Colloids and Surfaces A: Physicochem. Eng. Aspects 464 (2015) 8–16

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Dwelling on the adsorption of surfactant at the air/water interface in relation to its states in the bulk: A comprehensive analysis

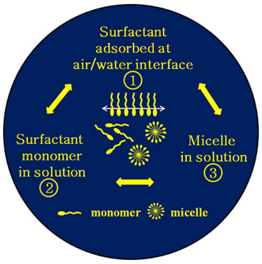
Animesh Pan[a], Animesh K. Rakshit[b], Satya P. Moulik[a,*]

[a] *Centre for Surface Science, Department of Chemistry, Jadavpur University, Kolkata 700032, India*
[b] *Indian Society for Surface Science & Technology, Department of Chemistry, Jadavpur University, Kolkata 700032, India*

HIGHLIGHTS

- Treatments of surfactant adsorption with reference to micelle formation.
- Free energy of adsorption at the interface, Traube's rationale.
- Adsorption free energy in relation to micellization, Rosen's rationale.
- Comparison between adsorption and micelle formation.
- A proposed Born–Haber type cycle for an overall correlation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 25 June 2014
Received in revised form 28 August 2014
Accepted 19 September 2014
Available online 28 September 2014

Keywords:
Surfactant
Adsorption
Micellization
Traube's rationale
Rosen and Aronson's rationale
Born–Haber cycle

ABSTRACT

The self-aggregation (micellization) of surfactants in the bulk in relation to their adsorption at the air/water interface has been analyzed and discussed. In this respect, the thermodynamic rationales of Traube, and Rosen and Aronson have been considered and analyzed at length. The first deals with adsorption at low surface pressure, the second hypothetically deals with concentration close to the critical micelle concentration having a constant surface excess and zero surface pressure. The question of possible micelle formation prior to completion of the process of adsorption has been also addressed. The standard Gibbs free energy of adsorption by Traube's method, and the method of Rosen and Aronson for ionic, non-ionic, zwitterionic, and bolaform surfactants have been evaluated: their differences have been attempted to account for and discussed. Considering a Born–Haber type cycle, the free energies of adsorption and micelle formation have been coupled together to describe the thermodynamic manifestation of the interrelated systems with a justification.

Although the standard free energy of adsorption is lower than the standard free energy of micellization, and hence it is relatively more favored, but it has been perceived that with increasing surfactant concentration (i.e., with the progress of the process), the apparent (non standard) free energy of adsorption of amphiphiles may become relatively more positive, resulting in micelle formation even before the surface saturation.

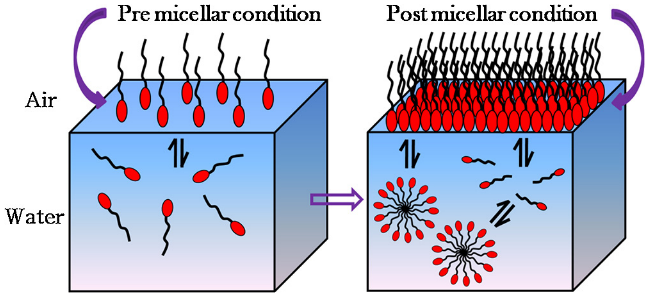
1. Introduction

Surfactants are amphiphilic molecules made up of hydrophobic tails and hydrophilic headgroups. Depending on the length of the hydrophobic chains and the nature of the hydrophilic head groups, the molecules may or may not dissolve in water. For example, stearic acid ($C_{17}H_{35}COOH$) is insoluble in water whereas its sodium

---

* Corresponding author. Tel.: +91 33 2414 6411; fax: +91 33 2414 6266.
E-mail addresses: akrakshi@yahoo.co.in (A.K. Rakshit), spmcss@yahoo.com (S.P. Moulik).

http://dx.doi.org/10.1016/j.colsurfa.2014.09.038
0927-7757/



Scheme 1. Pre- and post-micellar conditions of Surfactant in solution. Pre-micellar: A single equilibrium between bulk and unsaturated surface. Post-micellar: Three equilibria and a saturated surface.

salt, i.e., sodium stearate is soluble. The solubility depends on the relative strength of the favorable interaction of the hydrophilic group of the amphiphile and the non-favorable interaction of the hydrophobic tail with water. The stearate anion has favorable solvation effect that makes the salt well soluble in water. The insoluble acid and the soluble salt are known to form Langmuir and Gibbs monolayer, respectively at the air–water interface. The amphiphilic molecules which form Gibbs monolayer may also form self assembled units (or micelles) in the bulk of the solution, the unit's size depends on the type of the constituting molecules. Micelle formation arises from the hydrophobic effect by way of balancing the nonpolar and polar (also ionic) interactions, and it is entropy driven. The number of amphiphile molecules present at the interface and in the micelles present in the bulk solution are interrelated. It is acknowledged that formation of micelles commences on completion of the amphiphile adsorption at the air–water interface forming the Gibbs monolayer [1–3]. A detailed physicochemical discussion on the basics of the above issue with respect to the evaluation of the involved processes in a correlative manner has not been comprehensively done. A thermodynamic analysis of the problem has been herein attempted with a pictorial representation of the involved processes in the Scheme 1 [4]. It is a revisit to the issue with quantitative inputs and detailed perspectives.

