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ORIGINAL ARTICLE

The methods of determination of critical micellar concentrations of the amphiphilic systems in aqueous medium

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Abstract Science is the attempt to make the chaotic diversity of our sense-experience to a logically unified system of thought. A sound theoretical basis and a rational physicochemical understanding based on experimental findings lead to a proper understanding of a topic. Colloid chemistry strengthened its footing by the extensive studies on gold sols by Michael Faraday in 1850s, however, the term "colloid" was coined by Thomas Graham in 1861. Historically, the Stone Age paintings in the Lascaux cave in France and the written records of Egyptian pharaohs were produced with stabilized colloid pigments. The part of colloid science dealing with amphiphilic molecules is so diverse on its own that it is dealt in a separate branch called the "association colloid". A key development in the study of association colloids was the observation by James McBain that the osmotic pressure of salts of alkali metal fatty acid displayed a pronounced break in the concentration beyond a specific characteristic concentration, after which the osmotic coefficient remained almost constant (Evans and Wennerstrom, 1994). McBain attributed this fact to the self-association of these molecules among themselves (McBain, 1913, 1944) in solution. Here, we are providing a molecular as well as thermodynamic approach toward the micellization process.

1. Introduction

Surfactants are "schizophrenic" molecules possessing discrete polar and nonpolar domains and are the building blocks of the branch of chemistry called "soft colloids". They form a class by themselves since last 100 years in the field of colloid chemistry because of their importance in technology coupled with pure academic interest. The most important property of surfactants which enables their usages in detergency, emulsion stabilization, drug-delivery vehicle, etc. is their self-aggregation in solution. Due to the simultaneous presence of lipophilic and hydrophilic parts in their chemical structure, surfactants

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exhibit interesting concentration-dependent solubilization behavior in aqueous solution. At very low concentration, they preferentially adsorb at the air/solution interface in order to avoid the energetically unfavorable interaction between its nonpolar part with the water dipole in such a fashion that the polar head groups are solvated either by the dipole-induced dipole (for nonionic surfactants) or by ion–dipole interaction (for ionic surfactants) and pertain its apolar part in the air phase; of course maintaining the distribution coefficient (K_D^1) (Fig. 1) of the surfactant monomer $[S_m]$ in bulk $[S_m^b]$ and at air/solution interface $[S_m^i]$, under the constrain $[S_m] = ([S_m^i] + [S_m^b])$. Under this situation, K_D^1 $(= ([S_m^i]/[S_m^b]))$ is very large and we can assume that the surfactants populate at the air/solution interface as a whole. With increasing $[S_m]$, both $[S_m^b]$ and $[S_m^i]$ increase to maintain the constancy of K_D^1 and ultimately a situation is reached when the air/solution interface is completely saturated with the monomeric surfactants leading to a surfactant film at the interfacial zone (the Langmuirian monolayer) and beyond this, variation in $[S_m]$ can affect $[S_m^i]$ in no way. Further increase in $[S_m]$ beyond this limiting condition leads to the formation of a separate phase comprising the self-aggregated amphiphile structures in order to maintain $[S_m^b]$ unaffected to preserve the constancy of K_D^1; then a new equilibrium between the $[S_m^b]$ and $[S_m^a]$ (surfactant concentration in monomeric state in self-aggregated phase) sets in (Fig. 1) with another distribution constant K_D^2 $(= ([S_m^a]/[S_m^b]))$.

These self-aggregated structures are in general, spherical assemblies where the apolar amphiphile tail groups are disposed within a hydrophilic shell provided by the polar head groups of the amphiphiles, and the formed species is called the micelle (Fig. 2A). Depending on the structure and physicochemical conditions, viz., temperature, presence of electrolytes, the self aggregated structures can also be cylindrical (Fig. 2B) (Hakins and Mittelmann, 1949), worm-like (Fig. 2C) (Debye and Anacker, 1951), cylindrical double layer (Debye and Annu, 1949) or disk-like (Hakins and Mittelmann, 1949). Philippoff (1951) believed that micelles consist of partially hydrated and ionized double layer. Current discussions on micelles routinely depict micelles as the hypothetical Hartley spheroidal–ellipsoidal form (Menger, 1977; Fendler and Fendler, 1975). The threshold surfactant concentration required for the self-aggregation process is called the critical micellar concentration (*cmc*).

