# CHAPTER II
# LITERATURE REVIEW

## 2.1 Surfactants

### 2.1.1 Basic Principle

Nowadays, surfactants play an important role in which they are generally added to the process in order to produce various kinds of products that can be used in every human daily's life. They are used in many applications ranging from the mining industry to the nutrition industry. The largest market for surfactants is the households and personal-cared products. The personal-cared sector comprises of toilet soaps, hair-cared products, skin-cared products and oral-cared products (Behler *et al.*, 2000). The word *surfactant* is short for "SURFace-ACTive AgeNT". The term is literally descriptive because a surfactant does in fact concentrate at the boundaries between two immiscible phases: air-water interfaces, soil-solvent interfaces and fabric-water interfaces. Basically, the molecular structure of surfactants consists of a non-polar hydrophobic portion (lipophilic); usually a straight or branched hydrocarbon or fluorocarbon chain containing 8–18 carbon atoms, which is attached to a polar or ionic portion (hydrophilic). The hydrophilic portion can; therefore, be nonionic, ionic or zwitterionic. Figure 2.1 shows a typical structure of a surfactant. The hydrocarbon chain interacts weakly with the water molecules in an aqueous environment, whereas the polar or ionic head group interacts strongly with water molecules via dipole or ion-dipole interactions (Tadros, 2005). Surfactants also have the property of forming colloid-sized aggregates in a solution called micelles at sufficient high concentrations. The lowest total surfactant concentration at which micelles are present is called critical micelle concentration (CMC).

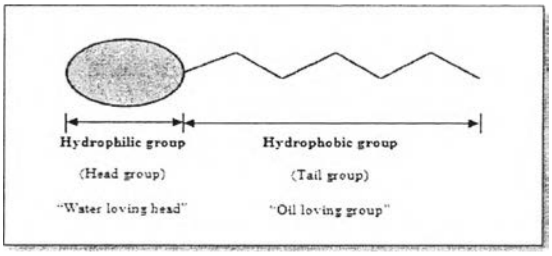


**Figure 2.1** Surfactant structures.

Generally, the hydrophobic part is a long-chain hydrocarbon but it may contain aromatic. For the hydrophilic part is carrying a positive or negative charge, giving rise to cationic or anionic surfactants, respectively otherwise contains ethylene oxide chains, sugar or saccharine group, as in the case of nonionic surfactants. Base on the charge present in the hydrophilic group, surfactants can be categorized into 4 types.

1. *Anionic surfactant.* The hydrophilic portion has a negatively charge, for example, $RCOO^-Na^+$ (soap), and $RC_6H_4SO_3^-Na^+$ (Alkyl Benzene Sulfonate).

2. *Cationic surfactant.* The hydrophilic portion has a positively charge, for example, $RNH_3^+Cl^-$ (salt of a long-chain amine), and $RN(CH_3)_3^+Cl^-$ (quaternary ammonium chloride).

3. *Nonionic surfactant.* No charge presents in the hydrophilic portion, for example, $RCOOCH_2CHOHCH_2OH$ (monoglyceride of long chain fatty acid), and $RC_6H_4(OC_2H_4)_xOH$ (polyoxyethylenated alkylphenol).

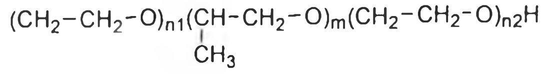
4. *Zwitterionic surfactant.* Both positive and negative charge may be present in the hydrophilic portion which leads to the head group hydrophilicity being an intermediate between the ionic and conventional nonionic classes. The charge depends on pH of solution. At low pH (acidic solution), they form cations, and at high pH (alkaline solutions), they form anions. For example, $RN^+H_2CH_2COO^-$ (long chain amino acid), and $RN^+(CH_3)_2CH_2CH_2SO_3$ (sulfobetaine).

### 2.1.2 Polymeric Surfactants

One of the main problems hindering utilization of surfactant-modified surface is surfactant desorption. Consequently, polymeric surfactant is used to reduce this problem because it can increase the stability of the surfactant coating on the solid surface (Atthaphong *et al.*, 2010).

#### *2.1.2.1 PEO-PPO-PEO Triblock Copolymer*

Water-soluble triblock copolymers of poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO), often denoted PEO-PPO-PEO or $(EO)_{n1}(PO)_m(EO)_{n2}$, are commercially available nonionic macromolecular surface active agents. PEO is hydrophilic part and PPO is hydrophobic part. Therefore, a block copolymer can self-assemble in a polar/non-polar mixture. When they form micelles at the critical micelle concentration (CMC), their core, the PPO part, tries to form a water avoiding shape, is dehydrated, and is protected by an outer water-swelled shell from the PEO part. Block copolymers form aggregrates of different kinds depending on the molecular weight, the block sizes, the solvent composition, and the temperature (Bakshi *et al.*, 2005). The general formula of this copolymer can be written as:



$$(CH_2-CH_2-O)_{n1}(\underset{CH_3}{\underset{|}{C}}H-CH_2-O)_m(CH_2-CH_2-O)_{n2}H$$

