symmetric double-chain surfactant, C12H25C12H25(CH3)2NCl,20 also indicated that cc was ~3cc1 (whereas cc2 was non-detectable).

The reduction of surface tension between cc1 and cc2 indicates that the aggregate(s) have a quantifiable effect on the surface tension. Here, we propose a possible mechanism, as illustrated in Figure 3: the formation of surface micellization. In this instance, surface micelles are formed when monomers from the bulk aggregate together with surfactant molecules on the surface. The micelles should have an asymmetric shape, such as a "hemisphere", as predicted theoretically by Israelachvili.9 The existence of "hemimicelles" on solid surfaces has been well-accepted21 and directly observed well below the cc.22 At the air/water surface, the surface micelles reduce surface tension by re-arranging the surfactant monolayer. Because of the steric repulsion between the two tails, adsorbed
monolayer of the surfactants have a looser packing, in comparison with single-chain surfactants. The notion that both tails of the surfactant are pointing to air phase was originated from the molecular simulation (Figure 4). It can be seen that the ends of both (CH$_3$− group) are clearly in the air/phase, ∼0.5 nm from the Gibbs dividing plane. As a result of the looser packing, the surface tension of double-tailed surfactant is higher than that of the single-tailed surfactant. Experimentally, the surface tension of C$_{16}$H$_{33}$C$_{12}$H$_{25}$(CH$_3$)$_2$NBr at $c_{c1}$ (Figure 2a) was 40 mN/m, which is ∼7 mN/m higher than the surface tension at the cmc of C$_{16}$TAB. Unfortunately, we cannot simulate the surface micelle formation because of the limited computing capacity. It has been verified that the simulation of bulk aggregates would require a timescale of 50 ns and simulation cell of more than 5 nm. For the surface micelles, the simulation box and time would be much larger to correctly simulate the unfolding of the carbon chains and fluctuation of the surface.

Previously, it has been proposed that the bulk micelles of double-tailed surfactants could consist of a combination of different size, from dimers and trimers to large bilayer vesicles. Hence, one might expect that the surface micelles can exist in a range of different size as well. Qualitatively, there is a key difference between the surface and bulk micelles. The bulk micelles of double-chains surfactants can contain both tails, especially when the second tail is longer than six carbons. In contrast, the adsorbed monolayer acts as “seeds” to lower the required entropy for aggregation. The relative ease between surface/bulk micelle formation is similar to heterogeneous/homogeneous nucleation. The surface micelles reach saturation at $c_{c2}$ above which all excessive surfactants form bulk micelles.

**DISCUSSION AND CONCLUSION**

The critical insight from this double-tailed surfactant is that the impact of micelles on surface tension can be significant enough to be measurable. The tension difference between $c_{c1}$ and $c_{c2}$ was more than 15 mN/m. On the other hand, the reduction of single-chain C$_{12}$TAB micelles was about 0.5 mN/m, which is in same order of the measurement errors. The difference was systematically observed for a large number double-chain surfactants with long hydrophobic tails. The second tail of the surfactant clearly plays a critical role in the surface aggregation and surface tension reduction. As this branch gets shortened, the tension difference between $c_{c1}$ and $c_{c2}$ is gradually diminished. Eventually, the surfactant is reduced to C$_{16}$TAB and the impact of micelles on surface tension becomes unobservable. Nevertheless, the micelles of C$_{16}$TAB can still affect the adsorbed surfactants at the surface, as reported via neutron reflectometry. The reduction was also smaller when the longer chain was reduced from 16 to 14 or 12 carbons. For these double-chain surfactants, $c_{c2}$ is the true threshold for surface saturation, which comprises a multilayer arrangement. While the available experimental techniques might not be able

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**Figure 2.** Surface tension (a) and conductivity (b) of hexadecyldimethyldodecyl ammonium bromide. Critical concentrations: $c_{c1} = 3.1 \times 10^{-6}$ M, $c_{c2} = 1.1 \times 10^{-4}$ M and $c_{cc} = 3.9 \times 10^{-5}$ M.

**Figure 3.** Proposed mechanisms of micelles/surface tension interaction: “surface micelle” and “adsorbed micelle”. The shaded areas represent the “hydrophobic core” of the micelles.

**Figure 4.** Density distribution of double-tailed surfactant at air/water interface, the Gibbs dividing plane was determined from water profile.
to distinguish the surface micelles, one might rely on the theoretical model or simulation. There are a number of mathematical formulae to model the gradual tension reduction by the surface micelles. For example, one of the possibilities is the theoretical combination of mass action law and Gibbs adsorption equation. Furthermore, the formation/adsorption of the surface micelles can be further examined by extending the molecular simulations.

The observation can be expected with other surfactant types of double-chain surfactants, either anionic or nonionic ones. Furthermore, the phenomena can be applicable to the famous double-chain surfactants, either anionic or nonionic ones.

Most importantly, the two measured critical concentrations correspond explicitly to different physical phenomena. To account for the different physical concomitants, the surface tension and the Gibbs equation to determine Surface Excesses of Cationic Surfactants. Langmuir 2014, 30, 6739–6747.

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