SURFACE CHMISTRY

MICELLES

Surface active agents

The word "Surfactant" is derived from three words "Surface Active Agents." Surfactants are materials that lower the surface tension (or interfacial tension) between two liquids or between a liquid and a solid. In the general sense, any material that affects the interfacial surface tension can be considered a surfactant, but in the practical sense, surfactants may act as wetting agents, emulsifiers, foaming agents, and dispersants.

Composition and structure

Surfactants are usually organic compounds that are amphiphillic i.e. they contain both hydrophobic groups (their tail) and hydrophilic group (their heads). Therefore, a surfactants contain both a water insoluble (and oil soluble) component and a water soluble component. Surfactants will diffuse in water and adsorb at interface between air and water or at the interface between oil and water. The water insoluble hydrophobic group may extended out of the bulk water phase, into the air or into oil phase, while water soluble head group remains in the water phase.

In the bulk aqueous phase, surfactants form aggregate, such as micelle where the hydrophobic tails form the core of the aggregate and the hydrophilic heads are in contact with surrounding liquid. Other type of aggregates can also be formed, such as spherical or cylindrical micelles or lipid bilayers. The shape of aggregates depends on the chemical structure of the surfactants i.e. the balance in size between hydrophilic head and hydrophobic tail.

Fig: Schematic illustration of the three most commonly observed geometrical shapes of surfactant micelles in aqueous solution.

Classification of Surfactants –

Most commonly surfactants are classified according to polar head group. There are four types of surfactants

(i) **Anionic surfactants** – it contain anionic functional groups at their head, such as sulfate, sulfonate, phosphate and carboxylates. Sodium lauryl sulfate (SLS), sodium dodecyl sulfate (SDS) and sodium lauryl ether sulfate (SLES).

(ii) **Cationic surfactants** – Permanently charged quaternary ammonium salts, cetrimonium bromide (CTAB), cetylpyridinium chloride (CPC), benzethonium chloride (BZT).

(iii) **Zwitterionic surfactants** – It have both cationic and anionic centers attached to the same molecule. The cationic part is based on primary, secondary or tertiary amines or quaternary ammonium cations. The most common biological zwitterionic surfactants have with an amine or ammonium.

(iv) **Nonionic surfactants –** It have covalently bonded oxygen containing hydrophilic groups which are bonded to hydrophobic parent structures. The water solubility of the oxygen groups is the result of hydrogen bonding. Hydrogen bonding decreases with increasing temperature and the water solubility of nonionic surfactants therefore decreases with increasing temperature.

Hydrophilic-Lipophilic Balance (HLB)

This term first suggested by Clayton, refers to the balance size and strength between the hydrophilic and hydrophobic arts of as surfactants. The HLB value is an empirical number assigned to non-ionic surfactants on the basis of a wide variety of experiments carried out on surfactants. The HLB values range from 1-40, the lower numbers generally indicating solubility in oil and the high numbers indicating solubility in water. An emulsifier has two different actions: it promotes the formation of an emulsion and it determines whether an oil/water(o/w) or a water/oil(w/o) emulsion will formed. The second action is closely connected with the HLB value.

On the basis of systematic experiments, Griffin found that the HLB values of mixtures of two or more emulsifiers are additive: the HLB value of a mixture is equal to the sum of the HLB values of the constituents multiplied by their mass fraction in the mixture x_i^m:

$$\mathrm{HLB} = \sum_i \quad x_i^m(\mathrm{HLB})$$

For most polyhydric alcohols, fatty acid and esters, approximate HLB value may obtained using the following equation:

$$\mathrm{HLB} = 20(1-S/A)$$

Where S is the saponification number of the ester and A is the acid number of the acid. This eq. can be written as:

$$\mathrm{HLB} = 20(1-M_h/M_m)$$

Where M_h is the mass of the hydrophobic group and M_m is the molar mass of the emulsifier.

