



## CHAPTER II

### THEORETICAL BACKGROUND AND LITERATURE REVIEW

#### 2.1 Surfactants

##### 2.1.1 Definition and Characteristic Features of Surfactants

Surfactants are major industrial products with millions of metric tons produced annually throughout the world. The word “surfactant” comes from “surface-active agent”. Surfactants, which are commonly known as soaps or detergents, are called amphiphiles because of their unique and interesting chemical characteristics. Surfactants are amphiphile molecules because they have both polar, hydrophilic head group (water-liking) and nonpolar, hydrophobic tail groups (oil-liking) in the same molecule. In the presence of a low concentration in the system, it is capable of adsorbing onto the interface of the system and changes the properties of the interface itself.

Most studies so far have been limited to single-chain surfactants. Recently, some researchers have tried to use a new type of surfactant on silica, dimeric or trimeric surfactants where two or three quaternary ammonium species are linked at the level of the head groups by a hydrocarbon spacer. This type of surfactant is often called a gemini surfactant. This surfactant is very different from single-chain surfactants with added salt (Esumi *et al.*, 1996). Thus, in our study we use this gemini surfactant as the additional surfactants (such as SDS, CTAB, and Triton X-100).

##### 2.1.2 Conventional Surfactants

There are four types of conventional surfactants: anionics, cationics, nonionics, and zwitterionics. In an anionic surfactant, some portion of the molecule appears to have a negative charge; for example,  $\text{RCOO}^-\text{Na}^+$  (soap) or  $\text{RC}_6\text{H}_4\text{SO}_3^-\text{Na}^+$  (alkylbenzene sulfonate). In a cationic surfactant, some portion of the molecule has a positive charge; for example  $\text{RN}(\text{CH}_3)_3^+\text{Cl}^-$  (quaternary ammonium chloride). Zwitterionic may have both negative and positive charges in the surface-active portion; for example,  $\text{RN}^+\text{H}_2\text{CH}_2\text{COO}^-$  (long-chain amino acid). For a nonionic

surfactant, there is no apparent ionic charge in the molecule for example;  $\text{RCOOCH}_2\text{CHOHCH}_2\text{OH}$  (monoglyceride) (Rosen, 2004).

#### 2.1.2.1 Cationic Surfactants

The most common cationic surfactants are the quaternary ammonium compounds with the general formula. A common class of cationics is the alkyl trimethyl ammonium chloride, such as dodecyl trimethyl ammonium chloride. Widely used cationic surfactants class is these containing two long-chain alkyl groups. These dialkyl surfactants are less soluble in water than the monoalkyl quaternary compounds, but they are commonly used in detergents as fabric softeners.

Advantages. Cationic surfactants are compatible with nonionics and zwitterions. This surface-active moiety has a positive charge, and thus adsorb strongly onto most solid surfaces (which are usually negatively charged), and can impart special characteristics to the substrate. This adsorption also makes possible the formation of emulsions that break in contact with negatively charged substrates, allowing for the deposition of the active phase on the substrate.

Disadvantages. Most types of cationic surfactants are not compatible with anionics (amine oxides are an exception). Generally, there are more expensive than anionics or nonionics and show poor detergency, and poor suspending power for carbon.

#### 2.1.2.2 Anionic Surfactants

Anionic surfactants are sodium and potassium salts of straight-chain fatty acids,  $\text{RCOO}^-\text{Na}^+$  (soap). These are the most widely used class of surfactants in industrial applications due to their relatively low cost to manufacture; they are used in practically every type of detergent. Several other anionic surfactants are commercially available, such as sulphosuccinates, isethionates, and taurates, and these are sometimes used for special applications.

Advantages. Anionic surfactants are easily prepared by the neutralization of free fatty acids or saponification of triglycerides using simple equipment. They can be made *in situ* by adding a fatty acid oil phase and alkaline material to in aqueous phase, or by the partial saponification of triglyceride oil. Anionic surfactants have excellent physical properties for use in toilet soap bars.

Disadvantages. Anionic surfactants form water-insoluble soaps with divalent and trivalent metallic ions, and insolubilize readily by electrolytes, such as NaCl. They are also unstable at a pH level below 7, yielding water-insoluble free fatty acid.

### 2.1.2.3 Nonionic Surfactants

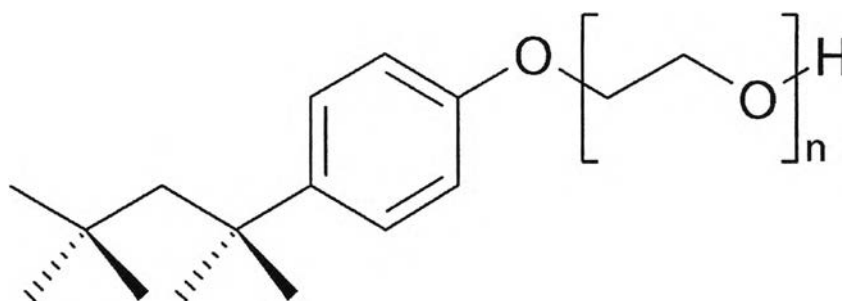
The most common nonionic surfactants are those based on ethylene oxide, commonly referred to as ethoxylated surfactants. Several classes can be distinguished: alcohol ethoxylates, sorbitan ester ethoxylates, and fatty acid ethoxylates.

Another important class of nonionics are the multihydroxy products such as glycol esters, glycerol (and polyglycerol) esters, glucosides and sucrose esters. Amine oxides and sulphinyl surfactants represent nonionics with a small head group.

Advantages. Nonionic surfactants are compatible with all other types of surfactants and are generally available as a 100% active material, free of electrolytes. They can be made resistant to hard water, polyvalent metallic cations, and electrolyte at high concentration; and they are soluble in water and organic solvents, including hydrocarbons. POE nonionics are generally excellent dispersing agents for carbon.

Disadvantages. Nonionic surfactant products are liquids or pastes, and are rarely nontacky solids. They are poor foamers (may be an advantage sometimes) and have no electrical effect. Ethylene oxide derivatives show an inverse temperature effect on solubility in water; they may become insoluble in water on heating. Commercial nonionic surfactant material is a mixture of products with a wide distribution of POE chain lengths. POE chains with terminal hydroxyl groups show yellowing (due to oxidation) in a strong alkali environment that can be prevented by etherifying (capping) the hydroxyl groups.

Triton X-100 (TX100) is a good example of a nonionic surfactant that is widely used in many applications. This nonionic surfactant is water-soluble containing polyoxyethylene chains as hydrophilic moieties. Its structure is given in Figure 2.1.



