

CHAPTER II

LITERATURE REVIEW

2.1 Surfactant Characteristics

Surfactants (or surface active agents) are organic compounds with at least one lyophilic (solvent-loving) group and one lyophobic (solvent-fearing) group in the molecule. If the solvent which the surfactant is to be used is water or an aqueous solution, then the terms hydrophilic and hydrophobic are used respectively. In the simplest term, a surfactant contains at least one non-polar group and one polar group and is represented in a form shown in Figure 2.1 (Farn, 2008).

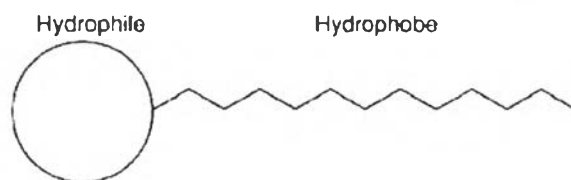


Figure 2.1 Simplified surfactant structure (Farn, 2008).

Depending on the hydrophilic head groups, surfactants are classified as follows (Farn, 2008):

1. *Anionic surfactants.* When they are in water, the hydrophilic head is negatively charged. Anionic surfactants are the most common and inexpensive surfactant and mainly used in detergency and personal care products.

2. *Cationic surfactants.* When they dissociate in water, the hydrophilic head is positively charged. They are generally used as fabric softeners, hair conditioners and antibacterial agents.

3. *Non-ionic surfactants.* They do not dissociate in water and the hydrophilic head has a neutral charge. Nonionic surfactants are commonly used in the formulation of emulsifier, dispersant and low temperature detergents.

4. *Amphoteric surfactants*. The hydrophilic head of amphoteric surfactants has a positive, negative or both positive and negative charges depending on pH. They are widely used in toiletries, baby shampoos, and daily cleaners.

2.2 Adsorption of Surfactants at the Solid-Liquid Interface

Surfactants adsorption is a process for transferring of surfactant molecules from the bulk phase onto the surface interface. The phenomenon of surfactant adsorption is studied in order to understand: (1) a measure of the amount of surfactants on surface that can be identified the performance of surfactant; and (2) the orientation of surfactant molecules on the surface that can be identified the effect of adsorption on surfaces (Paria and Khilar, 2004).

The adsorption of surfactants at the solid-liquid interface is strongly influenced by a number of factors (Rosen and Kunjappu, 2012): (1) the nature of the surface; (2) the molecular structure of the surfactant; and (3) the environmental of the aqueous phase such as pH, temperature, and electrolyte content or any additives.

2.2.1 Mechanisms of Surfactant Adsorption

There are number mechanisms by which surface-active molecules may adsorb onto the solid substrates from aqueous solution. In general, the adsorption of surfactants involves single ions rather than micelles (Paria and Khilar, 2004; Rosen and Kunjappu, 2012).

1. *Ion exchange*. Replacement of counter ions adsorbed onto the substrate from the solution by similarly charged surfactant ions.

2. *Ion pairing*. Adsorption of surfactant ions from solution onto oppositely charged sites by counter ions.

3. *Hydrophobic bonding*. Adsorption occurs when there is an attraction between a hydrophobic group of adsorbed molecule and a molecule present in the solution.

4. *Adsorption by polarization of π electrons*. When the solid surface has strongly positive sites and the surfactant contains electron-rich aromatic nuclei,

the attraction between electron rich aromatic nuclei of the adsorbate and positive sites of the adsorbent results in adsorption.

5. *Adsorption by dispersion forces.* Adsorption by London-van der Waals force between adsorbate and adsorbent increases with the increasing molecular weight of the adsorbate.

2.2.2 Adsorption Isotherm

An adsorption isotherm is a curve for describing the phenomenon governing the mobility of a substance from the aqueous solution to a solid phase at a constant temperature and pH. When an adsorbate is contacted with the adsorbent for sufficient time, and the adsorbate concentration in the bulk solution is in a dynamic balance with the interface concentration, this situation is called adsorption equilibrium.

In general, the mathematical models such as Langmuir, Freundlich, Brunauer–Emmett–Teller, and Redlich–Peterson are the modeling analysis which is used to construct and design the equilibrium isotherm (Foo and Hameed, 2010).