Davies suggested assigning an **HLB contribution group number** to each functional group in a molecule after studying the relative coalescence rates of stabilized oil droplets I water and water droplet in the oil. The **Davis equation** which is applicable to ionic and non-ionic surfactants is

$$\mathrm{HLB} = \sum(\text{hydrophilic group number}) - \sum(\text{hydrophobic group number}) + 7$$

MICELLE FORMATION

An important property of amphiphillic (surfactants) is the capacity to aggregate in solution. The aggregation process depends on the surfactants and condition of the system in which they are dissolved. The abrupt change in physicochemical properties seen when a specific concentration is exceeded which result in the formation of oriented colloidal aggregates. The narrow change in concentration over these change occur is called the

critical micelle concentration (CMC) and aggregation that are formed above the CMC are known as **micelles.**

CRITICAL MICELLE CONCENTRATION(CMC)

It is defined as concentration of surfactants above which micelles form and all the additional surfactants added to the system go to micelles ie. micelles only form when the concentration of surfactants is greater than CMC and the temperature of the system is greater the critical micelles temperature or Krafts temeperature. We can determine the value of CMC by using any of physical properties, but most commonly the break in molar conductance, surface tension, light scattering or refractive index versus concentration curves for this purpose.

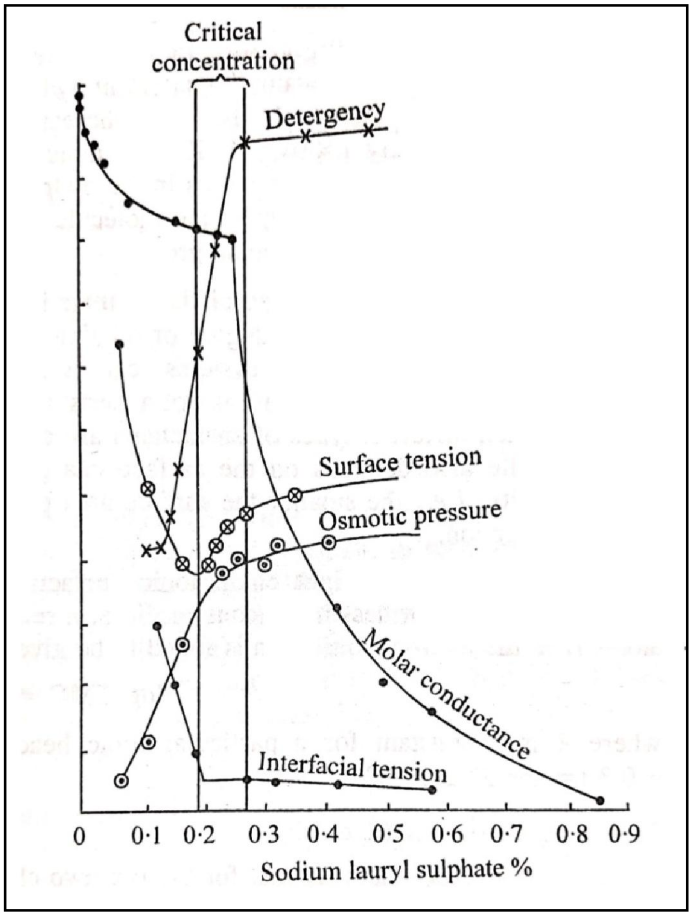


Fig: Changes in some physical properties of an aqueous solution of sodium lauryl sulphate in the neighborhood of the critical micelle concentration

Shape and structure of Micelles

In 1956, Hartley's spherical model was established by Reich from the viewpoint of entropy and the spherical form in now generally accepted. The formation of micelles by ionic surfactants is ascribed to a balance between hydrocarbon chain attraction and ionic repulsion. For non-ionic surfactants, however the hydrocarbon chain attraction is opposed by the requirements of hydrophilic groups for hydration and space. Therefore, the micellear structure is determined by equilibrium between the repulsive forces among hydrophilic group and short range attractive forces among hydrophobic groups. The chemical structure of a given surfactant determines the size and shape of micelles.

The shape and structure of micelles have been elucidated with the help of techniques such as NMR, ESR, neutron scattering etc. As the ionic concentration is increased, the shape of micelles changes in the sequences: spherical → cylindrical hexagonal → lamellar. For non-ionic micelles, on the other hand, the shape seems to change from spherical directly to lamellar with increasing concentration.