**Figure 2.1** Structure of Triton X-100

#### 2.1.2.4 Zwitterionic Surfactants

Zwitterionic surfactants are surfactants containing both cationic and anionic groups. The most common amphoteric surfactants are the N-alkyl betaines, which are derivatives of trimethylglycine. An example of a betaine surfactant is lauryl amido propyl dimethyl betaine. Amphoteric surfactants are sometimes referred to as zwitterionic molecules. They are soluble in water, but the solubility shows a minimum at the isoelectric point. Amphoteric surfactants show excellent compatibility with other surfactants, forming mixed micelles. They are commercially stable both in acids and alkalis.

The surface activity of amphoteric surfactants varies widely and depends on the distance between the charged groups, showing maximum activity at the isoelectric point. Zwitterionic surfactants have excellent dermatological properties. They also exhibit low eye irritation and are frequently used in shampoos and other personal care products.

Advantages. Zwitterionic surfactants are compatible with all the types of surfactants. They are less irritating to the skin and eyes than other types. And they may be adsorbed onto negatively or positively charged surfaces without forming a hydrophobic film.

Disadvantages. Zwitterionic surfactants are often insoluble in most organic solvents, including ethanol (Rosen, 2004).

### 2.1.3 Block Copolymer Surfactants

#### 2.1.3.1 *Characteristic Features of Block Copolymers*

Block copolymers consist of two different parts by—such as, PEO which is the hydrophilic part, and PPO, which is the hydrophobic part. Thus, 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 aggregates of different kinds depending on the molecular weight, the block sizes, the solvent composition, and the temperature (Bakshi *et al.*, 2005).

To obtain the better potential benefit of adsorption surfactants onto the surface and the adsolubilization capacity, we should use Pluronic block copolymer for studying adsolubilization in order to use it in various applications, especially in wastewater treatment. PEO-PPO-PEO block copolymers are recommended for adsolubilization. Some researchers have concluded that the adsolubilization is cost-effective, nontoxic.

#### 2.1.3.2 *Pluronic block copolymer (also termed Poloxamer or Synperonic)*

##### (i) *Commercial Pluronic Name*

Water-soluble poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide);  $(EO)_n(PO)_m(EO)_n$  and poly(propylene oxide)-poly(ethylene oxide)-poly(propylene oxide);  $(PO)_n(EO)_m(PO)_n$ , tri-block symmetric block copolymer or reversed block copolymer, produced by BASF, are often referred to by the trade name Pluronic, and Poloxamer, whereas the same compounds produced by ICI are known as Synperonics, a different trade name. The amphiphilic monomer units ethylene oxide (EO) and propylene oxide (PO) correspond to  $[-CH_2-CH_2-O-]$  and  $[-CH(CH_3)-CH_2-O-]$ , respectively (Ornella *et al.*, 2006).

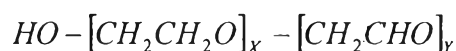
##### (ii) *Nomenclature of Pluronic*

Pluronic block copolymer code system is provided in order to estimate the characteristics of block copolymer. It consists of one letter, followed by two or three digit numeric code. Pluronic block copolymer nomenclature are classified as three letter; 'F', 'P', or 'L'. The letters stand for solid, paste, liquid,

respectively. The numeric code defines the structural parameters of the block copolymer. The last digit of this code encodes the approximate weight content of EO block in tens percentage of weight whereas the remaining digit encoded the molecular mass of the central PO block decoded by multiply by 300 to obtain the approximate molecular mass in Da unit. For example, the characteristic of the block copolymer code 'L64' is a liquid form which has a PO block 1800 Da (6\*300) and 40% wt. of EO (4\*10) (Kabnov *et al.*, 2002)

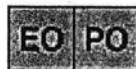
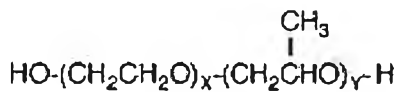
(iii) *General Structure of Pluronic Surfactants*

The chemical formula of Pluronic is presented as:

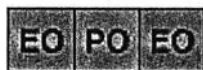
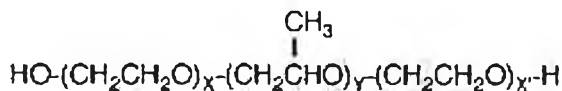


These amphiphilic polymers consist of a hydrophobic propylene oxide (PO) consists of ethylene oxide (EO) and propylene oxide (PO) blocks that are arranged in a basis  $EO_x-PO_y-EO_x$  triblock structure. A prominent feature of Pluronic copolymer is the ability of individual block copolymer molecules to self-assemble into polymeric micelles in aqueous solutions.

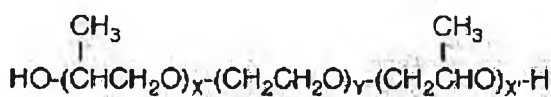
These amphiphilic triblock copolymer, a series of macromolecular weight nonionic surfactant, contain one or more hydrophilic blocks linear covalently linked to one or more hydrophobic blocks and self-assemble in aqueous solutions to form polymeric micelles. The number of hydrophobic PO; m and hydrophilic; n (also hydrophobic PO; n and hydrophilic; m in case of reverse Pluronic block copolymer) values are changed to vary the size, hydrophilicity and hydrophobicity. Structures and properties of EO/PO-block copolymer are shown in Figure 2.2 and Table 2.1, respectively.



### Diblock copolymers



### Triblock copolymers (Pluronic)



### Reversed triblock copolymers (reversed Pluronic)

Figure 2.2 Structures of EO/PO-block copolymer.

Notation	Mol. mass	EO wt%	Chemical formula <sup>a</sup>	HLB <sup>b</sup>
P103	4950	30	EO <sub>17</sub> PO <sub>60</sub> EO <sub>17</sub>	9
P104	5900	40	EO <sub>27</sub> PO <sub>61</sub> EO <sub>27</sub>	13
L64	2900	40	EO <sub>13</sub> PO <sub>30</sub> EO <sub>13</sub>	15
L44	2200	40	EO <sub>10</sub> PO <sub>23</sub> EO <sub>10</sub>	16
P105	6500	50	EO <sub>37</sub> PO <sub>56</sub> EO <sub>37</sub>	15
P85	4600	50	EO <sub>26</sub> PO <sub>40</sub> EO <sub>26</sub>	16
F87	7700	70	EO <sub>61</sub> PO <sub>40</sub> EO <sub>61</sub>	24
F88	11,400	80	EO <sub>101</sub> PO <sub>39</sub> EO <sub>104</sub>	28
F77	6600	70	EO <sub>52</sub> PO <sub>34</sub> EO <sub>52</sub>	25

Table 2.1 Example of Commercial Pluronic surfactants (Rui Zhang *et al.*, 2005)

Copolymers with various x and y values are characterized by hydrophilic-lipophilic balance (HLB).