2.3 **Critical Micelle Concentration of Surfactants**

The critical micelle concentration (CMC) is defined as the surfactant concentration at which micelles form and further surfactants added to the system go to micelles. In general, micelles are arranged with hydrophobic tails oriented inside and hydrophilic heads oriented toward the aqueous solution. There are a number of experimental methods to determine the CMC of a surfactant such as conductivity and surface tension. The method of choice depends on the availability of the various techniques and the relationship between the technique and the ultimate application (Myers, 2005).

2.3.1 Surface Tension of Surfactant Solution

The CMC is determined by measuring the surface tension of a series of surfactant concentration. As pure water, the surface tension reaches the highest value. Additional surfactant cause a decrease in surface tension. Above the CMC, the surface tension is independent of the surfactant concentration that is nearly constant.

The CMC is obtained from the surface tension vs. log concentration plot, shown in Figure 2.2, as the intersection point between the two best linear fitting for low and high concentrations.

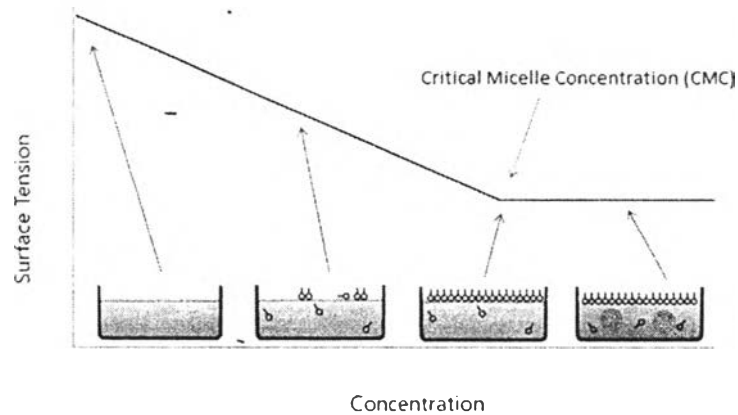


Figure 2.2 Simple plot between surface tension and a series of surfactant solution (KRUS).

2.3.2 Wilhelmy Plate Method

The Wilhelmy plate method is one of widely techniques for that measures contact angle on a solid sample as well as the surface tension acting on the perimeter of a plate. As the plate is moved into and out of a liquid, the change in force, F , due to the adhesion tension is shown in Equation 2.1 (Tiab and Donaldson, 2012; Yuan and Lee, 2013).

$$F = \gamma P \cos \theta \quad (2.1)$$

; where γ is the liquid surface tension, P is the perimeter of contact line, and θ is the contact angle. The experimental setup is shown in Figure 2.3. The plate is attached to a microbalance and the movement rate is determined by a computer.

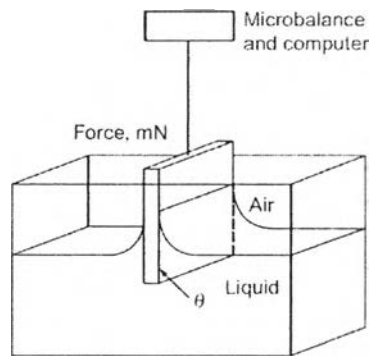


Figure 2.3 Wilhelmy plate method setup (Tiab and Donaldson, 2012).

2.4 Quartz Crystal Microbalance with Dissipation

A quartz crystal microbalance with dissipation (QCM-D) is a device which measures interfacial changes through their impact on piezo oscillation. The QCM-D has been used to determine changes in mass loadings from changes in oscillation frequency. QCM-D consists of a disk of single crystal quartz with metal electrodes deposited on each side of the disk. In general, gold quartz is used because it provides a more chemically stable surface (Binks, 1999).

QCM-D measures the change in resonance frequency of crystal quartz and energy dissipation. The change in resonance frequency relates to the amount of adsorbed mass which can be calculated using Sauerbrey equation shown in Equation 2.2 (Rodahl *et al.*, 1995; Merta *et al.*, 2004).

$$\Delta m = \frac{-C\Delta f}{n} \quad (2.2)$$

In Equation 2.2, Δm is the adsorbed mass, C is a constant characteristic of the crystal ($C = 17.7 \text{ ng}\cdot\text{cm}^{-2}\cdot\text{Hz}^{-1}$ for the crystals used at 5 MHz), Δf is the difference between the resonant frequency of the crystal sensor (f) and its nominal value (f_0), $\Delta f = f - f_0$, and n is the overtone number ($n = 1, 3, 5, \dots$). This relation based on the assumptions that the adsorbed mass forms a thin rigid film and uniform

distribution on the whole surface. In addition, equation (1) is also satisfied when the dissipation is 2×10^{-6} or less (Vogt *et al.*, 2004).

