Chapter I

Surfactant Aggregation in Solution: An Overview

1.1. Surfactant (Amphiphilic) molecules

Surfactants, a common contraction of the term surface-active agents, are versatile chemical substances that modify the surfaces or interfaces of the systems in which they are contained. Surfactants have the ability to adsorb (or locate) at interfaces, thereby altering significantly the physical properties of those interfaces [1]. Surfactants possess these characterstics because their molecular structure is amphiphilic (from the Greek amphi meaning 'on both sides' and phileein meaning 'to love') having polar as well as apolar parts within the same molecular unit. The polar part is called "head" and the apolar part usually a long chain hydrocarbon is called "tail"(figure 1.1). These compounds are most comfortable in a situation when each part is located in an appropriate environment, which is only possible at the interface between two media [2].

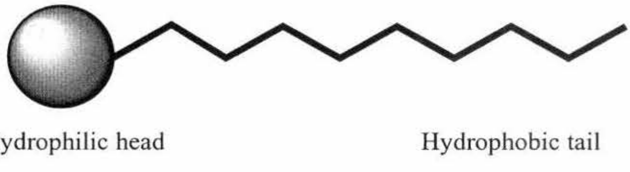


Figure 1.1. Common schematic representation of a surfactant molecule.

The hydrophobe is usually the equivalent of an 8 to 18 hydrocarbon, and can be aliphatic, aromatic, or a mixture of both. The source of hydrophobes are normally natural fats and oils, petroleum fractions, relatively short synthetic polymers, or relatively high molecular weight synthetic alcohols. The hydrophilic group gives the primary classification to surfactants, and are anionic, cationic and nonionic in nature. The anionic hydrophiles are the carboxylates (soaps), sulphates, sulphonates and phosphates. The cationic hydrophiles are some form of an amine product. The nonionic hydrophiles associate with water at the ether oxygens of a polyethylene glycol chain. 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 are called "gemini" surfactants. Amphiphilic molecules can also have two head groups (both anionic, both cationic or one anionic and the other cationic) joined by hydrophobic spacer [3]. 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).

1.2. Self-Assembly of Amphiphilic Molecules

Amphiphilic molecules have been the realm of interest in chemistry for over a hundred years with attention not only in pure science but also in their wide applications to industry. Self-assembly is a spontaneous organization of molecules driven by noncovalent interactions into stable aggregates. Self-assembly phenomenon is also well recognized in biological systems, e.g., lipid bilayers, the DNA duplex, and tertiary and quaternary structure of proteins. The process of spontaneous aggregation of simple molecules in solution into larger structures with a certain order is also an important phenomenon in every-day-life as well as an interesting subject for scientific investigation. The best-known example of aggregation in every-day-life is the formation of micelles by surfactant or detergent molecules. However, the most important type of aggregation, which is essential to life, is the formation of the lipid bilayer membrane by phospholipids. It has inspired chemists and physicists to study these and other similar types of aggregates because they mimic biological systems [1]. Aggregation of molecules often occurs at the borderline of solubility. An important molecular property in this respect is polarity, for which solubility follows the rule 'like dissolves like'. Polar (hydrophilic) compounds are well soluble in polar solvents, e.g. salt in water, and the same is true for apolar (hydrophobic) compounds and solvents, e.g. vitamin E and oil. Furthermore, polar compounds are insoluble in apolar solvents and vice versa.

Amphiphiles with longer hydrocarbon chains are found to be more surface-active compared to those having shorter hydrocarbon tail [4]. It is observed that amphiphiles with fluorocarbon chain are more surface-active than those with hydrocarbon chain [5]. When surfactants are added to water, they are adsorbed at the water-air interface, which actually arises from their dualistic character (polar and apolar character together in the same molecule). In aqueous solution the hydrophobic chain interacts weakly with the water molecules, whereas the hydrophilic head interacts strongly via dipole or ion-dipole interactions. It is this strong interaction that renders the surfactant soluble in water. However, the cooperative action of dispersion and hydrogen bonding between the water molecules tends to squeeze the surfactant chain out of the water (hence, these chains are referred to as hydrophobic). Therefore, surfactants tend to accumulate at the surface, which allows lowering the free energy of the phase boundary, i.e. the surface tension.

1.3. Structure and Shape of Aggregates: The Packing Parameter

The concept of molecular packing parameter has been widely cited in chemistry, physics, and biology literature because it allows a simple and intuitive insight into the self-assembly phenomenon [6]. The packing parameter approach permits indeed to relate the shape of the surfactant monomer to the aggregate morphology [7-9]. The molecular packing parameter P is defined as the ratio $v/a_o\, l_c$, where v and l_c are the volume and the extended length of the surfactant tail, respectively and a_o is the equilibrium area per molecule at the aggregate interface (or mean cross-sectional (effective) head-group surface area), as illustrated in figure 1.2. If we consider a spherical micelle with a core radius R, made up of N_{agg} molecules, then the volume of the core is $V = N_{agg} \times v = 4\pi R^3/3$, the surface area of the core $A = N_{agg} \times a_o = 4\pi R^2$. Hence, it can be deduced that $R = 3\ v/a_o$, from simple geometrical relations. If the micelle core is packed with surfactant tails without any empty space, then the radius R cannot exceed the extended length l_c of the tail. Introducing this constraint in the expression for R, one obtains 0 v / a_o l_c 1/3, for spherical micelles. These geometrical relations, together with the constraint that at least one dimension of the aggregate (the radius of the sphere or the cylinder, or the half-bilayer thickness, all denoted by R) cannot exceed l_c, lead to the following well-known connection between the molecular packing parameter and the aggregate shape [7], i.e., 0 v / a_o l_c 1/3 for sphere, 1/3 v/a_o l_c 1/2 for cylinder, and 1/2 v/a_o l_c 1 for bilayer. Inverted structures are formed when P>1.