(iv) *Mixed Pluronic Surfactant in solution*

For mixed micelles, the micellar mole fraction of the ionic component can be the effect on the mixed micelles properties. They found the mixed micelles are rich in triblock copolymer component in the ionic surfactant region of the mixed system. It's notable feature that many researches explore the way to improve adsorption and adsolubilization potential better than past. Most successful researches can be achieve by using binary surfactant or mixed surfactant to improve the single surfactant system performance. According to their synergism interaction (favorite) between surfactants, the  $\beta$  parameter is used for indicating the regular solution interaction (Mahajan *et al.*, 2005).

Mata *et al.* (2004) have studied aggregation behavior of a PEO-PPO-PEO block copolymer + ionic surfactants mixed systems in water and aqueous salt solutions and found that the addition of NaBr to copolymer can decrease cloud point, increase surface activity, shift micellization to lower concentration. Furthermore, more surfactant is needed for demicellization of P105 micelles in case of the presence of NaBr. However, the interaction of the mixed surfactant between P105 and ionic surfactants like sodium dodecyl sulphate; NaDS, and dodecyltrimethylammonium bromide; DTABr seem to diminish in the presence of NaBr. Ornella *et al.* (2006) also have investigated the interaction between cationic, anionic, and non-ionic surfactants with triblock copolymer Pluronic PE6200 and reverse block copolymer Pluronic 25R4. They were suggested that Pluronics are highly selective solutes. Both Pluronics and Pluronics R's efficiently interact with the anionic surfactant  $C_{10}OS$ , while this interaction is very weak in the case of cationic surfactant  $C_{10}TAB$  and almost completely absent for the non-ionic surfactant,  $C_{10}E_5$ .

The result suggests that the Pluronic-surfactants interaction is driven by a combination of different factors; the dipole-ion interaction between the polymer ether oxygen and the surfactant head-group. (i) the hydrophobic interaction between the polymer methylene groups and the surfactant hydrophobic



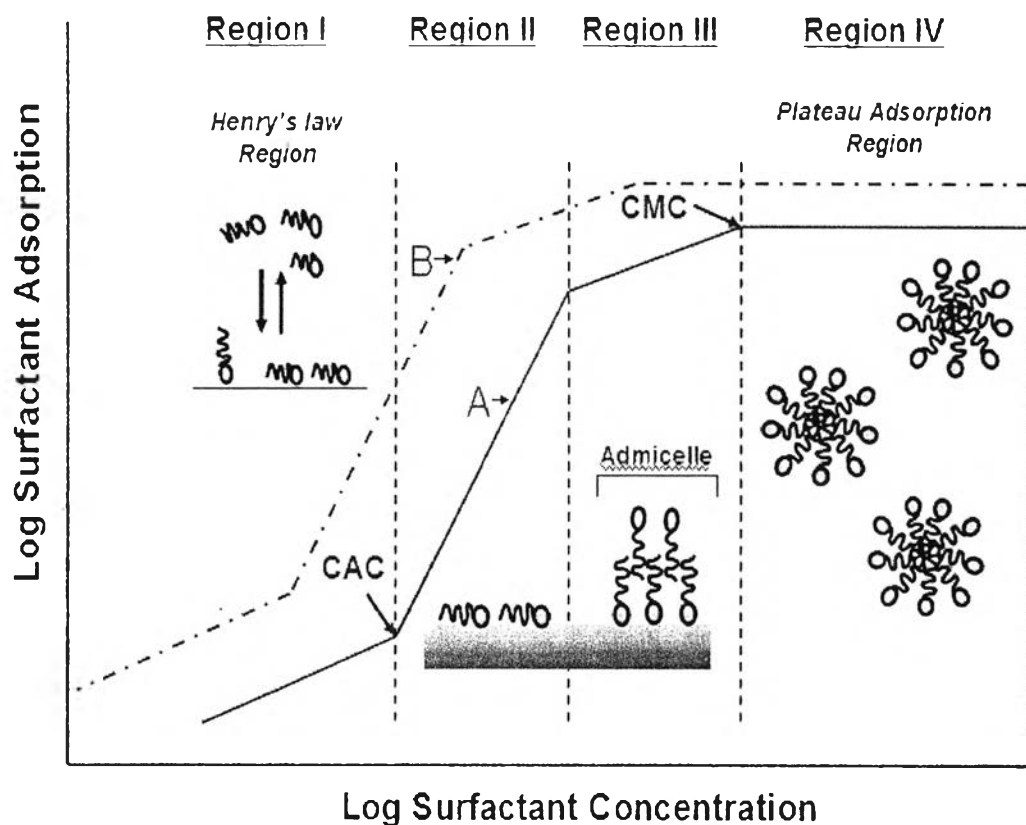
tail, and (ii) the cooperative aggregation of the surfactant tails in forming aggregates adsorbed to the polymer chain.

Ganguly *et al.* (2006) have studied that the effect of SDS on the self-assembly behavior of Pluronic block copolymer. The result showed that the aggregation number of the copolymer in the micelles decreased upon addition SDS, but a simultaneous enhancement in the degree of micellar hydration leads to a significant increase in the micellar volume fraction at a fix copolymer concentration. This enhancement in the micellar hydration leads to a marked increase in the stability of the micellar gel phase until it is destroyed at very high SDS concentration. Moreover, the composition of the copolymers plays a significant role in determining the influences of SDS on the gelation characteristics of the aqueous copolymer solutions. Copolymer with high PO/EO ratios shows an enhancement in the stability of the gel phase, whereas copolymers with low PO/EO ratios show a deterioration when the presence of SDS.

For the medical application, the mixed surfactants Pluronic P105 and D- $\alpha$ -tocopheryl polyethylene glycol 1000 succinate (TPGS) can improve the stability toward dilution among micelles because the aromatic ring of TPGS might lead to an increase in hydrophobic interactions between the polymer chains in the micelle's core and thus provide some advantages in particle stability towards dilution compared with Pluronic polymer. Hence, the more stable system and more efficient solubilization of the poorly soluble anticancer drug are available by using mixed surfactant with Pluronic (Gao *et al.*, 2008).