To study adsorption and micellization by a single method, measurements of surface tension is a general option, although there are a good number of methods (viz., conductometry, fluorimetry, refractometry, dye solubilization, calorimetry, etc.) for the determination of the latter [5,6]. Neutron reflectometry [7] is also a potential method, but the scope of its availability is only limited. The method of tensiometry is widely available and mostly used for the study. A general description of the tensiometric results is depicted in Fig. 1.

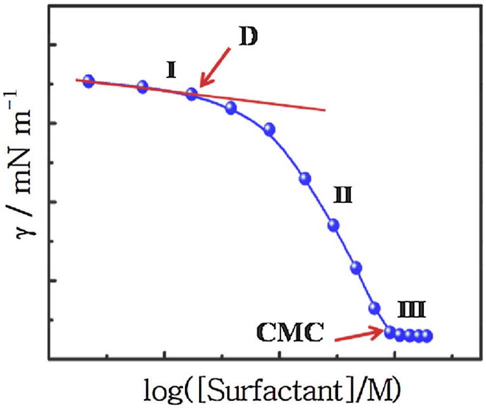


Fig. 1. Surface tension versus log [surfactant] plot in arbitrary scale. The sigmoidal curve has three distinct zones (described in the text below).

The plot of γ (surface tension) versus $\log C$ (surfactant concentration) at a constant temperature normally show three distinct regions: region I (mild decrease in γ), region II (rapid decline in γ, a co-operative process), and region III (almost unchanged or a very mild change in γ). The point of inflection or the start of the region III is called the critical micelle concentration (CMC) of the surfactant (the concentration at which surfactant assemblies, i.e., micelles begin to form). The deviation from the initial linear course to a nonlinear one (marked as D by an arrow head) in the region II is considered as the start of the co-operativity among the adsorbed surfactant molecules at the interface. The slope of the $\gamma - \log C$ isotherm thus continuously changes until the CMC point is reached. This slope is an essential and important parameter to calculate the relative surface excess of the surfactant (relative to water) at the air/water interface at concentrations $\leq$CMC using the Gibbs adsorption equation to be subsequently discussed.

Determination of the energetics of adsorption and micelle formation is physico-chemically very important for their quantification. There are different procedures for determination which are presented in current and past literatures [8–12]. Danov and Kralchevsky [11] and Janczuk et al. [12] have dwelt on it from fundamental considerations. A relation between the standard Gibbs free energy change of adsorption (ΔG^0_{ad}), and micellization (ΔG^0_M) has been proposed by Rosen and Aronson [13]. There are some reservations on the proposal's basic premises but its utility is recognized as it can explain the tensiometric results although criticisms exist [11]. The generally accepted concept of the behavior of surfactants in solution is that at the start there is adsorption of the surfactant at the air/water interface (since the process is strongly spontaneous), and because of the distribution of surfactant molecules between (a) the air/water interface and (b) the bulk solution, an equilibrium arises with the adsorbed molecules at the interface and those in the bulk. It is normally viewed that after the completion of adsorption at the air/water interface the micelle is formed in solution, in other words, $\Delta G^0_{ad} < \Delta G^0_M$ (both of negative sign as they are spontaneous). Recently, an opinion has emerged considering that the process micellization can also start before the completion of adsorption [14,15] although appropriate analytical reasons and/or rigorous experimental evidences (or favoring thermodynamic supports) are yet to be offered in its support. A recent publication has also argued against this opinion [16] supporting the existing view that micelle formation arises after the completion of the interfacial adsorption. We may herein add that if the proposition $\Delta G^0_{ad} < \Delta G^0_M$ holds, then the second does not commence until the first process is complete. But with the increased [surfactant] in solution the apparent (not standard) Gibbs free energy change of adsorption ΔG_{ad} may become $> \Delta G_M$ to make the second event to start before the completion of the first. Thus, in practice at CMC the interfacial adsorption may appear to remain incomplete.

It has been reported [7,17,18] that neutron reflectometry (NR) can determine the total surface coverage possible for a pure surfactant at the air/water interface which surface tension measurements generally underestimate. But Gurkov et al. [19] have proposed a method to determine the total surface coverage (θ) from tensiometric measurements, and opined that on the average at CMC the surface coverage is about 10% less than the actual. From a careful tensiometric study on a number of different types of surfactants [4], we have recently found that the lower surface coverage than actual at CMC could be to the extent of 20% but mostly within 10%. A procedure [4] has been suggested to compute the total surface excess (θ) values, which closely match the NR results. This shows the usability of the ST method in surface chemical research. In a recent publication, Li et al. [20] have empirically attempted to show the drawbacks of tensiometry measurements of cationic surfactants vis–vis NR method, more planned fundamental studies