CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Surfactants

Surfactants, a contraction of the phrase Surface Active agents, are materials that not only tend to accumulate at surfaces but also change the properties of those surfaces (Clint, 1992). The surfactant molecular structure is amphiphilic consisting of two distinct parts; one that has an affinity for the solvent, know as lyophilic group (hydrophilic group in case water is the solvent) or head group, connected to the other that has very little attraction for the solvent called lyophobic group (hydrophobic for water) or tail group. Due to the presence of two structurally dissimilar groups within a single molecule, surfactants form aggregates of molecules called micelles when the concentration of the surfactant solute in the bulk solution exceeds a limiting value, the so-called critical micelle concentration (CMC).

In an aqueous solution, the hydrophobic group is usually a long-chain hydrocarbon whereas the hydrophilic group is an ionic or highly polar group. Surfactants can be classified in many different ways. By indicating its polarity, which depends on the nature of hydrophilic group, surfactants can be classified as anionic, cationic, zwitterionic, and nonionic surfactants.

Nonionic surfactants carry no discrete charge when dissolved in aqueous solution. Hydrophilicity in nonionic surfactants is provided by hydrogen bonding with water molecules. Polyoxyethylene surfactants, which are the biggest group of nonionic surfactants, are used in many chemical industries. The solubility of these compounds is due to the forming of strong hydrogen bonding between oxygen atoms in hydroxyl groups with water molecules. With increasing temperature, ethoxylates become less soluble as a result of decreased hydration and increasing micellar size. Ethoxylates are general classed into the moderate foamer groups and do not respond to conventional foam boosters.

2.2 Foam

2.2.1 Foam Formation

Foam is a nonequilibrium dispersion of gas bubbles in a relatively smaller volume of liquid. The gas bubbles in foam are separated from each other by thin liquid films, the liquid being the continuous phase. Foam would have no stability unless there is a barrier to coalescence when two gas bubbles are touched. This barrier is provided by surfactant and the repulsion between surfactant layers sometimes called the disjoining pressure. This may be due to the electrostatic repulsion in ionic surfactant or steric hindrance in nonionic surfactant. Therefore, the surfactant is required in foam formation and stabilization because it is adsorbed at the interface between the air bubbles and the thin liquid film.

The adsorption of surfactants at the interface leading to the increasing of film elasticity which resists the localized thinning of the lamella surrounding the bubbles. The mechanism of operation of the film elasticity depends on two effects concerning the surface tension of the solution. Gibbs effect comes from the increase in surface tension with the decrease in the surfactant concentration below CMC. Marangoni effect depends on the time required for the surface tension to obtain its equilibrium because the initial surface tension of a new surface is always greater than the equilibrium. The two effects are complementary and provide mechanisms for the operation of film elasticity under different conditions (Rosen. 1989).

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 film of liquid. The formation of a foam form 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. At the surfactant concentration below CMC, there are only monomers in the thin liquid film as shown in Figures 2.1.

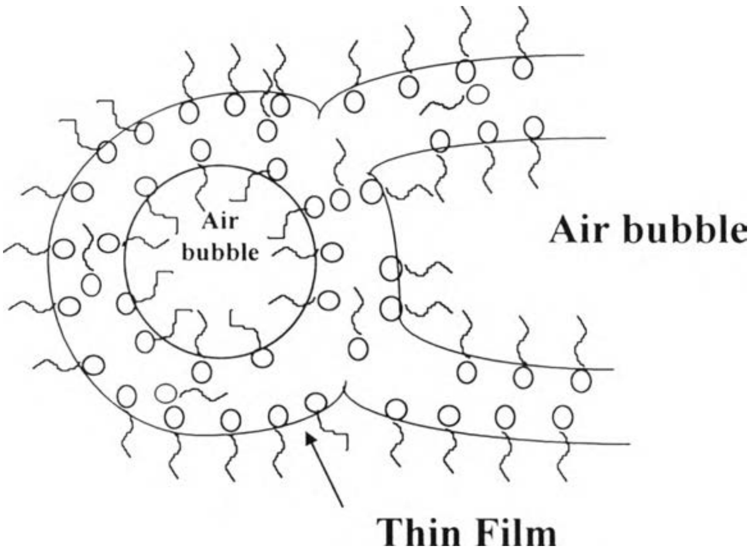

Figure 2.1 Formation of foam at the surfactant concentration below CMC.