## 2.2 Adsorption of surfactants at solid–liquid interface

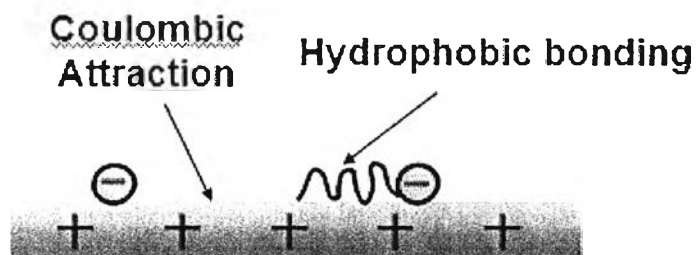
The adsorption of surfactants at liquid-solid surfaces is usually examined by the adsorption isotherm. It's the plot of the amount of surfactant adsorbed a solid surface versus the equilibrium surfactant concentration at constant temperature. Typically, the adsorption isotherm of an ionic surfactant onto an oppositely charge interfaces is commonly in an elongated sigmoid or S-shape. This S-shape adsorption isotherm can be divided into four parts, as shown in Figure 2.3.



**Figure 2.3** Schematic of S-shaped adsorption isotherm for an ionic surfactant on an oppositely charged substrate.

On the other hand, the adsorption isotherm of a nonionic type is describes by Langmuir isotherm (Schamahorn *et al.*, 1981-1982). They found that three levels of surfactant adsorption, corresponding to equilibrium concentration low in region II, high in region II, and low in region III (Asvapathanagul *et al.*, 2005).

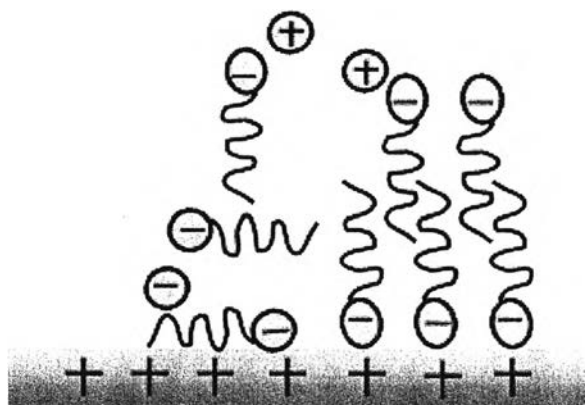
For the first region (region I: monomer adsorption region) as shown in Figure 2.4 is referred to as the Henry's law region and is considered as the infinite dilution region.



**Figure 2.4** Schematic of adsorption isotherm region I or monomer adsorption region.

Hence, the interaction between molecules of surfactants is negligible. A low concentration of surfactant results in a low amount adsorbed on the surface. Adsorbed surfactants in this region are viewed as being adsorbed alone and don't form any aggregate. The adsorption in this region occurs because of either the opposite charge attraction between ionic surfactant and the surface of the solid, or surfactant molecules lying prone on the surface of the solid in the nonionic type of surfactant.

In the second region (region II : surface aggregate formation) as shown in Figure 2.5, there is a remarkable increase in the slope relative to the slope in Region I, which is a general indication of greater numbers of surfactant adsorbed. The slope of the adsorption isotherm increases sharply. It is the consequence of hydrophobic interaction between the oncoming surfactant in the bulk solution and surfactant which have already been adsorbed onto the surface.

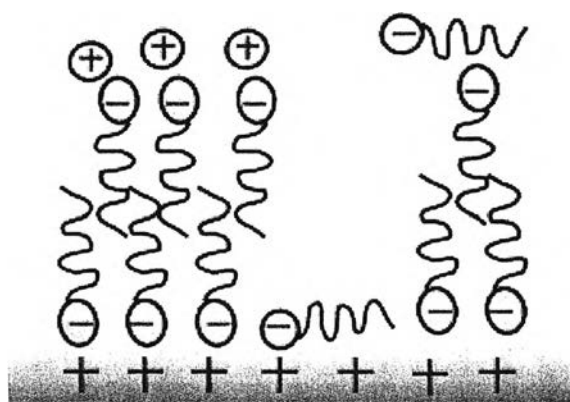


Surface heterogeneity  
plays an important role

**Figure 2.5** Schematic of adsorption isotherm region II or surface aggregate region.

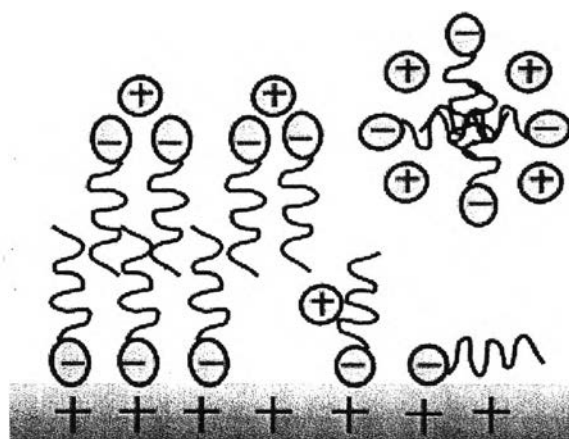
This aggregation, which occurs at concentrations well below the critical micelle concentration (CMC) of surfactant, is called admicelles or hemimicelles, depending on whether their structures are formed as being local bilayers or local monolayers, respectively. During this region, it occurs the transition point of adsorbed surfactant aggregates is called critical admicelle concentration (CAC) or the hemimicelle concentration (HMC).

The slope region III which connects continuously to region II decreases gradually because of electrostatic repulsion between oncoming surfactant and surfactant which have already been adsorbed as shown in Figure 2.6. At the end of region III as shown in Figure 2.7, critical micelle concentration (CMC) occurs. It is the point where the surfactant reaches the maximum coverage; there is no further surfactant capable to adsorb onto the surface.



### Ionic Surfactants on a Charge Surface

**Figure 2.6** Schematic of adsorption isotherm region III.



### Ionic Surfactants on a Charge Surface

**Figure 2.7** Schematic of adsorption isotherm region IV.

Typically, the equilibrium surfactant concentration at the transition point from region III to region IV is approximately at the critical micelle concentration (CMC). It is the plateau adsorption region for increasing surfactant concentration. At the point of CMC, micelles begin to form and no more surfactant adsorption is observed.

From the Figure 2.3 line B shows that the longer alkyl chain length or higher electrolyte concentration for ionic surfactants than A. The higher chain length, the easier adsorb so the CMC value is decreasing that appear moved the line B to the left.

The adsorption isotherm of a nonionic type of surfactant can be characterized by Langmuir isotherm which is based on four hypotheses.

