

## CHAPTER II

### LITERATURE REVIEW

#### 2.1 Mixed Micelle Formation

The critical micelle concentration (CMC) is the minimum surfactant concentration at which micelles form; The lower the CMC, the greater the tendency of a system to form micelles. When the total surfactant concentration equals the CMC, an infinitesimal fraction of surfactant is present in micelles. Therefore, the CMC is equal to the total monomer concentration in equilibrium with the micellar pseudo – phase. The CMC for monomer – micelle equilibrium is analogous to the dew point in vapor – liquid equilibrium. If two similarly structured surfactants of like charge are mixed together at the mixture CMC, an ideal system results. The mixture CMC,  $CMC_{mix}$ , lies between the CMC's of the individual surfactant CMC's. In analogy, the vapor pressure of a mixed ideal liquid is intermediate between the vapor pressures of the components of which it is composed, whether there is substantial liquid present or the system is at the dew point (where an infinitesimal amount of the liquid is present). For a binary system of surfactants A and B, the mixed micelle formation can be modeled by assuming that the thermodynamics of mixing in the micelle obeys ideal solution theory. When monomer and micelles are in equilibrium in the system, this results in :

$$\text{CMC}_{\text{mix}} = \frac{\text{CMC}_A * \text{CMC}_B}{y_A * \text{CMC}_B + y_B * \text{CMC}_A}$$

- Where  $\text{CMC}_{\text{mix}}$  = The mixture CMC value, M  
 $\text{CMC}_A$  = The CMC value for the component A, M  
 $\text{CMC}_B$  = The CMC value for the component B, M  
 $y_A$  = The monomer mole fractions of A  
 $y_B$  = The monomer mole fractions of B

The mole fractions are on a surfactant – only basis : i.e.,  $y_A$  is the moles of A in the monomer / total moles of surfactant monomer; therefore,  $y_A + y_B = 1$ .

## 2.2 Phase Boundaries and Krafft Points

There are two general approaches to present surfactant precipitation data in the literature: phase boundaries and Krafft points (or Krafft temperature).

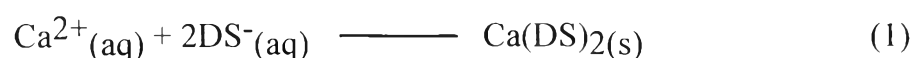
The Krafft point is the temperature at which the solubility of hydrate, surfactant crystals increases sharply with increasing temperature. This increase is so sharp that the solid hydrate dissolution temperature is essentially independent of concentration above the critical micelle concentration (CMC)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

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. Hardness tolerance of an anionic surfactant is defined as the minimum concentration of multivalent cation necessary to cause precipitation of surfactant (Scamehorn and Harwell, 1993).

The phase boundary approach involves forcing a surfactant to precipitate by adding another compound to solution, whereas the Krafft point involves forcing the precipitation by cooling the solution. Phase boundaries measurement is an increasingly popular method of measuring data in the recent literature 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, Krafft points are still reported. In this work, the phase boundaries were used to present precipitation data.

### **2.3 Precipitation Phase Boundary in Pure Component System**

There are many studies of the precipitation of pure surfactants (e.g. of SDS). The possible precipitation reactions occurring in the SDS system are represented by the following equation (1).



Below the CMC, all of the surfactant in the system is present as monomer, and precipitation depends on the total surfactant and total calcium concentrations. Therefore, as the surfactant concentration is increased in the solution, the amount of calcium required to cause precipitation decreases as described by the solubility product relationship:

$$K_{SP} = [Ca^{2+}] [DS^{-}]^2 \gamma_{Ca} \gamma_{DS}^2 \quad (2)$$

where  $K_{SP}$  is the activity based solubility product,  $[DS^{-}]$  is equal to the total SDS concentration, and  $\gamma_{Ca}$  and  $\gamma_{DS}$  are the activity coefficients of calcium and SDS, respectively. Precipitation above the CMC depends on the monomeric surfactant concentration,  $[DS^{-}]_{mon}$  and the unbound calcium concentration,  $[Ca^{+2}]_u$ :

$$K_{SP} = [Ca^{2+}]_u [DS^{-}]_{mon}^2 \gamma_{Ca} \gamma_{DS}^2 \quad (3)$$

The behavior above the CMC can be understood by examining the micelle-monomer-precipitation equilibria. These equilibria are shown in Figure 2.1 for SDS in the presence of calcium. Above the CMC, as the SDS concentration is increased, the additional surfactant tends to form micelles. A larger concentration of unbound calcium ions will then bind to the micelles, reducing the amount of unbound calcium available for precipitation of the surfactant monomers. The total calcium concentration must then be increased to meet the conditions required by the monomeric solubility product relationship in equation (3) for precipitation to occur.