Variation of the copolymer composition (PPO/PEO ratio) and molecular weight (PEO and PPO block length) during synthesis leads to the production of molecules with optimum properties that meet the specific requirements in various areas of technological significance. The ratio number of ethylene oxide units by number of propylene oxide units, also known as the hydrophilic/lipophilic balance (HLB) can be changed easily. Commercial names for PEO-PPO-PEO polymeric surfactants are Poloxamers (manufactured by ICI) and Pluronics (manufactured by BASF). In addition, this copolymer can be expected to be environmentally acceptable surfactant with no toxicity. As a result, PEO-PPO-PEO triblock copolymers are an important class of surfactants and find widespread industrial applications in detergency, dispersion stabilization, foaming, emulsification, lubrication, and formulation of cosmetics and inks, etc., along with more specialized applications in, for example, pharmaceuticals (drug solubilization and controlled release and burn wound covering), bioprocessing (protecting microorganisms against mechanical damage), and separations (solubilization of organics in aqueous solutions).

### 2.1.3 Linker Molecules

Linker molecules are ampliphiles that segregate near the microemulsion membrane either near the surfactant tail (lipophilic linkers) or the surfactant head group (hydrophilic linkers). Linker molecules can be divided into 3 types:

#### *2.1.3.1 Lipophilic Linker*

Lipophilic linkers which serve as a link between the surfactant tail and oil molecules segregate near the surfactant tail and help to improve the solubilization capacity. The linker molecules promote orientation of oil molecules in the oil phase and increase interaction deeper into the oil side of the interface, as shown in Figure 2.2. The impact of lipophilic linkers in oil–water–nonionic surfactant microemulsions was investigated by Salager *et al.* (1998) . His proposed model said that the best linker for improving oil solubilization should be the one which has a tail length that is intermediate between the length of the oil and that of the surfactant tails. Subsequently, Brinck *et al.* (1999) studied surfactant–alcohol mixtures at the silica–water interface and reported that long-chain alcohols promote the in-plane growth of the adsorbed nonionic surfactant aggregates. The thickness of the adsorbed layer is virtually unaffected by the alcohol though the adsorbed layer transforms from small discrete aggregates to larger lamellar structures. Tan and O'Haver (2004) studied the impact of lipophilic linkers (long chain linear alcohols) on the adsorption of and styrene adsolubilization in polyethyoxylated alkylphenols (Triton X) nonionic surfactants with varying EO units on amorphous precipitated silica. Results show that the presence of lipophilic linkers increases both surfactant adsorption and styrene adsolubilization. The enhancement of adsorption and styrene adsolubilization is thought to be caused by the linkers increasing interactions between styrene and surfactant hydrophobic groups.

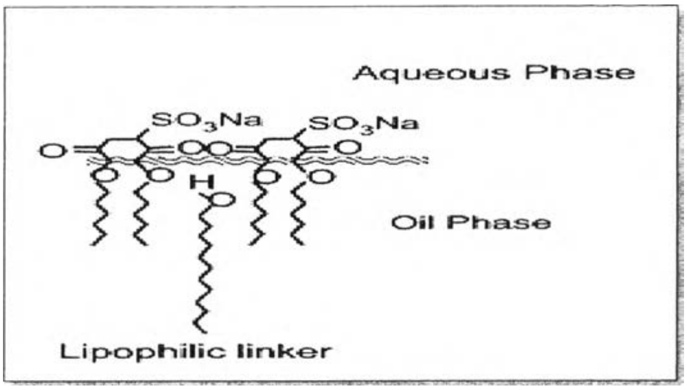


**Figure 2.2** Schematic of molecular interactions including lipophilic linker molecules.

### *2.1.3.2 Hydrophilic Linker*

Hydrophilic linkers are additives that can enhance the surfactant-water interaction. The hydrophilic linkers were found to have interfacial properties between a hydrotrope and a cosurfactant. More specifically, a hydrophilic linker is an amphiphile that coadsorbs with the surfactant at the oil/water interface but that has negligible interaction with the oil phase as shown in Figure 2.3 (Acosta *et al.*, 2002). Uchiyama *et al.* (2000) showed that the hydrophilic linker sodium mono and dimethyl naphthalene sulfonate (SMDNS) has limited capacity to improve the solubilization of chlorinated hydrocarbon. This was attributed to the lack of interaction between SMDNS and oil.