When the dissipation is larger than 2×10^{-6} , the adsorbed film is defined as soft layer (viscoelastic). The Voigt model is applied for viscous adsorbed layer. The additional parameters such as an effective layer density, layer thickness, shear elastic (storage) modulus, and shear viscosity (loss modulus) are added (Larsson *et al.*, 2003; Kou *et al.*, 2010).

The energy dissipation reflects the viscoelasticity of the adsorbed films and is measured based on that when the driving power to an oscillator is turned off, the voltage over the crystal decreases exponentially and a damped oscillating signal is recorded. The dissipation factor is showed in Equation 2.3 (Stålgren *et al.*, 2002).

$$D = \frac{E_{dissipated}}{2\pi E_{stored}} \quad (2.3)$$

; where $E_{dissipated}$ is the dissipated energy during one oscillation and E_{stored} is the stored energy during the oscillation cycle. With the QCM-D, the change in the dissipation factor, $\Delta D = D - D_0$, is measured, where D is the dissipation factor at any given time during the experiment and D_0 is the dissipation factor of a clean crystal immersed in the solvent.

A small ΔD represents for a rigid adsorbed structure. A large value for ΔD represents for a large energy loss, which is a soft film attached to the quartz crystal. The exact limits of this qualitative discrimination depend on the ratio between viscosity and elasticity of the adsorbed film (Voinova *et al.*, 1999; Shi *et al.*, 2009).

2.5 Surface Characterization

2.5.1 Atomic Force Microscopy (AFM)

The atomic force microscopy (AFM) first appeared in 1986 as an evolution from scanning tunneling microscopy (STM). The AFM was used to characterize the molecules of surfactants adsorbed on surface (Binks, 1999). The head groups of adsorbed surfactant must toward solution in order to provide a

repulsion force. For bilayer adsorbed surfactant, outside layer is scanned, but inner layer is still questionable. However, when AFM results are included with other information such as adsorption data, the surfactant structure can be predicted with strongly reasonable (Atkin *et al.*, 2003).

The adsorption and morphology of the cationic surfactant (CTAB) adsorbed onto the graphite were investigated by Manne *et al.* (1994) using AFM. They proposed that the surface morphology of CTAB on graphite was a hemicylindrical hemimicelles. The model agreed with their observations: (1) the model followed Langmuir isotherm data, and (2) graphite surface became more hydrophilic with increasing CTAB concentration due to exposing of cationic headgroups to the aqueous environment testified by the reduction of contact angle. At low surfactant concentrations (below the CMC), CTAB arranged a monolayer structure parallel to the graphite. They presumed that hemimicelles formation was based on this monolayer form so that the hemicylindrical shape did not need to relate to micelle in bulk solution.

Ducker and Grant (1996) presented the surface aggregate of the zwitterionic surfactant, DDAPS, on different types of surfaces. They used hydrophobic surface, graphite, and negatively charged hydrophilic surface, mica and silicon nitride. Silicon nitride was used to compare with mica in terms of the effect of surface roughness. The DDAPS adsorbed on graphite showed a hemicylinder shape and a lower curvature when comparing to mica resulting in aggregate shape could cover more surface leading to the reduction of the contact between surface and water.

Moreover, Ducker and Wanless (1996) also investigated adsorbed surfactant structure using mixtures of cationic and zwitterionic surfactant, DTAB and DDAPS respectively, on negatively charged hydrophilic surface, mica. They varied concentrations of DTAB and fixed a concentration of DDAPS. The result for pure DDAPS showed that there are 2 dimensions parallel to the mica with the length of each dimension about 5 nm. When the concentration of DTAB was increased, one dimension became longer whereas the other kept constant length. The authors explained that the shape of adsorbed surfactant was an intermediate between shapes of each surfactant and depended on the concentration of DTAB.