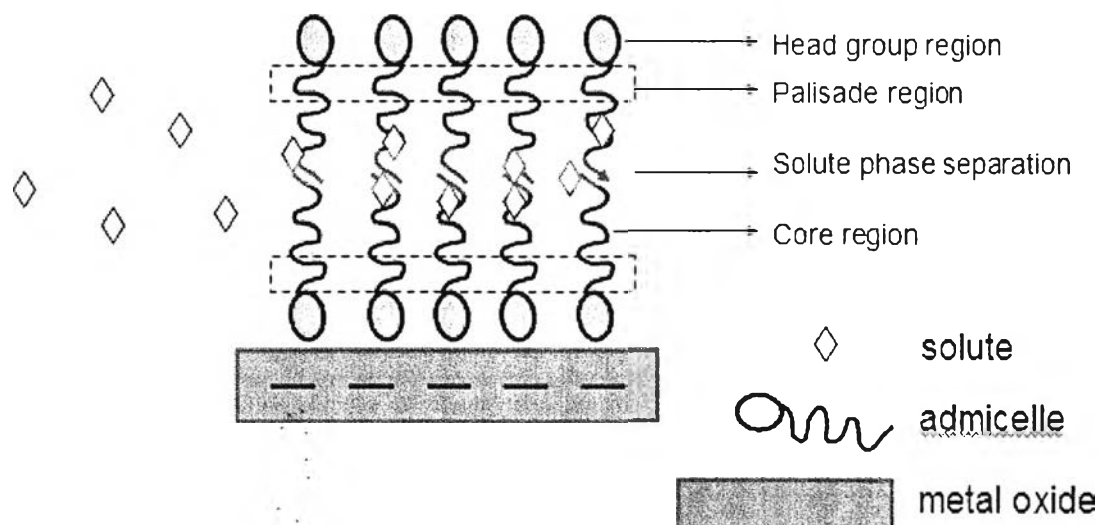
1. The surface of the adsorbent is uniform, that is, all the adsorption sites are equal.
2. Adsorbed molecules do not interact.
3. All adsorption occurs through the same mechanism.
4. At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

## 2.3 Adsolubilization

### 2.3.1 General Theory

#### 2.3.1.1 *Definition of Adsolubilization*

The ability to remove the organic solutes from aquatic environment using surfactant-modified solid surface through the process is called adsolubilization or surface solubilization as shown in Figure 2.8 (Adak *et al.*, 2005). This phenomenon of surfactant adsorbed layer formed on particles occurs by adsorption of surfactants which exhibit hydrophobic properties where water-insoluble compounds into the layer.



**Figure 2.8** Schematic of adsolubilization phenomenon.

According to the core admicelle is hydrophobic property so the admicelle can provide sites for capable of solubilizing water-insoluble components (Dickson *et al.*, 2002). Surfactant in admicelle form can be adsorbed at the variety of solid surface, especially silica surface.

### 2.3.1.2 The Applications of Adsolubilization

The adsorption of surfactants onto solids from solutions has received considerable attention because it can alter the properties of those solid surface turn to the expected surface, for example, its importance in fields as diverse as froth flotation detergency, enhanced oil recovery, drug preparations, pharmaceutical applications, engineer surface, pharmaceutical formulations, cosmetic product, paints, surface coatings, laundry detergents, wastewater treatment in order to remove organic pollutants., etc (Lee *et al.*, 2001, Adak *et al.*, 2005).

Surfactant adsorbed layers formed by the adsorption if surfactants onto particle constitute a hydrophobic environment. This adsolubilization phenomenon has been major used to modify surface properties of particle as well as to eliminate toxic substances in aqueous media (Esumi *et al.*, 2001).

### 2.3.1.3 Factors of Adsolubilization

There are a number of factors that are strongly involved in the adsorption isotherm of surfactant at the solid-liquid interface;

(1) The nature of the solid sites whether it is polar or non-polar, charge density and so forth.

(2) The nature and structure of the adsorbed surfactant.

(3) The systems of the aqueous phase, pH, ionic strength, temperature and so forth (Rosen, 2004).

### 2.3.1.4 The composition of adsolubilization

#### (i) Solid substrates (adsorbents)

There are many types of solid substrates used nowadays, such as alumina, carbon black, clay, titanium dioxide, zeolite, silica, and so forth. They are usually divided into three main types based on their surface charge-positive charge surface, negative charge surface, and hydrophobic surface. Alumina is an example of positive charge surface and carbon black is an example of hydrophobic surface. Most researchers found that the modification of the silica surface can improve both the physical and chemical properties. Silica is a great example of solid substrate which can apply in many applications.

Silica, which is also called silicon dioxide ( $\text{SiO}_2$ ), comprises two of the most abundant elements on the earth's crust; silicon and oxygen. Silica consumes about 59 percent of the earth's crust, and 95 percent of it is known as rocks. Silica is found in nature in several forms, including quartz and opal. In fact, 35 crystalline forms have been identified (Hart *et al.*, 1927). Under ambient conditions, silica is formed when silicon is exposed to air (oxygen). A very thin layer of silica, so-called native oxide, is built on top of the silicon surface. Silica also has covalent bonding and forms a network structure (also known as lattice or continuous), as shown in Figure 2.9. Silica's network structure can be attacked by hydrofluoric acid (HF). HF is capable of breaking down the silica pattern (Iler *et al.*, 1979).





**Figure 2.9** Structure of silicon dioxide ( $\text{SiO}_2$ ) or silica.

The point of zero charge of silica is between 2 and 3, in mildly environments, cationic surfactants readily adsorb onto silica. Although the type of surface directly on the properties of adsolubilization, surface treatment method is used in the adsolubilization phenomenon in order to catch up the expectation easily following the other factors (Esumi *et al.*, 2004). However, the morphology of the adsorbed surfactant is still being discussed.

(ii) *Contaminant or soluble organic solute.*

Various toxic organic chemicals, potentially hazardous to human health and also to the terrestrial and aquatic ecosystem, are being discharged into the environment as a result of industrial, agriculture and domestic activities. Many industrial wastes contain refractory organics, whose removals are rather difficult or impossible by conventional treatment process. Not only inorganic such as anions, heavy metal cations, but also organic compounds which are not expected to pose major health problems to the human population when wastewater is reused for agricultural purposes. The presence of organic environmental pollutants, such as styrene, poly aromatic hydrocarbons (PAHs) is considered to be harmful extremely.

