



Explaining the growth behavior of surfactant micelles



L. Magnus Bergström*

KTH Royal Institute of Technology, School of Chemical Science and Engineering, Department of Chemistry, Surface and Corrosion Science, SE-10044 Stockholm, Sweden

ARTICLE INFO

Article history:

Received 11 August 2014

Accepted 18 October 2014

Available online 4 November 2014

Keywords:

Surfactants

Micelles

Spontaneous curvature

Bending rigidity

Saddle-splay constant

Second CMC

ABSTRACT

The growth behavior of surfactant micelles has been investigated from a theoretical point of view. It is demonstrated that predictions deduced from the spherocylindrical micelle model, which considers micelles that are only able to grow in the length direction, are inconsistent with experimental measurements. Accordingly, the rise in aggregation numbers above a certain concentration, roughly corresponding to the second critical micelle concentration, appears to be much stronger than predicted by the spherocylindrical micelle model. On the other hand, predictions deduced from the general micelle model, which considers micelles that are able to grow with respect to both width and length, show excellent agreement with experimental observations. The latter theory is based on bending elasticity and it is demonstrated that the associated three parameters spontaneous curvature, bending rigidity and saddle-splay constant may all be determined for a micellar system from experimental measurements of the aggregation number as a function of surfactant concentration. The three parameters turn out to influence the appearance of a micellar growth curve rather differently. In accordance, the location of the second cmc is mainly determined by the saddle-splay constant and the bending rigidity. The shape of the growth curve, when going from the region of weakly growing micelles at low surfactant concentrations to strongly growing micelles above the second cmc, is mainly influenced by the bending rigidity.

© 2014 Published by Elsevier Inc.

1. Introduction

Surfactant molecules spontaneously self-assemble in an aqueous solvent above a certain concentration, the critical micelle concentration (cmc), to form micelles or bilayers. One well-known feature of surfactant micelles is their ability to grow in size as a response to, among other things, increasing surfactant concentration [1,2]. The extent to which micelles grow in size may differ widely among different surfactants and surfactant mixtures depending on molecular structure of the surfactant (tail length, size of head group, charge number, length of spacer in dimeric Gemini surfactants, etc.) as well as solution properties (electrolyte concentration, surfactant composition in mixed micelles, etc.) [1,3]. From a practical point of view it is very important to understand the growth behavior of micelles since it may, to a large extent, determine macroscopic properties of surfactant solutions such as viscosity, consistency, solubilization properties, etc.

There are a number of techniques available to determine aggregation numbers of surfactant micelles of which, perhaps, the most important ones are time-resolved fluorescence quenching (TRFQ), static light scattering (SLS) and small-angle neutron and X-ray

scattering (SANS and SAXS). With these techniques the aggregation number as a function of surfactant concentration have been determined for several common surfactants and the resulting growth behaviors are found to strongly depend on chemical structure of the surfactant as well as on solution properties. The growth behaviors of the cationic surfactants dodecyl trimethyl ammonium bromide and chloride (DTAB and DTAC, respectively) [4,5] with respect to surfactant concentration have been found to be very weak. The aggregation numbers of micelles formed by the anionic surfactant sodium dodecyl sulfate (SDS) [6,7] or the cationic surfactant hexadecyl trimethylammonium bromide (CTAB) [8] have been found to increase rather weakly with surfactant concentration but yet stronger than for DTAB/DTAC. The extent of growth of both SDS [9–12] and CTAB [13] micelles is found to significantly increase upon addition of salt whereas the growth behavior of DTAB micelles only slightly depends on electrolyte concentration [10].

One illuminating investigation of the changes in growth behaviors of micelles by means of modifying the chemical structure of surfactant molecules have been carried out by Lianos et al. [4] In accordance, micelles formed by cationic surfactants of the type $C_{12}H_{25}(C_mH_{2m+1})N(CH_3)_2Br$ (abbreviated 12, m -Br) were studied with TRFQ. It was found that micelles formed by surfactants with $m = 1-4$ do not grow at all with concentration within experimental

* Fax: +46 8 20 82 84.

E-mail address: magnusbe@kth.se

errors. In contrast, the two surfactants 12, 6-Br and 12, 8-Br, *i.e.* with a longer hydrocarbon chain attached to the quaternary amine head group, exhibit completely different growth behaviors. In accordance, both surfactants were observed to grow weakly at low surfactant concentrations followed by a much stronger growth behavior beyond a certain surfactant concentration. Such a more or less abrupt increase in the extent of growth has been observed for several surfactant systems and the surfactant concentration where the aggregation numbers start to grow rapidly is often referred to as *the second cmc* [14–21].

Another common example of a group of surfactants that may display a second cmc is dimeric Gemini surfactants, the growth behavior of which has been found to depend on the length of the spacer group that links the two unimeric units of a Gemini surfactant. [3] In accordance, Gemini surfactants with a short spacer group have been found to grow strongly with increasing surfactant concentration whereas Gemini surfactants with a longer spacer group grow much more weakly [22–24].