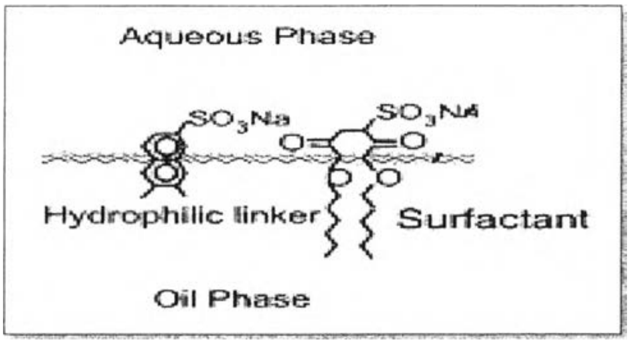


**Figure 2.3** Schematic of molecular interactions including hydrophilic linker molecules.

### *2.1.3.3 Combined Linker*

Combined linker is a linker system that combines with lipophilic linker and hydrophilic linker, as shown in Figure 2.4. When lipophilic and hydrophilic linker are added to the system. They show a special synergism reflected not only in an increased solubilization but also in an increased interfacial activity of each liner, they form a "self-assembled surfactant" at the interface.

Sabatini *et al.* (2003) investigated the role of hydrophilic linker in forming microemulsion. They investigated homologous alkyl naphthalene sulfonate: sodium naphthalene sulfonate (SNS), sodium mono- and dimethyl naphthalene sulfonate (SMDNS) and sodium dibutyl naphthalene sulfonate (SDBNS), for their role in forming SDHS-TCE microemulsion both with and without dodecanol as a lipophilic linker. They found that SNS shows no synergism when combined with dodecanol. For SMDNS, which acts as a hydrophilic linker, they note that, while alone it doesn't impact the solubilization capacity of the system. When SMDNS and dodecanol are combined, they show a synergistic effect that is reflected by an increased solubilization and increased partitioning of SMDNS into the interface. For SDBNS, it increases the solubilization capacity of the system in the absence of dodecanol, and strongly partition into the middle phase system. In addition, combining dodecanol and SDBNS increases the solubilization capacity of the system according to the lipophilic linker effect, but it doesn't show a special synergism since the SDBNS partitions into the interface remain at the same level with or without dodecanol.

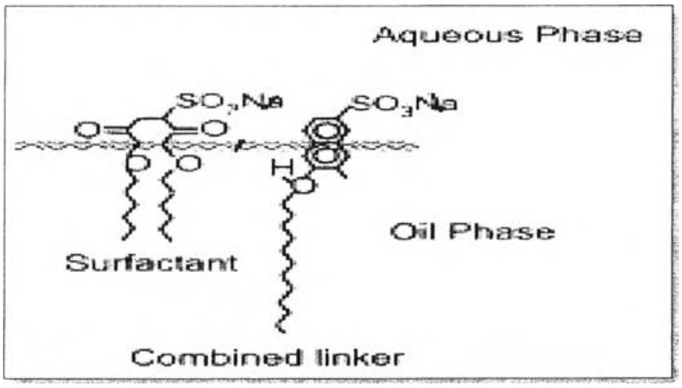


**Figure 2.4** Schematic of molecular interactions including combined linker molecules.

## 2.2 Surfactant Adsorption

### 2.2.1 Fundamentals

Surfactant adsorption is a process of surfactant molecules to transfer from the bulk solution phase to the interface. The adsorption of surfactant at solid-liquid interface is strongly influenced by a number of factors: (1) the nature of the structural groups on the solid surface (2) the molecular structure of the surfactant being adsorbed (the adsorbate) (3) the environment of the aqueous phase such as pH, electrolyte content (Rosen, 1989). The general adsorption isotherm of surfactants can be divided into 4 regions. Four-regime isotherm was typically observed for adsorption of ionic surfactant on oppositely charged solid surface and adsorption of non-ionic surfactant on silica surface (Paria, 2004). The schematic diagram of a typical adsorption isotherm of surfactant is illustrated in Figure 2.5.

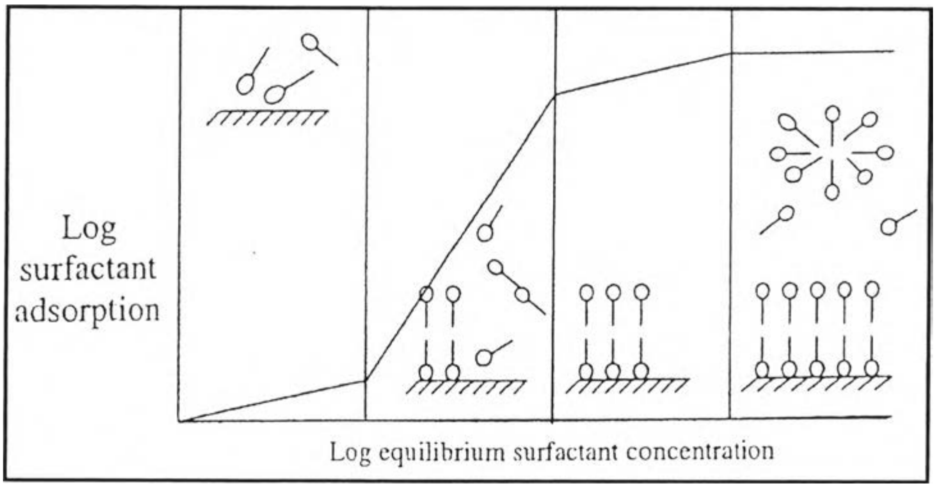


**Figure 2.5** Four- regime adsorption isotherm of surfactant.

**Region I:** The adsorption occurs at low surfactant concentration and it is commonly referred as the Henry's Law region due to the surfactant isotherms are linear and have a slope of unity (Somasundaran *et al.*, 1987). In this region, surfactants adsorb at the interface as individual ions and the adsorption occurs by ions exchange of counter ions. Under conditions with constant ionic strength, the adsorption occurs through the electrostatic interaction between the oppositely charge between solid surface and surfactants (Scamehorn *et al.*, 1982).