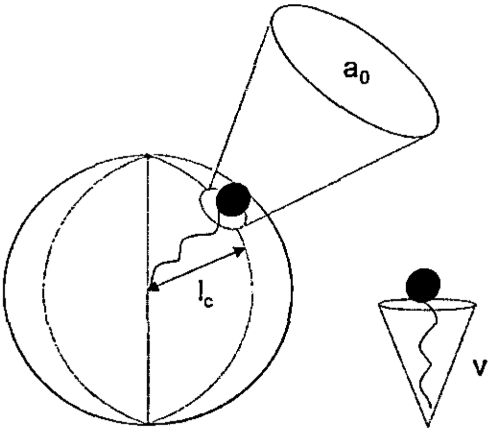
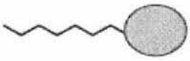
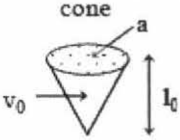
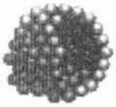
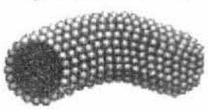
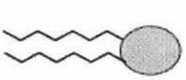
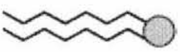
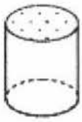
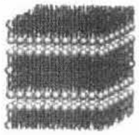
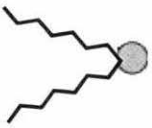


Figure 1.2. The critical packing parameter P (or surfactant number) relates the head group area, the extended length and the volume of the hydrophobic part of a surfactant molecule into a dimensionless number $P=V/a_o l_c$

Therefore, if the molecular packing parameter is known, the shape and size of the equilibrium aggregate can be readily identified. Nagarajan showed that the tail length influences the head group area (considering the tail packing constraints) and thereby the micellar shape [6]. It is important to note that a_o is often referred to as the "headgroup area" in the literature. This has led to the erroneous identification of a_o as a simple geometrical area based on the chemical structure of the headgroup in many papers, although a_o is actually an equilibrium parameter derived from thermodynamic considerations [6]. Needless to say, that for the same surfactant molecule, the area a_o can assume widely different values depending on the solution conditions such as temperature, salt concentration, additives present, etc.; hence, it is meaningless to associate one specific area with a given head group.

For example, sodium dodecylbenzene sulfonate forms micelles in aqueous solution whereas bilayer structures are formed when alkali metal chlorides are added [10] resulting in different experimental a_o values in these two cases. Moreover, the role of the surfactant tail has been virtually neglected. This is in part because the ratio v/l_c appearing in the molecular packing parameter is independent of the chain length for common surfactants (0.21 nm^2 for single tail surfactants) and the area a_o depends only on the head group interaction parameter. The predicted aggregation characteristics of surfactants are presented in Table 1.1.

Table 1.1. Schematic representation of surfactant structures and shapes derived from various packing parameters.

Possible surfactant type		$P(=V/a_o l_c)$	Shape	Structures formed
Single-tail surfactants with large headgroups		$< 1/3$	cone 	spherical micelles 
Single-chain surfactants with small headgroups		$1/3 < P < 1/2$	truncated cone 	cylindrical micelles 
Double-chain surfactants with large headgroups and flexible chains		$1/2 < P < 1$	truncated cone 	flexible bilayers, vesicles 
Double-chain surfactants with small headgroups or rigid, immobile chains		$P \sim 1$	cylinder 	planar bilayers 
double-chain surfactants with small headgroups, and bulky chains		$P > 1$	inverted truncat cone or wedge 	inverted micelles 

1.4. Self-Assembled Structures of Amphiphilic Molecules in Water

1.4.1. Micelles

The most intensely studied and debated type of molecular self-assembly and perhaps the simplest in terms of the structure of the aggregate is the micelle. Micelles formed by ionic amphiphilic molecules in aqueous solution are dynamic associations of surfactant molecules that achieve segregation of their hydrophobic portions from the solvent via self-assembly. They are loose, mostly spherical aggregates above their critical micellization concentration (cmc) in water or organic solvents [1].

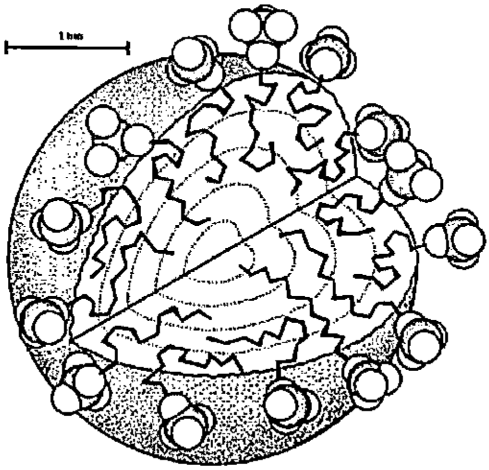


Figure 1.3. Schematic representation of a spherical micelle in aqueous solution.

Micellar aggregates are short-lived dynamic species, which rapidly disassemble and reassemble [11]. Hence, only average shape and aggregation numbers of micelles can be determined. Commonly, micellization of surfactants is an example of the hydrophobic effect. In micellization there are two opposing forces at work. The first is the hydrophobicity of the hydrocarbon tail, favouring the formation of micelles and the second is the repulsion between the surfactant head groups. The mere fact that micelles are formed from ionic surfactants is an indication of the fact that the hydrophobic driving force is large enough to overcome the electrostatic repulsion arising from the surfactant head groups. Figure 1.3 represents a spherical micelle formed in aqueous solution, where the hydrophobic chains are directed towards the interior of the aggregate and the polar head-groups point towards water, hence allowing the solubility/stability of the aggregate (no phase separation). Micelles are also known to be disorganized assemblies whose interiors consist of mobile, non-stretched hydrophobic chains [12]. In addition, it may be noted that in addition that water molecules can penetrate partially into the micelle core to interact with surfactant hydrophobic tails [13]. There are a large number of publications related to the micelles, micelle structures, and the thermodynamics of micelle formation. A huge amount of experimental and theoretical work devoted to the understanding of the aggregation of surface-active molecules has been carried out [14-16].

