

# THERMODYNAMICS OF MICELLIZATION: AN UNDERGRADUATE STUDY

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**Abstract:** Micelles are the simplest colloidal aggregates of amphiphiles with wide range of application in industrial, pharmaceutical, and biomedical fronts. Solubilization, dispersion and detergency are the most important features of micellar applications. Substrate binding and solubilization in the micelle are the primary reasons for influencing reaction kinetics, either enhanced or retarded as the case may be. Both natural and synthetic micellar system can be used as “carrier systems” for hydrophilic drug molecules. They are used in biochemical studies as a mimetic of cell membranes or to solubilize integral membrane proteins quantified by the micellar solubilization ratio, MSR. Pollutants can be solubilized by the micelles: both organic and inorganic pollutants are amenable to such conditions.

**Index Terms** – Micelle, hydrophobic, hydrophilic, double layer, counterion, critical micelle concentration.

## I. INTRODUCTION

Decades ago, McBain pointed out in a lecture to the Royal Society of London that surfactants behave strangely in water (Fuhrhop and Boettcher, 1990; Mukherjee, 1977; Columbus et al., 2006; McBain and Martin, 1914). Though he had been vehemently opposed by critics and disgracefully condemned as ‘Nonsense McBain’, today thousands of scientific publications like books, (Zana, 1986) monographs, (Tanford, 1980) review articles (Moulik, 1996; Mukherjee, 1967; Wennerstrom and Lindman, 1979) and proceedings (Mittal and Fendler, 1982) have unanimously acknowledged his proposition. Whereas dilute solution of amphiphilic molecules may be marginally different from non amphiphilic molecules, a pronounced change in both physical and chemical properties is observable at higher concentrations, beginning at a sharply definable concentration, the critical micellar concentration or cmc, characteristic of each system. A reversible spontaneous self-association of a large number of monomers, 20 to 100 in many systems, and a smaller number of counterions for ionic systems constitute a micelle, which is of colloidal dimension (2.5-6nm in diameter).

The characteristic feature that distinguishes association (or micellar) colloids from other colloids is that the former are in a state of dynamic association-dissociation equilibrium with monomeric amphiphiles in solution. This equilibrium is too rapid as compared to the time scale of most experimental methods. Physical studies have revealed that the breakdown time of micelles is in the order of 1-10 milliseconds.

## II. ON MICELLAR COMPONENTS

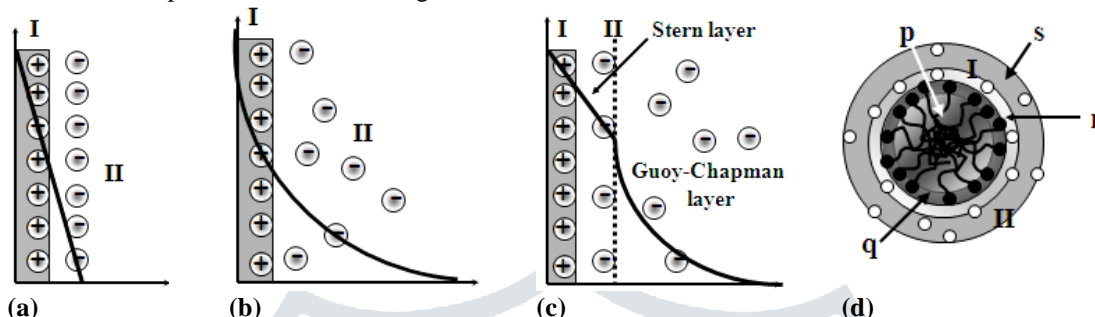
The hydrocarbon core of the micelle is probably oil-like, as per Hartley (Hartley, 1936), in view of the solubility of water insoluble or oil soluble materials in micelles or feeble water penetration up to a certain level, as per Menger (Menger et al, 1978). Traditionally, however, ‘hydrophobic interactions’ (attractive) are considered to be the major driving force for amphiphile aggregation (Evans and Miller, 1989). Since, temperature dependence of the thermodynamics of micellization in water is remarkably similar to that of the solvation of apolar compounds in water, it suggests that these processes have a common molecular origin described by the term ‘hydrophobic interactions’ (Blokzijl and Engberts, 1993). On the other hand, hydrophilic groups function as a deterrent to micelle formation (repulsive). They have a greater affinity for water molecules by an ion-induced dipole interaction for ionic surfactants and by hydrogen bonding for non ionic surfactants. Under the influence of strong electrostatic field, the nearest neighbor water molecules of an ionic group lack hydrogen bonds and become molecules of hydration.

