Chapter 1: Amphiphiles and their self-assembly

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A basic overview of amphiphiles and their self-assembly is provided in this chapter. First, the hydrophobic effect is described, followed by amphiphilic self-assembly and their stability thermodynamics. A succinct explanation of the relationship between the aggregate and molecular shapes is provided. The amphiphilic molecule's cylindrical shape is more suited for creating the bilayer assembly. Additionally covered is the general phase behavior of amphiphile compounds in aqueous solution. Direct hexagonal phase has a strong dominance in the phase diagram. At the end of the chapter, there is a brief discussion of intermediate phases such cubic, ribbon, and mesh phases as well as nematic, hexagonal, and lamellar phases.

1.1 Amphiphiles

The word amphiphile comes from the Greek prefix amphi, which means both or double, and the word phile, which means like or love. In general, an amphiphile is any molecule that consists of two parts, one which is soluble in a specific fluid and the other insoluble. When the fluid is water, one usually talks about hydrophilic and hydrophobic parts, respectively. The hydrophilic part is referred to as the 'head group' and hydrophobic part as the 'tail'. Examples of amphiphiles are surfactants, block copolymers, lipids, bile acids, and cholesterol [1–3]. Synthetic amphiphiles are often referred to as surfactants, whereas those of biological origin are usually called lipids. However, this classification is not standard, but this is the sense in which these two terms are used here. Amphiphilic molecules can be classified depending on the nature of their head groups as ionic, non-ionic and zwitterionic. The head groups of ionic amphiphiles dissociate in water and acquire an electric charge. For example, cetyltrimethylammonium bromide (CTAB) is a cationic surfactant (Fig. 1.1A) and sodium dodecylsulfate (SDS) is an anionic surfactant (Fig. 1.1B). The nonionic surfactant n-dodecyl tetra (ethylene oxide) (C12E4) does not contain any charge but its head group is polar (Fig. 1.1C). In the case of a zwitterionic amphiphile the head group acquires a dipole moment in aqueous solutions (Fig. 1.1D).

1.1.1 Hydrophobic effect

The interaction between water molecules involves orientation dependent hydrogen bonds. Molecules that have high water solubility are known as hydrophilic molecules. These molecules are believed to a have disordering effect on the water matrix around it, which in turn increases the entropy of the system and favors the molecules to be in contact with water [1]. On the other hand, molecules which are not capable of hydrogen bonding such as hydrocarbons and fluorocarbons, do not like to be in contact with water and are known as hydrophobic molecules. When such a molecule is placed in water, the water molecules around it, have to create a cavity to accommodate it. Since non-polar molecules cannot form hydrogen bonds, the creation of the cavity requires either breakage of hydrogen bonds, or rearrangement of the water molecules in a way that breaking of hydrogen bonds is avoided. Which process takes place depends on the details of the solute molecule. The shape of water molecules allows them to arrange themselves around most solutes to form cage-like structures, without breaking hydrogen bonds but in this process the water molecules become even more ordered than in bulk water which is entropically unfavorable. When many such molecules are present in water the loss of entropy becomes too great and it becomes more favorable to break hydrogen bonds and create larger cavities to accommodate an assembly of solute molecules. This leads to an effective attraction between the solute molecules, called the hydrophobic interaction [1, 4]. Due to the hydrophobic interaction, the solute molecules have stronger mutual attraction in water than they do in free space. Hydrophobic effect is very important in nature. It is the reason behind the formation of lipid membrane and affect many other biological processes, e.g. protein folding. It is an important effect which governs many phenomena in soft matter systems, in particular, it is the driving force for amphiphilic self-assembly.

