A BRIEF SYNOPSIS ON PHYSICOCHEMICAL ASPECTS OF AMPHIPHILES

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Abstract: A variety of molecular architectures displaying unique features flourish modern medicinal, pharmaceutical and industrial fields. They include lipid based drug-delivery vehicles that can be advantageously used to facilitate solubilization, stabilization, bioavailability and sustained release of drugs. These systems mostly include self-assembled colloidal carriers such as micelles, microemulsions, emulsions, vesicles/liposomes and liquid crystal nanostructures. In particular, micellar aggregates are considered the simplest colloidal organized media which solubilize hydrophobic part of drugs within their core or in the surface, depending on their structure. Amphiphiles are the basic units of such decorated structures. They have versatile applications in automobile oils, as detergents in laundry, in extracting petroleum, in pharmaceutical preparations, in DNA condensation for gene therapy etc.

Index Terms **– Amphiphile, Surfactant, HLB, Adsorption, Air – water interface.**

I. INTRODUCTION

The name ‘amphiphile’ is sometimes used synonymously with SurfActAnts (i.e., Surface Active Agents). They are compounds of low molecular weight (usually between 100-500) with a peculiar structural feature often described as ‘amphipathy’, i.e., they contain non polar hydrocarbon tail(s), usually a straight or branched hydrocarbon chain containing 8-18 carbon atoms which is attached to polar hydrophilic group(s), that may be non ionic, zwitterionic or ionic, accompanied by counterions in the last case. This dual nature endows a surfactant with their unique solution and interfacial characteristics.

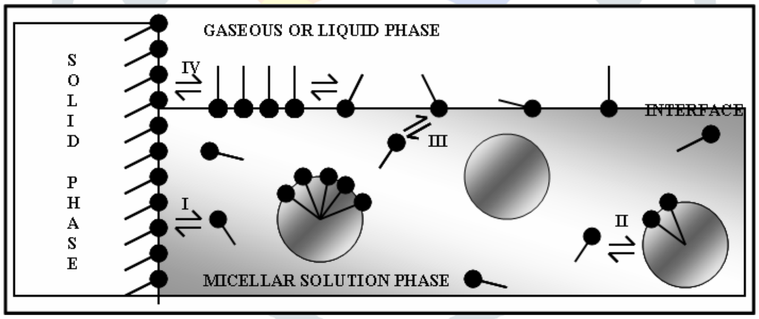


Fig. 1. Four fundamental processes for thermodynamical equilibria of amphiphilic molecules in solution.[1]

The fundamental processes that characterize the thermodynamical equilibria of amphiphilic (unimers or monomers) molecules in solution are (Fig. 1):

(I) Dissolution of amphiphiles (solid phase) into solution (liquid phase).

(II) Aggregation of dissolved amphiphiles in solution.

(III) Adsorption of dissolved amphiphiles at interface (boundary between any two immiscible phases) or surface (one of the phases is a gas, usually air e.g., in foams). The driving force for an amphiphile to adsorb at an interface is to lower the interfacial free energy (per unit area) of that phase boundary. The extent of adsorption depends on the amphiphile structure as well as on the nature of the two phases that meet at the interface.

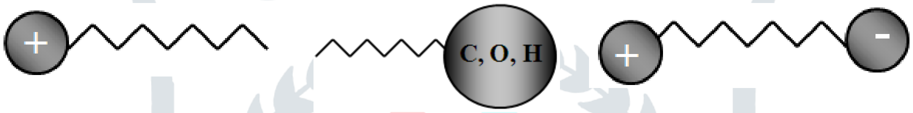
(IV) Spreading of amphiphiles at the interface to form condensed phase and solidification under compressed condition.

I and II involve either a solid-liquid (froth floatation) or liquid-liquid (emulsions) interface; III and IV are more universal and may arise at any interface.