Many of the common herbicides and insecticides contain the Phenolic moiety as a structure unit and are resistant to biodegradation. Phenolic compounds are popularly used in the preparation of antiseptics, dyes, antirust products, synthetic resins, biocides, photographic chemicals, ink, and

varnishes. They are present in the wastewater of many industries such as oil refineries, phenol production industries, explosive manufacturing industries (Adak *et al.*, 2006).

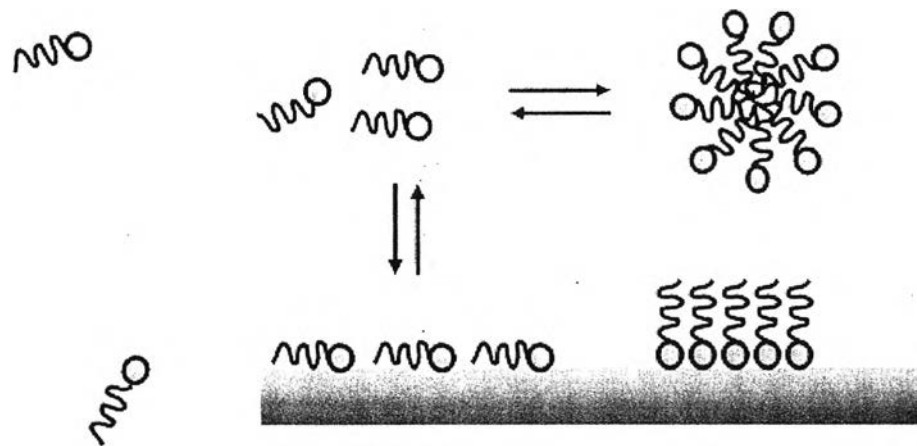
Moreover, the partition coefficient of the system depends on their varieties polarity of the solutes. The partition coefficients of  $\alpha$ -naphthol remain constant as the mole fraction of  $\alpha$ -naphthol in the admicelle increased, indicated that  $\alpha$ -naphthol adsolubilized both the core regions and palisade region. The slightly increased partition coefficient of the system as the increasing admicelle implied that the coefficient of solute is primarily partition to the core region. The changed component of the mixtures solute could also change the primary adsolubilization site for their system (Dickson *et al.*, 2002). Asvapathanagul *et al.* (2005) have pointed out that the presence of one solute affected on the other adsorbed solute into the admicelles. In mixed-solute systems, the presence of acetophenone had little effect on the toluene adsolubilization. In contrast, a synergistic interaction effect was observed in the adsolubilization of acetophenone in the presence of toluene.

### (iii) Surfactant

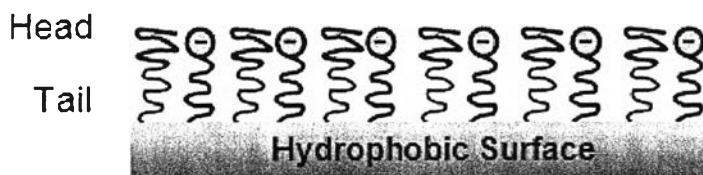
There are a lot of researches found that the amounts of admicelles have effected on somewhat the adsolubilization capacities—solute solubilize into the micelle like surface aggregate. The higher density of admicelles, the greater solute solubilizes onto the admicelles or selective the solutes. Typically, the adsorbed amount of ionic surfactants apparently increases with increasing ionic strength due to a decrease in the electrostatic repulsion force between the surfactants. Thus, mixed surfactant systems change markedly the adsolubilization behavior.

The surfactant form on the modified-surface is likely micelle-like structures on its surface particle having the potential to solubilize organic molecules into that structure formed, known as hemimicelle, micelle like surface aggregate, or admicelle. The admicelle is the characteristic of the surfactant behavior at the low surfactant concentration, similar the natural characteristic of micelle.

From Figure 2.10, depending on surfactant concentration in aqueous solution, surfactants are capable if it forms many different types of aggregates. At low surfactant concentration, the admicelles are adsorbed onto the solid surface monolayer form as shown in Figure 2.11.

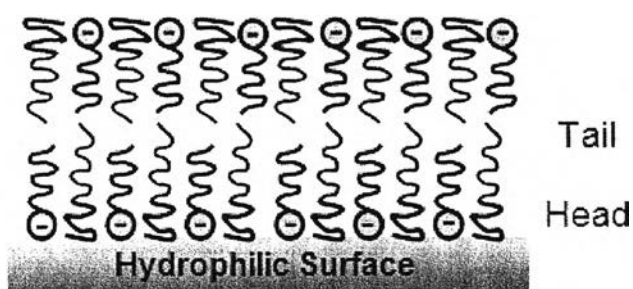


**Figure 2.10** Admicelle formation of surfactants.



**Figure 2.11** Monolayer of mix surfactant between nonionic and anionic adsorbed surfactants onto the hydrophilic surface.

The characteristic of monolayer admicelles is the head groups adsorbed on the substrate surface meanwhile the tail groups contact with the aqueous phase. After more increasing concentration, the admicelles are increasing adsorption onto the surface until coverage all surface area. It tends to presence in difference form; bilayer structure as shown in Figure 2.12. The surfactant aggregate formation plays an important part in addition to the amount of adsorbed surfactant (Asvapathanagul *et al.*, 2005).



**Figure 2.12** Bilayer of mix surfactant between nonionic and anionic adsorbed surfactants onto the hydrophilic surface.

When the surfactant concentration exceeds a certain level, surfactant monomers self-aggregate into spherical aggregates known as micelles. For micelle, the individual monomers are oriented with their hydrophilic group oriented into the interior of the spherical aggregates. Micelles form when the surfactant concentration first exceeds the critical micelle concentration (CMC), a value which varies for every surfactant. As additional surfactants are added above the critical micelle concentration (CMC), the incremental surfactants go to form additional micelles (West and Harwell, 1992).

## 2.3.2 Adsolubilization in single system

### 2.3.2.1 *The adsolubilization of cationic surfactant*

The adsorption on the silica surface of the surfactant, dodecyltrimethylammonium bromide, DTAB concentration below the CMC increased with increasing alcohol concentration in solutions whereas the adsorption of DTAB decrease with the DTAB concentration above the CMC. Besides, the co-adsorption of the alcohol increases with increasing alcohol concentration and benzyl alcohol is adsorbed stronger than phenol. The result showed that the surfactant modified silica ability is very high to incorporate phenol and benzyl alcohol. The adsolubilization showed the enhanced sorptive property toward organic compounds by the adsorbed surfactant layers (FØrland *et al.*, 2007).