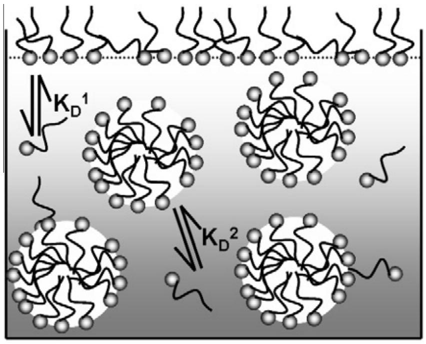

Figure 1 Schematic representation of a micellar solution and the existing equilibria.

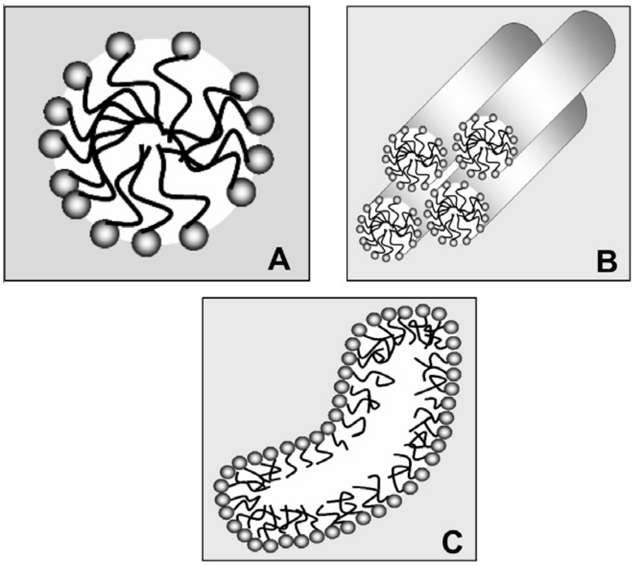

Figure 2 Concentration dependent structures of amphiphile aggregates. (A) Spherical, (B) cylindrical, and (C) worm-like micelle.

Although Hess and Gundermann (1937) reported the first X-ray diffraction pattern of soap micelle in 1937, still there exists considerable debate regarding the water penetration in the hydrophobic micellar interior. Svens and Rosenholm, in 1973, presented evidence that water permeates nearly to the center of the micelles (Svens and Rosenholm, 1973). At the other extreme, Stigter, in 1974, stated that water at the micelle surface meets a nonaqueous core at an abrupt interface; the surfactant methylenes proportional to the ionic head groups lie within this core (Stigter, 1974). These models are designated as "fjord" and "reef" model as schematically represented in Fig. 3. This feature was studied by Menger et al. (1978) using 13C NMR with chemical shift of an introduced carbonyl probe; as chemical shifts for carbonyls are solvent sensitive (Uejl and Nakamura, 1976) and its introduction perturbs the micellar structure nominally compared to other probes. Viscosity of micellar core, as observed from depolarization study of a fluorescence probe, was found to be 17–50 cP (Shinitzky et al., 1971). The micellar interior is thus liquid like, but more viscous than hydrocarbon solvents of similar chain length. Very high viscosity (151 cP) at the core of cetyltrimethylammonium bromide micelle (Pownall and Smith, 1973), however, suggested solid-like micellar interior. Intermediate schemes of Corkill et al. (1967) and Kurz (1962) revealed that the methylene groups adjacent to the ionic head group retain an aqueous atmosphere. Kresheck (1975) argued water penetration up to

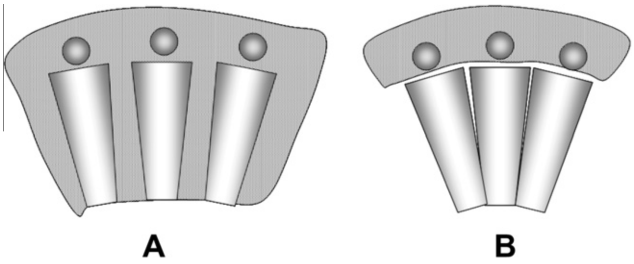

Figure 3 Schematic representation of (A) "fjord" and (B) "reef" model.