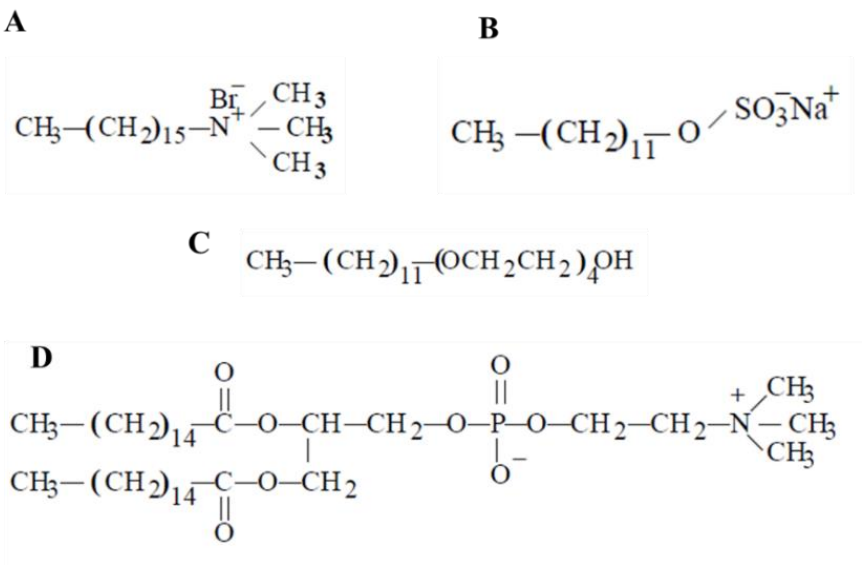

Figure 1.1: Chemical structure of (A) cationic surfactant cetyltrimethylammonium bromide (CTAB), (B) anionic surfactant sodium dodecylsulfate, (C) nonionic surfactant n-dodecyl tetra (ethylene oxide) (C12E4) and (D) zwitterionic lipid dipalmitoyl phosphatidylcholine (DPPC).

1.1.2 Amphiphilic self-assembly

At very low concentrations, amphiphiles form a monolayer at the air-water interface, by positioning their head groups at the water surface and keeping away the hydrocarbon part in the air. At higher concentrations, many of them self-assemble into aggregates of different structures in water, such that their hydrophobic parts are screened from water molecules by their hydrophilic parts. This phenomenon is referred as self-assembly and aggregates formed are called micelles. The amphiphile concentration at which self-assembly occurs is called the critical micellar concentration (CMC). Below CMC the amphiphiles are dispersed in water as monomers, whereas above CMC micelles coexist with monomers.

1.1.2.1 Thermodynamics of self-assembly

From a thermodynamic point of view, the system can be modeled using mass action considerations. That is, an analogy can be drawn between micellization and chemical equilibrium among reactants. Aggregates of different sizes can be treated as distinct chemical species and aqueous solution of an amphiphile can be considered as a multicomponent system with several phases in equilibrium. Each phase is taken to consist of aggregates of a given aggregation number, which is the number of molecules in an aggregate. For a very dilute solution, the interaction between the aggregates

may be neglected and one can apply the theory of dilute solutions to this system. The chemical potential of an amphiphile in an N-aggregate is given by [1, 5],

$$\mu_N = \mu_N^o + \frac{k_B T}{N} \, log \frac{X_N}{N}$$

The first term is the reference chemical potential arising from the mean interaction free energy per molecule (μ_N^o) and the other one comes from the entropy of mixing. $X_N$is the mole fraction of amphiphiles that form *N*-aggregates. The total mole fraction of the amphiphiles $X = \sum_{N=1}^{\infty} X_N \ll 1$. In chemical equilibrium, the chemical potential of the amphiphile (μ_N) remains the same for all *N*. Thus,

$$\mu_1^o + \frac{k_B T}{1} \, log \frac{X_1}{1} = \mu_2^o + \frac{k_B T}{2} \, log \frac{X_2}{2} = \ldots = \mu_N^o + \frac{k_B T}{N} \, log \frac{X_N}{N}$$

This gives the equilibrium distribution of the *N*-aggregates

$$\frac{X_N}{N} = X_1 Exp(\frac{\mu_1^o - \mu_N^o}{k_B T})$$

If we define $\alpha = (\frac{\mu_1^o - \mu_N^o}{k_B T})$, then $X_N = X_1 \, Exp(\alpha)$

Therefore, aggregation can take place only if α>0. Hence the energy per molecule must be lower in aggregates of size M, for some M > 1. In practice, M~50, and is determined by the optimal packing of the hydrocarbon chains within the micelles. Since X_N cannot exceed unity, the limiting value of monomer concentration, $X_1 \sim Exp(-\alpha)$. The critical micellar concentration (CMC), is the amphiphile concentration at which X_1 saturates and further addition of amphiphiles leads to the formation of micelles (fig. 1.2A). It is given by, $CMC \approx Exp(-\alpha)$.