**Region II:** The adsorption in this region is characterized by a sharply increased isotherm slope relative to the slope in the Henry's Law region. This is a general indication of the onset of cooperative effect between adsorbed molecules. It is widely accepted that this cooperative consists of the formation of micelle-like aggregates of adsorbed surfactants. These aggregates are frequently called admicelles or hemimicelles and self-assemblies (Harwell *et al.*, 1987), depending on whether their morphology is viewed as local bilayers or local monolayer, and the transition point from Region I to Region II is called the critical admicelle concentration (CAC) or hemimicelle concentration (HMC). As the driving force for micelle formation is the tail-tail interactions in the micelles, so for admicelles and hemimicelles their formation is driven by hydrophobic interactions between tail groups. In this region, the surface is not completely covered and enough sites on the surface are available for further adsorption.

**Region III:** In this region, the adsorption is characterized by a decrease in the isotherm slope relative to the slope in Region II because of the increasing in electrostatic hindrance to surfactant adsorption causing the surface becomes like-charged to the surfactant and the surface beings to repel the surfactant ions. In addition, the adsorption in this region occurs through the growth of exiting aggregates rather than the new aggregates formation of surfactants due to lack of adsorption sites.

**Region IV:** In this final region, the adsorption isotherm reaches a plateau region which corresponds to the maximum surface coverage. Generally, the region III/region IV transition occurs approximately at the CMC of surfactant, and reflects the effect of micelle formation on the chemical potential of surfactant monomer, the formation of micelle affects the variation of surface tension with surfactant concentration. In some systems; however, the Region III/ Region IV transition can be reached when the surface becomes saturated with adsorbed surfactant. For the adsorption of surfactants from aqueous solutions, this will correspond to bilayer completion for ionic surfactants adsorbed on oppositely charged surfaces, or to monolayer completion for adsorption on hydrophobic surfaces.

### 2.2.2 Adsorption of PEO-PPO-PEO Triblock Copolymers

The conformation of the triblock copolymer molecule that adsorbs onto the substrate surface depends on the properties of the surface and the quality of the solvent. For triblock copolymer adsorption from water onto a hydrophobic surface, the propylene oxide block which has high hydrophobicity acts as the anchor, being mainly situated near the surface because of its high surface affinity. The ethylene oxide segments which have high polarity are not found to adsorb, they have no affinity for the surface. The conformation of the adsorbed triblock copolymer is look like a brush. The thickness of a (saturated) brush layer depends mainly on the length of the ethylene oxide groups. For a hydrophilic substrate such a silica, the situation is different. Ethylene oxide has the highest surface affinity and will preferentially adsorb, thus the conformation of the adsorbed triblock copolymer is look like a pancake. Compared to a saturated brush layer, the pancake layer is in general less thick (Schroën *et al.*, 1995). Schematic representation of PEO-PPO-PEO triblock copolymers adsorbed at a hydrophobic and a hydrophilic surface, as shown in Figure 2.6.

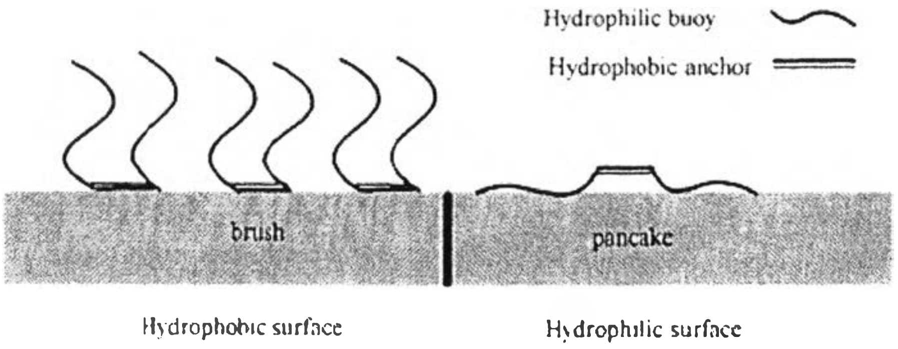


**Figure 2.6** Schematic representation of PEO-PPO-PEO triblock copolymers adsorbed at a hydrophobic and a hydrophilic surface (Schroën *et al.*, 1995).

