

Chapter 1

An Overview of Surfactant Self-Assemblies in Solution

1.1 Surfactants

Surfactants are molecules (ionic or nonionic) that upon adsorption at the air-water interface reduce surface tension of water. Therefore, surfactants are surface-active agents. Surfactants are normally amphiphilic molecules with a long hydrocarbon tail and a polar head group. The structural features of different types of surfactants are shown in Figure 1.1.1. The head group may be anionic, cationic or nonionic and accordingly the surfactants are classified as anionic, cationic or nonionic. There are some surface-active amphiphilic molecules that contain both anionic and cationic centers at the head group. These are called zwitterionic surfactants. Surfactants can also have two hydrocarbon chains attached to a polar head and are called double chain surfactants. On the other hand, surfactants containing two hydrophobic and two hydrophilic groups, called “gemini” surfactants. The gemini surfactants can be thought of “twin” surfactants as being made up of two typical surfactant molecules chemically linked at or near the head group. Amphiphilic molecules can also have two head groups (both anionic, both cationic or one anionic and the other cationic) joined by hydrophobic spacer [1]. These types of molecules are termed “bola-amphiphiles” commonly known as “bolaforms”. Surface activity of these molecules depends on both the hydrocarbon chain length and the nature of head group(s). Amphiphiles with longer hydrocarbon chains are found to be more surface-active compared to those having shorter hydrocarbon tail [2]. It is observed that amphiphiles with fluorocarbon chain are more surface-active than those with hydrocarbon chain. This is because the fluorocarbon chain is more hydrophobic than hydrocarbon chain [3].

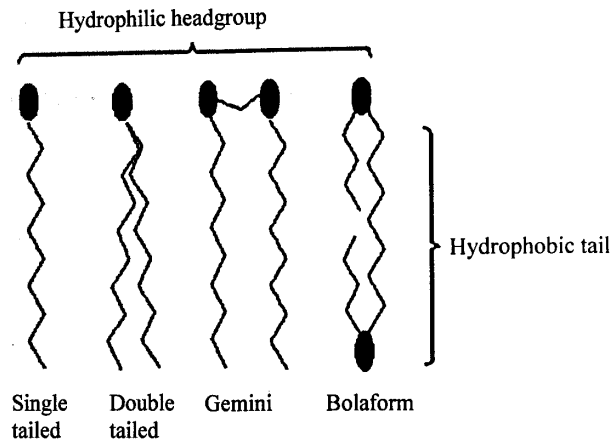


Figure 1.1.1 Structure of different types of vesicle-forming surfactants.

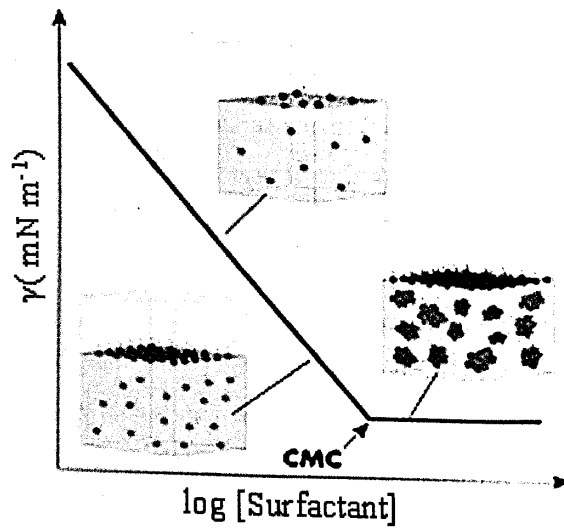


Figure 1.1.2 A representative plot of surface tension (γ) versus $\log[\text{surfactant}]$

1.1.1 Measurement of Surface Activity

At air-water interfaces, surfactants form monolayers due to specific adsorption on the interface. Upon addition of a surfactant in water the surface tension of water decreases due to adsorption of the amphiphiles at the air-water interface. The surface tension keeps on decreasing with the increase in concentration of surfactant until a critical concentration is reached after which surface tension remains unchanged. A typical plot of surface tension (γ) as a function of $\log[\text{surfactant}]$ is shown in Figure 1.1.2. The surface activity of an amphiphile is determined by the pC_{20} value [2] i.e., negative logarithm of the concentration of the surfactant required to reduce the surface tension of water by 20 units [2]. Higher value of pC_{20} means higher surface activity. As can be observed the break point correspond to the critical concentration at which the surface becomes saturated with the surfactant molecules. Above the critical concentration, the surfactant molecules go into water and form aggregates. The critical concentration is therefore, in general, called critical aggregation concentration (*cac*). The different steps of adsorption of surfactants are shown in Figure 1.1.2. The ratio (cac/C_{20}) of *cac* and C_{20} values is a measure of the tendency of the surfactant to form aggregates in water. The larger the ratio, the greater is the tendency of the surfactant to adsorb at the air-water interface relative to the formation of aggregates. In general, the cac/C_{20} ratios of conventional hydrocarbon monomeric surfactants are low, 3 or less [4]. The adsorbed amount of a surfactant at *cac* (Γ_{\max}) can be calculated according to the Gibbs adsorption equation [5]:

$$\Gamma_{\max} = -(1/nRT)(d\gamma/d\ln C) \quad (1.1)$$

where Γ_{\max} (molecules/m²) is the maximum surface excess concentration and n is the number of molecular species involved, and C is the concentration of surfactant. For nonionic surfactants $n = 0$, and for ionic surfactants (1:1) $n = 2$. Gibbs adsorption isotherm allows one to determine the minimum surface area (a_0) occupied by a surfactant head group at the air-water interface from the following equation:

$$a_0 = 1/(N_A \Gamma_{\max}) \quad (1.2)$$

where N_A is Avogadro's number. The greater the effectiveness of adsorption, the smaller

the area occupied by a surfactant head group. Usually a_0 values decrease with increasing hydrocarbon chain length of an amphiphile.

1.2 Interactions That Drive Self-Organization of Solutions

Self-organization is a general physicochemical process. There are no restrictions on the nature of solute and solvent to obtain an ideal organized solution. The only requirement is the amphiphilicity in solute-solvent interactions. However, studies in aqueous systems led to a skewed perspective of the origins of self-assembly and the role of the unique structural properties of water in promoting aggregate formation has been overemphasized. In fact, organized solutions of amphiphiles are found in many solvents such as hydrazine [5], ethylene glycol [6-8], glycerol [9], ethylammonium nitrate [10,11], and formamide [12,13] without the subtle structural properties of water.

1.2.1 What is Required From a Solvent for Amphiphilic Assembly?

A close look at the properties of the above-mentioned solvents suggests that high solvent polarity, and hence low solubilization of nonpolar solutes is necessary. Gordon "cohesiveness" parameter, $\gamma/v^{1/3}$ [14], and the Hildebrand solubility parameter, $\delta = (\Delta H_v/v)^{1/2}$ [15] are used to measure solvent polarity. Here γ is the surface tension of the solvent, ΔH_v its heat of vaporization, and v the molar volume. All solvents that have shown strong and confirmed evidence of surfactant assembly have Gordon parameters above 12.5 dyne/cm² and Hildebrand parameters greater than 16 (cal/cm³)^{1/2}. It is observed that the solubility of nonpolar molecules increases in going from water ($\gamma/v^{1/3} = 27$, $\delta = 23.4$) to ethylene glycol ($\gamma/v^{1/3} = 12.5$, $\delta = 16.1$) through hydrazine ($\gamma/v^{1/3} = 22$, $\delta = 19$) and glycerol ($\gamma/v^{1/3} = 15.1$, $\delta = 17.7$) [16]. This is manifested in the increased values of critical micelle concentrations (*cmc*) and decreased aggregation number (N_{agg}) [7,9,17-19].

Cohesive solvents have high surface tensions and heats of vaporization, which means that they have strong interactions among themselves. Such cohesiveness, and hence

ability to promote assembly of amphiphilic molecules is perhaps a result of high polarity and high hydrogen-bonding ability of the solvent. Indeed, all solvents capable of promoting solute self-organization have high polarity (π^*), and hydrogen-bond donating (α) and accepting (β) abilities. However, despite having high polarity dimethyl sulfoxide ($\pi^* = 1.0$, $\alpha = 0$) and nitromethane ($\pi^* = 0.85$, $\alpha = 0.22$) do not promote aggregation. This is due to hydrogen-bonding ability to them. On the other hand, methanol ($\pi^* = 0.60$, $\alpha = 0.93$) and ethanol ($\pi^* = 0.54$, $\alpha = 0.83$) can extensively hydrogen bond with themselves but lack the high polarity ($\pi^* > 0.9$). Although this is generally true, self-assembly formation in methanol is reported in the literature [20]. Similarly, a report of liquid-crystal formation in 3-methylsydnone [21], a highly polar, aprotic solvent with reasonably high Gordon parameter ($\gamma/v^{1/3} = 15$) suggests that cohesiveness from sources other than intramolecular hydrogen bonds can lead to amphiphilic assembly. This means that there should be other mechanisms, which can promote high solvent cohesiveness in addition to hydrogen bonding.

Table 1.2.1 Thermodynamics of micelle formation in Hydrazine

Surfactant	T (°C)	Hydrazine			Water		
		ΔG	ΔH	ΔS	ΔG	ΔH	ΔS
		(kcal/mol)	(kcal/mol)	(cal/mol)	(kcal/mol)	(kcal/mol)	(cal/mol)
DTAB	35	-7.1	-11	-13	-4.38 ^a	-0.42	13.07 ^a
SDS	35	-8.6	-14	-18	-3.92 ^b	-0.34 ^b	12.02 ^b

^aData are from ref. [22a]; ^bData [22b] for SDS corresponds to measurements at 25 °C.