

CHAPTER II

LITERATURE SURVEY

2.1 Wetting

Wetting is defined as the displacement of air from a solid or a liquid by an aqueous solution. In more basic terms, wetting refers to the ability of a surfactant solution to spread over a given surface. The ability to “wet” is a function of several parameters including molecular structure of the surfactant, its concentration, its environment, and the composition of the substrate to be wetted.

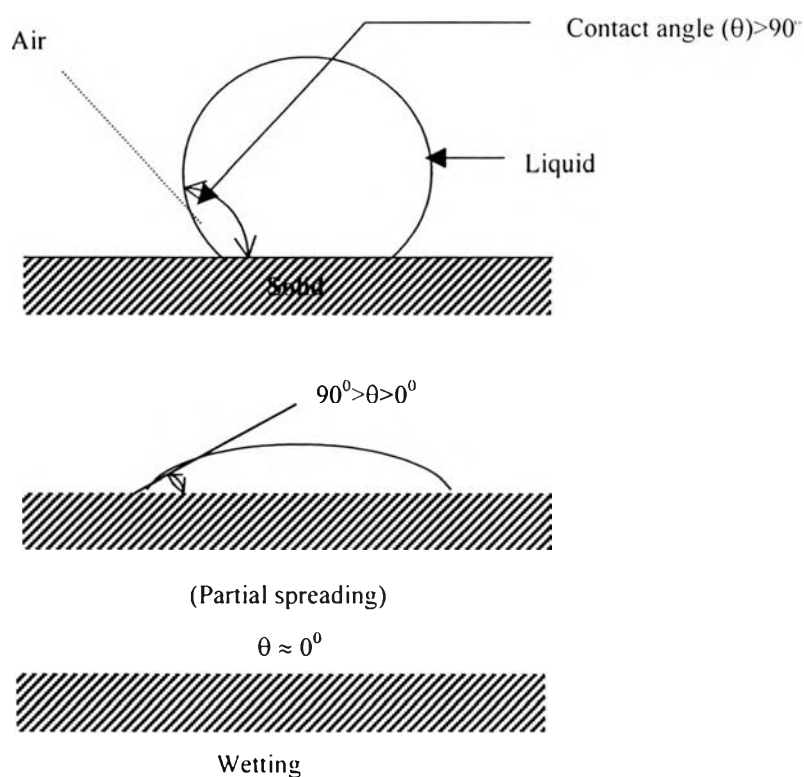


Figure 2.1 Contact angles for nonwetting, partial wetting, and wetting.

Wetting can be examined by measuring the “contact angle” of a drop of surfactant solution sitting on the substrate of interest. “Contact angle” is the angle between the substrate surface and the droplet (see Figure 2.1). The closer the contact angle is to zero, the better the wetting agent (surfactant).

Wetting in its most general sense is the displacement from a surface of one fluid by another. Wetting, therefore, always involves three phases, at least two of which are fluids: a gas and two immiscible liquids, or a solid and two immiscible liquids. Commonly, however, the term wetting is applied to the displacement of air from a liquid or solid surface by water or an aqueous solution. The term wetting agents apply to any substances that increase the ability of water or an aqueous solution in displacing air from a liquid or solid surface. Wetting is the process involving surfaces and interfaces and the modification of the wetting power of water is a surface property shown to some degree by all surface active agents, although the extent to which they exhibit this phenomenon varies greatly. When the surface to be wetted is small, as in the wetting of nongranular, nonporous solids (hard surface wetting), then equilibrium conditions or conditions close to it can be attained during the wetting process and the free energy changes involved in the process determine the degree of wetting attained. On the other hand, when the surface to be wetted is large, as the wetting of porous or textile surfaces or finely powdered solids, equilibrium conditions are often not reached during the time allowed for wetting. In this case the degree of wetting is determined by the kinetics rather than the thermodynamics of the wetting process.

It is observed experimentally that the contact angle for a material moving over a surface (the advancing contact angle) is different from that of the same material retreating from an interface (the receding contact angle). The receding angle is usually substantially lower than the advancing angle. The difference comes from several sources. First, most surfaces are not clean.

and the presence of contamination will cause the advancing angle to be higher than the contact angle made by the liquid as it withdraws over itself.