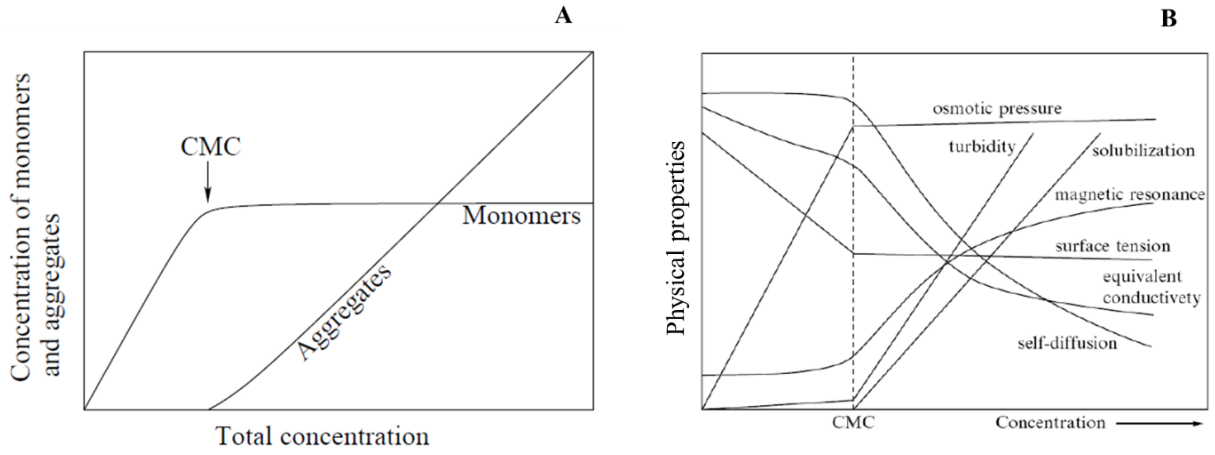

Figure 1.2: (A) Variation of monomers (X1) and aggregates concentration (XN) as a function of the amphiphile concentration (X) (from ref. [1]) and (B) Schematic representation of the concentration dependence of some physical properties of micelle forming surfactant solutions (from ref. [6]).

Experimentally, CMC is determined by studying the variation of certain physical quantities. Below the CMC value, some physical parameters such as turbidity, osmotic pressure and equivalent conductivity increase with concentration and surface tension decreases with concentration, but show a rather abrupt change in the concentration dependence above the CMC value [6], as in (fig. 1.2B).

The CMC depends on the chemical structure of the surfactant and many external factors, e.g., pH, temperature and pressure [7]. For example, it decreases strongly with increasing the hydrocarbon chain length of the surfactant. This is because the critical chemical potential, k_BT log(CMC), decreases linearly with chain length, with each methyl group contributing about 2-3 k_BT. The CMC of ionic surfactants (typically 10^{-3} - 10^{-2}M) is orders of magnitude higher than that of nonionic amphiphiles (typically 10^{-5} - 10^{-4}M). This is due to the smaller repulsion between the head-groups in the nonionic case. However, the CMC for lipids is typically~10^{-9}M, which is due to the large hydrophobic effect caused by their two chains. The addition of salt decreases the CMC of ionic surfactants by up to an order of magnitude. This effect is due to the electrostatic screening caused by the salt ions, which reduces the repulsion between the ionic head groups. However, salt has little effect on the CMC of nonionic amphiphiles and it can either increase or decrease.

1.1.2.2 Shapes of aggregates

The shape of aggregates in isotropic micellar solutions, just above CMC is usually spherical. In a mesomorphic state, aggregates can have different shapes, such as cylindrical, rod-like or disc-like. These shapes are subjected to a geometrical constraint; one of the three dimensions must be limited by the value 2*l*, where *l* is the length of the amphiphilic molecule. To classify and study these structures, the packing parameter *p* is introduced,

$$p = \frac{v}{a\,l}$$

where *a* is the optimal head group area, *v* the hydrocarbon chain volume and *l* the chain length. For $p < 1/3$, the molecules have a conical shape, which would force the aggregate to have a spherical shape. For other values of this parameter (*p*), the molecules can form cylindrical micelles, planer bilayer or inverted micelles (Figs. 1.3 and 1.4, Tab. 1). However, the shape of amphiphiles depends upon concentration, pH, temperature, etc.