4–6 carbons adjacent to the head group. The micellar structure is, therefore, diverse in nature and strongly depends on the particular surfactant in use. This diversity entails the field ever interesting. The micelle/water interface is a zone of high free energy region and is responsible for electrokinetic phenomena, electrolytic condensation, reaction catalysis (Fendler and Fendler, 1975), etc.

Surfactants are *surf*ace *act*ive *a*gen*t*s, in the sense that they preferentially adsorb at the air/solution interface in an aqueous solution at low concentration. Water has a very high surface tension (γ) arising out of the strong cohesive interaction among the water molecules as a result of the extensive intermolecular hydrogen bonding network among themselves. On interfacial adsorption, the hydrophobic part of the surfactant monomer acts as a dielectric media (or capacitor) between the water dipoles at the interface and hence decreases the degree of hydrogen bonding among the water molecules. Addition of surfactant in water, therefore, decreases γ of the solution, and the process continues till the interface becomes saturated with the monomeric surfactant; beyond which $[S_m^i]$ does not change significantly. The tensiometric profile (γ vs. analytical concentration of the surfactant, $[S_{anal}]$) therefore decreases up to *cmc* and remains constant thereafter. Conveniently, the tensiometric profiles are γ vs. $\log[S_{anal}]$ plots, firstly, because of the convergent nature of the logarithmic function with increasing $[S_{anal}]$, and secondly, the slope of the plots has a physical significance, as will be discussed later.

Depending on the charge of the head group, conventional surfactants can be nonionic, cationic, anionic, and zwitterionic. In all amphiphiles, there exists a long hydrocarbon chain in their structure. Nonionic surfactants contain no charge on its headgroup, e.g., polyoxyethylenes and polyglycidols, sorbitans etc. The polar groups in cationic surfactants are positively charged e.g., quaternary ammonium, pyridinium and phosphonium halide salts. In anionic surfactants, the polar groups are negatively charged as in sulfates, sulfonates, phosphates and carboxylates of alkali metal ions. Zwitterionic surfactants are amphoteric in the sense that it has both anionic and cationic charges in its structure, and behaves either cationic or anionic depending on the pH of the solution. There exists some surfactants with two hydrophobic chains attached with the head group, e.g., sodium salt of dioctylsulfosuccinic acid (Aerosol OT or AOT) and didodecyltrimethylammonium bromide (DDAB).

Geminis are new generation surfactants (Menger and Keiper, 2000; Hait and Moulik, 2002) and can be considered as twin surfactants. In gemini surfactant, two hydrophobic chains are attached with two different head groups and the head groups are linked by a spacer as if two monomeric surfactants are attached by a spacer and so they are named as dimer. Because of the presence of two hydrophobic chains per monomer, they are much more surface active than conventional surfactants. There exists a great variation in the nature of the spacer (Menger et al., 2000). The spacer may be short or long methylene groups; rigid (stilbene), polar (polyether), and nonpolar (aliphatic, aromatic) groups. The ionic groups may be positive (NH_4^+) or negative (PO_4^{3-}, SO_4^{2-}, COO^-), whereas the polar groups may be polyethers or sugar moieties. Solubility of the surfactant can be tuned by judicial choice of the spacer. A hydrophilic spacer increases its solubility in aqueous solution and vice versa. Because of its enhanced surface activity, gem in is deserve special importance in recent soft-colloid research.

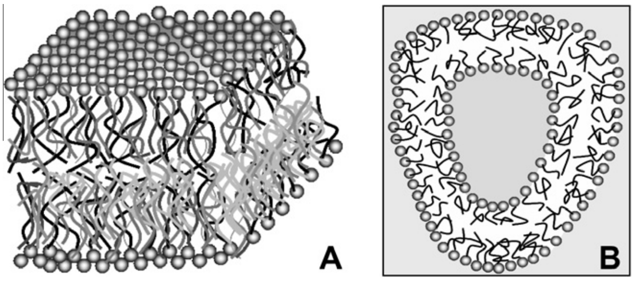

Figure 4 Schematic representation of (A) bilayer and (B) vesicle.

