CHAPTER II
BACKGROUND AND LITERATURE SURVEY

2.1 Surfactant

2.1.1 Structure and Behavior of Surfactants

Surfactants, which is a contraction of the term surface-active agent, is a substance that has the tendency to adsorb onto the surfaces or interfaces of the system accompanied with altering to a noticeable degree the surface or interfacial free energies of those surfaces or interfaces.

Surfactants consist of a structure known as amphiphatic structure, which includes two distinct structural groups: one that has very little attraction for the solvent called the lyophobic group and the other that has strong attraction to the solvent called lyophilic group. In an aqueous solution the lyophobic group or water-hating group is called a hydrophobic group, which is usually a long-chain hydrocarbon residue, while the lyophilic group or water-loving group is called a hydrophilic group, which in general is an ionic or highly polar group. Properties of a surfactant depend on the solvent system as well as the molecular structure.

According to the nature of the hydrophilic group, surfactants are categorized into four major types: anionic, cationic, nonionic, and zwitterionic surfactants.
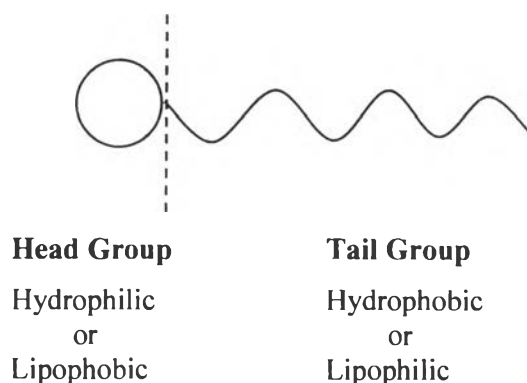

Head Group
Hydrophilic
or
Lipophobic

Tail Group
Hydrophobic
or
Lipophilic

Figure 2.1 General structure of a surfactant molecule.

2.1.2 Adsorption of Surfactants at Solid-Liquid Interface

The tendency to adsorb at interfaces in an oriented fashion is one of the characteristic features of surfactants. The performance of surfactant in many interfacial processes namely foaming, detergency, and emulsification depends on its concentration at the interface. Furthermore, study of adsorption can give the information about how the interface will be affected by the adsorption whether it will become more hydrophilic or hydrophobic, depending on the orientation of surfactant at the interface.

The most simple and widely used methodology to gain insight into a particular adsorption system is to study its adsorption isotherm. In general adsorption isotherms of anionic and cationic surfactants from aqueous solution onto nonpolar or hydrophobic surface are similar and are of the Langmuir type (Rosen, 1989) and appear to show surface saturation in the vicinity of critical micelle concentration of adsorbate as shown in Figure 2.1.
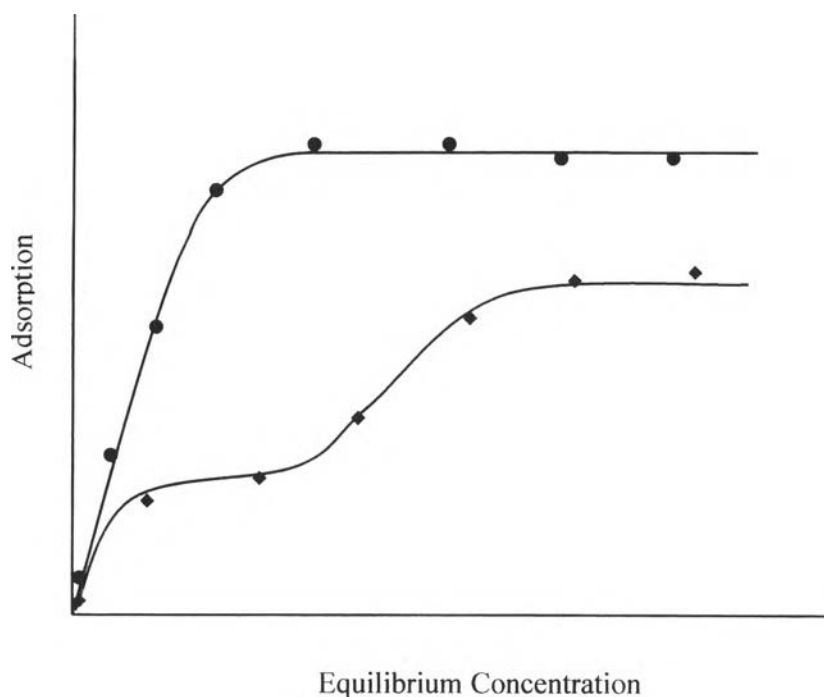

Equilibrium Concentration

Figure 2.2 Adsorption from aqueous solution onto hydrophobic surface.