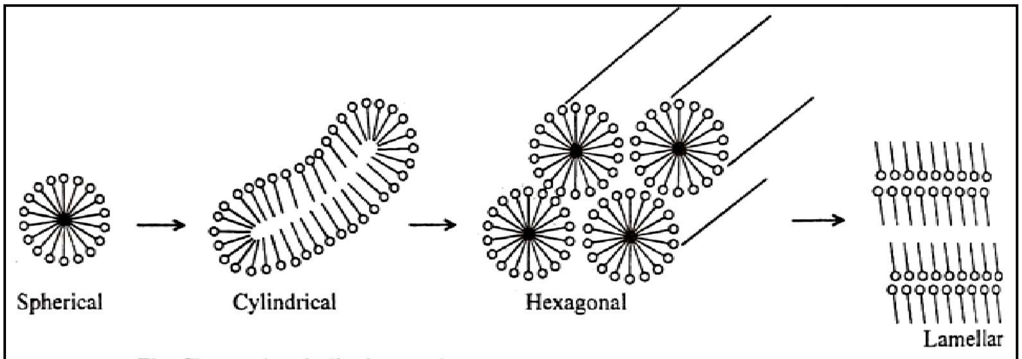


Fig. Changes in micelle shape and structure with change in surfactant concentration.

Factor Affecting Critical Micelle Concentration in Aqueous Media

Several factors such as the structure of the surfactant, concentration of electrolyte, addition of organics, presence of a second liquid phase and temperature affect the CMC in aqueous media. These are –

(I) Structure of Surfactants

(a) Role of hydrophobic group – In aqueous medium, the CMC decreases as the number of carbon atom in the hydrophobic group increases and for general rule for ionic surfactants is that the CMC is halved by the addition of one methylene group to a straight chain hydrophobic group attached to a single terminal hydrophilic group. For non-ionic and zwitter ions, the decrease with increase in the hydrophobic group is somewhat larger. When hydrophobic group is branched, the carbon atoms on the branches appear to have about one-half the effect of carbon atoms on a straight chain.

(b) Role of hydrophilic group – In aqueous medium, ionic surfactants have much higher CMCs than non-ionic surfactants containing equivalent hydrophobic groups.

(c) Role of degree of binding of the counter ion to the micelle – The CMS in aqueous reflects the degree of binding of the counter ion to the micelle. Increased binding of the counter ion, causes a decrease in the CMC of surfactant. The degree of binding also depends on the surface charge density of the micelle.

(II) Concentration of Elelectrolyte

It if found that ionic and non-ionic surfactants, the effect of concentration of electrolyte is given by

$$\log \mathrm{CMC} = -a \log c_i + b$$

where a and b are constants for given ionic head at particular temperature and c_i is the molar concentration of the counter ion. The decrease in the CMC in these case is due mainly to the decrease in the thickness of the ionic atmosphere surrounding the ionic head groups in presence of the additional electrolyte and consequent decreased electrical repulsion between them in the micelle.

(III) Addition of Organic materials

Small amount of organic materials may produce marked change in CMC in aqueous media. These are divided into two parts class I & II materials.

(a) Class I Materials – These are generally polar organic compounds such as alcohols and amides. They affect the CMC at much lower liquid phase concentrations than those in class II. They reduce the CMC. Shorter chain adsorbed mainly in the outer portion of micelle mainly at water-micelle interface. The long chain probably adsorbed mainly in the outer portion of the core, between the surfactant molecules.

(b) Class II Materials – These changes the CMC but at bulk phase concentration. These occur by modifying the interaction of water with the surfactant molecule by modifying the structure of water, its dielectric constant or its solubility parameters. These includes urea, formamide, short chain alcohols, water soluble esters, di-oxane, ethylene glycol.

(IV) The Presence of Second Liquid Phase

The CMC of surfactants in aqueous changes very little in the presence of a second liquid phase. When the hydrocarbon is a short chain unsaturated hydrocarbon or an aromatic hydrocarbon, the CMC is significantly less than the air, with the more polar hydrocarbon causing a large decrease. This is because some of the second liquid phase adsorbs on the outer portion of the surfactant micelle and acts as a class I material.