At the surfactant concentration above CMC, both monomers and micelles are present in the thin liquid film. The micelles can help to stabilize the thin liquid film by ensuring the maximum surfactant concentration at the air-liquid interface. These foams called micellar foams as shown in Figures 2.2. The foam height of a surfactants solution usually reaches the maximum at the CMC.

Foam can be generated by several techniques depending on the desired properties such as increasing in temperature will cause the dissolved gas to be released, mechanical agitation will lead to gas entrapment, and the simplest way is to disperse compressed gas directly into an aqueous solution through a glass filter.

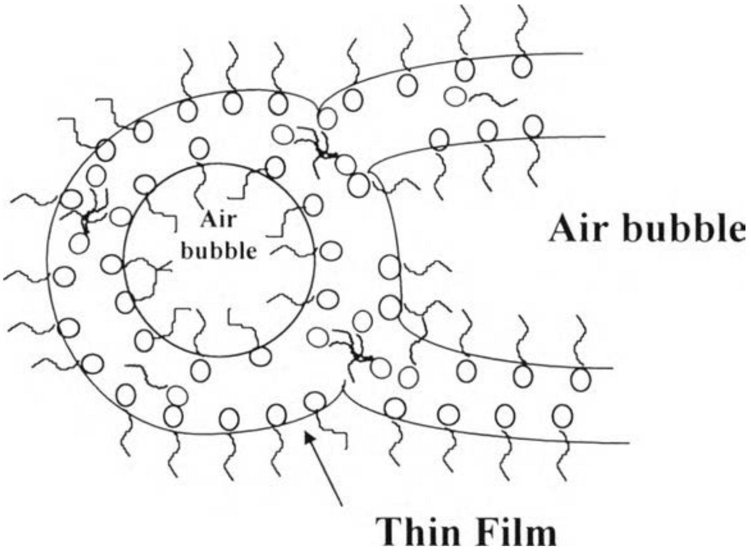

Figure 2.2 Formation of foam at the surfactant concentration above CMC.

2.2.2 Foam Structure

Foam has a more or less stable honeycomb structure of gas cells whose walls consist of thin liquid films with approximately plane parallel sides. The two-sided liquid films are called the lamellae of the foam. Where three or more gas bubbles meet, the lamellae are curved, concave to the gas cells, forming what is called the plateau border or Gibbs triangle as seen in Figure 2.3 (Rosen, 1989).

In a column of foam, liquid also drains as a result of hydrostatic pressure, with the result that lamellae are thinnest in the upper region of the column and thickest in the lower region. From this behavior, foams can be classified into two types, kugelschaum and polyederschaum. The kugelschaum foam has spherical shape and small size with a relatively low gas volume fraction, it has rather thick liquid film. The second type, polyederschaum, contains mostly gas phase separated by thin films or laminas. The foam has polyhedral shape and consists of plane-parallel films joined by channel called plateau border.