II. TYPES OF AMPHIPHILES

Amphiphiles may be of the following types:

2.1. Ionic (cationic, anionic)- It includes surfactants in which a single, double or branched hydrophobic (lyophilic) long alkyl/arylbenzene chains are connected to a headgroup [hydrophilic or hydrophobic] (Fig. 2a). Another class of ionic surfactant is the gemini surfactant where two monomeric surfactants are attached by a flexible or rigid spacer (methylene group, stilbene, polar or non polar groups) at the level of the head groups or very close to the head group (Fig. 3a).[2] Surfactants bearing one polar head group with two or more alkyl, acyl or mixed chain hydrophobic groups (forming vesicles or bilayers in solution) constitute another class, e.g., dioctadecyldimethylammonium bromide.[3] Recently, surfactants bearing four headgroups and four hydrocarbon chains have been also synthesized.[4] Self-assembly of symmetrical or asymmetrical bipolar amphiphiles (bolaamphiphiles) that can self-assemble and adsorb at air-water or liquid-solid interface form another variety (Fig. 3b).[5] They consist of one or two long hydrophobic central moiety(s) (mainly alkyl chain) and two polar head groups attached to their ends that can assume either a horse-shoe like conformation or lay perpendicular at the interface.[6] They have brought a revolutionary improvement in their performance because of high surface activity, low critical micelle concentration, multifarious aggregate structure and unusual viscosity behaviour. Amphiphilic copolymers[7] have been found to form various micellar morphologies such as spheres, rods, tubules, vesicles and cylinders, as evidenced from transmission electron microscopy (TEM) measurements.
Examples: Anionic surfactant includes salts of long chain carboxylic (fatty) acids, sulfonic acids, sulfuric acid, xanthic acid, dithiophosphoric acid, lower homologue tetraalkyl salts of dodecylsulfate etc. Cationic surfactants include long chain amines, quarternary ammonium salts, amine oxides, tertiary amines etc.



(a) (b) (c)

Fig. 2. Schematic illustrations of (a) ionic (e.g., cationic); (b) non ionic and (c) zwitterionic types of surfactants.

2.2. Non ionic- Here the surface active portion bears no apparent ionic charge (Fig. 2b). They are poor foamers, with no electrical effects and may become insoluble in water on heating. e.g., monoglycerides of long chain fatty acids, polyoxyethylenated glycols etc.

2.3. Zwitterionic- Both positive and negative charges are present in the surface active portion (Fig. 2c).[8] They are often insoluble in organic solvents (like ethanol) and are less irritating to skin and eyes than other types. e.g., long chain amino acids (pH sensitive, zwitterionic only near isoelectric pH), sulfobetaine (pH insensitive) etc.

III. MODELS FOR ADSORPTION OF AMPHIPHILES AT THE AIR-WATER INTERFACE

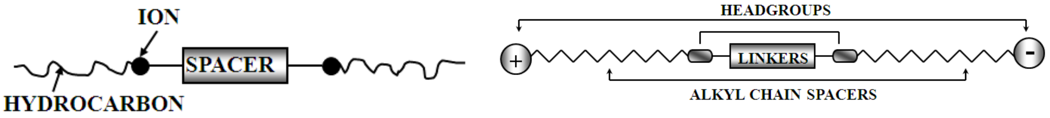
The major driving force for monolayer forming surfactant adsorption at the air-solution interface is the hydrophobic force attributed to the removal of the hydrocarbon chains from the aqueous environment. The major adsorption isotherms used in literature are:

3.1. The simplest non electrostatic approach used to describe the adsorption of surfactant molecules is the Langmuir model. This model assumes the adsorption of the surfactant molecules on N_o adsorption sites with a constant driving force, thus neglecting the interaction between the molecules within the adsorption layer.[9]

3.2. In surfactant adsorption, one of the most used extensions of the Langmuir model is the Frumkin model, which takes into account the lateral interaction of the adsorbed surfactant molecules by means of the Bragg-Williams lattice model giving rise to the linear dependence of the hydrophobic driving force on the surface coverage. The surface equations of states are derived assuming a monolayer of disk-like molecules.

3.3. Drawbacks

A thorough analysis of the surface tension data indicates that by using either the Langmuir or the Frumkin model, only the lower or upper part of the surface tension isotherms can be described, but a satisfactory fit to the entire concentration range is difficult to be achieved. Also the experimental values are much smaller than the values calculated from the Langmuir or Frumkin isotherms.



(a) (b)

Fig. 3. Typical illustrations of (a) gemini surfactant; (b) bolaamphiphile.

To overcome this discrepancy, a few theoretical approaches have been suggested which assume that the surfactant molecules can adsorb in two distinct states in the adsorption layer, and with increasing surface coverage the reorientation of the molecules takes place causing changes in the intrinsic compressibility of the interfacial layer.