Surfactant adsorption theories are based on a variety of surface equation of state or on different adsorption isotherms. In practice, the adsorption of ionic surfactants at the micelle-solution interface is described at three levels of approximation in literature (Overbeek and Stigter, 1956).

1. The simplest approach is the application of “pseudo non ionic” models. In this case, an adsorption isotherm derived for non ionic surfactants (e.g., Langmuir or Frumkin, discussed before) is used for the fitting of the data. They give limited physical insight due to the neglected electrostatic interactions.

2. A better approach is the use of adsorption isotherm (or equation of state) of non ionic surfactants by incorporating the electrostatic contribution in the adsorption free energy by means of Helmholtz model initially, and later by the Guoy-Chapman theory. von Helmholtz, in 1879, envisioned all the counterions as being lined up parallel to the charged surface at a distance of about one molecular diameter (Fig. 1a). The underlying concept of the Guoy-Chapman model is that the real charge distribution of the double layer is modeled by an idealized system in which the adsorbed ions form a uniformly charged adsorption layer at the interface whose charge is compensated by a diffuse cloud of point charges (Fig. 1b). The charge distribution of the diffuse layer is determined by the thermal motion of the point charges in the external electric field of the adsorption layer. In 1956, Overbeek and Stigter<sup>31</sup> analyzed the electrostatic effects involved in the formation of micelles and the charge distribution was illustrated on the basis of the non linearized

Poisson-Boltzmann equation. In order to take into account the finite size of the mobile ions, Stern proposed the introduction of a plane of closest approach. The region between the adsorption layer and the plane of closest approach is free of mobile charges (Stern-Mukerjee Layer). The head group and counterion concentrations within the Stern layer (Fig. 1c) of the micelles are considerably higher,  $\sim 1\text{-}3\text{M}$  (playing a major role in reducing the surface charge density and hence the double layer potential). This means that the theories of ionic surfactant adsorption based on the Guoy-Chapman-Stern model can differ not only on the generalized non ionic adsorption isotherm but also in the thickness, structure (counterion binding) and permittivity of the Stern layer. The limitations of the Guoy-Chapman-Stern theory originate from the arbitrary division of the real continuous charge distribution of the double layer into a compact and diffuse part, and from the neglect of the discrete nature of matter (structure and interaction) at the molecular level. However, effects like excluded volume, image forces, self atmosphere, cavity potential might cancel each other if the electrolyte concentration and the electric potential are not too large.



**Fig. 1. Model of the electrical double layer.** I represents charged surface, II represents solution phase.

*Variation of electric potential with distance from the charged surface is plotted in the y and x-axis respectively. (a) Helmholtz model; (b) Guoy-Chapman model; (c) Guoy-Chapman-Stern model; (d) typical ionic micellar model system. The outer two rings constitute the double layer; p, hydrocarbon layer, q, adsorbed surfactant molecule, r, inner Helmholtz plane, s, outer Helmholtz plane.*

3. Improvement in the modeling of the double layer has been made to accommodate counterion binding at the micellar interface. Kalinin and Radke (Kalinin and Radke, 1996) described the interface by a triple layer model, originally proposed by Grahame (Grahame, 1947). The first plane contains the adsorbed surfactant molecules. The second one (inner Helmholtz plane) contains the bound, partially dehydrated counterions, while the third plane (outer Helmholtz plane) represents the closest approach of the hydrated counterions of the diffused layer (Fig. 1d).

For non ionic surfactants, a layer (often termed as palisade layer) composed of polyoxyethylene chains to which hydrogen bonded solvent molecules are entrapped surrounds the outer region. The interfacial water concentration is substantially lower, (less than  $45\text{M}$ ), than their stoichiometric concentrations in the surrounding aqueous region ( $\sim 55\text{M}$ ) (Tada and El Seoud, 2002; Evans, 1956). Thus, the interfacial water is an integral part of the aggregate structure and is not a part of the bulk aqueous phase.