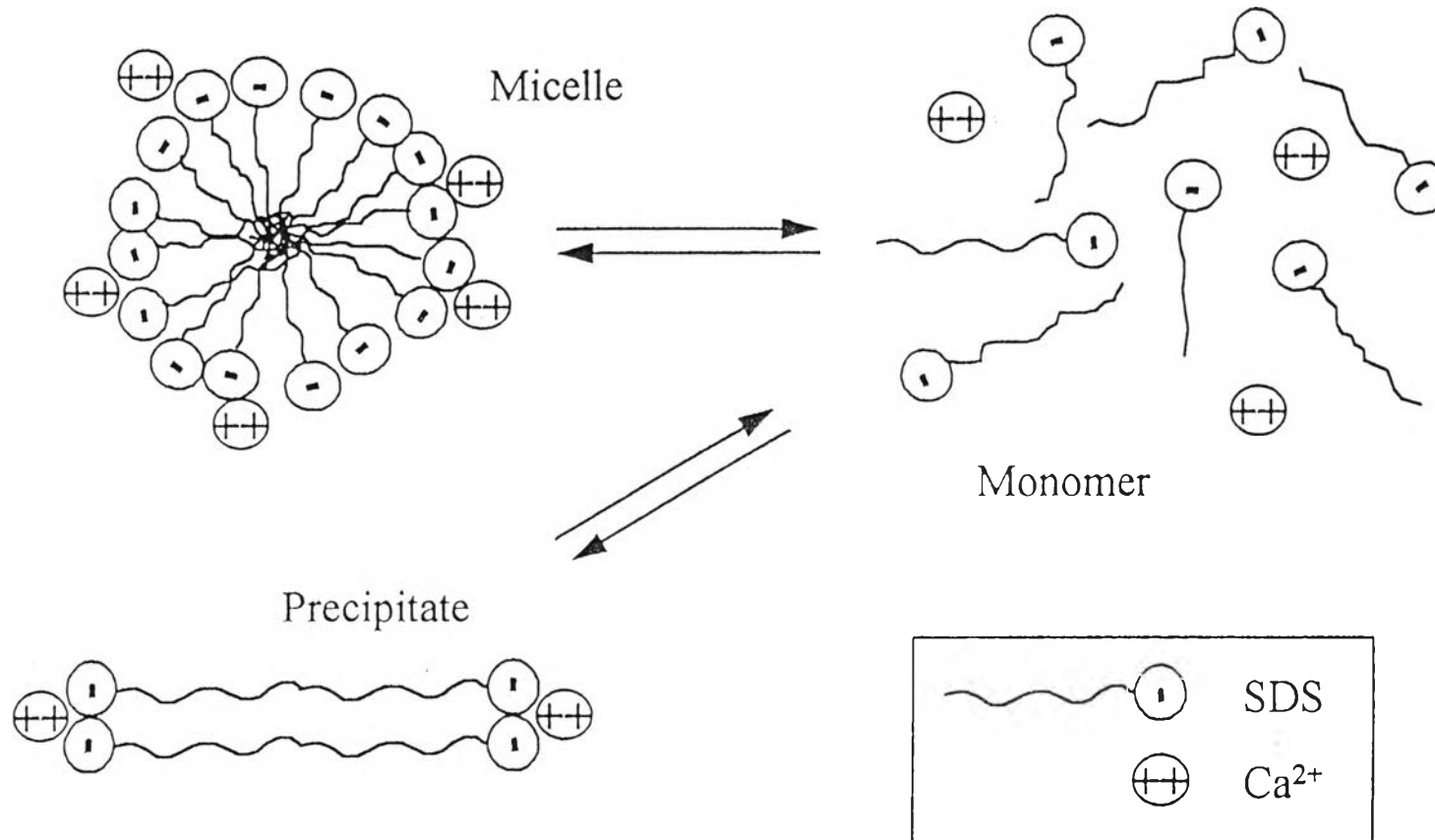


Figure 2.1 Schematic of equilibrium existing in pure SDS system.