(V) Temperature – The value of CMC first decreases with increase in temperature to certain minimum and then increases with further increase in temperature. The temperature causes decreased hydration of the hydrophilic group which favors micellization. However, temperature increases also produces distortion in the structure of water surrounding the hydrophobic group, an effect that disfavors micellization. The relative magnitude of the tow opposing effects, therefore, determines whether the CMC increases or decreases over a particular temperature range.

SOLUBILIZATION

A very important property of surfactants that is directly related to micelle formation is solubilization. It is particular mode of bringing into solution substances that are insoluble otherwise insoluble in the given electrolytes. A broad definition of solubilization is *“Solubilization is the preparation of thermodynamically stable isotropic solution of a substance normally insoluble or very slightly soluble in the given solvent by the introduction of an additional surfactant”*.

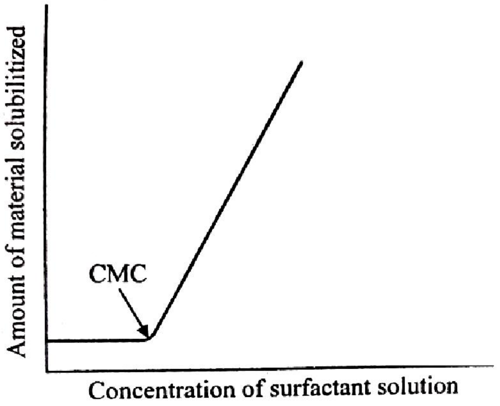


Fig: Plot of amount of material solubilized as a function of concentration of the surfactant in the bulk phase.

Several applications, for example, the dissolution of sparingly soluble drugs into water and their transport through the body, preparation of agricultural chemical solutions and the recovery of oil, etc. depend on solubilization by suitable surfactants. The mechanism of solubilization involved in (1) the removal of oily soil; (2) in micellar catalysis of organic reactions; (3) in emulsion polymerization where it appears to be important factor in the initiation step; (4) in the separation of material for manufacturing or analytical purposes; (5) in the formation of products containing water soluble ingredients where it can replace the use of organic solvents and (6) in enhanced oil recovery where solubilization produces ultra low interfacial tension required for mobilization of oil. Solubilization in non-aqueous media is of major importance in dry cleaning.

Micellar Aggregation Numbers

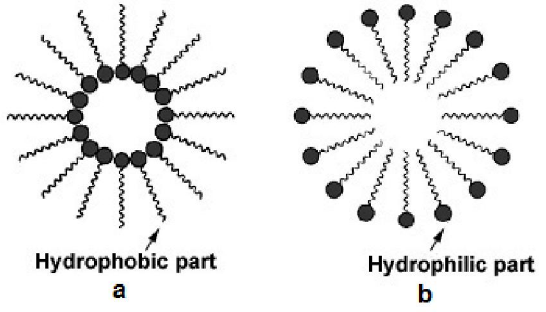
The number of molecules in a micelle ie. the sum of molecular mass of molecules forming a micelle.

$n = 4\pi(l_c+\Delta^2)/a_0,$ where Δ is the added length of the radius of the sphere due to the hydrophilic group, l_c is the length of hydrophobic group, a_0 cross sectional area of the hydrophilic group. Similarly, the volume of the hydrophobic cone is

$$n = (4/3)\pi(l_C)^3/V_h,\ V_h = \text{Volume of hydrophobic group}$$

Reverse Micelle

When the surfactant molecules in the oil –air interface become so packed in the monolayer that no further packing of molecule is not possible. They collect into a mass known as micelle. At a given temperature and pressure, the micelles of surfactants are monodisperse ie. they contain same number of molecules (25 -100) and diameter of a typical micelle is 3-8 nm. The nature of micelle depends upon the polarity of the medium used. In aqueous solution, the hydrophilic (polar head) groups are pointed towards the periphery (outside) and hydrophobic hydrocarbon chain group (tail) towards the center. If the polarity of the solvent is changed ie. if surfactant is dissolved in non-polar solvent (oil), a inverted micelle is formed is inverted.



(a) Reverse micelle (b) Normal Micelle