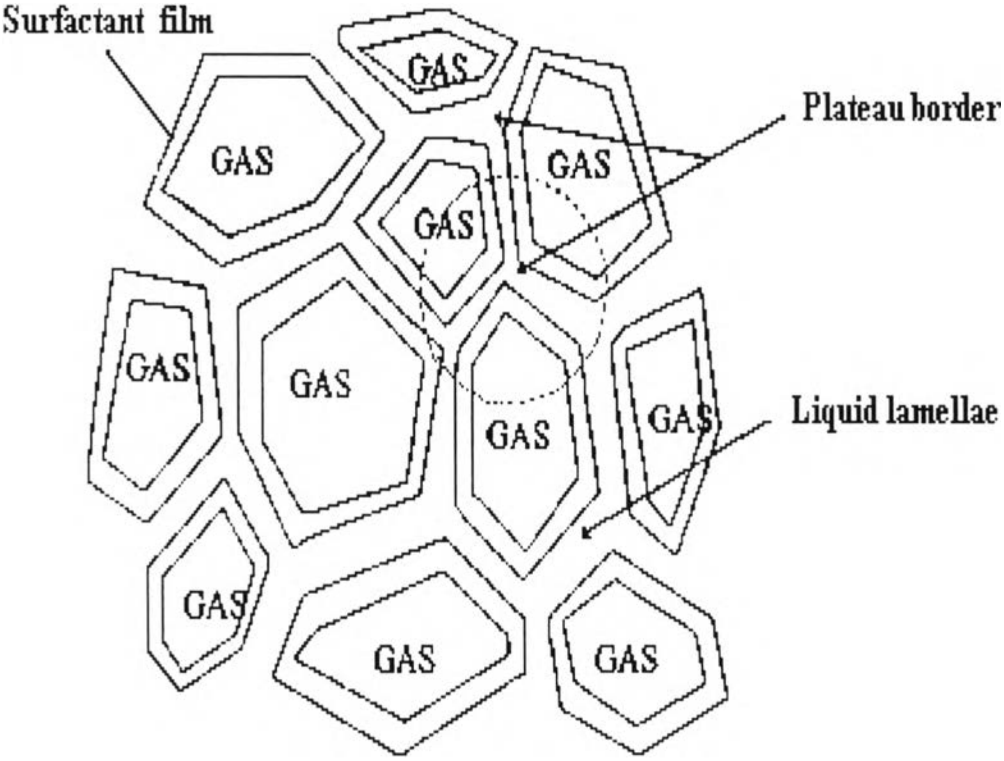

Figure 2.3 The structure of foam.

The two types of foam are shown in Figure 2.4 (Prud'homme, 1996 and Adamson, 1990).

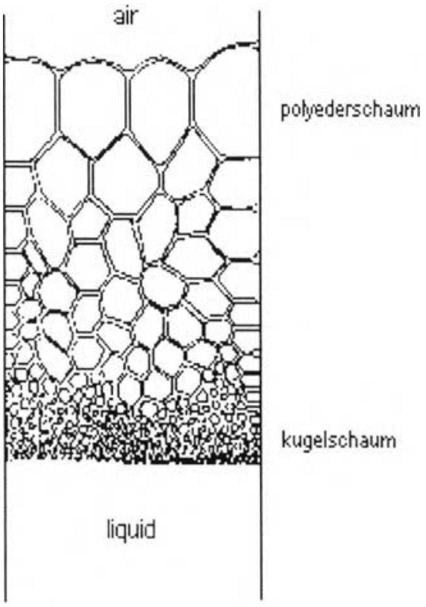

Figure 2.4 The two types of foam : polyederschaum, kugelschaum.

2.2.3 Foaming Properties

The discussion about foaming properties must distinguish between foamability (also know as foam capacity) and foam stability. The amount of foam formed under a given condition is a measure of the foamability, and the factors affecting the foam formation and immediate stabilization of the foam are important, like dynamic surface tension and surface rheology. Also, the foamability is related to physical factors within the liquid, for example, viscous effect. On the other hand, the decay rate of a foam volume is a measure of foam stability. Hence, the mechanisms causing destruction of the foam, like drainage, bubble coalescence, and gas diffusion are destructive for the stability.

There are many researchers who studied about foaming properties. Koczo et al. (1990) studied the foaming properties of liquids by characterizing their foamability which was defined as the foam volume obtained from a unit volume of liquid. They investigated the relations between the different parameters of foam beating and the properties of the foams formed by measuring the expansion ratio and drainage rate of the foams formed. The surfactant concentration was measured by high-performance liquid chromatography (HPLC). They found that the beater did not destroy the foam when its speed was increased up to a certain limit, but it redispersed the bubbles.

Schmidt et al. (1997) studied a high-foaming surfactant, AEO-Mild, by using the SEN foaming device, which is a useful way of measuring "flash foam", and the dynamic spray foaming, which is the Shell-designed device for measuring the foam height.

A new method to estimate the stability of short-life foams was studied by Iglesias et al. (1995). It was found that, under certain starting conditions, short-life foam decay exhibited a linear variation in the foam column height with the logarithm of the elapsed time.