2.2 The Contact Angle

When the substrate is a solid, the spreading coefficient must be evaluated by indirect means, since surface and interfacial tensions of solids cannot be measured directly. The method to doing this involves measuring the contact angle, which the substrate makes with the liquid in question.

The contact angle θ that the liquid makes when it is at equilibrium with the other phase in contact with it is related to the interfacial free energies per unit area of these two phases, gas and solid substrate. Diagram of the contact angle θ is shown in Figure 2.2. For a small reversible change in the position of liquid on the surface so as to cause an increase in the liquid-substrate (L/S) interfacial area of Δa , there is a corresponding decrease Δa in the area of the substrate-air (S/A) interface and an interface in the liquid-air (L/A) interface of $\Delta a \cos \theta$.

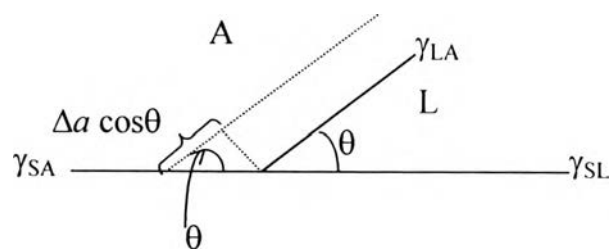


Figure 2.2 Contact angle.

$$\text{Thus } \Delta G_w = -\gamma_{SA}\Delta a + \gamma_{LS}\Delta a + \gamma_{LA}\Delta a \cos \theta. \quad (2.1)$$

$$\text{As } \Delta a \rightarrow 0, \Delta G \rightarrow 0$$

$$\gamma_{LA}da \cos \theta + \gamma_{LS}da - \gamma_{SA}da = 0 \quad (2.2)$$

Therefore,

$$\gamma_{LA} \cos \theta = \gamma_{SA} - \gamma_{SL} \quad (2.3)$$

or

$$\cos \theta = \frac{\gamma_{SA} - \gamma_{SL}}{\gamma_{LA}} \quad (2.4)$$

where

θ	=	contact angle
ΔG_w	=	surface free energy
Δa	=	interfacial area
γ_{SA}	=	interfacial free energy per unit area at the substrate-air interface
γ_{LS}	=	interfacial free energy per unit area at the liquid-substrate interface
	=	interfacial free energy per unit area at the liquid-air interface.
γ_{LA}		

Equation (2.3) is generally called Young's equation and the quantity $\gamma_{LA} \cos \theta$ the *adhesion tension*.

Note that γ_{SA} , the interfacial tension in equilibrium with the gas and liquid phases in the system, is not γ_S , the free energy per unit area of the solid in a vacuum, but $\gamma_S - \pi$, where π is the reduction in interfacial free energy per unit area of S resulting from adsorption of vapor of L; that is,

$$\pi = \gamma_S - \gamma_{SA} \quad (2.5)$$

The spreading coefficient cannot be positive or zero,

$$\text{since } S_{L/S} = \gamma_{SA} - (\gamma_{SL} + \gamma_{LA}) = \gamma_{SA} - \gamma_{SL} - \gamma_{LA} \quad (2.6)$$

$$\text{When } \theta > 0^\circ \quad \gamma_{SA} - \gamma_{SL} = \gamma_{LA} \cos \theta \quad (2.7)$$

substituting $\gamma_{LA} \cos \theta$ for $\gamma_{SA} - \gamma_{SL}$ yields

$$\begin{aligned} S_{L/S} &= \gamma_{LA} \cos \theta - \gamma_{LA} \\ &= \gamma_{LA} (\cos \theta - 1) \end{aligned} \quad (2.8)$$

2.3 Measurement of the Contact Angle

Many contact angle measurement techniques have been described in the literature. Contact angles are measured on macroscopic, smooth, nonporous, planar substrates by merely placing a droplet of the liquid or solution on the substrate and determining the contact angle by any of a number of techniques, although only a few have found wide application. Of these, the most frequently used is the goniometer-telescope measurement of sessile drop contact angles. The most obvious and widely used technique is to simply align a tangent with the sessile drop profile at the point of contact with the solid surface. This is most frequently done directly using a telescope equipped with a goniometer eyepiece.

Indirect measurement of the contact angle can be done by measuring the height h and the diameter d of the droplet as shown in Figure 2.3 and, assuming a spherical shape, by using the relation, $\tan \theta/2 = 2h/d$.