Grant *et al.* (2000) proposed the effect of hydrophobicity on the adsorbed nonionic surfactant, octa(oxyethylene) *n*-dodecyl ether ($C_{12}E_8$), on gold surface. They modified the surface became more hydrophobic by varied thiohexadecane groups from 0%, 25%, 50%, 75%, and 100% (contact angles increased linearly from 25° to 110°). They measured at the surfactant concentration twice of CMC. The overall results were shown in Figure 2.4. For the 0% and 25% of thiohexadecane, there was weak interaction between the surfactant and surface; hence water could create the hydrogen bond on surface. On the 50% thiohexadecane, the interaction between head group of surfactant and surface was increased so that close-packed micellar structure was occurred. When the degree of thiohexadecane was increased to 75%, surfactant structure formed a bilayer. At 100% thiohexadecane, a monolayer was observed with tail-down and head-up structure.

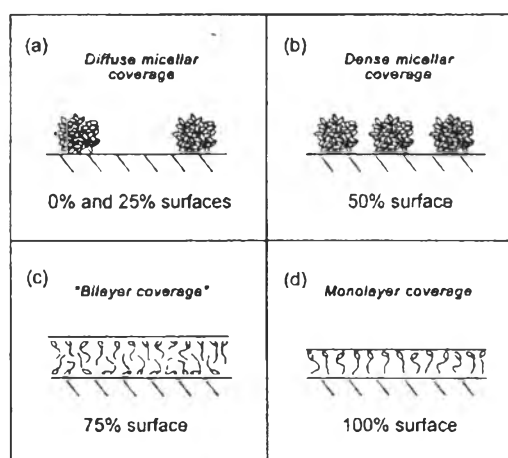


Figure 2.4 Proposed surfactant structure on gold surface at different hydrophobicity (Grant *et al.*, 2000).

Velegol *et al.* (2000) studied the influence of counterions on surfactant adsorption and adsorbed layer of surfactants on a silica surface. The cationic surfactants were $C_{16}TAB$ and $C_{16}TAC$ and the electrolytes were KBr and KCl . For the results of $C_{16}TAB$, it formed short rods at below the CMC ($0.9 \times CMC$) whereas it formed wormlike micelles onto silica at above the CMC ($10 \times CMC$) for both the presence and absence of KBr . As a result of the difference of AFM images

for both cases, this indicated that the mechanism of adsorption onto silica changed near the CMC. When the electrolyte was changed by KCl instead of KBr, adsorbed C₁₆TAC morphology showed the spherical shape for both concentrations. Besides, the presence and absence of KCl did not affected the self-assembly of surfactant onto silica.

AFM studies of cationic surfactant, CTACl, and cationic polyelectrolyte, poly(diallyldimethylammonium chloride) or PDADMAC, onto silica were presented by Liu *et al.* (2001). For pure CTACl adsorption, it formed a spherical shape at silica-water interface resulting from electrostatic force and then hydrophobic interaction. For pure PDADMAC adsorption, they cannot find any structures on the silica. They pointed out that PDADMAC formed a monolayer on the silica. For pre-adsorbed surfactant then polyelectrolyte, CTACl obstructed the adsorption of PDADMAC because CTACl formed the sphere first which showed the positive charge toward bulk solution so that there were a repulsion force to against the polyelectrolyte. On the contrary, for pre-adsorbed polyelectrolyte then surfactant, CTACl adsorbed on top of the polyelectrolyte because the negative charge of the silica surface was neutralized by the positive charge of the polymer and the surface became more hydrophobic. The aggregate of CTACl, as shown in Figure 2.5, was the hemispherical shape on the polyelectrolyte.

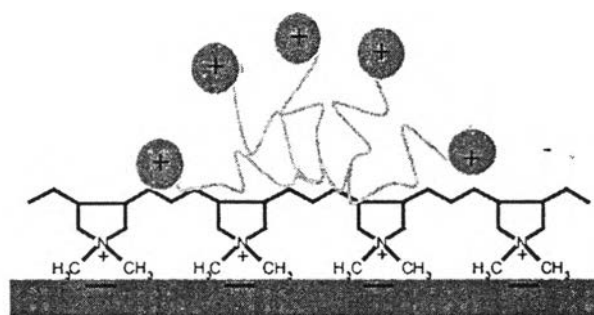


Figure 2.5 The hemisphere of CTACl on pre-adsorbed PDADMAC on silica (Liu *et al.*, 2001).