Sarma et al. (1987) studied the stability of aqueous foam by adding small amount of water-soluble polymers. They found that the addition of water-soluble polymer can significantly enhance the aqueous foam stability.

Prahan et al. (1990) studied the effects of temperature ranging from 30 to 80 ^{O}C to the stability of aqueous foams with polymer additives by determining the drainage half-life of foam and the initial drainage rate. They found that the stability of aqueous foams was reduced due to the decrease in drainage half-life and the increase in initial drainage rate at the higher temperature.

The stability of aqueous foams with polymer additives generated at different pressures was studied by Pradhan and Khilar, 1994. It was found that, without any additive, the foam stability increase significantly with the increase of generation pressure due to the decrease of bubble size of foam, when the foam was produced in a packed bed. However, it changed weakly with the change in generation pressure for foams with polymer additives.

Laheja et al. (1997) studied the stability of foams generated with ionic and nonionic surfactant solutions at concentration higher than the critical micelle concentration (CMC) and the influence of polymer addition on the stability of this foam. This study is useful in applications such as the manufacture of ultrafine carbonate particles, and in formulations of food and pharmaceutical products. The foam stability was indicated by the 80% drainage life, $\tau_{0.8}$. The $\tau_{0.8}$ of ionic surfactants (SDS and BKC) without any additives first decreased up to a concentration of 20CMC and then increased because the morphology of the micelle changed from globular to cylindrical micelles. For nonionic surfactant (TX100), $\tau_{0.8}$ increased and then leveled off at the higher concentration resulting from the decrease in bubble size resulting in the increase in viscosity of the solution. In the case of addition of the polymer sodium carboxymethyl cellulose (SCMC), the drainage time of TX100 increased, whereas the drainage time of SDS was not affected by this polymer.

2.3 The Cloud Point and Phase Separation of Nonionic Surfactants

The cloud point temperature which is an inherent property of nonionic surfactants is the lowest temperature at which turbidity and separation of immiscible surfactant phase occur(Clint, 1992). The higher the degree of polymerization in the polyoxyethylene surfactant, the higher the cloud point.

At the concentration above CMC, the micelles are formed in the solution. As the temperature increases, ethoxylates become less soluble as a result of the decrease in hydration force which is responsible for the repulsion force, and increasing in micellar size due to the reduction of ethoxylated head groups

(Triolo et al., 1982, Brown et al., 1983, Corti and Degiorgio, 1985). At the cloud point temperature, there is enough energy to break hydrogen bonding between oxygen in ethylene oxide chain and water molecule, thus more surfactant molecules can pack into the micelle leading to the enlarged micelles and the repulsive force becomes the attractive force (Degiorgio et al., 1985). Therefore the micelles come together to form micellar-rich phase which is immiscible in the micellar poor phase leading to the increase in the turbidity of the solution. This solution looks like an emulsion of oil droplets dispersed in water. If this solution is left for some time and allowed to separate under gravity force or in a centrifuge, then essentially clear micellar phase will be obtained (Clint, 1992). The solution separates into two isotropic phases consisting of a micellar-poor phase at the top of the solution and a micellar-rich phase, or coacervate phase, at the bottom . The dilute phase usually has a concentration a little above the CMC at that temperature (Corti et al., 1984).

The cloud point of nonionic surfactants had been studied by Galera-Gomez and Gu ,1996. The phase separation is shown in Figure 2.4.

