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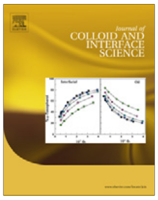

Tensiometric determination of Gibbs surface excess and micelle point: A critical revisit

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ABSTRACT

Amphiphile adsorption at the air/water interface lowers the surface tension (γ) of the solution. After a critical surfactant concentration (C), γ becomes constant (with a break in the γ–$\log C$ plot), which is considered the critical micelle concentration (CMC). At very low amphiphile concentration, γ decreases slowly, forming a plateau, then decreases sharply and often nonlinearly by a co-operative adsorption process till the second plateau is reached at CMC. To get the Gibbs surface excess (Γ) of the amphiphile relative to water, a polynomial equation of appropriate degree needs to be used, since the drop in γ progresses with continuous changing slope, which maximizes at CMC and becomes zero afterward. Recent research has evidenced that a complete saturated Gibbs monolayer may not always form at CMC; there may be formation of multilayer of micelles below the Gibbs monolayer, which cannot be assessed by ST measurements. A method like neutron reflectometry (NR) can evaluate the Γ beyond CMC. A procedure for determining $\Gamma_{\max}$ from tensiometric results is herein proposed. Amphiphiles do sometimes show a linear decline in γ with $\log C$ followed by a break with a plateau at CMC. There, a single slope leading to a single surface excess quantity is obtained for the Gibbs equation at all concentrations up to CMC. Possible reasons for such results are given. Current conflicting ideas and criticisms on the issue of Gibbs equation and determination of Γ and $\Gamma_{\max}$ have been addressed.

1. Introduction

Surface tension (ST) of water or air/water interfacial tension (γ) is reduced by the adsorption of surfactant at the interface, and the sigmoidal γ–log [surfactant] or $\log C$ course produces a distinct break in the plot with almost unchanged γ thereafter, which is taken as the critical micelle concentration (CMC) of the surfactant. By ST measurements and applying Gibbs adsorption equation [1], the surface excess of the surfactant (Γ) relative to the water can be estimated at any [surfactant] up to the CMC, where Γ is taken as the maximum. Gibbs equation for surface excess is

$$\Gamma = -\frac{1}{2.303nRT}\left(\frac{d\gamma}{d\log C}\right)$$

where the pre-factor, n is the number of species formed in solution by the dissociation of the surfactant (for a non-ionic candidate, $n = 1$; for uni–univalent totally dissociated ionic surfactant, $n = 2$), and R and T have their usual significance.

In the recent past [2–7], there has been debatable discussion on the meaning and applicability of the Gibbs surface excess equation, in relation to micelle formation. It has been considered that region II (Fig. 1) is saturated with the surfactant all through. Hence, this could be used to compute the characteristic value of the area per molecule of the surfactant. However, as the micelle formation is generally accepted to occur after saturation of the interface, the beginning of the region II might be assumed as the CMC point. Thus, the continuous decrease in surface tension with increase in surfactant concentration beyond the beginning of region II makes the above points highly questionable as micelles are nonsurface active. Near contemporary to the above, there has been a concept which considers near saturation of the surface in the beginning of region III (or the CMC) beyond which surfactant adsorption at the air/solution interface slowly continues [8–10]. The points that are therefore raised on the issue, and need discussion are the following:

(1) Meaning of different regions of the sigmoid, γ–$\log C$ plot, and location of the micelle forming point (CMC) in it.
(2) Requirement of surface saturation by the formation of Gibbs monolayer of amphiphile as a necessary condition for micelle formation.
(3) Analytical procedure for the evaluation of Gibbs surface excess.

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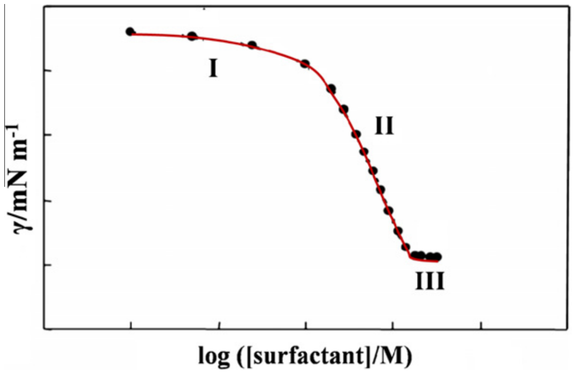

Fig. 1. A simple tensiometric profile.

(4) Explanation of frequently formed linear, non-sigmoid γ–log$C$ plots.

The above raised points demand explanation and rationalization to bring out a meaningful interrelated picture of amphiphile surface activity (adsorption, Γ and surface coverage (θ)) and bulk property (micelle formation). In this article, we intend to dwell on the subject by way of illustrations of present and past results of ours [11–13] and others [14–16] to allay the evolved misconception and confusion on the above mentioned macro picture of surfactant bearing bulk and interface system.