Malmsten *et al.* (1992) studied the adsorption of PEO-PPO-PEO block copolymers on silica. For a number of polymers with a total molecular weight of approximately 15000, they was found that the adsorbed amount is rather low (0.35-0.40

mg/m$^2$) and independent of the PPO content in the range 0-30% PPO. For a copolymer with a total molecular weight of 4000 and 50% PPO content, the adsorbed amount was approximately 0.20 mg/m$^2$. Thin adsorbed layers, with hydrodynamic thicknesses of about 2-5 nm, were performed by all polymers investigated. At higher pH, both the adsorbed amount and the hydrodynamic thickness decrease until complete desorption occurs. Because of at higher pH, the silica surface becomes increasingly (negatively) charged, increasing the affinity of cations for the surface, as well as decreasing the affinity of the polymer for the surface.

Shar *et al.* (1998) investigated the adsorption of a series of PEO-PPO-PEO triblock copolymers onto hydrophobic polystyrene latex. They found that the adsorbed amount of copolymers increases with increasing total molar mass and with the variable block molar mass. The copolymers with PEO block sizes smaller than or equal to the PPO block size adsorb more strongly than the copolymers of the corresponding molar masses predominantly consisting of PEO blocks. The random copolymers (50:50 ratio of PEO/PPO) and the high anchor-fraction of block copolymers adsorb at similar levels but are at substantially higher levels than the PEO homopolymers. In contrast, the low anchor-fraction (high PEO content) of block copolymers adsorb at levels lower than the random copolymers but higher than the PEO homopolymers of the corresponding molar masses. An increase in the adsorbed amount of the copolymers with increasing PPO block molar mass at fixed PEO block size also confirms the strong dependence of adsorbed amount on the anchor content. In addition, the hydrodynamic thickness of the adsorbed layer was determined. An increase in PEO block size increases the number of segments in tails which contribute more towards the hydrodynamic thickness of the adsorbed layer. However, an increase in the PPO block size increases the affinity between the surface and the polymer segments which raises the adsorbed amount; hence, in turn, the hydrodynamic thickness of the adsorbed layer. Random and block copolymers show higher hydrodynamic layer thickness values than the PEO homopolymers. For the block copolymers at high PPO content the layer thickness is greater than both the PEO homopolymer and the random copolymer.

In the following year, Shar *et al.*(1999) studied the adsorption of the same series of PEO-PPO-PEO copolymers from aqueous solution onto hydrophilic silica particles. They found that the adsorbed amounts presented in the study are about 5-6 times lower than those measured for the same copolymers on hydrophobic polystyrene latex. The adsorbed amount increased with increasing the total polymer molar mass. Comparison between the adsorption of these PEO-PPO-PEO triblock copolymers on silica and on polystyrene latex show higher maximum amount adsorbed at the interface ($\Gamma_{max}$) for the hydrophobic surface. Moreover, much lower adsorbed amounts were observed for PEO homopolymers than the copolymers. In the case of PEO homopolymers show overall lower amount adsorbed values suggests a flatten adsorption configuration for these polymers. In addition, they found that the adsorbed amount depends on both anchor and buoy blocks. Hydrodynamic thickness of the copolymers is found to be approximately 4 times lower for silica surface than that observed for the polystyrene latex surface. Copolymers show higher hydrodynamic thickness values than the PEO homopolymers of the corresponding molar mass. There is an increase in the hydrodynamic thickness of the adsorbed layer with increasing PPO block size for constant PEO block size. This effect, how ever, is smaller than that observed for the polystyrene latex.

## 2.3 Adsolubilization

### 2.3.1 Fundamentals

Scemehorn and Harwell (1988) suggested that the adsolubilization is "the incorporation of compounds into surfactant surface aggregates, which compounds would not be in excess at the interface in the absence of the surfactant". Adsolubilization system consists of three major components: the first is solid substrates such as silica, alumina, and titanium dioxide , the second is surfactant such as triblock copolymer, cetyltrimethylammonium bromide (CTAB), and sodium dodecyl sulfate (SDS), and the third is organic solutes such as phenol, 2-naphthol, and naphthalene. Adsolubilization mechanisms occur following these steps: firstly, surfactant molecule in aqueous solution adsorbs onto solid surface monolayer form. Then surfactant molecule will form second layer that is called admicelle. Thus, surfactant adsorbed layer exhibit hydrophobic properties. Finally, organic compounds in aqueous solution into surfactant adsorbed layer. The phenomena of adsolubilization are shown in Figure 2.7.