IV. ADSORPTION ISOTHERM FOR IONIC SURFACTANTS

The adsorption isotherms have been described with different approximations in the literature as categorized below:

4.1. The simplest approach has been the application of the “pseudo non ionic” model, in which an adsorption isotherm derived for non ionic surfactants is used for the fitting of the experimental data. This model has limited physical insight due to the neglect of electrostatic interactions.

4.2. A second model has considered an electrostatic contribution in the adsorption free energy by means of the Guoy-Chapman theory. One of the underlying assumptions of this model is that the real, continuous spatial charge density distribution of the electric double layer can be divided into a compact and a diffuse part. Here the fully dissociated adsorbed surfactant molecules form a uniformly charged monolayer and the point like counterions build up the diffuse part of the double layer. This model can successfully describe the experimental surface tension isotherms; on the other hand, it cannot interpret the effect of counterions on the surfactant adsorption. It predicts too high electric potential at the Helmholtz plane which gives rise to physically unrealistic counterion concentration in the close vicinity of the surfactant monolayer.

4.3. To overcome this problem, different counterion binding models are proposed in literature. Kalinin and Radke[10] have assumed that counterions can bind to the adsorbed surfactant molecules like an equilibrium chemical reaction. They have described the interface by a triple layer model. The first plane contains the adsorbed surfactant molecules. The second (inner Helmholtz plane) contains the bound counterions while the third plane (outer Helmholtz plane) represents the closest approach of the hydrated counterions of the diffuse layer to the adsorbed surfactant ions. The proposed model has been successfully fitted to the surface tension data measured for sodium dodecylsulfate (SDS) at air-solution and oil-solution interface. The model assumes strong chemical interactions between the adsorbed surfactant head groups and the counterions, which is a realistic assumption for weak electrolyte type surfactants but seems to be unnatural for strong electrolyte type surfactants that do not have the ability to complex (form covalent bonds) with the counterions.

4.4. Warszynski et al.[11] have used a model that assumes adsorption of the counterions in the same plane where the surfactant head groups are situated as there are considerable spaces between them. A second plane (outer Helmholtz plane) defines the closest approach of the hydrated counterions of the diffuse layer.

4.5. Gilanyi et al.[12] have considered that the closest approach of the mobile counterions to the air-water interface is limited by their hydrated size. As a consequence, if the hydrated counterion size is smaller than that of the surfactant head group, the counterions can enter the adsorption plane and reduce the surface charge density. On the other hand, if the hydrated counterions are larger than the surfactant head groups, a charge free Stern layer is formed with a thickness equal to the difference of the hydrated counterion and head group size. This model successfully describes experimental surface tension data and interprets the counterion effect but in the case of large counterions it predicts too high electrostatic potential and consequently physically unrealistic counterion concentration in the Helmholtz plane.

Table 1. (a) Typical interfaces and their corresponding interfacial tensions (γ in mN m^{-1}); (b) Typical HLB values of surfactants and their possible uses.

(a)		(b)	
Interface	γ	HLB	
Air-water	72-73	w/o emulsions	4-6
Air-10% aqueous NaOH	78	Wetting agents	7-9
Air-aqueous surfactant solution	30-50	o/w emulsions	8-12
Aliphatic hydrocarbon-water	28-30	Detergents	13-15
Aromatic hydrocarbon-water	20-30	Solubilizing	15-18
Hydrocarbon-aqueous surfactant solution	1-10	w/o emulsions	4-6

V. STRUCTURAL CHARACTERIZATION AND AMPHIPHILE ORIENTATION AT THE INTERFACE

Anisotropic liquid crystalline (lamellar or hexagonal) phases of surfactant in solution are optically birefringent, and show characteristic texture when viewed under optical microscope. However, quantitative information may be obtained from small angle X-ray diffraction (SAXD) analysis.[13]