2.5.2 Contact Angle Measurement

Contact angle is the angle between a solid surface and tangent of liquid droplet. The value of contact angle can interpret for characterizing surface properties such as wetting, hydrophobicity, and the solid-vapor or solid-liquid interfacial tensions (Garbassi and Occhiello, 1998).

The contact angle measurement depends on an equilibrium relation which is called Young's equation by Young in 1805. The contact angle (θ) of a liquid drop on a solid surface is defined by the three phase equilibrium of the drop under the action of interfacial tensions: solid-liquid (γ_{sl}), solid-vapor (γ_{sv}), and liquid-vapor (γ_{lv}), shown in Figure 2.6 (Kwok and Neumann, 1999). The Young's equation is shown in Equation 2.4.

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl} \quad (2.4)$$

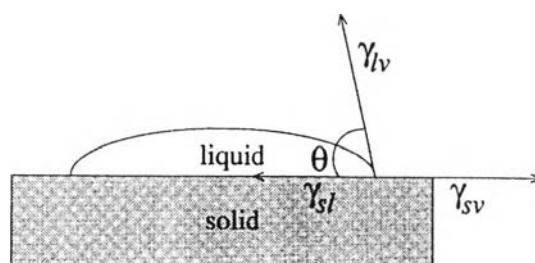


Figure 2.6 A sessile-drop contact angle system (Kwok and Neumann, 1999).

The low value of contact angle indicates that the liquid spreads well (high wettability) on surface, whereas high value points that less complete wetting (low wettability). If the contact angle is less than 90° , it means that the surface is the wetting surface. On the other hand, if the contact angle is more than 90° , it means that the surface is the non-wetting surface.

Contact angles are measured on macroscopic, smooth, nonporous, planar surfaces by dropping the liquid or solution on surfaces and determining the contact angle. There are various techniques to determine the contact angle namely Goniometer or sessile drop method, and Wilhelmy method. In general, the use of

microscope or photographing the droplet can use for measuring the contact angle (Rosen and Kunjappu, 2012).

2.6 Adsorption of Surfactant Mixtures

The role of mixed surfactant adsorption should be based on the comprehension of the mechanisms of adsorption and micelle formation of single system (Ogino and Abe, 1993). In the industrial products, there are very popular to use the mixtures of various types of surfactants; as a result, the mixtures show the synergistic interaction (Rosen and Kunjappu, 2012). The interactions between the combinations of surfactants at solid-aqueous interface are described below.

2.6.1 Anionic – Cationic Surfactant Mixtures

Huang *et al.* (1989) showed the adsorption behaviors of two mixed surfactant systems, DTAB – SDBS and DPB – SDS mixture, on silica surface. They found that the cationic surfactants, DTAB and DPB, were strongly adsorbed onto silica, but the anionic surfactants, SDBS and SDS, were not adsorbed onto silica for individual systems. However, in the mixed systems, the adsorption amounts of both cationic and anionic surfactants were increased and the excess adsorption of cationic ions was equal to excess adsorption of anionic ions. They concluded that cationic surfactants co-adsorbed with anionic surfactants as ion pairs onto uncharged silica via Van der Waals forces.

The formation of mixed anionic and cationic surfactants on laponite clay which was a negatively charged surface was investigated by Capovilla *et al.* (1991). Sodium dodecyl sulfate (SDS) and cetylpyridinium bromide (CPBr) were used as the anionic and cationic surfactant, respectively. The results showed that SDS favor tail-tail adsorption through Van der Waals interactions with a monolayer of adsorbed CPBr onto laponite clay. They proposed the model that the lower layer CPBr head groups adsorbed onto negatively charged clay and the head groups of the upper layer SDS toward aqueous solution formed in bilayers.

Paria *et al.* (2004) studied the effect of cationic surfactant, CTAB, to anionic surfactant, NaDBS, on cellulose surface, which had a negative charge. They

tested in both CTAB pre-adsorbed and mixture. The results revealed that the rate of adsorption and the amount of adsorption were increased in case of CTAB pre-adsorbed more than the mixture. The reason was that CTAB was expected to change surface charge of cellulose to hydrophobic site and followed by NaDBS. Moreover, both surfactants formed ion pair and had almost no charge in the mixture, which it impeded the adsorption on negatively charged surface.