Micelles are generally formed by cationic, anionic, zwitterionic as well as nonionic surfactants having short alkyl chains. The environment of a micelle varies in a regular manner as a function of distance from the center of the micelle, going from a relatively dense aliphatic medium near the center to a relatively diffuse region known as either Stern layer in ionic micelles, or as Palisade layer in neutral micelles [17-19], where the head groups, bound counterions, and solvent molecules coexist. The remaining counterions are contained in the Gouy-Chapman portion of the double layer that extends further into the aqueous phase. Fluorescence probe studies have indicated that micellar core is nonpolar, but less fluid than hydrocarbon solvents of equivalent chain length [20]. On the other hand, the Stern layer has polarity approximately equal to that of alcohols [21].

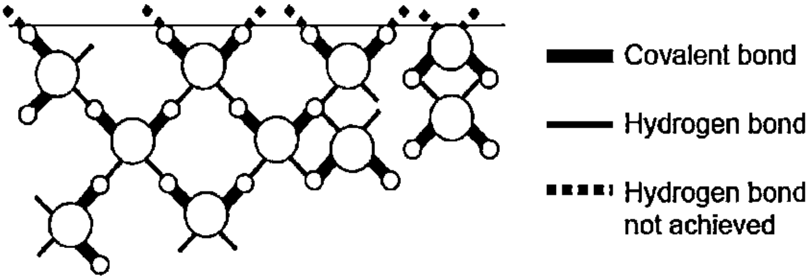


Figure 1.4. Water molecules at the liquid-air interface

Water is a very cohesive liquid due to the formation of a 3-dimensional hydrogen bond network (figure 1.4) in addition to attractive van der Waals interactions. This induces that the amount of work required to expand the interface air-water, characterized by the surface tension, is relatively high (~72.6 mNm^{-1}, for pure water at 20°C). When a nonpolar unit is introduced into an aqueous solution, the hydrogen bonding network formed by the existing water molecules is disrupted and the water molecules order themselves around the nonpolar entity to satisfy hydrogen bonds (figure 1.5 A). This results in an unfavourable decrease in entropy in the bulk water phase. As additional nonpolar units are added to the solution, they self-associate thus reducing the total water-accessible surface of the complex relative to the monodisperse state (figure 1.5 B). Now, fewer water molecules are required to rearrange around the collection of nonpolar groups. Therefore, the entropy associated with the complex is less unfavorable than for the monodisperse detergents. In short, hydrophobic association and the formation of micelles is driven by the favorable thermodynamic effect on the bulk water phase.

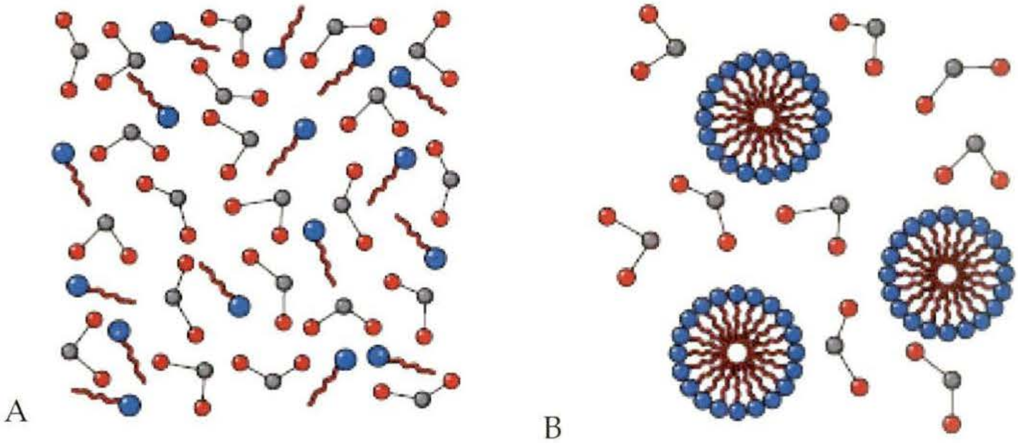


Figure 1.5. Water molecules ordered around surfactant monomers (A). Loss of total water-accessible surface as a result of micellisation (B).

A great deal of work has been done on elucidating the various factors that determine the cmc at which micelle formation becomes significant, especially in aqueous media. An extensive compilation of the cmc's of surfactants in aqueous media has been published [22]. Among the factors that are known to affect the cmc in aqueous solution are (i) the structure of the surfactant, (ii) the presence of added electrolyte (in the case of ionic surfactants) in the solution, (iii) the presence of various organic compounds in solution, and (iv) temperature of the solution.

Surfactant structure. In general, the ionic surfactants have higher cmc values compared to nonionic surfactants. The cmc in aqueous media generally decreases as the hydrophobic character of the surfactant increases. It has been observed that the cmc is halved by the addition of one methylene group to a straight-chain hydrocarbon tail. For nonionics and zwitterionics, the cmc value is decreased to one fifth of its previous value on the addition of one methylene group to the hydrocarbon tail. The branching of the hydrocarbon chain appears to have about one-half the effect of carbon atoms of a straight chain. When C-C double bond is present in the hydrocarbon chain the cmc value is higher than that of the corresponding saturated compound. An introduction of a polar group such as -O or -OH into the hydrophobic chain generally causes a significant increase in the cmc value in aqueous medium at room temperature. However, replacement of hydrocarbon chain by a fluorocarbon chain of same length causes a decrease in cmc value as has been already mentioned. For n-alkyl ionic surfactants, the cmc decreases in the order aminium salts > carboxylates > sulfonates > sulfates. It has been found that in quaternary cationics, pyridinium compounds have smaller cmc's than the corresponding trimethylammonium compounds.