The micellization followed by the formation of the Langmuirian monolayer formed at the air/solution interface depends on the structure of the surfactant. If the surfactant has a very long hydrocarbon chain ($\geqslant C_{18}$), increase in $[S_{anal}]$ results in phase separation (precipitation) of the amphiphile. For surfactants with more than one hydrophobic chain like naturally occurring lipids and gemini surfactants, the amphiphile has a cylindrical symmetry, and it is impossible to pack a sphere with such cylinders. In these cases, two surfactant monomers come closer facing their hydrophobic chains one another and spans in two dimensions forming a self-assembled structure called bilayer (Fig. 4A). Synthetic surfactants like AOT, DDAB, and gemini have an affinity of formation of such bilayer structures, which mimics the biological cell membrane structure. In lung, such bilayer structure plays the key role in exchange of oxygen and carbon dioxide in blood. Such bilayer structure can bend under suitable physicochemical conditions, leading to spherical or cylindrical aggregates. Such cylindrical aggregates with water both within the pool and at the outside of the aggregates are called vesicles (Fig. 4B). Vesicles can also be unilayer or multilayer depending on the solution conditions. Vesicular structures formed by naturally occurring lipids are called liposomes and are important constituents of biological systems.

2. Micellar microstructure

The hydrophobic part inside the micellar core is oil-like. Menger (1979) proposed that water can penetrate to some extent (3–4 carbon atoms attached with the head group) as supported by NMR and fluorimetric measurements. This ‘‘porous cluster’’ model of Menger explains the difference in polarity and microviscosity of the micellar core as determined by fluorescence measurements using dyes with different polarity. The polarizability of the head group also affects the water structure near its vicinity. The layer of water in immediate contact of the head groups solvates the surfactant head groups and are strongly bound to the self-aggregated structure and has a higher polarity compared to the bulk water, considered as free.

For ionic surfactants, in addition to the above microstructure, there exists some complexity arising out of condensation of the counterions onto the micelle/solution interface driven by Coulombic electrostatic interaction. The opposite charges on the surfactant headgroup and the counterion comprise an electrical double layer. A fraction of the adsorbed counterions are strongly attracted by the surfactant head group and are located just immediate to the surfactant head groups forming the Stern layer. The following less-dense counterion environment forms the Gouy–Chapman layer and constitutes the effective electrical double layer (Fig. 5). This electrical double layer onto the micellar surface stabilizes the system through dipolar interaction and the water of solvation (of surfactant head group) adds to the stabilization.

2.1. Determination of *cmc*

The determination of *cmc* of a surfactant is essential to surface scientists and technologists. Almost all physical properties of a surfactant solution exhibit a sharp concentration dependent discontinuity in the region of self-aggregation (or micellization) as schematically shown in Fig. 6. The grey zone corresponds to phase transformation of monomeric surfactant solution to micellar solution. The applicable methods depend on the nature of the surfactant.

2.1.1. Tensiometry

A positive work required to create a unit area at the interface is defined as the surface energy, and tensional force per unit length at the interface is the surface tension (γ) by definition. Thus,

$$\gamma = \left(\delta G_{surface}/\delta A_{surface}\right)_{P,T} \tag{1}$$

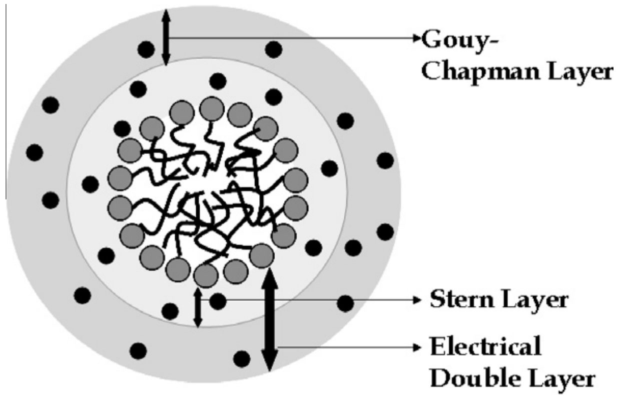

Figure 5 Schematic representation of micellar microstructure of ionic surfactant showing the electrical double layer.