Adsorption in this situation is mainly by dispersion forces with the orientation of the adsorbate initially maybe parallel to the surface of the solid or slightly tilted with hydrophobic group close to the surface. As adsorption continues, the adsorbed molecules become oriented more and more perpendicular to the surface. In some cases, the adsorption isotherm shows an inflection point that has been ascribed to a change in orientation of the surfactant from parallel to perpendicular.

The adsorption at the solid-liquid interface is strongly influenced by a number of factors namely the nature of the solid surface, the molecular structure of the surfactant being adsorbed, and the environment such as pH and temperature.

2.1.3 Micelle Formation and Factors Affecting the CMC Value

Micellization is a process of micelle formation of surfactants when the surfactant concentration is high enough to form aggregates of surfactant molecules. The surfactant concentration at which micellization starts appearing is called the critical micelle concentration (CMC) (Figure 2.3).

Micelle formation is an important phenomenon not only because a number of physical processes such as detergency and solubilization are governed by micelle compositions, but also because it affects other interfacial phenomena such as surface or interfacial tension reduction as well.

The determination of the value of the CMC can be made by the use of several measurable physicals properties, but most commonly, the breaks in the electrical conductivity, surface tension, light scattering, or refractive index concentration curves have been used for this purpose.

There are various factors known to affect the CMC in aqueous solution namely the structure of surfactant, the presence of added electrolyte, the presence of organic compounds or a second liquid phase, and the temperature.
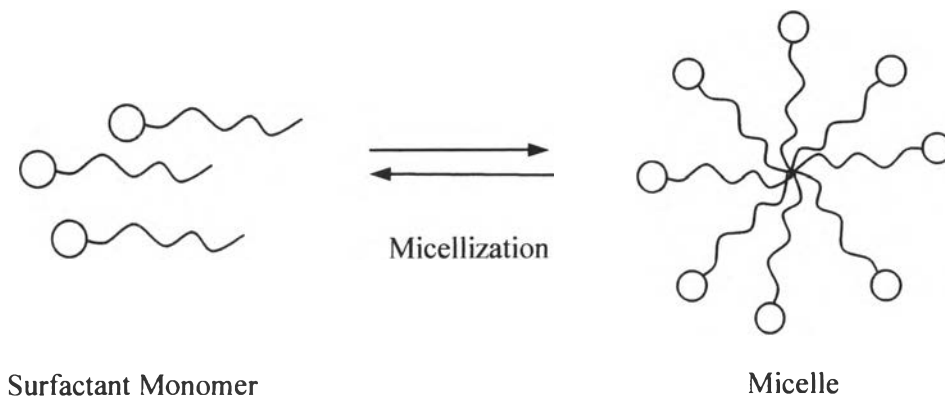
Figure 2.3 Micelle formation.

2.1.4 Precipitation of Surfactant

Anionic surfactants tend to precipitate in the presence of high salinity or hardness levels. Hardness tolerance is the maximum concentration of a divalent cation possible without precipitating the anionic surfactant. It is necessary to understand the mechanism of surfactant precipitation in order to maximize its detergency performance.