2.6.2 Anionic – Nonionic Surfactant Mixtures

Esumi *et al.* (1990) investigated the adsorbed structure of mixed surfactants on positively charged alumina. Lithium dodecyl sulfate (LiDS) and lithium perfluoro-1-octanesulfonate (LiFOS) were used as anionic surfactants. Sodium dodecyl sulfate poly(oxyethylene) nonylphenyl ether (NP) with different chain lengths, 7.5, 10, and 20 were used as nonionic surfactants. Individual LiDS or LiFOS adsorbed on alumina became flocculation. Further addition of NP with different chain lengths resulted in the mixed bilayer, as shown in Figure 2.7. These bilayers were formed easily when the length of NP chain decreased; nevertheless, they made the redispersion of alumina particles simply with an increase in NP chain length because of the steric repulsions associated with the chain length.

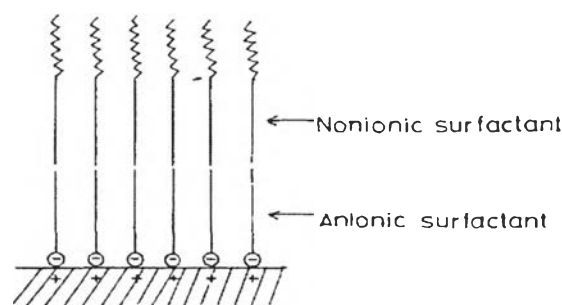


Figure 2.7 A model of mixed bilayer on alumina (Esumi *et al.*, 1990).

The behavior of mixed surfactants system, an anionic surfactant sodium dodecyl sulfate (SDS) and a nonionic surfactant pentaethylene glycol monodecyl ether ($C_{10}E_5$) was revealed on the silica surface by Thibaut *et al.* (2000). They observed that $C_{10}E_5$ itself could adsorb onto silica, but no adsorption for the

SDS. In the mixtures, when SDS existed, the adsorption of $C_{10}E_5$ was limited owing to the fact that there was the mixed micelles formation. As a consequence, the adsorption of $C_{10}E_5$ decreased in the mixtures. Their further investigation was that the preadsorbed of $C_{10}E_5$, followed by the addition of SDS- $C_{10}E_5$ mixtures. The results showed that the $C_{10}E_5$ -preadsorbed onto silica was desorbed due to the mixed micelles formation as well.

Penfold *et al.* (2002) determined the adsorption mechanism and structure of mixed anionic surfactant, sodium dodecyl sulfate (SDS), and nonionic surfactant, hexaethylene glycol monododecyl ether ($C_{12}E_6$), on negatively charged silica surface. They found that individual SDS did not adsorb onto silica whereas $C_{12}E_6$ adsorbed by the formation of hydrogen bond between ether oxygens of ethylene oxide group of $C_{12}E_6$ and OH groups on silica surface. In the presence of $C_{12}E_6$, SDS can coadsorb with $C_{12}E_6$ onto silica. Increasing SDS molar ratio in mixtures, the adsorbed amounts of surfactant decreased. Furthermore, the SDS was not next to the silica surface but it was in outer layer of surface layer formed like bilayer.

The interaction forces for mixed surfactant adsorption on alumina were proposed by Sakai *et al.* (2003). Anionic sodium dodecyl sulfate (SDS) and nonionic hexaoxyethylenedodecyl ether ($C_{12}E_6$) were used in this study. They pointed out that the coadsorption of between SDS and $C_{12}E_6$ caused the synergism from the hydrophobic interaction of the surfactants. At lower $C_{12}E_6$ concentrations, there is the stronger SDS adsorption resulting from the reduction of electrostatic forces between ionic headgroups of SDS admicelles. With increasing in $C_{12}E_6$ concentrations, the formation of the closed packed adlayers was formed as compared to individual SDS admicells.

2.6.3 Cationic – Nonionic Surfactant Mixtures

The adsorption behaviors on alumina surface of mixed surfactant using the cationic surfactant, tetradecyl trimethyl ammonium chloride (TTAC), and the nonionic surfactant, pentadecylethoxylated nonyl phenol (NP-15) were measured by Huang *et al.* (1996). The results showed that TTAC adsorbed onto negatively charged alumina with the electrostatic force whereas no adsorption of NP-15 was

detected in the individual system. For the adsorption isotherms of TTAC in the presence of NP-15, the adsorption of TTAC increased below saturation adsorption because the synergism of TTAC and NP-15 to reduce the repulsion among the TTAC headgroups and decreased it above due to the competition of bulky NP-15. For the adsorption isotherms of NP-15 in the presence of TTAC with increasing in TTAC molar ratio, the adsorption of NP-15 was increased due to the co-adsorption of NP-15 with TTAC aggregates.

