CHAPTER II
BACKGROUND AND LITERATURE SURVEY

2.1 Structure and Behavior of Surfactants

Surfactants, a contraction of the terms surface active agent, are materials that tend not only to accumulate at surface but they also change the properties of those surfaces. A surfactant has a characteristic molecular structure consisting of structural group that has very little attraction for solvent, known as a lyophobic group (hydrophobic group in case water is the solvent), or tail group, together with a group that has strong attraction for the solvent, called the lyophillic group (hydrophilic group for the water), or head group. This is known as an amphipathic structure. The amphipathic structure of the surfactant not only leads to high concentration of surfactant at the surface and reduction of surface tension of water, but also orientation of the molecule at the surface with its hydrophilic group in the aqueous phase and its hydrophobic group oriented away from it.

The chemical structure of groupings suitable as the lyophobic and lyophilic portions of the surfactant molecule varies with the nature of the solvent and the conditions of use.

The hydrophobic group is usually a long chain hydrocarbon residue, and less often, a halogenated hydrocarbon or siloxane chain; the hydrophilic group is an ionic or highly polar group. Depending on the nature of the hydrophilic group(head group), surfactants are classified as:

1. Anionic surfactant : the surface active portion of the molecule bears a negative charge, for example, $C_{12}H_{25}SO_3^-Na^+$ (sodium dodecyl sulfate).
2. Cationic surfactant : the surface active portion of the molecule bears a positive charge, for example, $RNH_3^+Cl^-$ (Salt of a long chain amine), $RN(CH_3)_3^+Cl^-$ (quaternary ammonium chloride).
3. Zwitterionic surfactant : both positive and negative charges may be present in the surface active portion, for example, $RN^+H_2CH_2COO^-$ (long chain amino acid)
4. Nonionic surfactant : the surface active portion of the molecule bears no apparent ionic charge, for example, $R(C_2H_4O)_{10}OH$ (ethoxylated alcohol)

2.2 Foam Formation

Foam is produced when air or some other gas is introduced beneath the surface of a liquid that expands to enclose the gas with a liquid film . So foam is a dispersion of gas in a liquid, with (normally) a high dispersed-phase (gas) volume fraction.

The formation of a foam from a bulk involves the expansion of the surface area due to the work acting upon the system. Since surface tension is the work involved in creating a new surface, it is easier to form new surface with lower surface tension. Therefore surfactant is necessary in foam formation because it can reduce the surface tension of the new surface area as illustrated in Fig.2.1.

2.3 Structure of Foam

Foams usually have a stable honeycomb structure of gas cells whose walls consist of thin liquid films. These two-sided films are called the lamellae of the foam. Where three or more gas bubbles meet, the lamellae are curved, concave to the gas cells, this region of intersection called the Plateau border or Gibbs triangles is shown in Fig. 2.2.

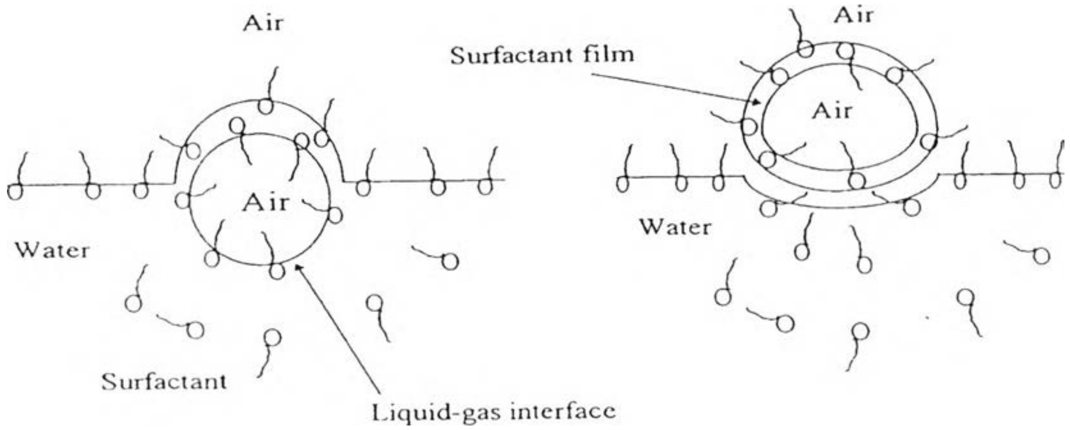


Figure 2.1 Formation of foam.