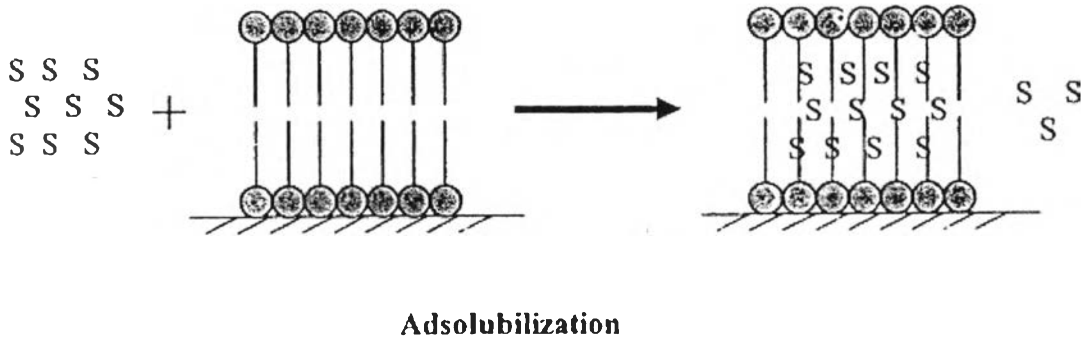


**Figure 2.7** The phenomena of adsolubilization.

Basically, the admicelle is devided into three regions. Figure 2.8 shows the structure of admicelle. The outer region, consisting of the surfactant head groups, is the most polar and forms the admicelle/water and admicelle/solid interfaces. The inner region is referred to as the core region. This region consists of the hydrocarbon chains and is non-polar in nature. The region between the headgroups and the core is the palisade region. This region is intermediate in polarity, consists of the carbons near the headgroups, and is also characterized by water molecules that have penetrated the admicelle (Dickson and O'Haver, 2002).

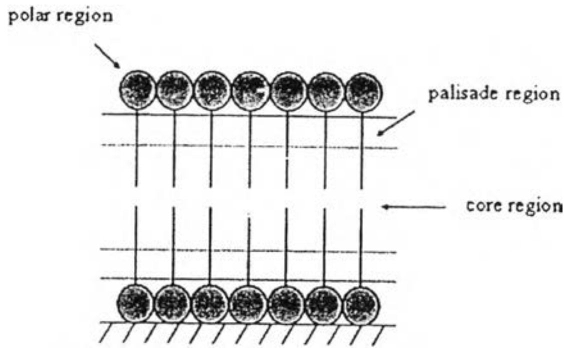


**Figure 2.8** The admicelle structure.

Factors influencing adsolubilization behavior are as follows: (1) the nature of the structural groups on the solid surface (2) the molecular structure of the surfactant being adsorbed (the adsorbate) (3) the environment of the aqueous phase such as pH, electrolyte content. Nowadays, the adsolubilization has been widely used in many industries in order to improve product qualities such as admicellar polymerization process, adsolubilization of drugs, admicellar chromatoghaphy, enhance oil recovery, water and soil remediation, wastewater treatment, Yu *et al.* (1992) began to investigate the use of adsolubilization for admicellar catalysis, a surface analogue of micellar catalysis which may give greater stereo selectivity than micellar catalysis and may be more amenable to development into industrial scale processes because it can be employed in a fixed bed mode.

### 2.3.2 Adsolubilization in Single-Surfactant System

For a past decade, the adsolubilizations of various organic compounds in single surfactant system have been studied. Kitiyanan *et al.* (1996) studied the adsolubilization of styrene, isoprene and their mixtures into cetyltrimethylammonium bromide (CTAB) bilayers (admicelles) on precipitated silica. The result showed that the adsolubilization equilibrium constant or partition coefficient of styrene is constant. This implies that styrene is adsolubilized into both the palisade region and the core of the admicelle. While the isoprene adsolubilization equilibrium constant decrease with increasing mole fraction implies that isoprene is adsolubilized into the palisade region of the admicelle.

Esumi and Yamamoto (1998) investigated the adsorption of sodium dodecyl sulfate (SDS) on hydrotalcite and adsolubilization of 2-naphthol. They found that the amount of SDS adsorbed increased sharply at low SDS concentration and then reached a plateau. The adsorption of SDS would occur at two sites: one is the external surface and the other is the interlayer. The microenvironment in the SDS adsorbed layer becomes hydrophobic with increasing SDS concentration. The amount of SDS adsorbed in the presence of 2-naphthol was almost the same as that in the absence of 2-naphthol. The amount of 2-naphthol adsolubilized increased with increasing SDS concentration and reached a maximum, and then gradually decreased. This gradual reduction is not correlated with the solubilization in SDS micelles in aqueous solution. But it come from the 2-naphthol adsorbed would desorb by adsorption of SDS due to electrostatic repulsive interaction between SDS and dissociated 2-naphthol.

Dickson and O'Haver (2002) studied the adsolubilization of naphthalene and α-naphthol with similar structures but different in polarities in $C_nTAB$ (n = 12, 14, 16) admicelles. They investigated the adsolubilization capacities of the core and palisade regions within the admicelle and their interactions within the admicelle. The partition coefficients for α-naphthol remained constant as the mole fraction of α-naphthol in the admicelle increased, implying that α-naphthol adsolubilized to both the core and palisade regions. The partition coefficients for naphthalene in the $C_{16}TAB$ and $C_{12}TAB$ system remain essentially constant as the mole fraction in the admicelle increased due to the intermediate polarity of naphthalene, indicating that naphthalene adsolubilized to both the core and palisade regions. In the $C_{14}TAB$ system, the partition coefficient increased slightly as the mole fraction of naphthalene in the admicelle increased. This increase in the partition coefficient implied that the component was partitioning primarily to the core of admicelles.