Soboleva *et al.* (2004) presented the study of adsorption behavior of mixed surfactants. The cationic tetradecyl trimethyl ammonium bromide (TTAB) and nonionic p-tret-octylphenyl ether of deca(ethylene glycol) (TX-100) were used for adsorption onto silica. At low concentrations of surfactant, a synergistic interaction between the hydrocarbon chains of both surfactants occurred and the contact angles in this region reached maximum values. When surfactant concentrations were increasing, the contact angles decreased because the aggregation of mixed surfactants which polar groups oriented toward the aqueous solution was formed onto silica as shown in Figure 2.8.

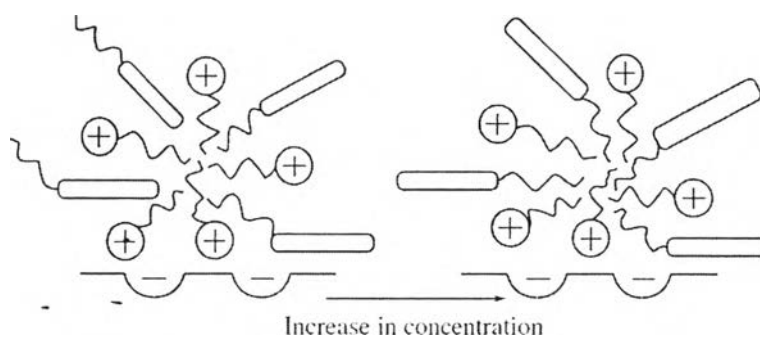


Figure 2.8 The structure of mixed surfactant on silica at high concentrations (Soboleva *et al.*, 2004).

The effect of pH on the adsorption of surfactant mixtures of cationic dodecylpyridinium bromide (DDPB) and nonionic p-tret-octylphenyl ether of deca(ethylene glycol) (TX-100) on silica was studied by Kharitonova *et al.* (2005). They studied the adsorbability at pH 3.6, 6.5, and 10. The result showed that the

synergistic interactions occurred at entire range of pH used. At higher pH values, they observed that DDPB adsorbed more and TX-100 adsorbed less than lower pH values. These are consistent with Atkin *et al.* (2003) that the negatively charged densities remained low until the solution pH reaches 6, but increased dramatically between pH 6 and 11.

The interaction energy between the mixtures of surfactants on hydrophobic silica was investigated by Ivanova *et al.* (2007). They studied both individual surfactants and their mixtures using dodecylpyridinium bromide (DDPB) and p-tret-octylphenyl ether of deca(ethylene glycol) (TX-100) which are a cationic and nonionic, respectively. The results demonstrated that the interaction energies for the mixed surfactants were lower than the individual surfactant so that the synergistic force of both surfactants took place. The Rubini-Rosen model was used to identify the adsorbed layer. It was shown that the TX-100 adsorbed adjacent to hydrophobic silica surface. The cause of this synergism came from chain-chain interactions between DDPB and TX-100.

2.7 Surfactants Adsorption Kinetics

The kinetics of surfactant adsorption at the solid-water interface plays an important role in a wide-range of applications of surfactants. The examples are the wetting of fabrics in detergency, the spreading of agricultural sprays on leaves, the adsorption of collectors on ore particles, and the deposition of conditioners on hair and textiles (Woods *et al.*, 2011).

A model which describes the kinetic of adsorption of single nonionic surfactants at a silica surface was presented by Brinck *et al.* (1998). A series of poly(ethylene glycol) monoalkyl ethers, $C_{10}E_6$, $C_{12}E_5$, $C_{12}E_8$, and $C_{14}E_6$, was used. The model, as shown in Figure 2.9, was described as a two-step process where the first step was diffusion of monomer and micelle from the bulk solution to a subsurface, and the second step was the transportation into the solid surface. Due to simultaneous occurrence of both steps, there was continuous equilibrium between monomer and micelle.