Soaps (fatty acids) tend to have poor hardness tolerance because of the high attraction of the calcium/magnesium for the carboxylate head group to form soap scum. Figure 2.4 illustrates the precipitation of an anionic surfactant or soap system in the presence of counterions.
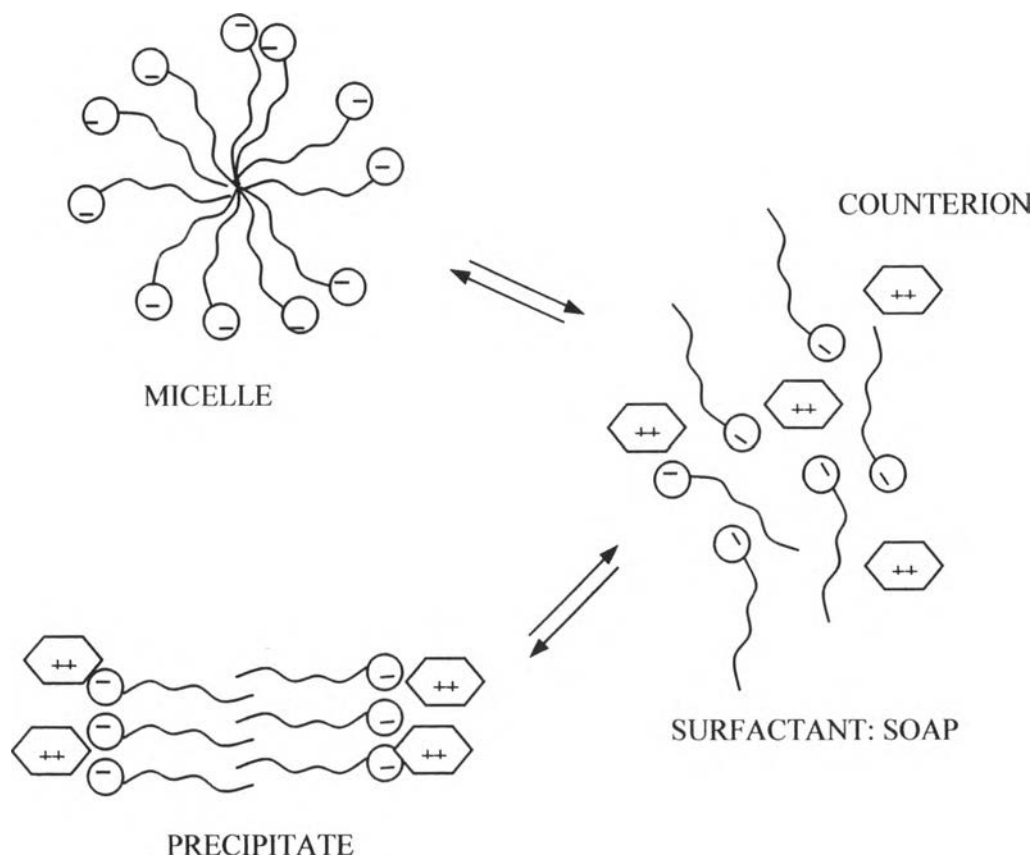
Figure 2.4 Schematic diagram of monomer-micelle-precipitate equilibrium in an anionic surfactant system.

2.2 Wetting and Its Modification by Surfactants

Wetting can occur spontaneously as long as the surface tension of the liquid is less than the critical surface tension of the solid to be wetted. When a droplet of a high surface tension liquid is placed on a low surface energy solid, the liquid surface tension will cause that liquid to form a drop of spherical shape since the spherical geometry has the lowest surface area resulting in the lowest energy requirement. In contrast, if the drop of liquid with lower surface tension than the solid to be wetted is deposited on that solid, the drop of liquid will be flattened or tends to spread over the solid substrate.

For nonporous hard surface having a small area, the process of wetting is governed by its thermodynamics, the change in surface free energy. In contrast, the wetting process for porous surfaces and large area surfaces is determined by the kinetics.

Normally, near equilibrium wetting occurs on hard surfaces because areas in general are small. For low-energy surfaces, the Zisman correlation is useful. The Zisman equation is as follows:

$$\cos \theta = a + b\gamma_{LV} \qquad (2)$$

or

$$\cos \theta = 1 - \beta(\gamma_{LV} - \gamma_{LV}^{C}) \qquad (3)$$

where γ_{LV}^{C} is the critical surface tension characteristic of the solid, a, b, and β are constants. Solid has a characteristic critical value of surface tension that cannot be exceeded by a wetting liquid. In other words, a liquid that spreads spontaneously must have a lower surface tension than γ_{LV}^{C}. The critical surface tension suggested by Zisman can be obtained from the relationship of $\cos \theta$ and liquid/vapor interfacial tension, the point corresponding to $\cos \theta = 1$ as shown in Figure 2.5.
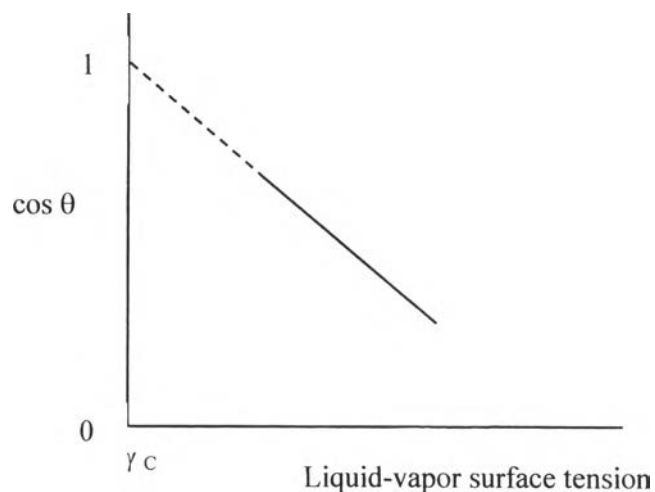

Figure 2.5 A Zisman plot.

Since surfactants are highly surface active, one of their main functions is to reduce surface tension by adsorption at the interfaces. Surfactant alignment in a vapor/liquid/solid system is illustrated in Figure 2.6.
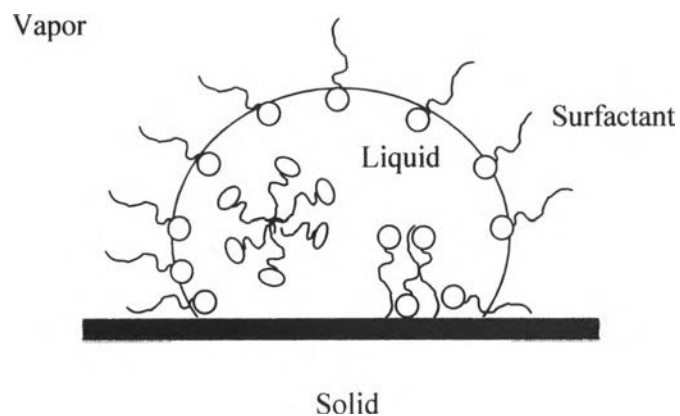

Figure 2.6 Surfactant alignment in a vapor/liquid/solid system.

Many works are focused on investigation of wetting mechanism and its modifications by surfactants. Modaressi and Garnier (2002) studied the mechanism of wetting and adsorption of water droplets on sized paper and they reported that the adsorption started only after the drop had wetted the surface to a certain extent. Wetting on a partially hydrophobized porous surface had the rate lower than in hydrodynamics wetting by a factor that is a function of surface roughness. At the same time, the wetting dynamics was found to be independent of the chemical heterogeneity of the surface. Loukkala *et al.* (2001) stated that surfactant solutions exhibited a wide variety of wetting and dewetting behaviors on high-energy surfaces. These behaviors were driven by surfactant self-assemblies at the moving contact line. Moreover, Qu *et al.* (2002) correlated the autophobing phenomenon and surfactant self-assemblies event. They reported the essence of autophobing of ionic surfactant solution lies in the interplay of surfactant self-assembling at the contact line and the driving of fluid motion by that self-assembly. The other evidence that elucidates surfactant self-assembly and its implications

for wetting was proposed by Kumar *et al.* (2003). The presence of a region with unusual higher wetting behavior ahead of advancing and receding contact line provides direct indication of the self-assembly and carryover of surfactant.

2.3 Contact Angle

Contact angle measurement is the most common method for evaluating wettability. Furthermore, contact angle measurements have also been a major experimental approach to many problems concerned with solid-liquid interface (Erbil *et al.*, 1999). There are three main techniques for measuring the contact angle on flat plates. These are the sessile drop (or captive bubble in liquid), the Wilhelmy plate, and inclined plane method.

In the sessile drop method, a liquid drop is placed on a horizontal solid surface so that the edge of the drop and its reflected image are both visible when viewed in cross section using a microscope. This allows the tangent to be determined at the point of contact between the drop and the surface. Several measurements are often made on both sides of the drop and an average between those values will be taken.