In the past, the growth behavior of surfactant micelles has usually been rationalized in terms of small and strictly spherically shaped micelles that may grow in only one direction to form cylindrical rod-shaped micelles with hemi-spherical end caps, so called spherocylindrical micelles [14,19,25–30]. In accordance, the observation of a second cmc, and the transition from weakly to strongly growing micelles, has usually been interpreted as the result of a transition from spherical to rod-shaped micelles, a so called sphere-to-rod transition [31,32]. However, due to geometrical constraints, micelles can only be strictly spherically shaped below a certain aggregation number. For instance, surfactants with a tail consisting of C_{12} aliphatic chain has a maximum aggregation number $N_{max} = 56$ [33]. As a consequence, already Tartar [34], more than 50 years ago, and later on Tanford [33], realized from simple geometrical considerations that micelles formed by common surfactants, that grow rather weakly with surfactant concentration, are too large for being strictly spherical and must assume some kind of non-spherical shape. Likewise, micelles showing a second cmc, *e.g.* 12, 6-Br and 12, 8-Br [4], usually start to grow strongly in size at an aggregation number largely exceeding N_{max} , indicating that the second cmc does not correspond to a sphere-to-rod transition.

The present paper is organized as follows. In Section 2.1, the micellar growth behavior according to the conventional spherocylindrical micelle model is derived from fundamental equations based on the thermodynamics of self-assembly and it is demonstrated that the spherocylindrical micelle model is inconsistent with experimental results. In Section 2.2 we make a brief outline of the basic principles and equations behind the recently derived general micelle model [35]. This theory is based on thermodynamics of self-assembly combined with bending elasticity theory. In Section 3, we propose a completely novel approach to rationalize the growth behavior of surfactant micelles. Predictions based on the general micelle model are being compared with experimentally determined aggregation numbers and their dependence on surfactant concentration. In accordance, we are able to demonstrate that the growth behavior of ordinary surfactant micelles may be rationalized in terms of the three bending elasticity constants spontaneous curvature (H_0), bending rigidity (k_c) and saddle-splay constant (\bar{k}_c).

2. Methods

2.1. The growth behavior of spherocylindrical micelles

2.1.1. Thermodynamics of self-assembly and the size distribution of micelles

The process of self-assembling surfactant molecules to form micelles is unfavorable from an entropy of mixing point of view

and always imposes a driving force endeavoring to dissociate surfactant self-assemblies and favoring small aggregates. Moreover, it is possible to demonstrate from straightforward thermodynamic arguments that the driving force for micelles becoming smaller in size increases with decreasing free surfactant concentration [36]. As a result, the entropic driving force of dissociating micelles must increase with decreasing total surfactant concentration giving rise to the important property of micelles growing in size with increasing surfactant concentration.

The growth behavior of micelles with a minimum aggregation number N_s may be rationalized from the following completely general expression for the size distribution of surfactant micelles [25,37]

$$\phi_{mic} = \int_{N_s}^{\infty} e^{-E(N)/kT} dN = \int_{N_s}^{\infty} \phi_{free}^N e^{-N\Delta\mu_{mic}/kT} dN \quad (1)$$

k is Boltzmann's constant, T is the absolute temperature and ϕ_{mic} and ϕ_{free} are the concentrations of surfactant aggregated in micelles and free surfactant, respectively. $\Delta\mu_{mic}$ denotes the “interaction” free energy per molecule of forming a micelle and $E(N) \equiv N(\Delta\mu_{mic} - kT \ln \phi_{free})$ is the free energy of forming a single micelle out of N surfactant free monomers. More details including the full derivation of Eq. (1) is provided in the [Supplementary Material](#).

2.1.2. The spherocylindrical micelle

In Eq. (1), we have denoted quantities related to concentrations ϕ_{free} and ϕ_{mic} , where ϕ stands for volume fraction. The use of volume fraction rather than mole fraction in the logarithmic terms in expressions for the entropy of mixing particles or molecules with different sizes is well established and was derived independently by Flory and Huggins for case of polymeric molecules dispersed in a solvent of small molecules [38–40]. The Flory–Huggins derivation treats the macromolecules as flexible species but the expression has been demonstrated from more general arguments to also be valid for rigid particles mixed with smaller solvent molecules. For instance, based on lattice statistical mechanics Guggenheim and coworkers have derived expressions for the entropy of mixing particles of various size and shape with smaller solvent molecules [41]. For all cases treated, the expression for the free energy of mixing with volume rather than mole fraction in the logarithmic terms was obtained in the limit where the solvent is treated as a continuum medium. For the special case of solute and solvent with equal molecular volumes, the two concentration quantities become identical, volume fraction may be replaced with mole fraction, and the conventional free energy of mixing expression is recovered.

It is perhaps less known that the choice of volume or mole fraction in the expression for the free energy of mixing has a large and decisive impact on the predicted growth behavior of surfactant micelles. We may illustrate this with the example of rodlike or spherocylindrical micelles growing exclusively in the length direction. The free energy of a spherocylindrical micelle may be written as a sum of two contributions [25–27]

$$E(N)/kT = \alpha + \beta N \quad (2)$$

The free energy of forming the cylindrical part of a micelle out of free surfactants in solution (βN) is an extensive quantity that is proportional to the aggregation number, where β is the free energy per surfactant aggregated in the cylinders, whereas the free energy of forming the hemispherical end-caps out of surfactants aggregated in the cylindrical part (αkT) is constant with respect to aggregation number.

Inserting Eq. (2) in Eq. (1) gives the total volume fraction of spherocylindrical micelles

Download English Version:

<https://daneshyari.com/en/article/6997504>

Download Persian Version:

<https://daneshyari.com/article/6997504>

[Daneshyari.com](https://daneshyari.com)