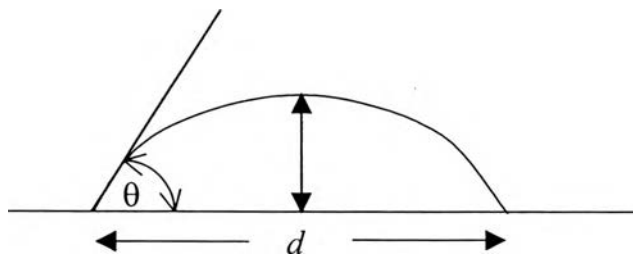


Figure 2.3 A sessile drop of liquid resting on an ideal solid substrate.

However, to obtain a valid, reproducible contact angle is more complicated and difficult than it appears for a number of reasons:

1. Contamination of the droplet by adsorption of impurities from the gas phase tends to reduce θ if $\gamma_{L,A}$ and/or $\gamma_{S,L}$ is reduced and $\gamma_{S,A}$ remains more or less constant.
2. A solid surface, even when apparently smooth, may have impurities and defects that vary from place to place on the surface and from sample to sample. Roughness reduces θ when the value on a smooth surface is $< 90^\circ$, and increases it when the value is $> 90^\circ$.
3. The contact angle may show hysteresis. In this case the advancing contact angle will always be greater than the receding contact angle, sometimes differing by as much as 60° . Contact angle hysteresis is always present when the surface is not clean or when it contains a considerable amount of impurity. However, even when the surface is clean and the substrate is pure, it may show hysteresis. For example, steric acid becomes more wettable (shows a smaller contact angle) after being contacted with water. The explanation has been advanced that there is a change in orientation of the surface molecules in the presence of water, with more of the molecules becoming oriented with their carboxylic acid groups facing the water, thus decreasing the interfacial free energy. Other reasons for low receding angles are penetration of the wetting liquid into the substrate, removal of an adsorbed surface film from the substrate by the wetting liquid, and microscopic surface roughness.

Contact angles on finely divided solids are more difficult to measure, but are often more desirable and more important than those on large solid surfaces. One method of obtaining such angles is to pack the powder into a glass tube and measure the rate of penetration l in time t of a liquid of surface tension $\gamma_{L,A}$ and viscosity η is given by the modified Washburn equation,

$$l^2 = \frac{(kr)t\gamma_{L,A}\cos\theta}{2\eta} \quad (2.9)$$

Where r is the mean equivalent radius of the capillary passages through the powder and k is a constant to allow for the tortuous path through them. The (kr) product depends on the packing of the powder. When the powder is packed to the same bulk density, (kr) is assumed to be constant. The (kr) product is evaluated by passing through the powder a pure liquid of known $\gamma_{L,A}$ whose contact angle is known or assumed to be 0° . A limitation of the method is the assumption that (kr) will not change with change in the nature of the wetting liquid. This is only justified when the particle size of the powder is not changed by flocculation or dispersion produced by the passage through it of the surfactant solution.

This method is not reliable for dilute solutions of surfactants in many cases since it depends upon knowing the (constant) value of $\gamma_{L,A}$. If adsorption of the surfactant onto the solid decreases its solution phase concentration to a value below the CMC, then $\gamma_{L,A}$ will change and it will be impossible to determine θ accurately.

Adsorption of the surfactant onto the solid also makes this an unreliable method for determining the wetting effectiveness of dilute surfactant solution for powdered solids. Because of the small ratio of solution volume to solid-liquid interface, solutions that contain highly surface-active material that adsorbs well at the solid-liquid interface are rapidly depleted of surfactant and may penetrate more slowly than solutions of weakly surface-active material.

Another method of measuring contact angles of powders involves measuring the height h of a drop of the wetting liquid on a cake of the powder, prepared by compressing it in a mold. The contact angle is obtained from

$$\cos \theta = 1 - \sqrt{\frac{1}{3(1-\varepsilon)(1/Bh^2 - 1/2)}} \quad \text{For } \theta < 90^\circ \quad (2.10)$$

$$\cos\theta = -1 + \sqrt{\frac{2}{3(1-\varepsilon)}\left(\frac{2}{Bh^2} - 1\right)} \quad \text{For } \theta > 90^\circ \quad (2.11)$$

Where

$$B = \rho_L g / 2\gamma_{LA} \quad (2.12)$$

ρ_L = density of wetting liquid

γ_{LA} = surface tension between liquid-air interface

g = gravitational constant

ε = porosity of the cake.