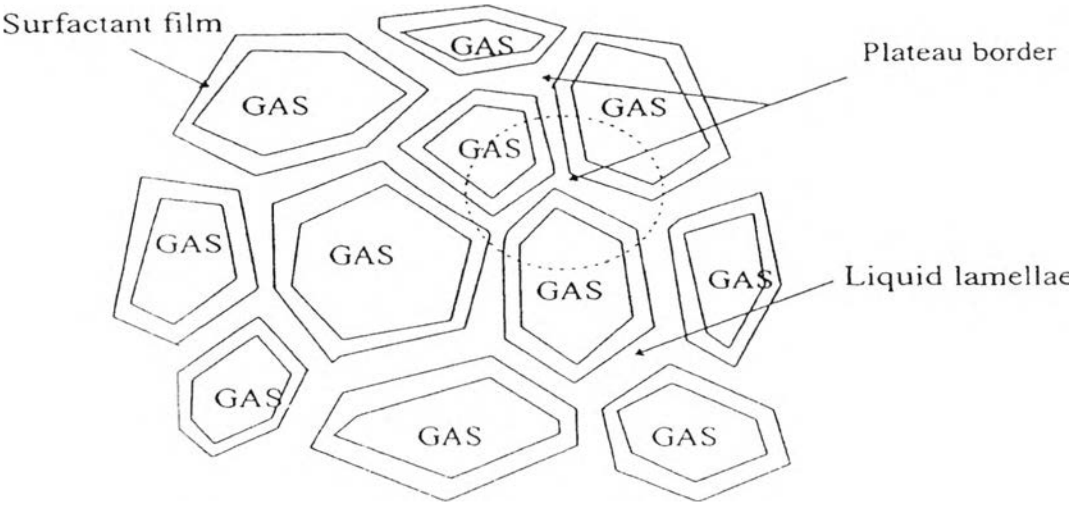


Figure 2.2 The structure of foam.

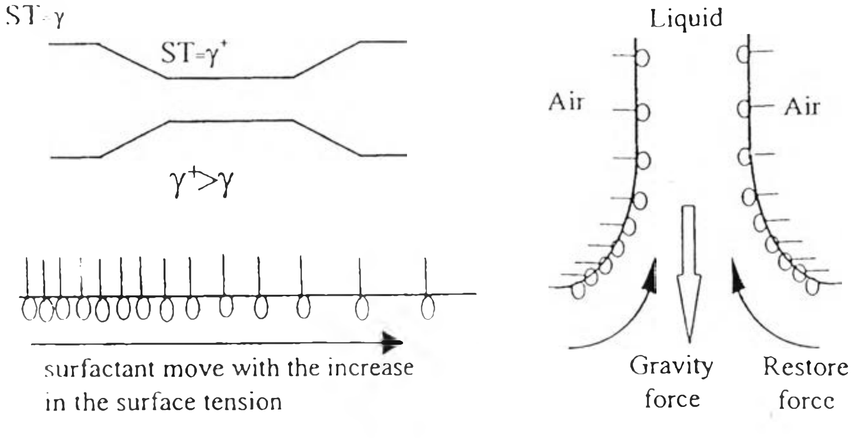
2.4 Foam Stability

The stability of foam can be split into two parts, film elasticity and film drainage.

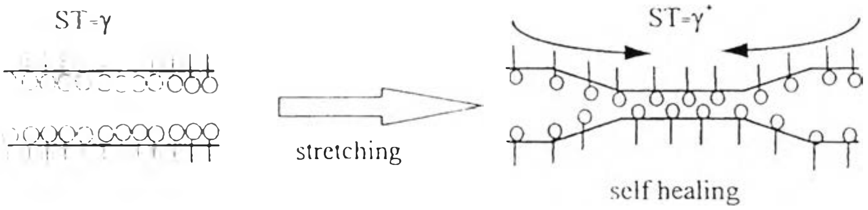
Film elasticity can be explained by two theories, Gibbs surface elasticity and the Marangoni effect. Both effects postulate that film elasticity is due to the local increase in surface tension when the new surface area is created. The increasing in surface tension causes liquid to flow from the thick section to the thinner section. which is called healing. There is the restoring force from the Gibbs elasticity and the Marangoni effect bringing surfactant molecules back into the region of high surface tension, as depicted in Fig. 2.3.