Young initiated the understanding of wettability relating to the contact angle in 1805 (Marmur, 1996). He correlated the static contact angle with the free interfacial energies between solid-vapor (γ_{SV}), solid-liquid (γ_{SL}), and liquid-vapor (γ_{LV}) through the equation known as Young's equation (equation (1)). This equation can be derived using the principle of energy minimization as well as a force balance along the surface at the contact line. Furthermore, this is only valid for a liquid drop resting at equilibrium on a smooth, flat, homogeneous, impermeable, and nondeformable surface, which can be used as a model for explaining wetting phenomenon in most systems. However, it is unfortunate that evaluation of the various interfacial tensions required is not always straightforward and only the interfacial tension between liquid-vapor can be measured directly. The surface tension of a liquid can be measured by using tensiometry, drop profiles, capillary rise, etc (Dalal, 1987). The solid-vapor and solid-liquid interfacial tensions are not directly accessible.

2.4 Factors Affecting Contact Angle and Wettability

There are several factors affecting contact angle, for examples, method of measurement, drop evaporation, droplet contamination, surface roughness, surface heterogeneity, temperature and other environmental conditions.

Rosen (1989) reported that surface roughness reduced contact angle when the value on a smooth surface is less than 90° and increased the contact angle when the value on the smooth surface is greater than 90°. Furthermore, contamination of a droplet by adsorption of impurities from the gas phase tends to reduce contact angle.

The effect of surface heterogeneity on the drop size dependence of contact angles was observed by Lin and Li (1995). They noticed that the fluctuations of contact angle can be due to surface heterogeneity and the contact angle can decrease, increase or remain relative constant as the drop size increases, corresponding to positive line tension, negative line tension and negligible line tension effect, respectively. In addition, they stated that real surfaces used in contact angle measurements always have some degrees of heterogeneity due to, for example, polycrystalline materials, impurities of surface materials and solutions used in the preparation processes, as well as pollutants from air.

Static advancing and low rate dynamic contact angle measurements by using conventional goniometer and automated axisymetric drop shape analysis (ADSA) technique, respectively were done by Kwok *et al.* (1997). They found that in a specific case, slip and stick contact angle behavior, which could be observed from the ADSA method, could not be observed in the conventional goniometer method. This circumstance is necessary in the decision whether or not the experimental contact angles can be used to interpret surface energetic in conjunction with Young's equation.

Basu *et al.* (1998) stated that the dynamic and static contact angles of bitumen decreased above a certain NaCl concentration for a particular pH when compared to the results with no salt. The dynamic and static contact angles of bitumen decreased significantly with increasing NaCl concentration at high pH and decreased with increasing pH. Furthermore, it has been reported that bitumen oil on a glass surface in the presence of water at pH 11 reaches a higher equilibrium contact angle than when in the

presence of water at pH 3 because of the decrease in the interfacial tension (Starkweather *et al.*, 2000).

McHale *et al.* (2001) examined the effects of drop flattening and substrate surface heterogeneity on the cross sectional and planar shapes of droplets of liquids resting on solid surfaces by using simultaneous planar and side view video microscopy of sessile drop. They found that the planar view often shows deviations from a circular shape whereas these are not apparent from a side view observation of droplet. This demonstrated that the large variation in measured contact angle possibly depends upon the direction of side view.

Sefiane *et al.* (2003) reported that the dynamic contact angle in the system of binary mixtures between water and ethanol was highly dependent on the concentration of the more volatile component.

Ghannam (2002) proposed that whereas $CaCl_2$ and $AlCl_3$ slightly changed the wetting behavior of the polyacrylamide aqueous solution over polyethylene substrate, NaCl significantly lowered the contact angle and enhanced wettability, especially for the higher concentration of polyacrylamide solution.

Synergistic effect on the spreading of the mixed surfactant solution onto the hydrophobic polyethylene film has been observed by Zhou *et al.* (2003). It was suggested that the mixed hydrocarbon-chain surfactant systems enhanced spreading behavior and also lowered dynamic contact angles, which implied greater dynamic spreading coefficients.

2.5 Applications and Related Work

The effect of sodium octanoate (SO) and pH on the precipitation of sodium dodecyl sulfate (SDS) with calcium in water was investigated by Rodriguez and co-workers (1998). They showed that, above critical micelle concentration (CMC), the hardness tolerance of SDS increased with decreasing pH due to synergism in the SDS/SO mixtures.