This method assumes that the powder consists of identical spheres.

2.4 Contact Angle Hysteresis

Contact angle hysteresis is caused by the existence of multiple thermodynamic metastable states for systems having three-phase (solid/liquid/vapor) boundaries. Each of these states is characterized by a contact angle. These states can be produced by surface heterogeneity, surface roughness, or surface deformability. A different contact angle is associated with each metastable state. The most generally useful contact angle for describing wetting behavior is the static (zero-velocity) advancing contact angle, and it is this angle that will be implied when simply referring to “the contact angle”. The maximum stable angle is called the advancing (or advanced, θ_A) angle. The minimum stable angle is referred to as the receding (or receded, θ_R) angle as shown in Figure 2.4. Hysteresis is the difference between the two.

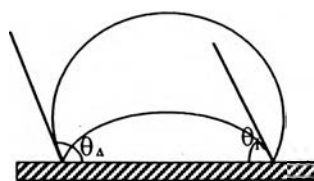


Figure 2.4 Schematic of a sessile drop on a surface.

Measurement of contact angle hysteresis is usually done by one of two methods. A finite volume of liquid is placed on a substrate, and this volume is given differentially increment until the contact line is observed to advance. The contact angle obtained just before the meniscus moves is called the advancing contact angle. To obtain the receding contact angle, the volume of the drop is differentially reduced until the contact line is again observed to move; the liquid meniscus shape just before the drop moves is used to obtain the receding contact angle. An alternate strategy is to place a sessile drop on a substrate, then tilt the substrate until the drop just begins to slide because of an imbalance between the gravitational and capillary forces. The angle subtended at the front of the drop is the advancing contact angle, whereas that at the rear is the receding contact angle. Both these techniques are illustrated in Figure 2.5.

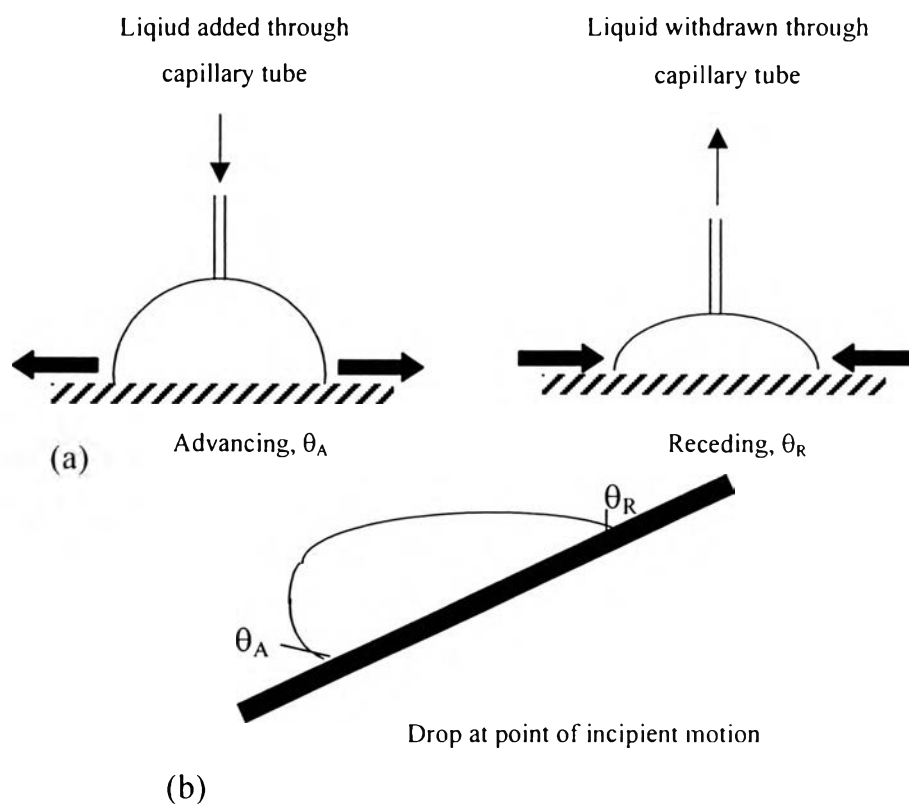


Figure 2.5 Techniques for measurement contact angle hysteresis.