Dickson *et al.* (2002) founded that the adsolubilization of naphthalene in the presence of the different amounts of  $\alpha$ -naphthol in  $C_n$ TAB admicelles indicated that naphthalene and  $\alpha$ -naphthol actively competed for sites which is the result of reduced maximum adsolubilization of naphthalene and a shift in the adsolubilization isotherms—within all surfactant system studied ;  $C_n$ TAB (n=12, 14, 16). The amount of  $\alpha$ -naphthol required to produce the maximum competition between two solutes in  $C_{12}$ TAB admicelles was much greater than in the other. They varied the polarities of organic solutes,  $\alpha$ -naphthol and naphthalene, whereas similar structures for studies its effect of adsorption into CTAB admicellar surfactants. The result is not clear to indicate the correlation between the surfactant tail length and the maximum solute adsolubilization. However, the data of the adsorption isotherms indicated that  $C_{14}$ TAB and  $C_{12}$ TAB were the tightest and loosest packed admicelles, respectively. As the results, the packed admicelles property affects directly on the adsorption of the solute into the admicelles, because of tightly packed  $C_{14}$ TAB admicelles on the surface, the adsolubilization is decreased into its region. On the other hand,  $C_{12}$ TAB can promote the incorporation of the polar solutes into their loosed packing region. For effects of the molar ratio of CTAB to OPEO<sub>10</sub>, Dickson *et al.* (2002) also found that the suitable molar ratio influence on the adsolubilization capacity which depends on the type of solute and surfactant.

Pradubmook *et al.* (2003) have studied the effect of pH on adsolubilization of toluene and acetophenone into adsorbed surfactant on precipitated silica. They found that the adsorption of the CTAB surfactant on the silica surface is increasing with increasing pH. And the type of solute also affects on the adsolubilization. In this research, pH 5 and 8 were investigated both single solute system and mixed solute system. For single solute systems, pH had a little effect on the adsolubilization of toluene on silica surface, in contrastly, the adsolubilization of acetophenone is increasing where increasing pH.

For mixed solute systems, the type of solutes and its amount can be depended on the adsolubilization. They found that the presence of acetophenone had a mildly synergistic effect on toluene adsolubilization whereas that the presence of toluene had a strongly synergistic effect on acetophenone adsolubilization. And in case of pH, the solute synergism is not a strong as single systems even changed pH. For ionic surface, most researches studied about adsorption and adsolubilization of the ionic surfactant from the aqueous solution onto the solid surface such as oxides. In the aqueous solution, the protonation or deprotonation of adsorbed water causes the solid surface to bear a charge, dependent on the solid surface and solution pH.

Adak *et al.* (2007) observed that the removal phenol efficient from the water by surfactant-modified alumina through adsolubilization was increased due to the present of anionics and decreased a little due to the present of cationics while temperature and humic acid had no effect on the removal of phenol. The result showed that phenol could be desorbed from surfactant-modified alumina (SMA) surface by shaking the material with rectified spirit and then the surfactant modified alumina (SMA) could be reused.

#### 2.3.2.2. *The adsolubilization of anionic surfactant*

Esumi and Yamamoto (1997), and Upadhyaya *et al.* (2007) have pointed out that anionic surfactants onto alumina surface was dramatically reduced owing to their presence of cationic-rich micelles whereas the adsorption of cationic surfactants on silica was substantially reduced in the presence of anionic rich micelles. In the next year, Esumi and Yamamoto (1998) were studied that the amount of SDS adsorbed increased sharply at low SDS concentration and occurred at two

sites: one is the external surface and the other is the interlayer. A further addition of higher SDS concentrations considerably enhanced the dispersion stability due to the formation of bilayer. At high anionic surfactant concentration, the adsorption of anionic surfactant on alumina surface occurred due to electrostatic attraction between anionic head group of surfactant and positively charged alumina surface and interaction between the hydrocarbon chains. At this stage, the exhausted alumina (containing micelle-like aggregates on its surface) can be utilized for the removal of organic pollutant such as phenol by solubilizing them into the micelle (Adak *et al.*, 2005).

Normally, the adsorption of the different type surfactant onto the same solid surface also showed the different adsorption efficiency. In single surfactant system, hexadecyltrimethylammonium bromide; HTAB and 1,2-bis(dodecyl dimethylammonio) ethane; 2RenQ, which are cationic surfactants, was very similar and greater than for hexaoxyethylenedecyl ether; C<sub>10</sub>E<sub>6</sub> which is nonionic surfactant (Esumi *et al.*, 1996). The alkyl chain length of the surfactants is important factor to correlate with the adsolubilization (Esumi *et al.*, 2001). The amount of 2-naphthol adsorbed altered with the alkyl chain length; it is increased with increasing the alkyl chain length (Esumi *et al.*, 2007). However, the most studies have been limited in the single system so the binary system or mixed surfactant system are studied later on. In 1996, Yamanaka and Esumi are reported that the adsorption of HEC on alumina increases remarkably owing to the presence of SDS, and the amount of SDS is unaffected by the presence of HEC. Due to the complex formation, the similar trend is observed for the SDS-HMHEC. Moreover, the binary surfactants can enhance by HEC or HMHEC adsorption. Comparing between HEC and HMHEC adsorption, the amount of former is almost constant in the presence of SDS, whereas in case of the latter decrease because of the formation of SDS-HMHEC complex in the bulk solution.

Even if the different solid surface; titanium dioxide having dodecyl chain, the dodecyl chain involves the adsolubilization of naphthalene and 2-naphthol. The amount of both solubilized solutes enhance because of the admicellar partition. And it was shown that 2RenQ was adsolubilized preferentially rather than 2-naphthol (Esumi *et al.*, 1997). In the next year, Esumi *et al.* (1998) changed the

surfactant to be SDS which is in the same classification of alkyl chain as dodecyl chain. The results indicated that the quaternary ammonium groups grafted on titanium dioxide interact with SDS by electrostatic attraction and hydrophobic interaction. Thus, the adsorption of SDS was greater than on untreated titanium dioxide. However, the amount of adsorbed solutes was not increased. Comparing with the same solute; 2-naphthol by using tetradecyltrimethylammonium bromide (TTAB) on Na-Kaolinite, the presence of polyacrylamide (HMPAM) at much lower TTAB concentrations the adsolubilization of 2-naphthol onto the Na-Kaolinite surface was also enhanced greatly. However, the stability of the solid surface dispersion was supposed to concern. In case of using the clay as the solid surface, the stability was found to be strongly diminished by presence of HMPAM. And the presence of HMPAM at the suitable concentration was also supposed to concern too. If it was added in the region of the CMC, the adsolubilization is fairly not different (Wang *et al.*, 1999).