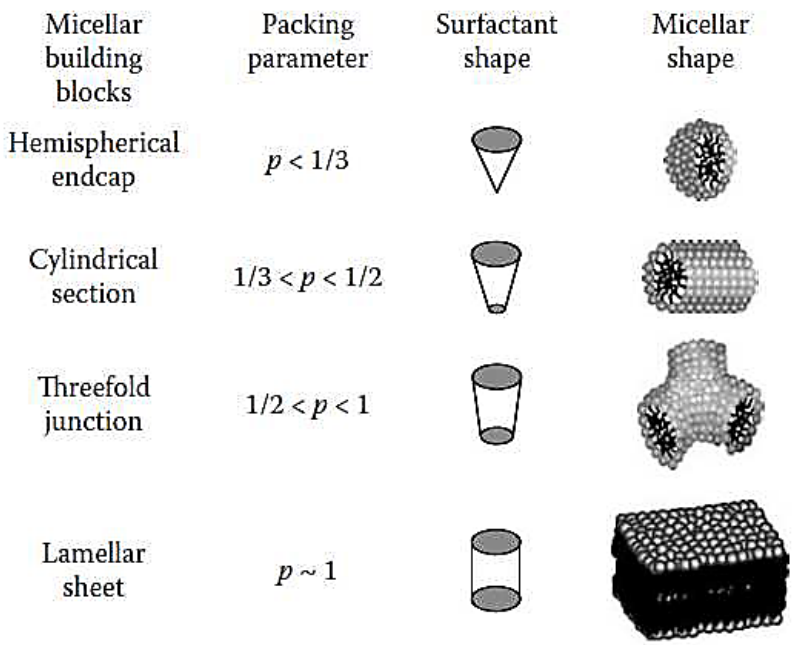

Figure 1.3: Dependence of aggregate morphology on the packing parameter (from ref. [8]).

In the case of spherical micelles, radius of the micelles is determined by chain length of amphiphilic molecule. As a result, the size distribution of spherical micelles is fairly mono-disperse. The radius of a cylindrical micelle is again set by the length of the amphiphile. Cylindrical micelles have hemispherical end-caps, which cost additional energy to create. This end-cap energy is clearly independent of the length of the cylinder. The length distribution of cylindrical micelles is determined by the competition between entropy, which would favor shorter and hence larger number of micelles, and end-cap energy, which would favor longer and hence smaller number of micelles. Since the end-cap energy is independent of the length of the cylinder, this results in a very broad length distribution of these micelles. The end-cap energy can be made very large by adding certain salts and alcohols to the amphiphile solution. This results in the formation of very long, flexible micelles that become entangled to form a viscoelastic gel. These are known as 'worm-like' micelles and these micelles may be microns long and have either a circular or elliptical cross section of a few nanometers. They behave in many ways similar to polymers [9]. Another kind of micelles is disc-like, have semi-toroidal rims in order to prevent the hydrocarbon chains from being in contact with water. The formation of these curved edges, however cost energy. The difference in the behavior of disc-like and rod-like micelles arises from the fact that the perimeter of the rim of a disc increases with the disc radius, whereas the size of the end cap on a cylinder is independent of the length of the cylinder. Generally, disc-like micelles are unstable and coalesce to form an infinite bilayer in order to decrease the edge energy. However, disc-like micelles are found in some multi-component amphiphilic systems [10–12].

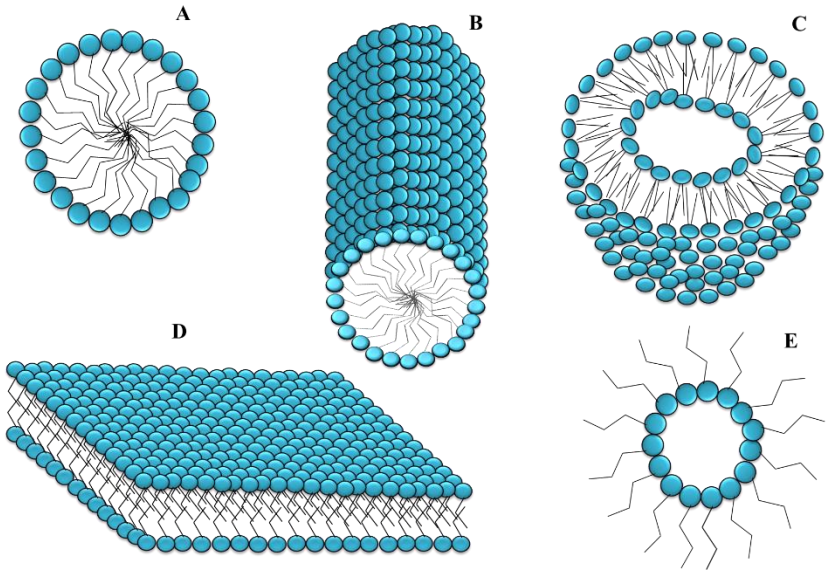

Figure 1.4: Schematics of various self-assembled structures of amphiphilic molecules: (A) spherical micelle, (B) cylindrical micelle, (C) vesicle, (D) bilayer and (E) inverted micelle.

Micelles are very useful in many fields of science and technology [3, 13, 14]. In chemistry micelles are used as catalysts and solubilizing agents in many organic and inorganic reactions. In colloid chemistry spherical micelles are used as a model system for studying many problems, for example the various interactions between colloid particles. They are very important in cosmetics and oil industry. Viscoelastic solutions of amphiphiles are widely used as lubricants. They are also used in medicine for encapsulating drugs in their hydrocarbon cores, in oil recovery for solubilizing oil droplets. Some of these systems have also been used for protein crystallization [15]. The recent development of nanotechnology has again expanded their field of application. For example, various liquid crystalline phases exhibited by these molecules have been used as templates for the synthesis of mesoporous materials and nano particles.