Counterion. The degree of counterion binding, β (=1-α), has also an effect on the cmc value of ionic surfactants. The larger the hydrated radius of the counterion (ionic size follows the order $NH_4^+ > K^+ > Na^+ > Li^+$ and $F^- > I^- > Br^- > Cl^-$), the weaker the degree of binding, and hence larger the cmc. Thus in aqueous medium, for anionic lauryl sulfates, the cmc increases in the order $Ca^{2+} < N(C_2H_5)_4^+ < N(CH_3)_4^+ < NH_4^+ < Cs^+ < K^+ < Na^+ < Li^+$. On the other hand, for cationic dodecyltrimethylammonium and dodecylpyridinium salts, the order in aqueous medium is $I^- < Br^- < Cl^- < F^-$.

Electrolyte. In aqueous solution the presence of electrolyte causes a decrease in the cmc, the effect being more pronounced for anionic and cationic than for zwitterionic surfactants and more pronounced for zwitterionic than for nonionics.

Charge screening of the surfactant head groups by the ions of the added electrolytes is mainly responsible for such decrease in cmc. The change in cmc of nonionics and zwitterionics upon addition of electrolyte is mainly due to the "salting out" or "salting in" of the hydrophobic group in aqueous solvent.

Organic additives. Water-soluble polar organic compounds such as alcohols and amides reduce the cmc at much lower concentrations. Shorter-chain alcohols are mainly adsorbed in the water-micelle interfacial region. The longer-chain compounds are adsorbed in the outer portion of the micelle core, between the surfactant molecules. Additives that have more than one group capable of forming hydrogen bonds with water appear to produce greater depression of cmc. On the other hand, additives like urea, formamide, N-methylacetamide, guanidinium salts, short-chain alcohols, ethylene glycol, and other polyhydric alcohols, such as fructose and xylose increase cmc at relatively higher concentrations by modifying the interaction of water with surfactant molecules.

Temperature. The effect of temperature on the cmc of surfactants in aqueous medium is complex, the value appearing first to decrease with temperature to some minimum and then to increase with further increase in temperature. Increase of temperature causes decrease of hydration of the hydrophilic group, which favors micellization and also causes disruption of the structured water surrounding the hydrophobic group, which disfavors micellization. The relative magnitude of these two opposing effects, therefore, determines increase or decrease of cmc. Temperature effects are more dramatic in the case of double chain surfactants. For example, turbid, liposomal dispersions of didecyldimethylammonium bromide at room temperature become a clear solution when heated to 60°C due to formation of small micellar aggregates [23,24].

1.4.2. Worm-like micelles

Worm-like micelles are long, flexible, cylindrical chains with contour lengths of the order of a few micrometers. These structures are formed at very high surfactant concentrations or in presence of organic or inorganic salts via alteration of micellar surface curvature. The entanglement of these wormlike chains into a transient network imparts viscoelatic properties to the solution [25,26]. A schematic representation of the microstructure of a typical worm like micelles is shown in figure 1.6. The dynamics of these systems differs from those of conventional polymers in that the wormlike micelles are continuously breaking apart and recombining. The rheological behavior of these surfactant solutions is known to follow "reaction-reptation model" which is an extension of the reptation model of polymer relaxation to cylindrical micelles of surfactant molecules undergoing reversible scission and recombination processes [27]. The linear and nonlinear viscoelastic properties of surfactant solutions have been extensively studied over past few years, both theoretically [28,29] and experimentally [30-40].

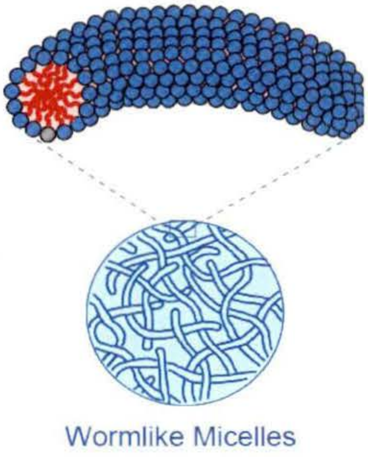


Figure 1.6. Microstructure of a typical wormlike micelle.

In general, it is observed that there is a critical shear rate above which the viscosity dramatically increases for dilute concentration of surfactant solution. The cause of this shear thickening phenomenon is believed to be the flow-induced structure formation of surfactant aggregates under shear flow [30,36]. With increasing flow intensity, the micelles undergo coalescence or tend to be stretched toward the flow direction, and as shear flow is going with time, the shear-induced structure of wormlike micelles continuously breaks down and re-forms at high shear rate [41]. This shear-induced structure (SIS) behaves like a gel and shows strong flow birefringence in solution state [33]. The classic example of such an 'abnormal' system is a solution containing cationic surfactant cetyl pyridinium chloride (CPC) with sodium salicylate (NaSal) as the additive. For semidilute surfactant solutions, zero shear viscosity initially increased with concentration, reached a maximum, and then decreased [2,34,42]. Also, the shear viscosity of semi-dilute CPC/NaSal solutions showed almost a constant value until the critical shear rate and then shear thinning began, followed by shear thickening at higher shear rate.