(a) Sessile drop volumes are incrementally increased or decreased until the contact line is just set in motion. Images of the drop at these limits are used to obtain θ_A and θ_R . (b) Alternatively, sessile drops are placed on a substrate that is subsequently inclined until the point of incipient drop motion. Drop images at this critical position simultaneously give the advanced and receded contact angles.

The advancing contact angle, which is the lowest, energetically possible metastable state that can exist on the heterogeneous surface, was shown to be equivalent to the case of an ideal surface composed entirely of the low-energy component. Likewise, the receding contact angle was similarly shown to be equivalent to case of an ideal surface composed of the high-energy material. If roughness is the major cause of contact angle hysteresis, then neither the advancing and receding angle has any physical interpretation within the context of Young's equation, since the apparent angle is influenced to a greater extent by geometrical factors than by interfacial energetic.

The measurement of the receding contact angle has been recommended as a means of characterizing the quality of the solid surface. Ideal surfaces with no vapor adsorption should have zero contact angle hysteresis (i.e., advancing angle equal receding angle); however, the measurement of receding contact angles is complicated by the strong influence of the rate of liquid removal from the drop. It is argued that the receding contact angle is not a unique property of the solid-liquid-vapor system, even when it is measured after extremely low rates of liquid removal.

2.5 Precipitation of Surfactant

It is necessary to understand the mechanism of surfactant precipitation in order to maximize its detergency property. Figure 2.6 illustrates

precipitation of the anionic surfactant and soap system under the presence of counterions.

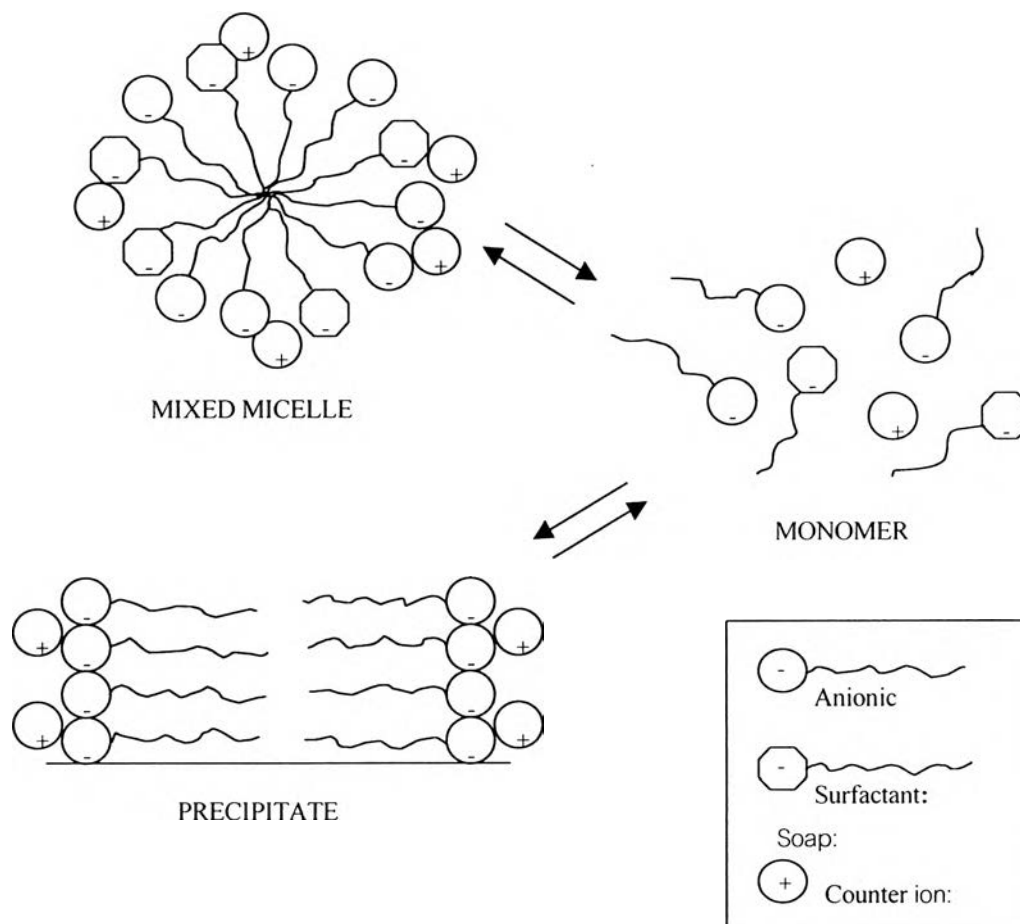


Figure 2.6 Schematic of equilibrium existing in system.