1.2 Phase behavior of aqueous solutions of amphiphiles

Figure 1.5 presents the generic temperature-composition phase diagram of binary surfactant-water systems. Below the CMC, amphiphiles form an isotropic molecular solution. However, just above the CMC, they usually form a solution of spherical micelles. The next phase is a cubic phase built up of discrete globular micelles. Due to the free energy penalty of packing globular micelles at high volume fractions, the micelles deform and become elongated into cylindrical micelles to form finally a 2D hexagonal lattice, with their long axes aligned normal to the plane of the lattice. This hexagonal phase is usually observed over a wide range of composition. Thereafter, the hexagonal phase transform to a lamellar phase (L_α), consisting of a periodic stack of bilayers separated by

water layers; due to free energy penalty of packing cylindrical micelles at high volume fractions. This lamellar L_α phase is a one-dimensional (1-D) lattice of bilayers, with liquid-like short range positional ordering of the molecules within the bilayers. Further increase of surfactant concentration gives-rise to a hexagonal phase of inverted micelles in some systems. This hexagonal phase can be looked at as consisting of a 2D lattice of water columns in the hydrocarbon matrix. The Kraft point or Kraft temperature shown in figure 1.5 is the temperature below which the amphiphile is in the crystalline phase and is insoluble in water. Schematics of various lyotropic liquid crystalline phases are shown in figure 1.6.

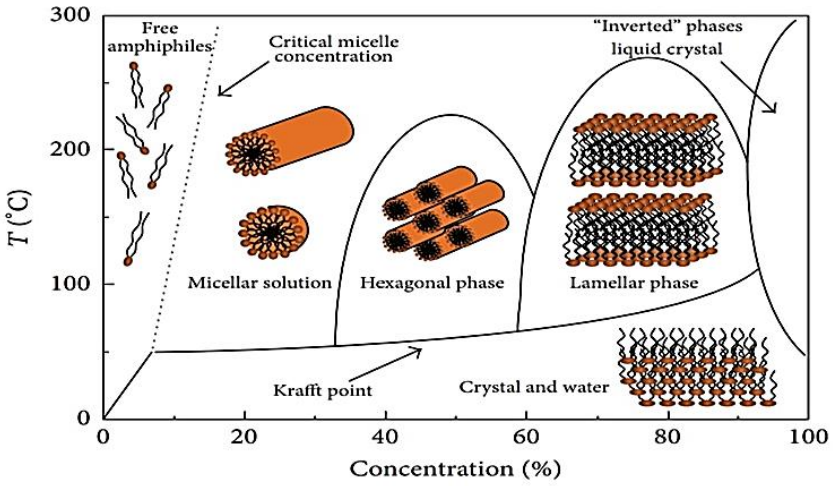

Figure 1.5: Schematic of phase diagram of amphiphile-water system (from ref. [16]).

For double chain surfactants the phase diagram looks different as in the case of dioctyl sodium sulfosuccinate (Aerosol OT or AOT) and dioctadecyl dimethyl ammonium chloride (DODMAC) [17, 18]. As for the single chain surfactant, the chain melting temperature strongly depends on the chain length. In the case of DODMAC the chains are long, which leads to a high melting temperature. The important feature of phase diagram of this class of surfactant is the stability of the lamellar phase over a wide composition range. In addition, this type of surfactant generally shows bicontinuous cubic phase and inverted hexagonal phase at higher surfactant concentrations. Double-chained lipids, such as dipalmitoyl phosphatidylcholine (DPPC), form only bilayers at all concentrations, except at extremely low water content. Hence, lamellar phases are very common in these systems. Above, the chain melting temperature, fluid lamellar (L_α) phase is found in this system and lamellar 'gel' phase is seen at lower temperatures, where the hydrocarbon chains are mainly in the all-trans conformation and arranged on a 2-D lattice within each bilayer.

In some systems, in between the isotropic and hexagonal phases, the rod-like micelles acquire long range orientational order to form a nematic phase denoted as N_c [19, 20]. Disc-like micelles, in

between isotropic and lamellar phase, also exhibit the nematic phase [21], referred as N_d. Here, rod like (disc-like) micelles director ($\vec{n}$). These nematics are uniaxial in character. Another kind of nematic of biaxial character, so called 'biaxial nematic' N_B has also been reported in the literature [22, 23] (Fig. 1.7). Generally, these three nematics are not found in one amphiphile. However, the potassium laurate/ decanol/water [25] system displays all the three nematic phases.