Atthapong *et al.* (2010) studied the adsorption and adsolubilization of styrene and ethylcyclohexane by using polymerizable surfactants on aluminum oxide. For this study, a bilayer of anionic polymerizable surfactant and non-polymerizable surfactant was adsorbed onto alumina. The results of adsorption studies showed that as the number of ethylene oxide (EO) groups of the surfactants increased, the area per molecule increased and the maximum adsorption decreased. This variation in adsorption was attributed to the increased bulkiness of the head group with increasing number of EO groups. In addition, they found that the number of EO groups does not impact the adsolubilization potential for styrene and ethylcyclohexane. For surfactant desorption studies, they found that the polymerization of polymerizable surfactant increased the stability of surfactant adsorbed onto the alumina surface and reduced surfactant desorption from the alumina surface.

Sieburg *et al.* (2010) investigated the adsolubilization of poorly water-soluble 2-naphthol into amphiphilic invertible polymers (AIPs). The results showed that the polymers adsolubilized molecules of sparingly 2-naphthol into the adsorbed layer on both substrates. AIP macromolecules represented different surface activity depending on length of the hydrophobic fragment in macromolecules. Different AIP fragments are related to polymer adsorption on hydrophilic and hydrophobized silica. It is expected that mainly AIP hydrophobic fragments interact with 2-naphthol molecules and facilitate adsolubilization. The amount of adsolubilized 2-naphthol does not depend on substrate nature and length of the hydrophobic fragment in polymer. It is primarily regulated by the total length of the adsorbed macromo lecules.

### 2.3.3 Adsolubilization in Mixed-Surfactant System

Adsorption of mixed surfactant system can provide several advantages over single surfactant system because the adsorption of surfactants on substrate can be controlled using appropriate surfactants and solution properties. For mixed surfactant system, If the different types of surfactant can show the special synergistic interaction among them; consequently, the properties of mixed surfactant system are better than single surfactant system.

Esumi *et al.* (2000) investigated the adsolubilization of 2-naphthol using surfactant mixtures of an anionic surfactant, sodium dodecyl sulfate (SDS), and a nonionic surfactant, hexaoxyethylenedodecyl ether ($C_{10}E_6$), on alumina. The results showed that in a single- surfactant system, $C_{10}E_6$ itself showed a very low adsolubilization of 2-naphthol, whereas SDS has an appreciable adsolubilization capacity. In a mixed-surfactant system, the adsolubilization become greater with an increase in the SDS content in the initial mixtures. On the other hand, the ratio of adsolubilized amount to surfactant adsorbed amount become smaller when the SDS content in the initial mixtures increased. They use the ratio of adsolubilized amount to surfactant adsorbed amount to compare the efficiency of adsolubilization. When the ratio of SDS to $C_{10}E_6$ becomes small, the efficiency of adsolubilization becomes greater. The surfactant adsorbed layer for both SDS:$C_{10}E_6$ = 1:3 and 1:1 provides greater efficiency of adsolubilization than that for SDS alone.

In the following year, Esumi *et al.* (2001) investigated the adsolubilization of 2-naphthol by binary mixtures of cationic and nonionic surfactants on silica. Two cationic surfactants used were hexadecyltrimethylammonium bromide (HTAB) and 1,2-bis(dodecyldimethylammonio)ethane dibromides (2RenQ), and a nonionic surfactant used was hexaoxyethylenedecyl ether ($C_{10}E_6$). In the single surfactant systems, adsolubilization of 2-naphthol for HTAB and 2RenQ was very similar and was greater than that for $C_{10}E_6$. In the HTAB/$C_{10}E_6$ system, the adsolubilization of 2-naphthol was enhanced by surfactant mixtures of HTAB and $C_{10}E_6$ compared to those of single systems. On the other hand, in the 2RenQ/$C_{10}E_6$ system the adsolubilization of 2-naphthol by surfactant mixtures of 2RenQ and $C_{10}E_6$ was rather smaller than that of 2RenQ alone but still larger than that of $C_{10}E_6$. It is suggested that the hydrophobic properties in the mixed surfactant adsorbed layer for adsolubilization of 2-naphthol are affected by the structure of cationic surfactant.

### 2.3.4 Adsolubilization in PEO-PPO-PEO Triblock Copolymer System

Desorption of the adsorbed surfactant from substrate surface is the main problems hindering utilization of surfactant-modified surface. Nowadays, polymeric surfactant is used as adsorbate in adsolubilization system in order to reduce that problem because it can increase the stability of the surfactant coating on the solid surface.