2.6 Precipitation Phase Boundaries

There are two general approaches to the present surfactant precipitation data in the literature: phase boundaries or Kraft points (sometimes called Kraft temperatures).

A phase boundary represents the minimum or maximum concentration of an additive required to form an infinitesimal amount of precipitate in the aqueous surfactant solution at constant temperature at various surfactant concentrations. The boundary separates concentration regimes in which precipitation occurs at equilibrium from regimes where no precipitate is present. A phase boundary can represent the hardness tolerance or minimum concentration of calcium required to precipitate an anionic surfactant (Scamehorn and Harwell, 1993).

The Kraft point is the temperature at which the solubility of hydrated surfactant crystals increases sharply with increasing temperature. This increase is so sharp that the solid hydrate dissolution temperature is essentially independent of concentration above the critical micelle concentration (CMC) and is, therefore, often called the Kraft point without specifying the surfactant concentration (Scamehorn and Harwell, 1993).

The phase boundary approach involves forcing a surfactant to precipitate by adding another compound to solution, whereas the Kraft point involves forcing the precipitation by cooling the solution. Phase boundaries are a more popular method of data presentation in recent literatures because isothermal results are easier to model and are more useful, particularly in mixed surfactant systems. Temperature effects can then be incorporated in model parameters derived from isothermal phase boundaries. However, Kraft points are still reported. The phase boundary of pure surfactant system is shown as Figure 2.7.

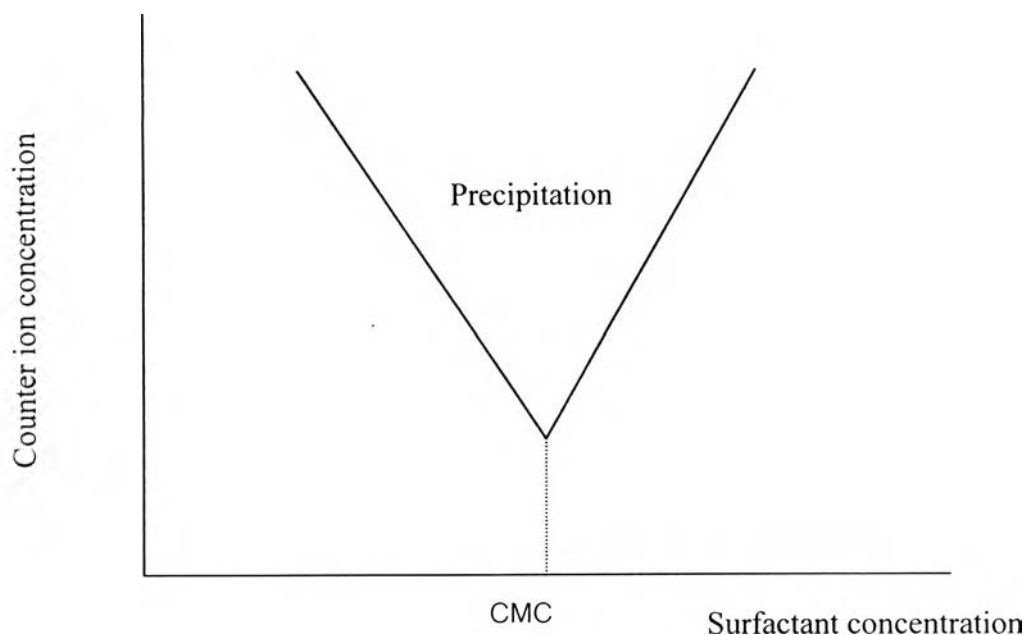


Figure 2.7 Phase boundary of pure surfactant.