## 2.4 Precipitation of Surfactant Mixtures

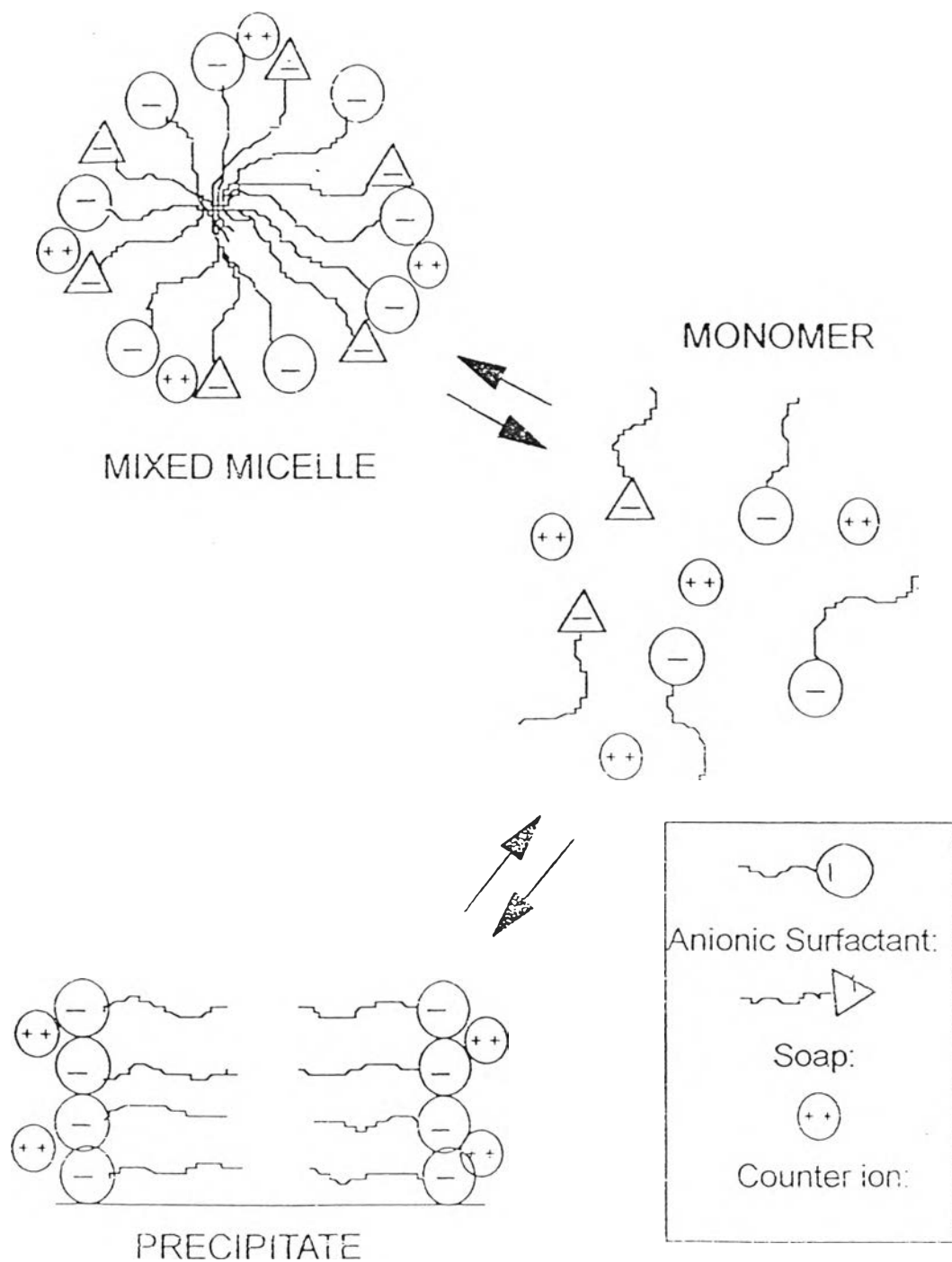
The use of surfactant mixtures permits considerable manipulation of precipitation behavior. More generally, surfactant mixtures can have a number of synergistic advantages over the use of a single surfactant (Scamehorn, 1986). The use of surfactant mixtures can be superior because mixed micelles form which are composed of all the surfactant components while only one component is present in the precipitate when the first precipitate forms (on a phase boundary or at the Krafft temperature). Therefore, surfactant mixtures can precipitate with more difficulty than pure component surfactant. Figure 2.2 illustrates precipitation of the anionic surfactant and soap system in the presence of counterions.