In ionic association colloids and biomembranes, a delicate balance between the cooperative (attractive) or anticooperative (repulsive) forces determines aggregate morphology. This is termed as the 'short range interaction' within the interfacial region. The physical origin of this attractive or repulsive contributions to the free energy of aggregation was clarified with explicit expressions by Nagarajan and Ruckenstein (Nagarajan and Ruckenstein, 1991). 'Long range interactions' between the charged surface and free counterions i.e., the electrical double layer, reflect the balance of thermal induced ion dissociation from the aggregate interface and electrostatic attraction between the interface and counterions. The latter does not significantly contribute to the former (Geng et al., 2005).

### III. PRE CMC ASSOCIATION

The phenomenon of appearance of aggregation at a concentration below cmc is referred to as pre micellization. Any kind of pre cmc association had already been conjectured by McBain and others a long time back (Mukerjee et al., 1958). They have reported such phenomena from conductance study, by evaluating transference number, osmotic coefficient etc of dilute surfactant solutions. Recent studies have strongly supported premicellar aggregation at concentration down to four times lower than the macroscopically determined cmc from various studies [nuclear magnetic resonance spectroscopy, ( $^1\text{H}$  NMR)] (Jiang et al., 2008).<sup>39</sup> Tensiometric profile quite different from conventional surfactant systems probably also indicates such features as reported by Moulik and co-workers on cationic systems (Mitra et al., 2006). Bile salts display an unique aggregational phenomena, as modeled by Small (Small et al., 1971). By means of hydrophobic interaction, primary micelles are formed initially, which later form large secondary micelles via polymerization in a linear fashion by means of hydrogen bonds.

### IV. THERMODYNAMICS OF MONOMER-MICELLE EQUILIBRIUM

The physicochemical features of surfactant self-assembly were elucidated by the pioneering model of Tanford (Tanford, 1974) for the free energy change associated with micellization. Aggregation is constrained by both an increase in electrostatic energy (for ionic surfactants) and a decrease in entropy. But, in reality, the transfer of a hydrocarbon from an aqueous environment at infinite dilution to a liquid hydrocarbon phase is always accompanied by a decrease in free energy followed by a positive entropy change. Ideally, two consecutive processes accounts for such an anomaly on transfer of a non polar solute from aqueous to a hydrophobic environment:

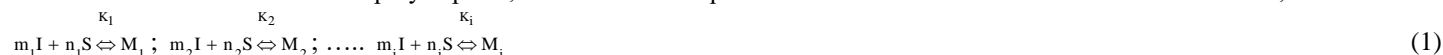
- (i) condensation of alkyl chains from dispersed monomers in solution to aggregate via hydrophobic interaction, and

(ii) release of water molecules in the vicinity of non polar solutes which are 'hydrophobically hydrated' forming 'icebergs' around the hydrophobic part of monomer, as put forward by Frank and Evans (Frank and Evans, 1945).

The former accounts for a negative entropy change, whereas a large positive entropy change of the latter played a determinant role in the overall micellar entropy change. The micelle formation of surfactants generally follows the following two models depending on whether the micelle is considered as a chemical specie or as a separate phase. The mass action model takes the former point of view (Philips, 1955), whereas the phase separation model regards micelles as a separate phase (Shinoda and Hutchinson, 1962).

#### 4.1. Mass action model

To apply the mass action model strictly, one must know every association constant over the whole stepwise association from monomer to micelle. Micelles are polydisperse, with a series of equilibria between counterion 'I' and surfactant ion 'S',



This model has the disadvantage that either monodispersity of the micelle aggregates is endorsed, or numerical values of each association constant have to be assumed. The simple association equilibrium based on assuming the formation of a monodisperse ionic or non ionic micelle with relatively small aggregation number (<100) is represented as (Mukerjee, 1972),



where 'm' is the number of counterions  $I^{\mp}$  associate with the micelle having 'n' number of  $S^{\pm}$  (amphiphile ions) to form a micelle  $M^{\pm(n-m)}$  having resultant charge  $\pm(n-m)$  signifying that  $n > m$ . For the non ionic, the case is simpler with 'n' number of S forming micelle M. From Equation 2, the micellization constant  $K_M$  or  $K'_M$  may be written as

$$K_M = a_M / a_S^n \quad \text{OR} \quad K'_M = a_{M^{\pm(n-m)}} / a_{S^{\pm}}^n a_{I^{\mp}}^m \quad (3)$$