Precipitations are formed in solutions at concentrations above the curve in Figure 2.7. Solutions with total concentrations below the curve remain clear and no crystals appear. The minimum in these plots represents the CMC. Below the CMC, surfactant, which precipitates, behaves the same as any simple electrolyte; i.e., as the concentration of one ion is increased, the concentration of the other ion required to cause precipitation decreases as dictated by equation (2.13).

$$K_{sp} = [\text{counterion}]_{un} [\text{surfactant}]_{mon} \quad (2.13)$$

Where

- K_{sp} = The concentration-based solubility product
- $[\text{counter ion}]_{un}$ = The concentration of unbound (or unassociated) counter ion, M
- $[\text{surfactant}]_{mon}$ = The monomer concentration of surfactant, M

This equation shows that an increase in surfactant concentration below the CMC results in decrease in hardness tolerance. At the CMC, however, micelles begin to form and the precipitation phase boundary drastically changes. This is primarily due to counterion binding onto micelles. At the CMC, the hardness tolerance is at minimum. Any surfactant added beyond the CMC can form micelles. Therefore, a small change in surfactant concentration beyond the CMC results in a relatively large change in concentration of unbound counter ion. The solubility product above the CMC is a function of the unbound counterion and monomer surfactant concentration only, as shown in equation (2.10), since the monomer concentration can be assumed to be equal to the CMC.

The effect of pH on the precipitation phase boundary of SDS (sodium dodecyl sulfate) with calcium ion can be seen clearly that as the solution pH is varied from 5 to 9, the hardness tolerance for the SDS and Ca^{2+} system was not much different. (Chintanasathien, 1993). The effect of pH on the precipitation phase boundary of soap has the same characteristics as the SDS precipitation phase boundary. However, a slight significant change in the precipitation phase boundary with pH can be seen. It can be explained in the same way as the precipitation phase boundary of SDS except that the effect of pH on the precipitation phase boundary of soap is more pronounced. It can be seen that pH affects the precipitation phase boundary of soap by increasing the minimum hardness tolerance when pH is lowered. It can be explained that hydrogen ions can enhance micelle formation. Hydrogen ions will insert themselves between the charged head groups (carboxyl head group, $-\text{COO}^-$) of the micelle. This results in the decrease of charge-charge repulsion between the head groups of the micelle. Therefore, micelles can form more easily in the presence of hydrogen ions. Hence, the minimum hardness tolerance increases when pH is lowered. (Chintanasathien, 1993).

2.7 Literature Review

Chandra *et al.* (1996) studied the effect of liquid-solid contact angle on droplet evaporation. They found that addition of a surfactant to a water droplet reduces surface tension and increase its spreading on a solid surface. Spreading of the droplet resulted in a significant decrease in droplet evaporation time. As the liquid layer became thinner, heat transfer from the solid to the liquid-vapor interface was enhanced. Spreading of the droplet also increased the heat transfer area. Bigelow and Brockway (1956) reported that the most important factor in determining the oleophobic properties of film of fatty acid, and similar polar organic compounds, adsorbed on solid surfaces was the density of the adsorbed molecule on the surfaces. The length of the adsorbed polar molecules was not a major factor in determining the oleophobic properties of film. The same maximum contact angle was observed for drops of cetane on films of all the acids which were prepared from their nearly saturated solutions. Furthermore, Buckton *et al.* (1995) found that significant roughness increased the effective perimeter compare to the measured perimeter, and consequently the measured contact angle would be in error. Shiao *et al.* (1998) reported the chain length compatibility effect in the contact angle spreading coefficient and the surface tension of sodium alkyl/alkanol mixture. It was demonstrated that the spreading coefficient, the contact angle, and the surface tension were minimum when the chain length of the surfactant was equal to that of the alkanol. This phenomenon was determined to result from the closer packing of the monolayer expected for matched surfactant/alkanol pairs. The minimum in the contact angle was better spreading when the surface had a tighter surfactant/alkanol packing. Under most laboratory conditions, preparation of completely homogeneity solid surfaces is an extremely difficult task. Therefore, the contact angle measurements always had some degrees of heterogeneity. due to, for example

polycrystalline materials, impurities of surface as well as pollutants from air. The degree of surface heterogeneity affected, significantly, drop size dependence of contact angles. These effect had been explored by Lin (1995). In addition, Horr *et al.* (1995) studied a relationship between the alkyl chain length of molecules separating hydrophilic surfaces from hydrophilic liquids and the resulting contact angle was investigated. The decreased contact angle for dimethylsilanes and silanes (hydrophilic liquids) with branching groups could result from disruption of molecular packing due to steric effects and suggests that microscopic factors affected the measured macroscopic contact angle.