Hauthal *et al.* (1999) examined synergism in the wetting properties of ternary surfactant mixtures on the basis of nonideality parameter of binary subsystem derived

from advancing contact angles of appropriate surfactant mixtures. They found that the advancing contact angle increased with decreasing polarity for all surfactant species and the contact angle for surfactant solutions was between 20 and 60% lower than that for pure water so that the surfactants proved especially effective. Moreover, in most binary systems, decreasing in the value of advancing contact angle showed a weak synergistic behavior. The experimental and calculated advancing contact angles of ternary surfactant mixtures on the basis of nonideality parameters of binary subsystem have an average deviation of about 10%. Erbil and co-workers (1999) determined the receding contact angles of water drops on poly (methyl methacrylate) (PMMA) and poly(ethylene terephthalate) (PET) by using video microscopy of sessile drop. Depending on the initial drop size, receding contact angles equalled to 54-64° for PMMA and 64-66° for PET. Furthermore, advancing and receding contact angles were also determined from needle–syringe and the inclined plane methods for comparison. The variations of the values were obtained from both methods, which they stated that these apparent variations depended on the rate of liquid flow and the size of the drops.

Starkweather *et al.* (2000) reported the effect of pH and SDS surfactant concentration on the change in the contact angle of oil on stainless steel and glass surfaces. The change in contact angle was compared between an initial contact angle and a final contact angle measured at 300 s after. Over the range of pH values and SDS concentrations studied, increasing pH and surfactant concentration above the CMC hindered the change in the contact angle of the oil on both surfaces despite the interfacial tension between the oil and surfactant solutions decreased. The critical micelle concentration (CMC) values of Triton X-100 (nonionic surfactant) and sodium dodecylsulfate (anionic surfactant) were determined from the point of sudden change in the graph that plotted between surface tension vs. surfactant concentration or contact angle vs. surfactant concentration for each type of surfactant obtained by measuring the surface tension and the contact angle of these surfactant solutions at several concentrations on Teflon by using Du Nuoy-type tensiometer and goniometer. (Dionisio and Sotomayor, 2000). Furthermore, the goniometer was used to measure the contact angle of several organic liquid droplets on the solid surfaces for determining the surface tension of those solid surfaces by utilizing the Zisman plot (Kabza *et al.*, 2000).

Contact angle of several saturated surfactant solutions such as fatty acids (C_{10} – C_{18}), sodium and calcium salt of fatty acids, and sodium and calcium salt of alkyl sulfates on its precipitated surfaces measured by sessile drop method was studied by Luangpirom and co-workers (2001). They stated that free fatty acids and calcium salts of fatty acids have advancing contact angle between 77 and 92° with little dependence on alkyl chain length for C_{12} and higher alkyl chains. The lower advancing contact angle was found for sodium salts of fatty acids. At the same number of carbon atoms, calcium dodecyl sulfate has lower advancing contact angle than calcium salt of dodecanoic acid ($\theta_A = 46$ vs.82°) whereas the same advancing contact angle was found for calcium salt of 18-carbon fatty acid and alkyl sulfate. Moreover, they showed that greasiness and slipperiness or scummy feel of precipitated surfactant does not necessary correspond to a hydrophobic surface.

Balasuwatthi (2003) proposed that presence of subsaturated sodium dodecyl sulfate (NaDS) solutions could reduce contact angle of calcium salt of dodecanoic acid (CaC_{12}) on its precipitated surface. Contact angle of this system decreased with increasing in NaDS concentrations until reaching the CMC of the surfactant mixture.

Amirfazli *et al.* (2003) investigated the line tension for the system near wetting by measuring contact angles of heptane, octane, and nonane on two different self-assembled surfaces. They concluded that the observed drop size dependence of contact angles was due to line tension, however, the line tension decreased as the contact angle decreased and was likely to vanish at complete wetting.

Adsorption and contact angle of single and binary mixtures of sodium oleate and ethoxylate nonylphenol type nonionic surfactants on apatite minerals were studied by Sis and Chander (2003). The results show multilayers of oleate adsorbed on apatite surface. The presence of Ca^{2+} ions increased the adsorption by causing surface precipitation of oleate salt as calcium oleate. However the presence of nonionic surfactant decreased oleate adsorption due to competition between surfactants and prevention of oleate ions from precipitation as calcium oleate.