The average micellar length is a thermodynamic quantity, and it responds to changes in solution composition and temperature. Normally when a wormlike micellar solution is heated, the micellar length decays exponentially with temperature [1,43]. The reduction in micellar length leads to an exponential decrease in viscosity of the solution. The reduction in micellar length, in turn, leads to an exponential decrease in rheological properties such as the zero-shear viscosity η_0 and the relaxation time t_R. Accordingly, an Arrhenius plot of ln η_0 versus 1/T (where T is the absolute temperature) falls on a straight line, the slope of which yields the flow activation energy E_a. Values of E_a ranging from 70 to 300 kJ/mol have been reported for various micellar solutions [43-45]. Inorganic and organic salts have been widely used as additives to facilitate the structural transition of micelles in ionic surfactant solutions [46-49]. Inorganic counterions promote gradual micellar growth by reducing the head group repulsions in the ionic micelles. On the other hand, organic salts in aqueous micellar systems, dissociate to produce ionic species with a hydrophobic moiety, which affects the packing of the surfactant tails and leads to changes in the effective packing parameter. The growth of cationic surfactant such as CTAB micelles has been extensively studied in the presence of salts such as KBr [50], sodium salicylate [51,52] chlorobenzoates [53], and benzyl sulfonates [54]. Single chain ionic surfactants, e.g., cetyltrimethylammonium bromide (CTAB), favor convex-up surface geometry of the micelles due to strong headgroup repulsion and form spherical or near spherical micelles at the cmc, while either at much higher surfactant concentrations (~1.0 M) or in the presence of high inorganic salt concentrations (>0.1 M), morphological changes occur to rod-like micelles and vesicles [2, 55-57]. Hydrotropic salts like sodium salicylate (NaSal) also promote sphere to worm-like micellar transition at considerably lower concentration (e.g.,

~1.0 mM in CTAB) by increasing the packing parameter above the critical value of 1/3 via efficient charge screening of the surfactant head groups [7]. These worm-like micellar solutions at low concentrations show complex and unusual rheological phenomena. The increased salt concentrations cause the microstructure to change from globular to wormlike micelles. Addition of anionic surfactant, for instance, sodium dodecyl benzenesulfonate (SDBS) to solutions of cationic surfactants has also been found to generate wormlike micelles [58]. The effect of nonionic additives on micellar shape has also been investigated by many research groups. Hedin and co-workers have reported the elongation of CTAB micelles upon the solubilization of benzene [59]. Zhang and coworkers investigated the effect of benzyl alcohol on CTAB/KBr micellar systems by a combination of rheology and NMR studies and have suggested elongation of micelles upon alcohol solubilisation [60]. The addition of alcohols has also been shown to promote growth of worm-like micelles in such transitions [61-63].

Although, studies related to the microstructural transitions of micelles to worm-like micelles and vesicles have been going on for quite some time, a common element in most of the works summarised above is the presence of an anion salt like NaSal. A number of studies on micellar shape transition in cationic, anionic, and catanionic surfactant systems induced by polar and nonpolar organic species have been reported in the literature. However, these systems trigger the shape transition only at very high concentrations and make themselves unsuitable for certain applications. Recent studies show that the above mentioned transitions takes place even in presence of neutral aromatichydroxy dopants like 1- and 2-naphthols. Studies on the microstructural modifications of charged amphiphiles by neutral aromatichydroxy compounds are rather recent and will be discussed later in more detail.

1.4.3. Vesicles

Vesicles are closed bilayered structures similar to those of the lamellar phase characterized by two distinct water compartments, one forming the core and other the external medium [64,65] (figure 1.7). Like micelles, the formation of vesicles is a result of energetically favorable hydrophobic association of the hydrocarbon tail(s) of an amphiphilic molecule. However, unlike micelles, vesicles have two distinct domains: the lipophilic membrane and the interior aqueous cavity. Specifically, the surface of micelles is a lipid monolayer, while the surface of liposomes is a lipid bilayer and the inner core of micelles is composed of hydrocarbon chains, while the inner core of vesicles is an aqueous phase (figure 1.7).

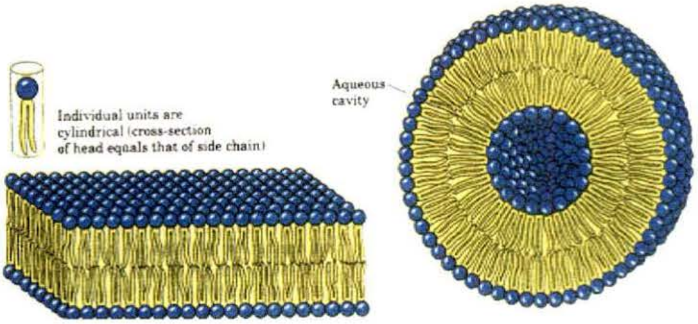


Figure 1.7. Figure showing bilayer and the individual unit of the surfactant forming the bilayer. The folding of the bilayer due to hydrophobic interaction forms the vesicle.