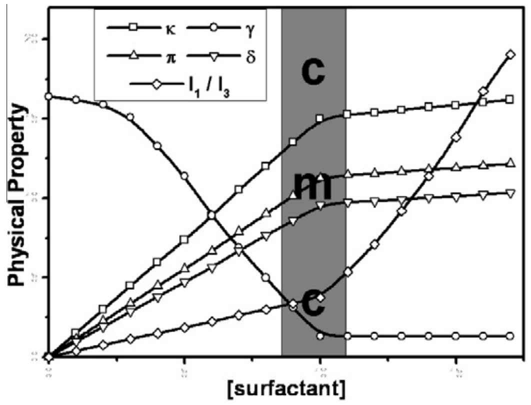

Figure 6 Determination of critical micellar concentration. Any physical property of a surfactant solution changes sharply at the onset of *cmc* formation.

where the terms G and A represent the Gibbs free energy and area, respectively. In a surfactant solution, amphiphile monomers are distributed between the interface and the bulk with an excess energy for the latter state of ΔE_{ex} following the relation:

$$\left([S^b_m]/[S^i_m]\right) = \exp(-\Delta E_{ex}/kT) \tag{2}$$

where S_m represent surfactant monomer, and superscripts i and b stand for interface and bulk, respectively.

Water has high surface tension ($\gamma = 72\,\mathrm{mN\,m^{-1}}$) arising out of strong cohesive force among the water molecules as a result of extensive intermolecular hydrogen bonding. Because of preferential adsorption of surfactant molecules, at low concentration, surfactant monomers hinder the degree of intermolecular hydrogen bonding among water molecules at the air/solution interface. This decreases the interfacial tension (γ) gradually with increasing analytical surfactant concentration till the air/solution interface becomes saturated with amphiphiles. Beyond complete interfacial saturation, surfactants self-assemble to form micelles and populate essentially the bulk phase without perturbing the interfacial rheology. The tensiometric profile (conventionally, the γ vs. $\log[S_{anal}]$) thus decreases up to complete interfacial saturation and remains unaltered thereafter. The surfactant concentration at the breakpoint means interfacial saturation and it is considered that the interfacial saturation corresponds to amphiphile self-aggregation (or micellization). The break point thus is a measure of *cmc*.

The simplest model describing the interfacial amphiphile adsorption is the Langmuir model, which assumes the adsorption of surfactant monomers at the adsorption sites with constant driving force, and there, the monomer–monomer interaction is neglected. In Frumpkin model (Hill, 1962), consideration of the lateral interaction of the adsorbed surfactant molecules by means of Bragg–Williams lattice model was introduced and this led to linear dependence of hydrophobic driving force on the surface coverage. One limitation of surface equation of state is that it is derived assuming a monolayer of disk-like molecules, which is reads orbed for a dilute surfactant monolayer but an oversimplification arises when the hydrophobic chains overlap at the adsorption layer. The Langmuir or Frumpkin model can only describe the lower and upper limits of tensiometric isotherm (Varga et al., 2007).

In some surfactants, where the hydrophobic part of the surfactant contains some hydrophilic substitution (Menger and Chelbowski, 2005; Menger and Galloway, 2004), there may be some additional complexity in the tensiometric profile at the post interfacial saturation region (Varga et al., 2007). This arises out of the change in rheology and very slight change in $[S^i_m]$. In these cases, the additional breaks in the tensiometric profiles, following the sharp break arises out of the small tilt in the surfactant at the interfacial monolayer. Due to the presence of the hydrophilic substitution in the tail, surfactants are tilted at the interfacial region (as shown in Fig. 7) and with increasing $[S_{anal}]$, the tilted monomers can subsequently orient themselves in an upright conformation to make the interface to accommodate some more surfactant molecules causing a finite decrease in γ.

In most of the earlier reports (Moulik and Ghosh, 1997; Ghosh and Moulik, 1998; Ghosh, 2001; Chakraborty et al., 2005), linear decrease in γ was observed from a very low concentration ($[S_{anal}] \sim 0$). A nonlinear decrease in γ to attain the saturation has been also reported (Ghosh and Chakraborty,

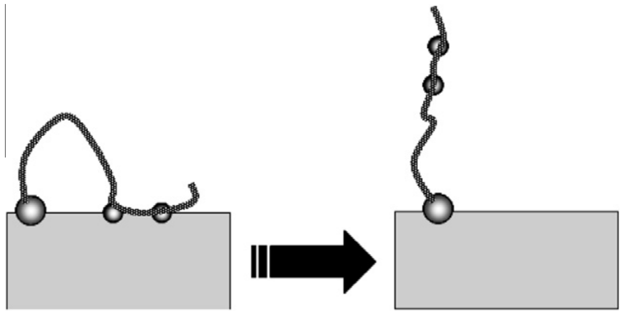

Figure 7 Schematic representation of concentration dependent conformational change at the surface saturated interfacial monolayer.