2. Measurements, data acquisition and analysis

In establishing our opinion, we have used data of our works [11–13] on MEGA-10, (*N*-methyl-*N*-decanoyl glucamide); C-3 (*N*-hexadecyl-*N*,*N*,*N*-tris(2-hydroxyethyl)ammonium bromide) and AOT (ethylhexyl sulfosuccinate), available in the PhD dissertations (Jadavpur University, Kolkata, India) of G. Basu Ray (2007), D. Mitra (2009), and A. Chatterjee (2001). Two sets of data of Addison and Hutchinson [14] and Mysels [15] on sodium dodecylsulfate (SDS) were also acquisitioned from literature and used. A set of data on Ionic liquid (1-[*n*-(*N*-carbazole)decyl]-3-methylimidazolium bromide) [carbazoleC$_{10}$mim][Br]) was obtained by courtesy of B. Dong of Key Laboratory of Colloid and Interface Chemistry, Shandong University, China, discussed in Ref. [16]. These surfactant molecules are essentially text book examples of non-ionic surfactant (MEGA 10) and anionic surfactants (AOT, SDS); the former produces neutral micelles, whereas the latter two form anionic micelles. We have also made fresh measurements of surface tension of cationic surfactant CTAB (cetylthrimethylammonium bromide) in our laboratory with a du Noüy tensiometer (Kruss, Germany) by the ring detachment technique (measurement details can be found in our publication) [17]. All micelles, neutral and ionic, are not surface active and hence do not affect surface tension in the post-micellar state; any change in γ after CMC ought to be the result of adsorption or desorption of surfactant monomers to or from the surface (or interface). It may be added that tensiometry is the most versatile method to probe into both bulk and interfacial properties of all types of surfactants (non-ionic and ionic). The common method of conductance has limitations; it can only probe into the solution properties of ionic surfactants. Other methods also have their specific limitations.

The collected and experimented γ values were then plotted against log$C$, and different regions in the constructed profiles were identified. For the determination of the surface excess (Γ) at any concentration, the plots were fitted to polynomial equations, and the calculated slopes at the required concentrations were used in the Gibbs equation; the slope at the CMC or micelle formation point was eventually the maximum.

3. Results and discussion

The questions presented above cropped up because of some recent (if not earlier also) thoughts on the nature of the reported sigmoid γ–log$C$ tensiometric (ST) plots [18]. We have attempted to rationalize them on the basis of experimental results, concept, and thermodynamic grounds.

3.1. Meaning of different regions of sigmoid γ–log$C$ plot, and location of the micelle point in it.

In practice, the γ–log$C$ plots for micelle forming amphiphiles are mostly sigmoid in nature. In the initial stage (region I), γ changes mildly in the region of low [amphiphile] with sparsely surfactant-populated air/water interface until the region (II) begins (Fig. 1). Thereafter, the amphiphile molecules co-operatively get populated/adsorbed at the surface (interface) with a sharp decline in γ.

The start of the region (II) is thus not the surfactant saturation point and not to be identified with CMC. From the start of this region, surfactant molecules get proficiently adsorbed at the interface consequently γ rapidly decreases: at the saturation point, surfactant monomers are hardly accommodated at the interface, and γ remains constant (or unchanged). It can be physicochemically considered that the polar or ionic head groups of surfactants at the interface remain hydrated. With increasing concentration, the available area at the interface per solvated ion or group decreases by way of competitive accommodation causing their desolvation, which in turn adds more surfactant molecules at the interface leading to the increase in concentration of the surfactant molecules at the interface and hence to the decline in γ. In this way, the interface gets significantly populated at the beginning of the region (III), after which γ does not practically change with increasing [surfactant] which, most often, is found in reports defining it to be the point of CMC (critical micelle concentration i.e., the start of micelle formation) [11–13,19,20].

Further addition of surfactant in the solution results in the increased formation of micelles, which are not surface active, and remain in the bulk. In this condition, the surfactant monomers in solution are considered to be in thermodynamic equilibrium with the micelles in one hand and with the adsorbed molecules (or ions) at the interface on the other. Also, the micelles are taken to be in equilibrium with the adsorbed molecules (or ions) at the interface. The aforesaid equilibrium concept of ours on surfactant self-aggregation and adsorption is depicted in Fig. 2. Thus, throughout the region (II), the surface excess continues to increase up to the CMC.

3.2. Requirement of surface saturation by a Gibbs monolayer of amphiphile as a necessary condition vis a vis micelle formation

Dual polar-nonpolar nature of amphiphile molecules makes them to prefer the air/water interface than the bulk water having

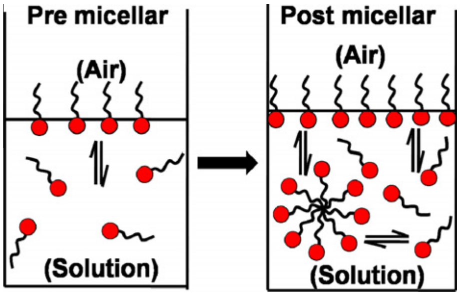

Fig. 2. Schematic representation of equilibriums at pre and post 'CMC' zones.