Vesicles have been found useful as agent in many practical applications and also a basis for several theoretical investigations. Micelles can solubilize amphiphiles and organic compounds, while vesicles can solubilize (or encapsulate) organic compounds and amphiphiles in the lipid bilayer, and inorganic compounds and amphiphiles in the aqueous core. Vesicles can be prepared as small unilammellar vesicles (SUV), large unilamellar vesicles (LUV) or large multilamellar vesicles (liposomes). Multilamellar vesicles can be large having diameter of several μms and they are also termed as onions [66,67]. Vesicles are classified in terms of number of lamellae and size. Multimembrane vesicles are divided into three groups: multilamellar vesicles (MLVs) also called as onion-shaped vesicles, oligolamellar vesicles (OLVs), and multivesicular vesicles (MVVs). OLVs are composed of several lamellae. Unilamellar vesicles consist of a lipid bilayer separating an aqueous solution from the bulk phase, forming roughly spherical structures with an inner aqueous core [15, 68]. These vesicles (ULVs) are usually divided into three groups in terms of size: small unilamellar vesicles (SUVs), large

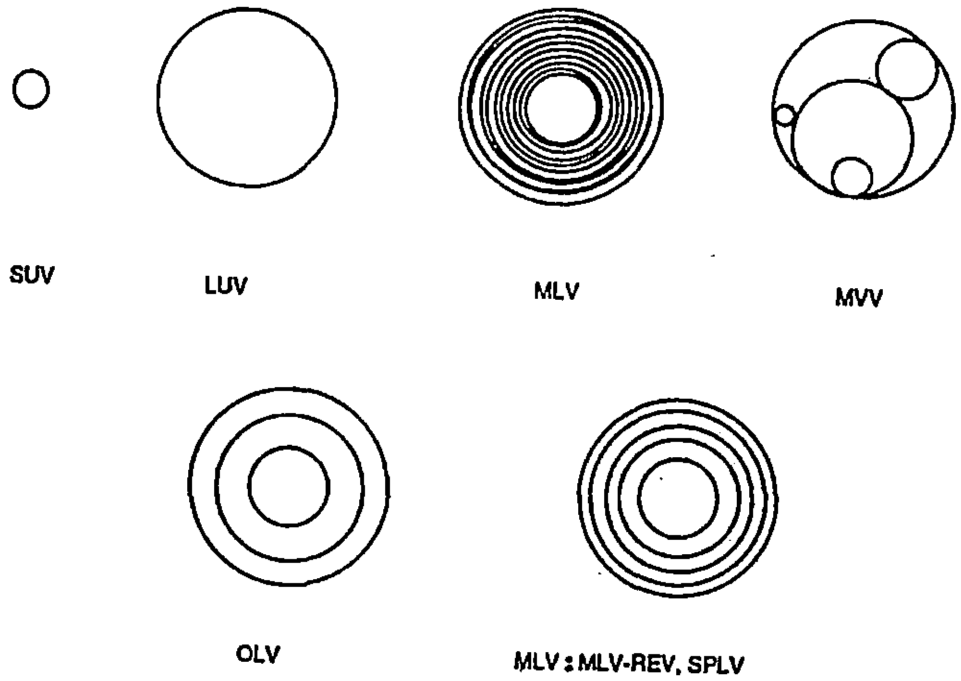


Figure 1.8. Morphology of different vesicle structures

unilamellar vesicles (LUVs), and giant unilamellar vesicles (GUVs). Figure 1.8 presents a schematic view of the major liposome types. Vesicles with diameter under 100 nm are normally considered as SUVs, whereas those greater than 100 nm are LUVs. GUVs are those, which have sizes greater than 10 µm. The disadvantage of MLVs is their heterogeneous size distribution. The advantage of SUVs is the homogeneous size distribution and their disadvantage is low encapsulation efficiency. For LUVs, encapsulation efficiency is relatively high and even macromolecules can be encapsulated. Vesicles have been found to form from synthetic surfactants that contain one, two, or three alkyl hydrocarbon chains and quaternary ammonium, carboxylate, sulfate, sulfonate, hydroxide, or phosphate, zwitterionic or functionalized head groups. Vesicles are also generated by polymeric surfactants and block copolymers.

Vesicles formed by double-tailed surfactants. Vesicles are normally formed by double-tailed surfactants having cylindrical shape, i.e., a packing parameter close to 1. The most common membrane lipids are double-chained phospholipids or glycolipids, with 16-18 carbons per chain. Double-chain amphiphiles with anionic head groups, such as sulfonate, phosphate and carboxylate also form stable bilayer membrane when the alkyl chain contains more than ten carbon atoms [69]. Mortara et. al. reported vesicle formation from dihexadecyl phosphate [70]. Hoffmann and coworkers have shown the formation of vesicles in diethylammonium perfluorooctanoate solution by small angle neutron scattering studies [71]. In 1977, Kunitake et. al. demonstrated that tetraalkylammonium salts with two long alkyl residues form vesicles similar to those of phospholipids [72]. They have shown that the synthetic surfactant, dioctadecyldimethylammonium bromide (DDOAB), can also form vesicles in large excess of water [73]. In fact, this is the first example of a totally synthetic bilayer membrane. Dioctadecyldimethylammonium chloride and bromide (DODAC and DODAB), and most probably the other halide-based homologues, self-assemble spontaneously to large unilamellar vesicles above their gel-to-liquid crystalline phase transition temperature, T_m (~48 and 45°C, respectively) at low concentrations (e.g., 1.0 mM). When cooled to room temperature, these vesicle structures remain (meta) stable, and most of their physical properties have been reported [74-77]. Recently, Bhattacharya and coworkers have synthesized double-chain cationic surfactants that form vesicles in water [78,79].