The film drainage is the second factor that affects the stability of foam. Drainage of the film occurs under two influences: gravity and surface tension. Drainage by gravity is an important effect on the thickness of lamellae. The bulk viscosity of the foam solution is a major factor in determining the rate of drainage by gravity in thick lamellae. At high concentration of surfactant, the viscosity of the bulk solution is high and therefore the drainage rate in the lamellae decreases when the amount of surfactant in the lamellae increases.

The pressure difference causes drainage of liquid into the plateau border at point A from point B (Fig. 2.4). The greater the surface tension, the greater the pressure difference and the greater the liquid drainage, hence the lower the stability of foam. Foams are destroyed when liquid drains out between the two parallel surfaces of the lamellae causing it to become thinner. At a certain critical thickness, the film collapses and the bubble bursts. Thus the stability of foam depends on many factors that have influence on film drainage such as type of surfactant, concentration of surfactant, temperature, etc.



a) Marangoni effect



b) Gibbs film elasticity

Figure 2.3 The Marangoni effect and Gibbs film elasticity.

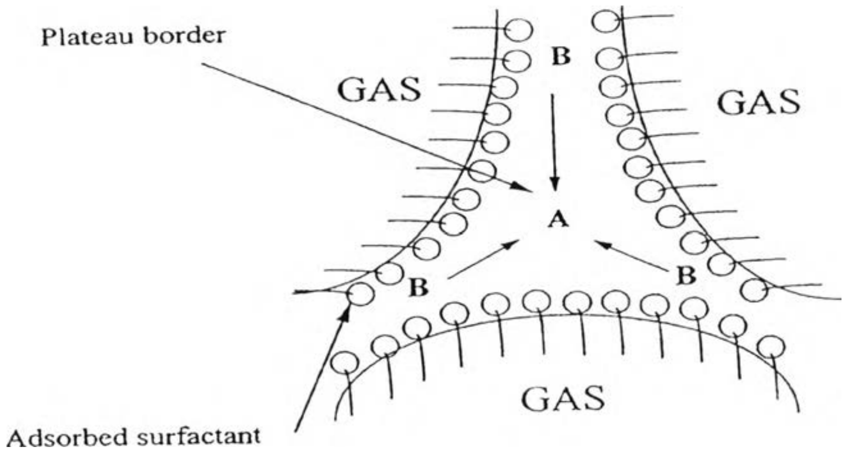


Figure 2.4 Gas bubble.

2.5 Phase Boundaries

A phase boundary represents the minimum or maximum concentration of an additive required to form an infinitesimal amount of precipitate in 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 precipitation boundary, consisting of line segments MSL(the micelle saturation line) and SPL(surfactant precipitation line), divides the graph into two regions of clear solution and cloudy mixtures. Below line segments SML(surfactant micellization line) and SPL, only surfactant monomers are present in solution. Below line segments SML and MSL, both micelles and monomers are present. In the region between MSL and SPL, saturated solution exists in equilibrium with the precipitate of calcium salt of the surfactant. These are shown in Fig. 2.5.