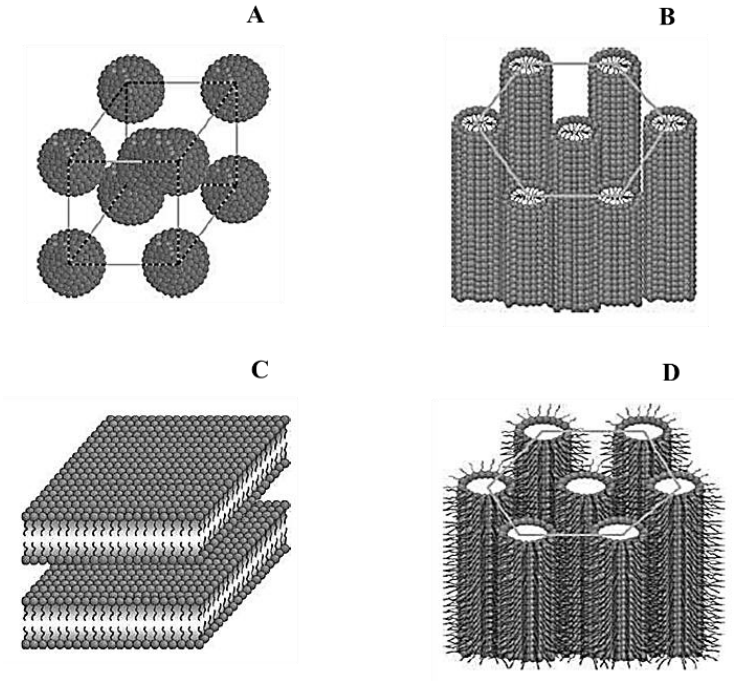

Figure 1.6: Schematics of various lyotropic liquid crystalline phases: (A) micellar cubic (bcc) phase, (B) direct hexagonal (H_I) phase, (C) lamellar (L_α) phase and (D) Inverted hexagonal (H_{II}) phase (from ref. [24])

A cholesteric phase can be formed if a nematic phase is doped with a chiral molecule. Three types of lyotropic cholesterics have been reported in the literature, Chc, Chd, and ChB [26]. The labels c, d, and B refer to the original nematic phases (calamitic, discotic, and biaxial), which were cholesterized by the addition of the chiral dopant. It has been observed that micelles spontaneously pack in a helicoidal structure (Fig. 1.8) whose pitch depends on the physico-chemical parameters [27], such as temperature, concentration of the chiral dopant (c_m) and micellar shape anisotropy (Sa). In cholesterics, the typical length scale of the pitch is of the order of micrometers.

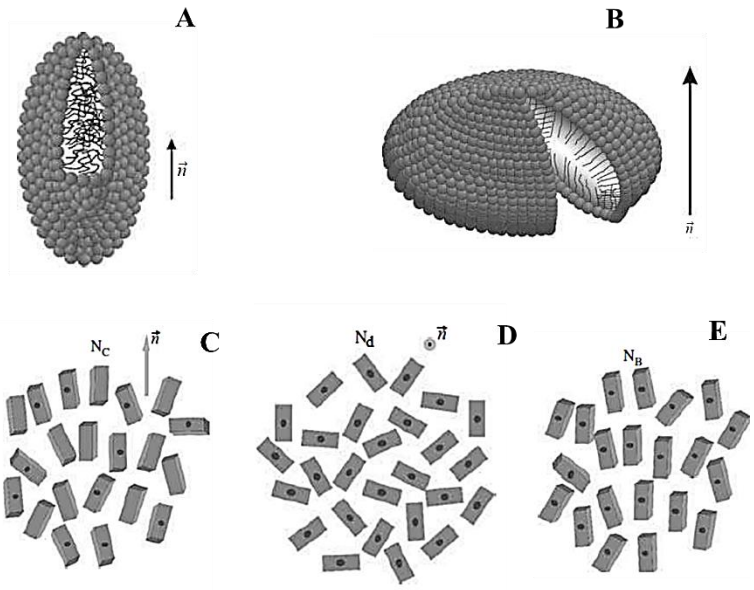

Figure 1.7: Schematics of micelles in lyotropic mixtures: (A) prolate ellipsoid or rod-like, (B) oblate ellipsoid or disc-like; ~n is the director and cuts show the paraffinic chains in inner part of micelles. Sketch of the order in the context of the intrinsically biaxial (brick-like) micelles model. The dots represent a particular surface of the micelles: (C) N_c phase, (D) N_d phase and (E) N_B phase (from ref. [24]).