5.1. Amphiphilic alignment at the interface

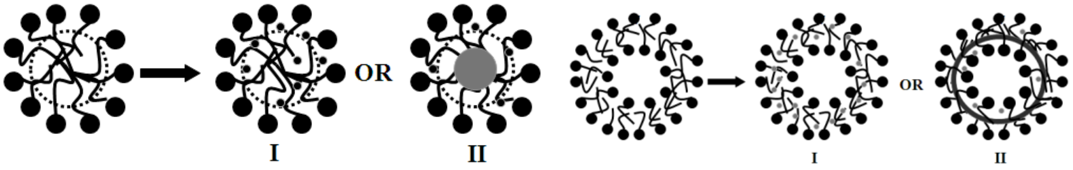
Information on the possible conformation and packing mode of amphiphile molecules at the interface can be deduced from the molecular area at the point of film collapse [from Langmuir Blodgett (LB) method, discussed later], but evidence about the molecular orientation can be obtained using X-ray diffraction, neutron reflectivity, infrared reflection absorption spectroscopy measurements etc.[14] Dynamic surface tension gives an insight to the interfacial adsorption layer which has been analyzed in the light of Frumkin's model.[15]

5.2. Lowering of surface energy

Surface energy of a liquid actually gives rise to 'surface tension' (γ). It is defined as either a force acting to oppose any increase in surface area of the liquid or the work done to increase a liquid's surface area by unity. The reversible work (w_{rev}) done on a closed system of phases α and β (with a plane interface separating them) includes work associated with a reversible volume change (dV) against a constant pressure P in each bulk phase in addition to the work required to change the interfacial area (dA), $dw_{rev}=-PdV+\gamma^{\alpha\beta}dA$. The energy or work required to create new water-air surface during respiration is so crucial to a new born baby that nature has developed lung surfactants specially to reduce this work by about a factor of three. An amphiphile can lower the aqueous surface tension to a value of 30-50mN m^{-1} and oil-water interfacial tension to 20-30mN m^{-1} from 72-73mN m^{-1} (Table 1a). Ultra low O/W interfacial tension in the range of 10^{-3} mN m^{-1} or below can be achieved in a microemulsion system. This minimizes the related positive free energy change of dispersion associated with new surface formation.

VI. HLB AND ITS IMPORTANCE

Griffin[16] defined the hydrophilic-lipophilic balance (HLB) of a surfactant as its tendency to partition between the polar and non polar media. Strongly hydrophilic surfactants have a HLB ~40, whereas strongly lyophilic surfactants have HLB ~1. The HLB values computed by Griffin have been studied with a varying oil-water interfacial structure. HLB of a surfactant depends on the presence of polar and non polar groups in the molecule. Depending on their HLB values, surfactants find application in a variety of use (Table 1b). Further mention of HLB will be made in subsequent sections.



(a) (b)

Fig. 4. (a) Type I solubilization; (b) Type II solubilization.

6.1. Solubilization and Related Features of Assemblies

One of the distinguishable features of aqueous surfactant solution is there ability to enhance the solubility of hydrophobic solutes that have otherwise very poor solubility in water. If the solubilizate molecules are entirely located in the region of the surfactant tails, they belong to Type I solubilization (Fig. 4a). Alternately, they may constitute a domain themselves in the interior of the aggregates in addition to being present among the surfactant tails (Type II solubilization) (Fig. 4b). The former stands for a micellar solubilization, the latter aggregates are referred to as microemulsions (discussed in subsequent section).

VII. USES AND APPLICATIONS

In agriculture. 1. Formulation aids: used as emulsifiers and dispersing agents in emulsifiable concentrates, water dispersible granules etc. 2. Activity enhancers: use of a surfactant along with a pesticide enhances the activity of the functional ingredients such that lower quantities of the active ingredients are released.

In foam control. Defoamers: application as defoamers for their lower surface tension than the foaming medium, positive spreading coefficient at the air-liquid interface, resistant to degradation and insolubility in the foaming environment.

In electrochemistry. Catalysts in electrochemical reactions: in electroplating technique, they inhibit corrosion, improve battery performance etc.[15]

VIII. CONCLUSION

It can be stated that equilibria III and IV (in Fig 1.) involve universal properties of amphiphile as it chooses different kinds of interface such as: (A) micellar system is the simplest form of aggregation that constitutes air-water interface, and (B) microemulsion system is a complex form of aggregation involving oil-water interface. The physical constraints on the surfactant molecule dictates the type of aggregate which it can form to exclude water. Double chain surfactants do not form micelles, but instead form multi-lamellar bilayers, vesicles, liposomes (spherical vesicles with bilayer membranes composed of amphiphilic phospholipids used for biocompatibility, non toxicity, and biodegradability for use in medicinal chemistry as drug delivery) etc. These remarkable aggregates closely mirror the kinds of structures observed in living cell membranes. The amphiphilic self-assembly thereby has a versatile importance in cell biology.

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