Vesicles from catanionic mixtures. Vesicles are formed by amphiphiles that roughly have the shape of a cylinder, having packing parameter value close to 1. Another common way to achieve the packing parameter value close to 1 is by using two single-tailed amphiphiles, one cationic and the other anionic [80]. In this case, each individual surfactant molecule resembles a cone because of the electrostatic repulsion from its headgroup. Thus, when present alone, each surfactant would form micelles. When mixed together, however, the cationic and anionic headgroups cancel out their electrostatic effects, causing a significant reduction in their headgroup areas. The combination thus resembles a cylinder and thereby forms vesicles. Interestingly, formation of these vesicles occurs spontaneously when the two surfactants are added into water. Moreover, the vesicles are indefinitely stable, which suggests that they may actually be equilibrium structures [80]. Recently, spontaneously formed vesicles have attracted attention of researchers for simplicity of their preparation and good dispersibility in water [81-85]. The discovery of the spontaneous formation of vesicles in mixtures of cationic and anionic surfactants is a particularly fascinating consequence of controlling and modulating interfacial curvature through charge interactions. They have been intensively investigated due to their possible applications in medicine, biology and pharmacy [86-95]. The first published results concerning this problem came from Hargreaves and Deamer [94]. Temperature was found to be an important factor, which has to be taken into account in investigations of vesicles properties, emphasizing their stability and ability of incorporation and exemption of drugs. Common examples of such mixtures are SDS/DTAB [95-97], CTAB/SDBS [80, 98-103], CTAB/SOS [104-107], and DeAC/SDeS [108]. Precipitation within the equimolar ratio of cationic and anionic surfactants is typical of such mixtures. However in the excess of one of the surfactants, the formation of stable unilamellar vesicles occurs. It was observed that the area of the vesicular phase in the phase diagram depends on the choice of cationic as well as of the anionic surfactants. In the case of equal chain lengths but oppositely charged heads, precipitation appears even much stronger compared to the phenomena appearing in cases of a big difference in chain lengths (CTAB/SOS) [109]. The exchange of chloride with bromide ions in the DTAB/SDBS mixture leads to the spreading of vesicular phase area. These investigations indicate that counterion is an important factor in the formation of the vesicular phase. Spontaneous formation of vesicles was observed in the mixture of double-tailed didodecyl dimethyl ammonium bromide (DDAB) and single-tailed SDS [110-117]. Kondo et al. published the phase diagram of that mixture; the sizes of aggregates were determined by Dynamic Light scattering (DLS) [118]. Besides, they also investigated the ability of glucose entrapment. Different areas were found in the phase diagram, i.e., homogeneous solution, liquid crystals, multiphases. Within the area of a great excess of SDS, spherical micelles were found. The vesicular phase was presented within the area of the great excess of DDAB. Between these areas, the area with micelles and vesicles appeared. Spontaneous formation of vesicles was observed in the highly diluted area of surfactants ($\omega_{\text{surfactant}} < 0.001$). Addition of DDAB to the spherical micellar solution of SDS induces growth and transition of spherical to cylindrical micelles

Marques et al. investigated the DTAB/SDBS mixture using Cryo-TEM; they determined the stability and sizes of vesicles [110, 112, 119]. Vesicles in the aqueous DDAB/DTAC mixture within the high-dilution region were most easily formed at a considerable excess of DTAC after a gentle mixing. The vesicles were polydispersed with two main populations around *d* = 40–50 nm and *d* = 500–600 nm [120]. Also, intact vesicles, vesicles with ruptured membranes, small bilayer disks, and globular micelles were visualized by Cryo-TEM.

Vesicle formation by single chain surfactants. Vesicles can also be formed by mixing a single-tailed cationic surfactant with an aromatic acid. This approach is similar to the mixtures of surfactants discussed above because the surfactant and the acid tend to bind very strongly. The difference is that only one of the two components in the mixture is a surfactant. The fact that vesicles form in these systems is still not very well known and the vesicle formation process is not fully understood. Mixtures of CTAB and 5-methyl salicylic acid (5mS) have been previously studied by Lin et. al. [121]. Surprisingly, at a molar ratio around 1.1, the authors found that their solution contained unilamellar vesicles. This result was inferred from a cryo-transmission electron microscopy (cryo-TEM) image, which showed vesicles around 100 nm in diameter. In a subsequent paper, Zheng, Zakin and co-workers [122] again used cryo-TEM to infer the presence of vesicles; this time in mixtures of CTAB and the sodium salt of 3-methyl salicylic acid (3mS). These vesicles were reported to transform into cylindrical micelles upon shearing. In the system studied by Manohar et. al., the surfactant was obtained by mixing equimolar amounts of CTAB with sodium 3-hydroxynaphtalene 2-carboxylate (SHNC), followed by removal of excess counterions [123]. This surfactant when added to water at room temperature assembled into multilamellar vesicles around 1 - 10 μm in diameter [124]. Due to the formation of these large MLVs, the solutions were highly turbid and quite viscous (viscosities ca. 100 times that of water). Upon increasing the temperature, the samples transformed into clear solutions containing wormlike micelles, thereby leading to an increase in viscosity by about an order of magnitude. It is not clear if the MLVs in these samples at low temperatures were stable or if they aggregated and eventually phase-separated to form a lamellar phase. Recently, Davies and co-workers using turbidimetry, rheological techniques, and small-angle neutron scattering (SANS) measurements have demonstrated that the aromatic derivative, 5-methyl salicylic acid (5mS), can induce the cationic surfactant, CTAB, to form either wormlike micelles or unilamellar vesicles depending on the solution composition [55]. A qualitative mechanism to account for the vesicle-to-micelle transition involves the desorption of bound 5mS molecules from the vesicles as temperature is increased.

Methods of preparation of vesicles. It should be noted that many naturally occurring and synthetic surfactants and phospholipids are unable to undergo simple aggregation to form vesicles spontaneously when dispersed in water due to their high energy of formation. For MLVs, appropriate lipids are first dissolved in Chloroform-methanol mixture (9:1 vol %) in a small round-bottom flask. The solvent is then evaporated off under vacuum while the flask is warmed in a water bath to produce a thin film on the wall of the flask. To remove residual solvents completely, the flask is allowed to stand in desiccators under reduced pressure for several hours. Water or an aqueous buffer is added and lipid film is hydrated at a temperature above the phase transition temperature (T_m) of the lipid. The flask is then agitated on a vortex mixer for more than 5 min above the T_m. The resulting milky dispersion thus obtained contains MLVs of wide size distribution. The SUVs are typically prepared by sonicating the dispersion of MLVs by use of either a bath-type or probe-type sonicator. However, other methods e.g. Ethanol Injection, Cholic Acid Removal, Triton X-100 Batch, French Press Extrusion, and prevesicle are also used for preparation of SUVs depending upon the nature of the lipid and requirements.