2007). The interfacial tension has been also found to remain more or less unaltered till a finite $[S_{anal}]$ region (Chakraborty and Ghosh, 2007) followed by a decreasing thereafter. Menger et al. (2005) have proposed that the presence of a few monomer at the surface can promote interfacial adsorption for other monomers, resulting in the following sharp decrease in γ. This phenomenon is often found in biological processes manifested with hydrophobicity. The critical surfactant concentration required to induce sharp decrease in γ is termed as critical monolayer concentration (c_m) (Chakraborty and Ghosh, 2007; Menger et al., 2005). The interfacial saturation and hence *cmc* corresponds to the saturation in γ value.

Some more physicochemical parameters can be calculated from the tensiometric profile between γ and $\log[S_{anal}]$. The slope of the profile $((\delta\gamma/\delta \log[S_{anal}])_{[S_{anal}]\sim cmc})$ near the point of discontinuity (*cmc*) is a measure of the efficiency of the maximum adsorption of surfactant at the air/solution interface and is given by the Gibbs adsorption equation,

$$\Gamma_{\max} = -\frac{1}{2.303nRT}[S]^{Lt}_{anal} \sim cmc(\delta\gamma/\delta \log[S]_{anal}) \tag{3}$$

where, $\Gamma_{\max}$ is the Gibbs relative surface excess, n is the total number of chemical species produced in solution per surfactant monomer, R is the universal gas constant and T is the temperature in absolute scale. The $\Gamma_{\max}$ has been defined as the excess interfacial surfactant concentration in comparison with the bulk value when the excess of the solute component is set to zero. In this rationale, the thickness of the interface has been considered negligible. Near *cmc*, the interface is almost saturated (Rosen, 1978; Osipow, 1962) to make linear dependence between γ and $\log[S_{anal}]$ to yield a constant surface excess. Area of exclusion per surfactant head group at the completely surfactant saturated air/solution interface ($A_{\min}$) follows from the relation (Rosen, 1978):

$$A_{\min} = \frac{10^{18}}{N_0\Gamma_{\max}}\ \text{nm}^2\ \text{molecule}^{-1} \tag{4}$$

where N_0 is the Avogadro number.

Another important parameter called pC_{20} (Chakraborty and Ghosh, 2007; Rosen, 1978; Rosen et al., 1999; Tsubone and Tajima, 2002; Tsubone et al., 2003; Kunieda et al., 2000; Tsubone and Ghosh, 2003, 2004) evaluated from the tensiometric profile is the efficacy of the surfactant monomer to populate the air/solution interface in the low concentration region defined as

$$pC_{20} = -\log C_{20} \tag{5}$$

where C_{20} is the $[S_{anal}]$ required to decrease the surface tension of pure solvent by 20 mN m^{-1} (i.e., $\gamma_{\mathrm{H_2O}}$ to $(\gamma_{\mathrm{H_2O}} - 20)$).

2.1.2. Conductometry

For ionic surfactants, in monomeric form (below *cmc*), the surfactants behave like a strong electrolyte and dissociate completely. The ions contribute to the electrical transport of the solution as measured by the specific conductance (κ) or equivalent conductance (Λ). In the monomeric region, κ increases sharply with increasing $[S_{anal}]$. At and above micellization, a certain fraction of the counterions condenses on the micellar interface inside the Stern layer as a result of Coulombic (electrostatic) attraction. On counterion condensation, the net number of charge carriers decreases causing decrease in the rate of increment in κ with increasing $[S_{anal}]$. Thus, the conductometric profile (κ vs. $[S_{anal}]$) has a sharp break at the point of amphiphile self-aggregation. The degree of counterion binding (denoted as f) can be calculated using the ratio of the slopes of the conductometric profile in pre and post micellar region, M_1 and M_2, respectively, using the equation (Evans et al., 1984; Lianos et al., 1984)

$$F = (1 - M_2/M_1) \tag{6}$$

Degree of counterion condensation (f) can also be evaluated from Evans equation (Evans et al., 1984),

$$1000M_2 = \frac{(N-m)^2}{N^{4/3}}(1000M_1 - \lambda_C) + \frac{(N-m)}{N}\lambda_C \tag{7}$$

with "N" being the aggregation number of a micelle with "m" number of counterions condensing per micelle and λ_C is the equivalent conductance of the counterion, where $f = m/N$.