#### 2.3.2.3 *The adsolubilization of nonionic surfactant*

The properties of mixed micelles of cationic gemini surfactants and nonionic surfactant Triton X-100: effect of the surfactant composition and the spacer length was investigated by Wang *et al.* (2005). The results showed the decrease of CMC with increasing  $X_{TX100}$  was much more significant and the changes for three gemini surfactants showed distinct differences at  $X_{TX100}$  lower than 0.4. These properties of mixed micelles occurred due to the changes of the electrostatic repulsion between headgroups of cationic. Gemini surfactant and the steric repulsion between hydrophilic headgroups of TX100 caused by the variation of surfactant composition, as well as the spacer conformation of gemini surfactants.

Tan and O'Haver (2004) were investigated the impact of lipophilic linkers (long chain linear alcohols) on the adsorption of and styrene adsolubilization in polyethoxylated alkylphenols (Triton X) nonionic surfactants with varying EO units on amorphous precipitated silica. They found that the presence of lipophilic linkers increases both surfactant adsorption and styrene adsolubilization and the percent increase of styrene adsolubilization was greater than the percent increase of surfactant adsorption for all studied systems. The adsolubilization



capacity of surfactants increased, up to a certain value, with increasing lipophilic linker tail length or concentration. Styrene adsolubilization at the water-silica interface decreased with increasing numbers of ethoxylated (EO) units in the surfactant, especially at higher styrene loading levels. The enhancement of adsorption and styrene adsolubilization was thought to be caused by the linker increasing interaction between styrene and surfactant hydrophobic groups.

#### 2.3.2.4 *The adsolubilization of block copolymer surfactant*

Triblock polymers (TBP) interact with ionic surfactants and the ionic surfactant binds to the PPO block preferentially and can change the TBP aggregation even at low concentration. Commonly, the surfactant structure formation changes mainly following to the surfactant concentration. In order to control structure, stability and rheology of the solutions and to stabilize the colloidal solution, the triblock copolymers which were mixed in the system can adjust those properties well (Bakshi *et al.*, 2005).

Amphilic diblock copolymer can provide an important alternative to small molecule surfactants, especially when replacement of the solution phase is required in multistage synthesis or processing. For example, amphilic diblock copolymers adsorbed at the solid/aqueous solution interface have been used in a wide variety of the applications, such as nano-structured templates nanoreactors for preparing metallic nanoparticles (Sakai *et al.*, 2007).

Bharatiya *et al.* (2008) have studied the influence of a hydrophobic diol (Surfynol 104) on the micellar transitions of Pluonic P85 [(EO)<sub>26</sub>(PO)<sub>39</sub>(EO)<sub>26</sub>] in aqueous solution. The addition of diol affected to decrease cloud point (CP) and gelation temperature of aqueous Pluronic solution. Diol got incorporated in the block copolymer micelles and led to structural transition of the micelles. Besides, temperature will increase if the presence of sodium chloride is added.

## 2.4 Adsorption and adsolubilization of mixed conventional surfactant and Pluronic block copolymer

Adsorption of mixed-surfactants system is outstanding in many industrial processes more than the individual surfactants system. The different types of surfactant exhibit their synergistic interaction among of them. As a result, the properties of process can improve better than single surfactant system. It depends on many factors such as the amount of components, the ratios of the surfactants, and the optimal systematic manner of surfactant components.

Understanding of the interactions between the components of a surfactant mixture is, therefore, important to get their best performance. Thus, a significant research has been focused on the field of polymer-surfactant interactions in recent decades and several reviews exist. Surfactants are expected to bind strongly with the copolymer if they are more hydrophobic than PEO. The surfactants will preferentially bind to the PPO block and will interfere with polymer aggregation at low concentrations (Zhang *et al.*, 2005). Bakshi *et al.* (2005, 2006) have studied the synergistic interactions in both mixed micelles, the increasing temperature induced much stronger for the mixture of Pluronic F127 than Pluronic P103 because of the greater PPO units. The synergistic interactions are mainly responsible for mixed micelle formation between the different surfactant components. For Pluronic F127/Pluronic P103 and 12-2-12 mixtures system, the former case has the much stronger rather than the latter because the greater PEO units reduce particularly the cationic polar head group better (Bakhashi *et al.*, 2005).

Comparing the mixture of Pluronic F127 between zwitterionic-alkyldimethylammonio propane sulfonates + anionic surfactant-SDS, SDBS and zwitterions + nonionic surfactant-TX-100, Bakhashi *et al.* (2006) has pointed out the former mixtures system is stronger synergistic interaction due to the increased hydrophobicity of zwitterionic component. On the other hand, the latter system is closer to ideal or unfavorable interaction because of the bulkiness of the hydrophilic groups of zwitterionic and TX-100 component.

Mahajan *et al.* (2005) did the mixed micelles of conventional surfactants-tetradecyltrimethylammonium bromide (TTAB), hexadecyltrimethylammonium bromide (HTAB), and polyoxyethylene(23)laurylether(Brij35), with triblock polymers, Pluronic L64 and P127. They varied the micellar mole fraction of the ionic component and suggested that the mixed micelles are rich in triblock polymer component in the ionic surfactant rich region of the surfactant mixture. Comparing Pluronic F127 and L64, the former surfactant is greater hydrophobic than the latter because of its greater number of PPO unit.

Bakshi *et al.* (2005) reported that the interaction of Pluronic L64 and F68 with SDS form mixed micelles well and the addition of SDS can reduce the size of TBP micelles remarkably. While Zhang *et al.* (2005) has suggested that the addition of a small amount SDS leads SDS micelles to disrupt the F127-g-PVP graft copolymer aggregates to a lesser extent than Pluronic F127. A small decrease of CMT changes the solvent quality and encourages the formation of micelles. At intermediate concentrations of SDS, the CMT is somewhat shifted to a lowest temperature. A further increase in the SDS concentration leads to the formation of SDS micelles, which started to be bound to the polymer chain. The graft copolymer is found to have a higher CMC than that of Pluronic F127. And this modification of Pluronic F127 with PVP improves its solubility in water. Where as, the presence of conventional surfactants in the TBP solution is important for changing the physico-chemical of block copolymer. Castro *et al.* (2006) reported that  $E_{67}S_{15}E_{67}$  micelles formation and their sizes were changed with the amount of adding SDS in the solution.

Mahajan *et al.* (2005) reported the result of the stronger synergistic interaction were observed for the cationic combinations with Pluronic F68 rather than TX-100 because of the reduction in the cationic polar head group repulsions by the interaction of non-ionic surfactants in the mixed micelle.