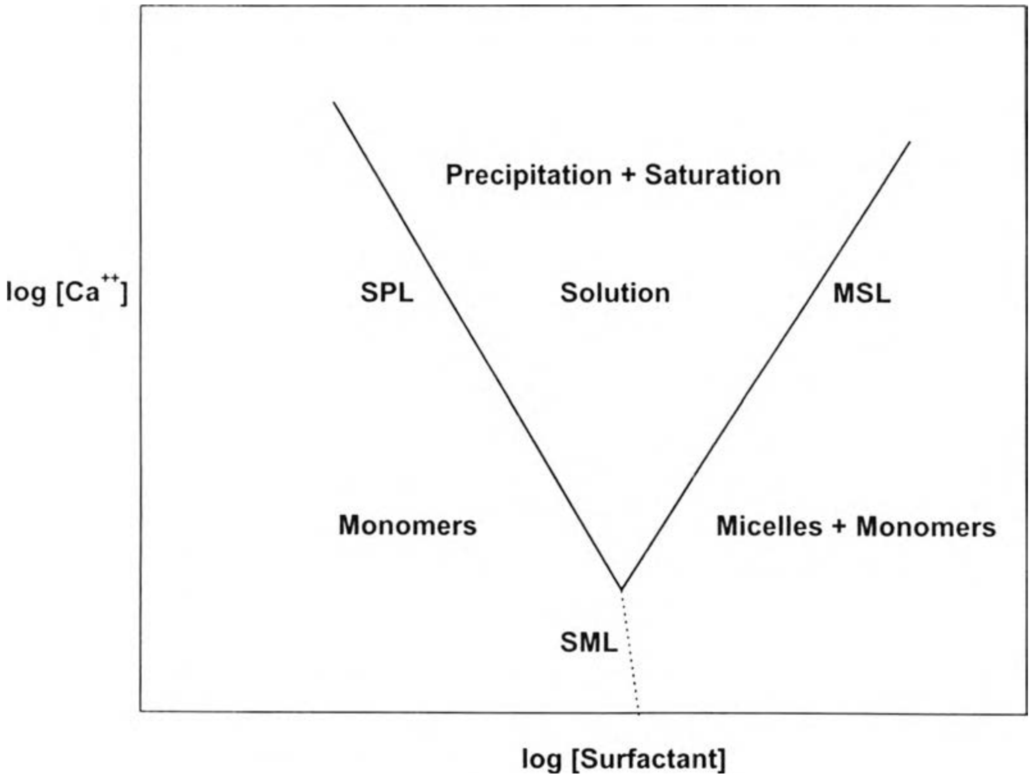


Figure 2.5 Generalized calcium sulfonate precipitation boundary diagram.

In this work, the foaming properties of Soap/SDS mixtures inside and outside of the Soap/SDS-Calcium Phase Boundary Diagram were studied.

2.6 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. It has been found that, surfactant mixtures precipitate with more difficulty than pure component surfactants, and hence a higher hardness tolerance can be achieved.

2.7 Mixed Micelle Formation

The critical micelle concentration (CMC) is the lowest 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 as micelle. Therefore, the CMC is equal to the total monomer concentration in equilibrium with the micellar pseudo-phase. The CMC for mononer-micelle equilibrium is analogous to the dew point in vapor-liquid equilibrium. If two similarly structured surfactants of like charges are mixed together, an ideal system results. The mixture CMC(CMC_{mix}) lies between the CMC's of the individual surfactants. Analogously, the vapor pressure of a mixed ideal liquid is intermediate between the vapor pressure of the components of which it is composed. For a binary system of surfactant A and B, the mixed micelle formation can be modelled by assuming that the thermodynamics of mixing in the micelle obeys ideal solution theory. When mononer and micelles are in equilibrium in the system, CMC_{mix} is given by the following equation:

$$CMC_{mix} = \frac{CMC_A * CMC_B}{Y_A * CMC_B + Y_B * CMC_B} \qquad \text{-----}1$$

where CMC_{mix} = Mixture CMC value, M

CMC_A = CMC value for component A, M

CMC_B = CMC value for component B, M

Y_A = Mole fraction of component A

Y_B = Mole fraction of component B

2.8 Literature Review

Stellner and Scamehorn (1989) reported the influence of a nonionic surfactant. nonylphenol polyethoxylate with an average of 10 ethylene oxide groups, on the hardness tolerance of an anionic surfactant(sodium dodecyl sulfate). It was shown that the addition of the nonionic surfactant raised the hardness tolerance of the anionic surfactant. This phenomenon was found 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 mixtures.

Rodriguez, et al.(1995) studied precipitation in solutions containing mixtures of anionic surfactant and soap. The hardness tolerance(precipitation as a function of pH, and the mole ratio of soap/anionic surfactant. It was concluded that CMC and solubility limit of soap increased with increasing pH. Changing the pH had no effect on the CMC and precipitation phase boundaries of the anionic surfactant. The hardness tolerance of the anionic surfactant was also found to increase when soap was added.

Cohen, et al.(1993) studied the influence of anionic concentration and water hardness on foam properties of a linear alkylbenzene sulfonate. Foam height and foam stability of solutions of a linear alkylbenzene sulfonate (LAS) were measured according to the Ross-Miles test at a constant temperature(49 ^{o}C) with varying anionic concentration and water hardness. $CaCO_3$ was used to give the water hardness in that study. The results show that precipitation of LAS by calcium ion causes an increase in the CMC of the remaining LAS in solution due to the precipitation of the heavier homologs. Maximum foam height was therefore obtained at a higher concentration of LAS than in the system with no calcium. Experiments with varying amount of calcium concentration also show that foam height is almost independent of calcium concentration until a “critical” calcium concentration is reached, where the amount of precipitated LAS is substantial, and therefore, there is a dramatic decrease of foam height. The results show that foam stability does not decrease beyond the CMC in the presence of calcium due to the higher stability of the calcium micelles as compared to the sodium micelles.