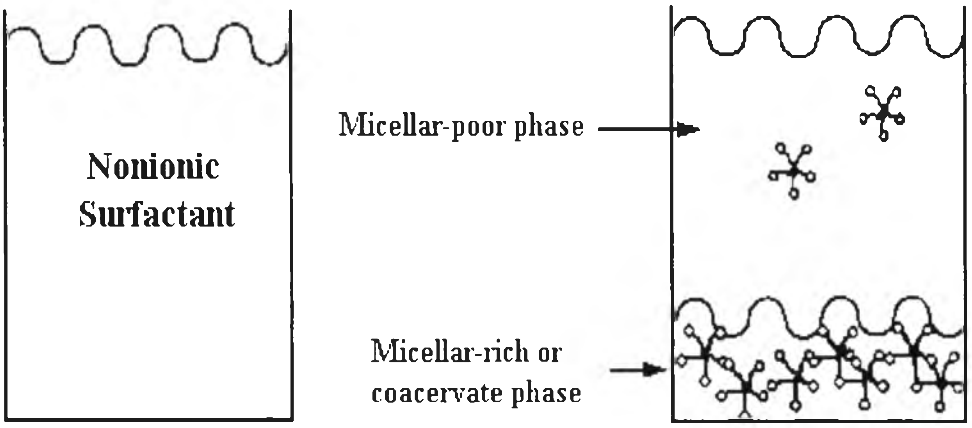

Figure 2.4 Schematic diagram of phase separation in nonionic surfactant.

It is important to emphasize that any factors affecting the dehydration of nonionic micelles can alter the cloud point of a given nonionic surfactant, either increasing or decreasing it.

Sadaghiania et al. (1991) studied the cloud point of Triton X-100 aqueous system. The cloud point of Triton X-100 aqueous system has been measured over the concentration rage from 0.1 - 24 wt%. They found the lower consolution temperature at 0.2 wt%. The cloud point is found to decrease sharply with concentration for the very dilute solutions, going through a minimum at about 0.2 wt%. Above 0.2 wt%, the cloud point increases slowly with increasing concentration, and above 20 wt%, there is a monotonous increase of the cloud point. At a low concentration (1 wt%) of nonionic surfactant, lechitin drastically depresses the cloud point, but the degree of cloud point depression is found to diminish with increased concentration of Triton X-100. On the other hand, the addition of decanol registers only a small decrease of cloud point for the concentration of Triton X-100 employed (1-24 wt%). The uncharged cationic surfactants have no significant effect on the cloud point of the nonionic surfactant solution but ionic surfactants lead to a substantial increase in the cloud point.

Aveyard et al. (1989) studied the effects of alkanol chain lengths on cloud points and vicosities of $C_{12}EO_5$. The results show that the longer chain homologous of alkanols depresses the cloud point and increases the viscosity of aqueous $C_{12}EO_5$. This is due to the penetration of the alkanols into the surfactant alkyl tail region, which would increase the effective value of chain area for the surfactant. This would promote the formation of more asymmetrical structures leading to lower cloud point and increase in the viscosity.

Sukulwongyai (1997) studied the effect of three different chlorination degrees of ethane. The results show that the cloud point depression is greater as the degree of chlorination of ethane increased because the higher the chlorination degree, the higher the hydrophobicity.

It has been proposed that the foam height of nonionic surfactants decreases sharply at the temperature above the cloud point due to the presence of the micellar-rich phase in the solution. Two mechanisms has been proposed for the antifoam property of the micellar-rich phase, ie. the spreading mechanism and the bridging mechanism. In the spreading mechanism, the micellar-rich phase droplets enter the air-water surface and spread. The spreading effect is due to the surface tension difference between the water surface and the micellar-rich phase which produces a shear force. It drags the underlying liquid away from the films and this causes a faster thinning and leads to film rupture. The spreading coefficient can be calculated from the equation 2.1.

$$S = \gamma_{aw} + \gamma_{ow} - \gamma_{oa} \qquad (2.1)$$

Where γ_{aw} is the air-water surface tension, γ_{ow} is the micellar-rich phase-water surface tension, γ_{oa} is the micellar-rich phase-air surface tension. If the spreading mechanism occurs, the calculated spreading coefficient will have a high positive value.

In the bridging mechanism, the micellar-rich phase still enters the air-water surface of foam films but it does not spread. When the film thickness becomes comparable to the size of the micellar-rich phase , if the contact angle between the liquid and the micellar-rich phase is larger than 90°, the liquid film is unstable and breaks. This contact angle condition is equivalent to a positive bridging coefficient. The bridging coefficient can be calculated from the equation 2.2.

$$B = \gamma_{aw}^2 + \gamma_{ow}^2 - \gamma_{oa}^2 \qquad (2.2)$$

If the bridging mechanism occurs, the calculated bridging coefficient will have a high positive value (Colin & Langevin, 1997).