1.4.4. Aggregation in non polar solvents: Reverse Micelles

When surfactants aggregate in non polar solvents, their polar or charged groups are located in the interior, or core, of the aggregate, while their hydrocarbon tails extend into the bulk solvent (figure 1.9). These aggregates are referred to as reverse micelles. Reversed micelles are the subject of constantly increasing interest because they can provide "tailored-to-size microreactors" for chemical (whether organic or inorganic), biological, electron-transfer reactions, etc. [125,126]. Moreover, water encased in such aggregates is thought to mimic water close to biological membranes or proteins [127]. Among the surfactants capable of forming reversed micelles, Aerosol OT (AOT, sodium bis (2-ethylhexyl sulfosuccinate) has a remarkable ability to solubilize large amounts of water, up to water-to-surfactant molar ratios of 40-60, according to the surrounding nonpolar medium. Owing to interactions with the polar heads of the surfactant, solubilized water exhibits peculiar properties [128]. Various investigations have shown a transition region at molar ratios of 10-12 between a reversed micellar state (where water is involved in surfactant and sodium ions' hydration) and a microphase domain corresponding to a water- in-oil microemulsion (where part of the solubilized water is "apparently free") [129,130]. The solvent pool is defined over a wide range of solvent and surfactant concentration by a single parameter,

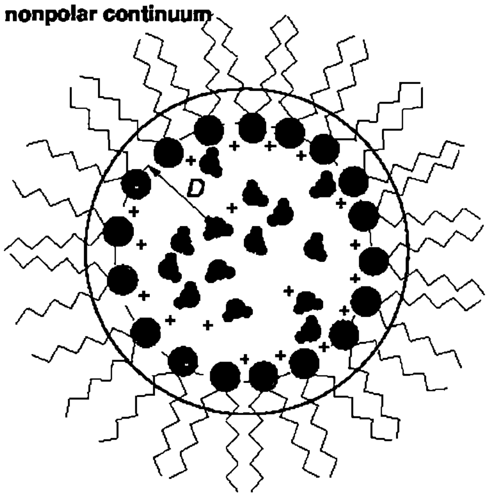


Figure 1.9. Schematic representation of a reverse micelle formed from a double tailed surfactant.

$$Ws = [H_2O]/[AOT]$$

This confinement makes the polar solvent different in behaviour from pure solution. Thus, studies of many interesting photophysical works, charge transfer, energy transfer, exciplex formation, etc. have been carried out in reverse micelles.

1.5. Practical Applications of Molecular Self-assemblies of surfactants

In recent years, there has been extensive fundamental and applied research about the properties of surfactants in aqueous solution because of their uses in wide-ranging chemical and technological areas such as organic and physical chemistry, biochemistry, polymer chemistry, pharmaceuticals, petroleum recovery, detergents, cosmetics, paints and coatings, photographic films, mineral processing, and food science [1,4]. Wormlike micelles have potential applications as viscosity enhancer, in drag reduction [131], as oil field fluids [132], and as templates for material synthesis [133,134].

Among the above-mentioned structures of the amphiphiles, vesicles have recently become a fascinating object in surfactant science. This is because of their importance in chemistry, biology as well as in the industry. There is a huge body of literature that addresses vesicles and liposomes used in various scientific fields [135,136]. Vesicles are increasingly being used in commercial products. Since the vesicles can entrap large quantities of reagents either in the lipophilic membrane or in the aqueous cavity, they have been used as encapsulants of cosmetic substances and pharmaceutical drugs [137,138]. Liposomes have potential use as controlled drug delivery vehicles in the pharmaceutical industry. In fact, liposomes were the first vesicle species to be studied in any great depth for drug delivery [139]. Since the vesicles have numerous uses in biological and industrial fields, they are of great interest in sensor technology [140] and waste water treatment [140,141]. Vesicles are widely used as micro reactors for artificial photosynthesis, and as substrates for a variety of enzymes and proteins [4]. Also vesicles have some important characteristics that allow them to be used as protectors of sensitive reagents for analytical detection [142]. Lundhal and Yang have used liposomes for separating biomolecules [143].

Molecular gels, one type of soft matter have potential applications involving nanomaterials such as sensors, molecular electronics, and catalysts and drug delivery or modification agents for paints, inks, cleaning agents, cosmetics, polymers, drugs, etc. [144]. Recovery of spilled crude oil or disposal of used cooking oil frequently involves gels or complex microemulsions. Many aqueous gels are employed for macromolecular separations, protein crystallization, etc. Gels of calyx [4]arenes are potential membrane filters [145]. Ajayaghosh and coworkers have reported light-harvesting organogels based on π-conjugated systems [146]. Gels can also be used as a matrix for molecular recognition. Feringa et al. demonstrated chiral recognition through cooperative interactions between aggregates and gels of bis (ureide)-cyclohexane-based gelators with a coaggregating guest of the same structure bearing an azobenzene chromophore [147]. A further practical relevance is the use of organogel superstructures as templates for creation of inorganic structures [148-150]. One of the most challenging goals is the transcription of chirality in inorganic materials. By using the template effect of cholesterol-based organogel system, Ono et. al. demonstrated that the chirality of organic compounds and their assemblies could be transcripted into inorganic materials [151].

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