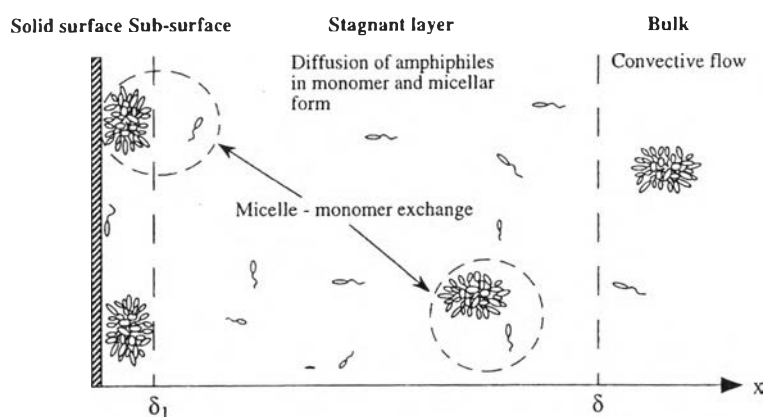


Figure 2.9 The solution profile outside the silica surface (Brinck *et al.*, 1998).

Biswas and Chattoraj (1998) studied the kinetics of adsorption of cationic surfactants, CTAB, MTAB, and DTAB, on the silica surface at various values of bulk concentration, pH, ionic strength, and temperature. It appeared that the adsorption kinetics follow the two-steps first-order kinetic rate equation with two different rate constants, k_1 and k_2 . The rate constants of adsorption on silica increased with increasing temperature as well.

In addition, Atkin *et al.* (2000) studied the adsorption kinetics using a cationic surfactant, CTAB, onto silica. The initial rate of adsorption was expressed as a function of CTAB concentration in the presence and absence of electrolyte. The result showed that when the CTAB concentration increased, the adsorption rate also increased. Above the CMC for both systems which there was no increase in monomer concentration, the initial rate of adsorption continued increasing. The reason was that the micelles transported surfactant monomers to a surface and they then left the micelles and adsorbed on surface as monomers. Hence, the monomers in micelles would penetrate the surface layer more effectively than individual monomer.

The adsorption and desorption kinetics of cationic surfactant onto silica in the water and the toluene system was investigated by Tabor *et al.* (2009). They used the dialkyldimethylammonium bromide (Di- C_{12} DAB). For a particular bulk surfactant concentration, the kinetic behavior in both solvents had the same trend at the beginning which was very rapid. The equilibrium adsorbed amount from water

was twice as much as from toluene indicating that in water, surfactants form a bilayer, whereas they formed the monolayer in toluene. The desorption of Di- C_{12} DAB from aqueous system was rapid and seemed to be a single-rate process. In the contrary, the desorption from toluene was slower than water and consistent with two-rate model which was the faster step (the tightly bound mode) and the slower step (the loosely bound mode).

Furthermore, Tabor *et al.* (2009) also published another article related to the adsorption kinetics of nonionic surfactants onto silica in toluene. A range of Poly(ethylene glycol) monoalkyl ethers (C_nE_mS), $C_{12}E_3$, $C_{12}E_{10}$, $C_{12}E_{23}$, and $C_{16}E_5$, was used. The result showed that the initial rate of each surfactant was almost the same. They suggested that the adsorption process was limited by the hydrodynamics of the flow cell which was the transportation to the surface and the diffusion of surfactant molecules. They found that the larger “m” (more EO groups) could reach to the equilibrium more quickly. The explanation was that the surfactant which contained larger EO groups was required fewer molecules to adsorb all sites.

Recently, there was a series of two articles involved in surfactant adsorption kinetics had been published by Woods *et al.* (2011). The first one was the adsorption of pure surfactants on silica. The cationic surfactant, CTAB, and the nonionic surfactant, Triton X-100, were used in this study. For both surfactants, their data fitted the Frumkin isotherm. They adopt the kinetic equation from Curwen *et al.* (2007) to investigate in their study. They pointed out that the rate constants of adsorption and desorption decreased with increasing surface coverage because of the steric hindrance to adsorption. The second one was the adsorption of CTAB and Triton X-100 mixtures on silica. For the various molar ratios of mixed surfactants, both types of surfactants showed a smooth increase in amount adsorbed with time. Besides, the rate of adsorption of Triton X-100 in mixtures was faster than pure component because small amounts of CTAB bounded electrostatically to the negatively charge of the silica surface.