## 2.5. Contact Angle

### 2.5.1. Wetting as a Contact Angle Phenomenon

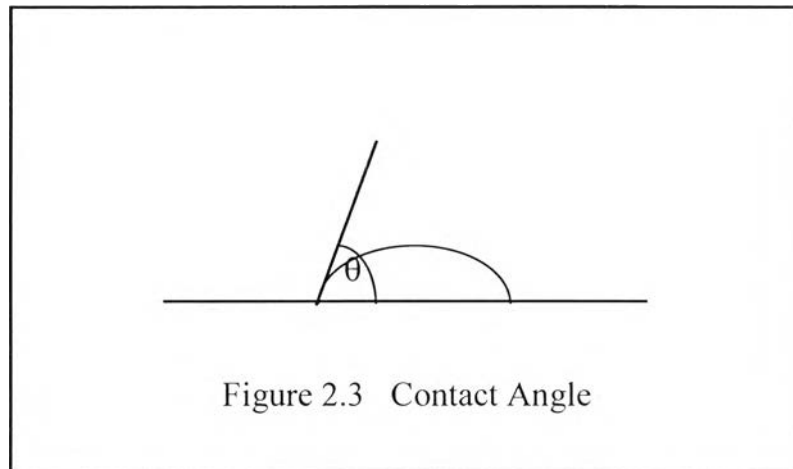
The terms wetting and nonwetting as employed in various practical situations tend to be defined in terms of the effect desired. Usually, however, wetting means that the contact angle between a liquid and a solid is zero or so close to zero that the liquid spreads over the solid easily, and nonwetting means that the angle is greater than  $90^\circ$  so that the liquid tends to ball up and run off the surface easily (Adamson, 1990).

The contact angle  $\theta$  that the liquid makes when it is at equilibrium with the other phases in contact with it is related to the interfacial free energy per unit area of those phases. When the liquid is at equilibrium with other two phases, gas and solid substrate, we can diagram the contact



**Figure 2.2** Schematic of equilibrium existing in mixed system.

angle  $\theta$  as shown in Figure 2.3



The central relationship is the Young equation,

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

For the case of finite contact angle, it is larger than  $0^\circ$ . The spreading coefficient  $S_{LS}$  is

$$S_{LS} = \gamma_{SV} - \gamma_{LV} - \gamma_{SL}$$

where  $\gamma_{SV}$  = The interfacial free energy per unit area of the substrate in equilibrium with liquid-saturated air above it.

$\gamma_{SL}$  = The interfacial free energy per unit area at the liquid-substrate interface.

$\gamma_{LV}$  = The surface tension of liquid, L.

### 2.5.2. Measurement of the Contact Angle

Contact angles are measured on macroscopic, smooth, nonporous, planar substrates by merely placing a droplet of the liquid or solution on the



substrate and determined the contact angle by any of a number of techniques (Adamson, 1976). The contact angle can be measured directly by use of a microscope fitted with a goniometer eyepiece or by photographing the droplet. Indirect measurement of the contact angle can be done by measuring the height  $h$  and the diameter  $d$  of the droplet and, assuming a spherical shape, by using the relation

$$\tan \theta/2 = 2 h/d$$

## 2.6 Literature Review

Rodriguez, Scamehorn, and Chanin (1997) studied the precipitation in solutions containing mixtures of synthetic anionic surfactant and soap. They studied the effect of sodium octanoate on hardness tolerance of sodium dodecyl sulfate. They concluded that increasing the pH increased the CMC and the hardness tolerance of SDS increased when soap was added. Amante, Scamehorn, and Harwell (1988, 1991) studied the precipitation of mixtures of anionic and cationic surfactants (sodium alkyl sulfate and dodecylpyridium chloride) as a function of pH, temperature, and anionic surfactant alkyl chain length. They concluded that increasing temperature and decreasing surfactant alkyl chain length generally tended to decrease the tendency to precipitate. Noik et al. (1987) presented the entire precipitation phase boundary for a four-component mixture containing an anionic surfactant, butanol,  $\text{CaCl}_2$  and  $\text{NaCl}$ . They concluded that butanol increased the hardness tolerance which resulted from enhancement of formation of micelles. Stellner and Scamehorn (1989) reported the influence of nonionic surfactant, nonylphenol polyethoxylate with an average of 10 ethylene oxide groups per molecule on the hardness

tolerance of an anionic surfactant (sodium dodecyl sulfate). It was demonstrated that the addition of the nonionic surfactant raised the hardness tolerance. This phenomenon was determined to result from the formation of mixed micelles. Shiau (1990) studied the precipitation of ternary mixtures of surfactants consisting of anionic, cationic, and nonionic surfactants. He found that increasing the concentration of nonionic surfactant decreased the tendency for precipitation of anionic – cationic surfactant or coacervate to occur. Kwok et al. (1997) presented the contact angle measurement and contact angle interpretation. In this work, the contact angle was measured by axisymmetric drop shape analysis and a goniometer sessile drop technique.