2.1.3. Fluorescence spectroscopy

There is a considerable change in the absorption and emission spectra of an organic dye depending on the neighboring environment that affects the electronic spectra of the dye. The choice of dye plays an important role in determining *cmc* of the surfactant. Generally, water-insoluble dye is used in determination of *cmc* such that the distribution coefficient ($K_d = (D_C/D_W)$) of the dye between the micellar core (D_C) and the aqueous phase (D_W) is sufficiently large. In pre-micellar stage, the dye accommodates itself in a polar environment of water and beyond micellization, the dye partitions itself between the aqueous and hydrocarbon-like micellar core.

The commonly used dye in the study of micellization is pyrene, which shows significant fine structured emission spectrum (vibronic bands). In absence of any solvent–solute interaction (either individually or collectively), the relative intensities of these vibronic bands in the fluorescence spectrum are governed, as in UV absorption spectra, by the relative positions of the potential energy surfaces of the excited singlet states relative to the ground singlet state and by the Franck–Condon principle. The solvent-dependent vibronic band intensities of pyrene were firstly studied by Nakajima (1971, 1974, 1976). The intensities of various vibronic bands were found to show a strong dependence on the solvent environment. In presence of polar solvents, there is an enhancement in intensity of the 0–0 band at the expense of others. The UV absorption and fluorescence of pyrene undergo perturbation in intensities due to vibronic coupling (Nakajima, 1971, 1974). Though the intensity enhancement of forbidden vibronic bands were found to be due to solute–solvent interactions, no conclusions could be drawn to the extra mechanisms involved in the above solute–solvent interaction. Both solvent dipole moment and dielectric constants were found to be important in these effects. The major contributions to vibronic band intensities are from specific solute–solvent dipole–dipole coupling, although other effects due to π-orbital interactions between solute and solvent and bulk dielectric constant cannot be neglected (Kalyansundaram and Thomas, 1977). Pyrene has five predominant peaks in the fluorescence spectrum at 372 (0–0), 379, 383, 388, and 393 nm (Kalyansundaram and Thomas, 1977). Conveniently, the peak intensities are normalized with respect to the 0–0 peak. Since the intensity of the peak at 383 nm (I_{III}) is the most sensitive to the environment relative to that at 372 nm (I_{I}), the ($I_{\mathrm{III}}/I_{\mathrm{I}}$) ratio is considered in indexing solvent polarity. It is observed that, in hydrocarbon solvents of very low dielectric constant ($\varepsilon \leqslant 2$), the relative peak intensities show minimum variation ($I_{\mathrm{III}}/I_{\mathrm{I}} = 1.65$–$1.75$) for a wide variation in hydrocarbon configuration. In presence of micelles and other macromolecular systems, pyrene is preferentially solubilized in the interior hydrophobic regions of these aggregates. In a typical experiment, amphiphile concentration is varied from below *cmc* to above it in presence of a constant concentration of pyrene. Below *cmc*, there are no micelles in the solution and pyrene fluorescence corresponds to that in water with $I_{\mathrm{III}}/I_{\mathrm{I}} \sim 0.66$. However, as the amphiphile concentration increases beyond *cmc*, pyrene is distributed among the micellar core and water with a major fraction being at the hydrocarbon-like environment inside the micellar core as illustrated by the increased $I_{\mathrm{III}}/I_{\mathrm{I}}$ ratio. Since both the fluorescence lifetime (τ_{f}) as well as $I_{\mathrm{III}}/I_{\mathrm{I}}$ ratio in the vibronic band intensities are functions of environment around the probe, both τ_f and $I_{\mathrm{III}}/I_{\mathrm{I}}$ show sharp breaks at *cmc*. Above *cmc*, $I_{\mathrm{III}}/I_{\mathrm{I}}$ remains fairly constant and independent of the probe as well as the surfactant concentration. It has been observed that $I_{\mathrm{III}}/I_{\mathrm{I}}$ for pyrene is quite dependent on the surfactant head group, but is independent of the surfactant concentration, length of the hydrocarbon chain, or presence of external additives like hexane or electrolytes like NaCl or NaBr.

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