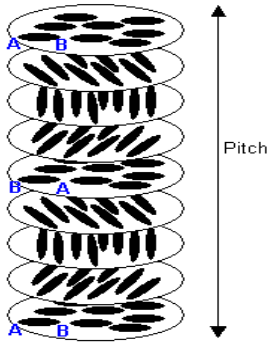

Figure 1.8: Sketch of a sequence of micelles in a cholesteric structure. A and B denote the two ends of the rod-like micelles.

As described above, the hexagonal phase consists of cylindrical micelles with uniform curvature of the surfactant-water interface (neglecting the hemispherical end caps), whereas the lamellar phase is made up of planar bilayers. Many studies indicate that the morphological transformation from cylinders to bilayers does not take place abruptly, but through a sequence of intermediate shapes, giving rise to a sequence of so-called intermediate phases between the hexagonal and lamellar phases [28]. In ionic surfactants the intermediate phases usually occur only over very narrow ranges of composition. Further, the phase boundaries in these systems are almost

independent of temperature [29]. Intermediate phases are frequently observed in the presence of a co-surfactant over a wide range of composition [30].

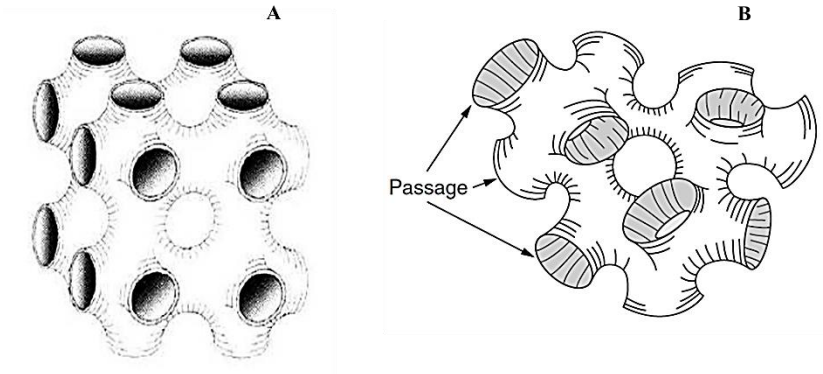

Figure 1.9: Schematic of (A) a bicontinuous cubic phase and (B) a sponge (L_3) phase (from ref. [33]).

Frequently a bi-continuous cubic phases, which are optically isotropic, have been identified between the hexagonal and lamellar phases [28, 31, 32]. They form the first class of intermediate phases (Fig. 1.9A). Their identification is made easier by the fact that they are optically isotropic, unlike all other phases found at comparable surfactant concentrations. Hence, their formation can be easily visualized using polarizing optical microscopy observations. Cubic phases can be classified into two types. Type I cubic phases consist of two interpenetrating, topologically identical networks of cylindrical micelles, separated by water. In type II cubic phases two interpenetrating water channels are separated by a surfactant bilayer. Interestingly, the surface separating the two networks into two equal volumes can be described as a triply periodic minimal surface characterized by vanishing mean curvature everywhere on the surface. Three cubic structures have been reported belonging to the space groups Im3m, Ia3d and Pn3m, usually associated with the P, gyroid and D triply periodic minimal surfaces respectively. Although some bicontinuous non-cubic intermediate phases have been proposed in the literature, their existence has not yet been unambiguously established [28].

Another type of intermediate phase seen in some surfactants is the ribbon phase consisting of long micelles with roughly elliptical cross-section (Fig. 1.10A). These arrange on a two-dimensional rectangular lattice. Two types of structures have been reported, corresponding to the plane groups cmm and pgg [34–36].

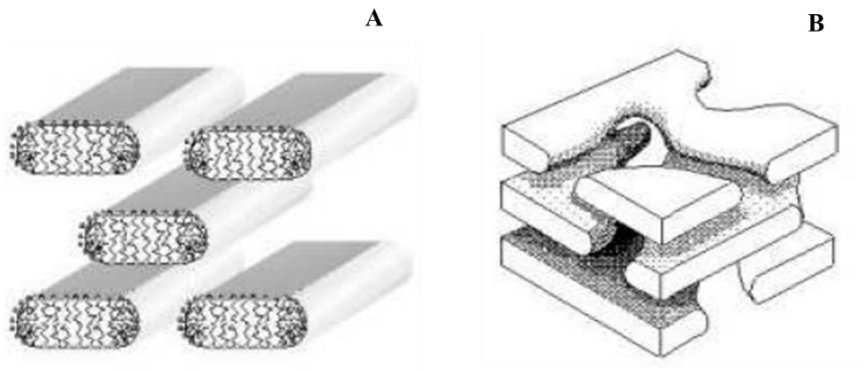

Figure 1.10: Schematic diagram of (A) centered rectangular lattice made up of ribbon-like aggregates, (B) a random mesh phase (from ref. [28]).