Montarges *et al.* (1998) studied the adsorption of organic toxicants from water onto $Al_{13}$-pluronic modified clay. This organic toxicants are 4-monochlorophenol (4-MCP) and 2,5-dichlorophenol (2,5-DCP). In the case of 4-MCP, the presence of co-intercalated PEO-PPO-PEO triblock copolymers leads to higher adsorbed amounts than what is observed for a classical aluminum-pillared clay. In acid conditions the highest adsorbed amounts are obtains for the clay modified with the most hydrophobic polymer. In basic conditions a reverse trend is observed as the highest adsorbed amounts are obtained for the clay modified with the most hydrophilic polymer. In the case of 2,5-DCP, the highest adsorbed amounts are obtained in the case of clay modified with the most hydrophobic polymer for both pH domains.

Tsurumi *et al.* (2006) investigated the adsolubilization of 2-naphthol into an adsorbed layer of PEO-PPO-PEO triblock copolymers on hydrophilic silica. The result showed that the order of the adsorption in the saturation level was found to be P123 $\approx$ P103 > P105 >> F108, meaning that copolymers with higher hydrophobicity can adsorb preferentially to the silica surface. In other words, the adsorbed amount increases as the HLB value decreases. Indeed, this order was parallel to the order of the adsolubilization amount of 2-naphthol. This suggests that an enhancement of copolymers adsorption provides a number of hydrophobic sites that is sufficient to enable adsolubilization of 2-naphthol. In the case of co-addition of copolymers and 2-naphthol, the adsolubilization amount increased gradually at lower surfactant concentration regions, reached a maximum, and then decreased with increasing concentration of copolymers. The maximum amount appeared at CMC of each copolymer. The decrement in the adsolubilization amount is interpreted as incorporation of the 2-naphthol takes place not only into the adsorbed layer but also into the solution micelles simultaneously. On the other hand, the final decrement was not observed when 2-naphthol was added after replacement of the copolymers supernatant by free surfactant solution.

The same experimental was investigated on hydrophobically modified silica particles by Tsurumi *et al.* (2006). The result showed that the amount of the PEO-PPO-PEO adsorbed of the maximum/saturation adsorption level was increases with a decrease in the HLB value, suggesting that the more hydrophobic copolymers (P103 and P123) adsorb preferentially onto the hydrophobic silica surface over the more hydrophilic copolymers (P105 and P108). The greater adsorbed amount of the more hydrophobic surfactants resulted in a greater amount of 2-naphthol adsolubilized into the adsorbed copolymers layers. In the case of simultaneous addition of the copolymer and 2-naphthol, the amount adsolubilized into the adsorbed P123 and P103 layers increased, reached a maximum, and then decreased. On the other hand, for both P105 and P108, a decreased in the adsolubilized amount was not observed. When 2-naphthol was added after replacement of the copolymers supernatant by a surfactant free solution, the final decrease was insignificant for all copolymers.

Wattanaphan (2008) studied the adsorption of EO/PO block copolymers L31, P123, L64, 17R2, 25R4, and 10R5 onto hydrophilic silica surfaces and adsolubilization of phenol, naphthalene, and 2-naphthol into EO/PO block copolymers adsorbed layer. The results showed that L31 and 17R2 with HLB values lower than 7 could not appreciably adsorb onto hydrophilic silica due to the small number of EO groups capable of interacting with the silica surface. Four factors are considered for the adsorption of block copolymers onto silica; HLB value, configuration, EO/PO ratio, and molecular weight. Consequently, the maximum amount of adsorbed surfactant is thus affected by the copolymer configuration, EO/PO ratio, and molecular weight as well. For adsolubilization study, for a given HLB value, the copolymers which have a larger number of PPO groups and higher molecular weight appear to appreciably adsolubilize organics more than those with a lower number of PPO groups and lower molecular weight. In addition, the effect of size and polarity of organic compounds were investigated. The small molecules prefer to be adsolubilized more than the larger one and the polar compounds tend to have significantly higher in the amounts of organics adsolubilized than the non-polar compounds.

Sahasyodhin *et al.* (2010) focused on the modification of hydrophobic silica particles with EO/PO triblock copolymer surfactants, which are Pluronic L31, P123, L64, 17R2, 25R4, and 10R5, and used the modified hydrophobic silica to adsolubilize various aromatic organic compounds, including phenol, 2-naphthol, and naphthalene. The adsorption results show that all triblock copolymers used in this study were shown to preferentially adsorb onto the hydrophobic silica surface. The configuration, HLB values, and EO/PO ratio of copolymers were found to be important factors affecting adsorption and found that the hydrophobic silica is a better substrate for EO/PO triblock copolymers than hydrophilic silica because larger range of HLB values can be used. In the adsolubilization study, the hydrophobic silica modified with copolymers has shown to be very effective in adsolubilizing the model aromatic organic molecules from aqueous phase. The EO/PO ratio and number of EO groups of copolymers were found to affect the phenol adsolubilization. While 2-naphthol adsolubilization was affected by only the number of EO groups in the same trend with phenol. For naphthalene, the adsolubilization has shown to be nearly the same for all copolymers studied with the exception of L31. In addition, the hydrophobic silica modified with EO/PO triblock copolymers shows higher ability to adsolubilization of aromatic organic compounds than the hydrophilic silica.