The activity coefficient  $f_{\pm}$  below the cmc can be obtained from the extended Debye-Huckel theory, where the following equation can be used,

$$\log f_{\pm} = \frac{-A |z^+ z^-| \sqrt{\mu}}{1 + \sqrt{\mu}} + b\mu \quad (4)$$

where  $z^+$  and  $z^-$  are the ionic charges,  $\mu$  is the ionic strength of the solution,  $A$  ( $=0.5141$ ) is a constant involving dielectric constant ( $\epsilon$ ) and absolute temperature ( $T$ ) of water and  $b$  ( $=0.1 |z^+ z^-|$ ) is an adjustable parameter according to Davies (Robinson and Stokes, 1955). Intermicellar bulk phase is generally richer in counterion than surfactant ion above cmc, with a repulsive interaction between the former resulting in an increase in  $f_{\pm}$  with surfactant concentration. For dilute solutions (cmc values are usually in mM concentration), activity terms can be conveniently replaced by concentration terms in mole fraction scale. The standard state is the hypothetical state of unit mole fraction. Taking logarithmic operation on the relations, we get,

$$\Delta G_m^\circ = RT \ln X_{cmc} - (RT/n) \ln X_M \quad \text{for non ionic} \quad (5)$$

$$\text{and } \Delta G_m^\circ = RT \ln X_{cmc} + (m/n) RT \ln X_{cmc} - (RT/n) \ln X_{M^{\pm(n-m)}} \quad \text{for ionic} \quad (6)$$

where  $(m/n)$  is the fraction of counterions condensed on a micelle, and  $\Delta G_m^\circ$  is the standard Gibbs free energy change per mole of monomer unit involved in the process of micellization. In either case,  $X_S$  or  $X_{S^{\pm}}$  or  $X_{I^{\mp}}$  is taken equal to the cmc for micelles of aggregation number more than 50 (Moroi et al., 1988).

##### 4.1.1. Estimation of counterion binding ( $m/n$ )

For ionic surfactants, the electroneutrality of the solution holds following the relation,

$$C_{I^{\mp}} - C_{S^{\pm}} - (n-m)C_{M^{\pm(n-m)}} = 0 \quad (7)$$

The mass balance for surfactant ion and counterion are respectively expressed as,

$$C_t = C_{S^{\pm}} + nC_{M^{\pm(n-m)}} \quad (a)$$

$$\text{and } C_t = C_{I^{\mp}} + mC_{M^{\pm(n-m)}} \quad (b) \quad (8)$$

where  $C_t$  is the total concentration of 1-1 ionic surfactant. Replacing  $C_{M^{\pm(n-m)}}$  in Equation 8 by Equation 7, it becomes,

$$C_{S^{\pm}} = (1-n/m)C_t + (n/m)C_{I^{\mp}} \quad (a)$$

$$\text{and } C_{I^{\mp}} = (1-m/n)C_t + (m/n)C_{S^{\pm}} \quad (b) \quad (9)$$

Taking logarithm of Equation 3 one obtains,

$$\ln C_{S^{\pm}} = -(m/n) \ln C_{I^{\mp}} - (1/n) \ln K'_M + (1/n) \ln C_{M^{\pm(n-m)}} \quad (10)$$

It can be easily assumed that the term  $\ln C_{M^{\pm(n-m)}}$  is negligibly small in magnitude compared with that of  $\ln K'_M$ , as estimated by Mukerjee (Mukerjee, 1967) or Funasaki (Funasaki, 1993) to lie within ~5%. In other words, the last two terms of Equation 10 can be set constant in high accuracy to estimate  $(m/n)$  from the slope by plotting  $\ln X_{S^{\pm}} (= \ln X_{cmc})$  vs.  $\ln C_{I^{\mp}}$  (similar to Corrin-Harkins plot Corrin and Harkins, 1947). Equation 10 may be rewritten involving the Equations 9b and 8a as,

$$\ln C_{S^{\pm}} = -(m/n) \ln [(1-m/n)C_t + (m/n)C_{S^{\pm}}] - (1/n) \ln K'_M + (1/n) \ln [(C_t - C_{S^{\pm}})/n] \quad (11)$$