Mesh phases are the third type of intermediate phases seen in many surfactant systems. They consist of two-dimensional mesh-like aggregates, which can also be described as bilayers with a regular array of mono-disperse pores. Mesh phases are of two types-ordered and random mesh phases. In the ordered mesh phase, the mesh-like aggregates lock into a three-dimensional lattice. On the other hand, the random mesh phase consists of a periodic stacking of these aggregates with no long-range positional correlations of the in-plane structure (Fig. 1.10B). All known structures of ordered mesh phases are either rhombohedral (space group: $\bar{R}3m$) or tetragonal (space group: I4mm). The former consists of a 3-layer stacking of 3-coordinated hexagonal mesh, whereas the latter has a 2-layer stacking of 4-coordinated square mesh (Fig. 1.11).

Most of the studies on mesh phases, reported in the literature, have been carried out on the non-ionic surfactants, poly (oxyethylene glycol) alkyl ethers (C_nEO_m), where they occur over a rather wide range of composition [38–46]. The role of the length of the hydrocarbon chain of the surfactant in stabilizing different intermediate phases has been well studied in this class of surfactants. Shorter hydrocarbon chains are found to favor the bi-continuous cubic phase, whereas longer ones induce mesh phases [45]. The structures of both these bi-continuous and mesh phases are consistent with the theoretical predictions of Hyde [47, 48]. However, the theory does not explain the role of chain length in determining the structure. It has been conjectured that the increase in micellar curvature due to an increase in the head group size gives rise to the cubic phase, whereas the decrease in the flexibility of the aggregate due to an increase in the chain length induces the intermediate mesh phase. A variety of intermediate phases, such as ribbon, ordered mesh and bi-continuous cubic, have been seen in the sodium dodecyl sulphate (SDS)-water system, albeit over very narrow ranges of composition.

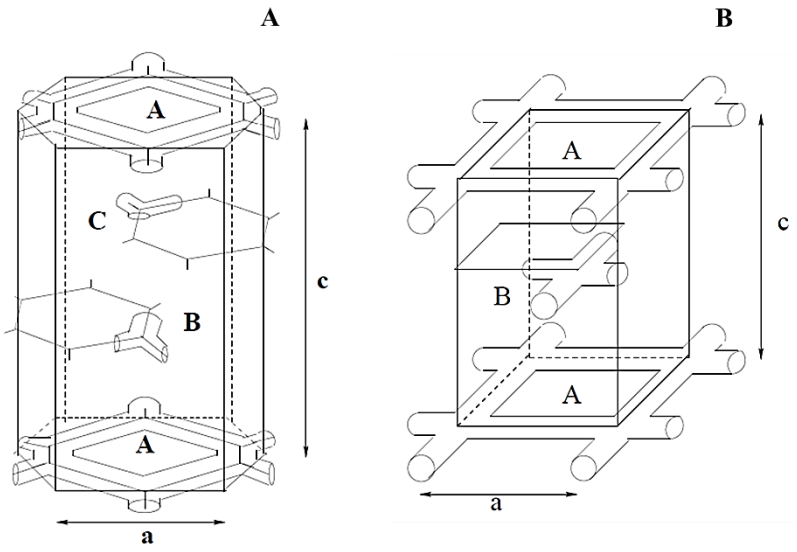

Figure 1.11: Schematic of an ordered mesh phase: (A) hexagonal unit cell and (B) a tetragonal unit cell (from ref. [37]).

Worm-like micelles that occur most frequently upon increasing the concentration of the surfactant or of an added salt, or in the presence of specific counterions. These micelles can be cross-link into a network and break and reform spontaneously or under stress, and so are often called 'living polymers' [49].

In many systems the isotropic (L_3) sponge phase observed in narrow phase regions adjacent to the domain of stability of the L_α phase [50]. Sponge phase exhibits no long-range order and consists of one extended bilayer in a convoluted morphology, which is randomly interconnected throughout space and divides the sample volume into two equivalent strongly interwoven sub volumes (Fig. 1.9B). The relative stability of the isotropic L_3 and L_α structures depends critically on the membrane flexibility which can be tuned by varying temperature, electrolyte concentration, and co-surfactant surfactant ratio. The confinement of a sponge phase between two rigid macroscopic walls of a surface forces apparatus can lead to a first-order transition to a lamellar phase [51].

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