##### 4.1.2. Estimation of $K'_M$ .

Thus, it is worthy to have a knowledge on  $m$ ,  $n$  and  $K'_M$  for characterization of a micellar solution. But it is quite difficult to determine these three parameters precisely. Recently, Moroi et al. (Moroi et al., 1997) have developed a new approach to determine the three

micellization parameters ( $n$ ,  $m$ ,  $K'_M$ ) of SDS by combining electrical conductivity and either  $C_{s^\pm}$  or  $C_{i^\mp}$  (determined from electrometric methods). The micellization constant, on the other hand, can be derived from the definition of cmc (Israelachvili et al., 1976),

$$1/K'_M = 2n(n+m)(X_{cmc})^{n+m} \quad (12)$$

or enumerated from cmc and from either  $C_{s^\pm}$  or  $C_{i^\mp}$  (Moroi and Sakamoto, 1988).

#### 4.1.3. Estimation of other thermodynamic parameters.

Following physicochemical rationale, the second or the third term of Equations 5 and 6 respectively including the negative sign may be replaced by  $(RT/n)[\ln 2 + 2\ln n]$  and  $(RT/n)\ln[2n^2(1+m/n)]$  respectively according to Moroi's proposition (Matsuoka et al., 1993). The enthalpy and entropy changes for the process are evaluated using van't Hoff's and Gibbs equations respectively, in combination with  $\Delta G_m^\circ$  obtained by Equation 5 or 6,

$$\left[ \frac{\partial \{(\Delta G_m^\circ)/T\}}{\partial (1/T)} \right]_p = (\Delta H_m^\circ)$$

$$\text{and } \Delta S_m^\circ = (\Delta H_m^\circ - \Delta G_m^\circ)/T \quad (13)$$

#### 4.2. Phase separation model

This model is based on the assumption that

- (i) the activity of a surfactant remains constant at and above the cmc, and
- (ii) with increasing concentration above cmc, only micelles with increasing concentration are formed. In reality, electrochemical techniques measuring the activity of both surfactant ion and counterions, found activity to vary above cmc. Also the model is inconsistent with the degrees of freedom of the phase rule. If the micelle is regarded as a phase, three phases coexist above the Krafft point (discussed later)- intermicellar bulk phase, surfactant solid phase and micellar phase. Based on the phase equilibrium, monomer  $\rightleftharpoons$  micelle, at a constant temperature, chemical potential of a surfactant monomer in solution ( $\mu_s$ ) is equal to the chemical potential of the monomer in the pseudomicellar phase ( $\mu_M$ ), thus

$$\mu_s = \mu_M$$

$$\text{Or, } \mu_s^\circ + RT \ln a_s = \mu_M^\circ + RT \ln a_M \quad (14)$$

where  $\mu_s^\circ$  and  $\mu_M^\circ$  are the standard chemical potentials of monomer and micelle respectively,  $a_s$  and  $a_M$  are their corresponding activities in molarity and mole fraction scale respectively ( $a_M=1$  for the pseudophase is taken to be a pure phase). From here, we get the same expression of the Gibbs free energy as in Equation 5 or 6.<sup>23</sup>

Various other prevalent models of micellization includes that by Israelachvili, Mitchell and Ninham from thermodynamic point of view (Israelachvili et al., 1976), or models developed from the molecular effects involved in micellization<sup>36</sup> or taking into account different configurational statistics of the hydrocarbon tails (Dill and Flory, 1981), or from a host of computer models for amphiphilic self-assembly (Stephenson et al., 2006), all displaying the various critical steps involved in such an aggregation.

### VIII. CONCLUSION

Micelles are amphiphilic colloidal structures, with particle diameters from 5 to 100 nm range. Micellar amphiphilic molecules at low concentrations exist separately in aqueous medium. The aggregation of micellar molecules takes place if their concentration is increased. But aggregation of micellar molecules happens only within a limited concentration interval. The critical micelle concentration is the concentration of a monomeric micellar amphiphile at which aggregation begins and micelles appear. Mass action model and phase separation model describes the process of micellization from a theoretical point of view.

### IX. ACKNOWLEDGEMENT

The author thanks the Centre for Surface Science, Jadavpur University and the Department of Chemistry, Rishi Bankim Chandra College for the work.

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