

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Surfactants

Surfactants, a diminutive form of the phrase SURFace ACTive AgeNTs, is a molecule that when they are added to a liquid at low concentrations, the properties of that liquid at a surface or interface can be altered significantly.

2.1.1 Structure of Surfactants

The general structure of a surfactant includes a structural group that has strong attraction with a solvent, known as a lyophilic group (solvent-loving), together with a group that has little attraction with the solvent, called the lyophobic group (solvent-hating). This is known as an amphipathic structure as shown Figure 2.1. In most cases, water is a common solvent. The amphipathic structure of the surfactant therefore causes not only concentration of the surfactant at the surface and reduction of the surface tension of the 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 (Rosen, 1988).

The hydrophobic group is usually a long chain hydrocarbon residue, and less often a halogenated or oxygenated hydrocarbon or siloxane chain while the hydrophilic group is an ionic or highly polar group. This dual functionality, hydrophobic and hydrophilic, provides the basis for characteristics useful in cleaner and detergent formulation, including surface tension modification, foam, and cloud point (Scamehorn *et al.*, 1992).

2.1.2 Types of Surfactants

Surfactants are generally characterized by the nature of the hydrophilic group as the following categories:

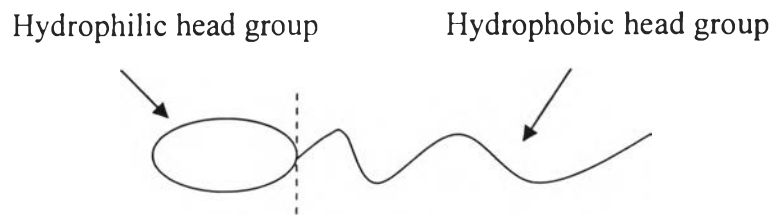


Figure 2.1 Schematic of a surfactant molecule.

1. Anionic surfactants: The surface-active portion of the molecule bears a negative charge, for example, $\text{RC}_6\text{H}_4\text{SO}_3^-\text{Na}^+$ (alkylbenzene sulfonate), $\text{C}_{12}\text{H}_{25}\text{SO}_3^-\text{Na}^+$ (sodium dodecyl sulfate).

2. Cationic surfactants: The surface-active portion bears a positive charge, for example, $n\text{-C}_{16}\text{H}_{33}\text{N}(\text{CH}=\text{CH})_2\text{CHCl}$ (Cetylpyridinium chloride or CPC), $\text{RNH}_3^+\text{Cl}^-$ (salt of a long-chain amine), $\text{RN}(\text{CH}_3)_3^+\text{Cl}^-$ (quaternary ammonium chloride).

3. Nonionic surfactants: The surface-active portion bears no apparent ionic charge. They are a class of synthetic surfactants that are prepared by attaching ethylene oxide molecules to a water-insoluble molecule, such as $\text{RCOOCH}_2\text{CHOHCCH}_2\text{OH}$ (monoglyceride of long-chain fatty acid).

4. Zwitterionic surfactants: Both positive and negative charges may be present in the surface-active portion, for example, $\text{RN}^+\text{H}_2\text{CH}_2\text{COO}^-$ (long-chain amino acid).

2.2 Foam

2.2.1 Foam Formation

Foam is a gas dispersed in a liquid that is produced when air or another gas is introduced beneath the surface of a liquid that expands to enclose the gas with a film of liquid (Rosen, 1988). Foams would have no stability unless there were barriers to prevent coalescence when two gas bubbles touch. The barrier

(liquid film) is produced by the presence of a water-soluble surfactant (Sebba, 1987). The formation of foam from a bulk involves the expansion of the surface area due to the work action upon the system. As surface tension is the work involved in creation a new system, the amount of new area formed will be greater with the lower surface tension. Therefore the surfactant is required for foam formation because it can reduce the surface tension of the new surface area as shown in Figure 2.2.

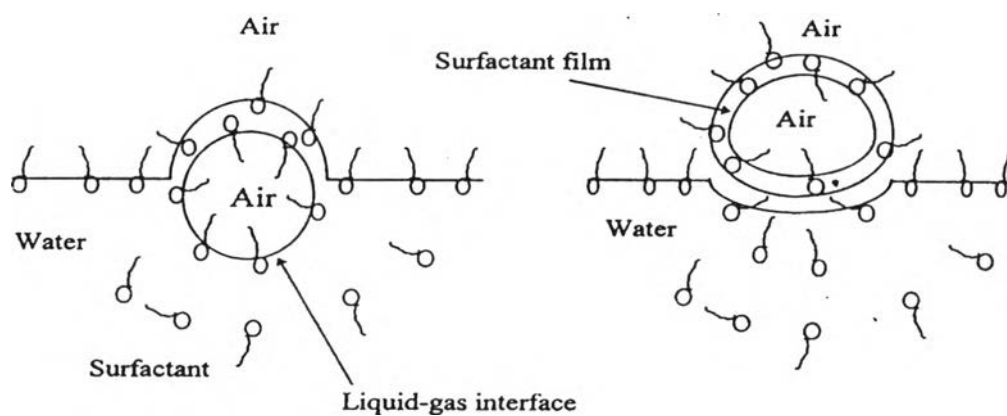


Figure 2.2 Formation of foam (Rosen, 1988).

2.2.2 Structure of Foam

Foam consists of a high-volume fraction of gas dispersed in a liquid. Liquid is a continuous phase. The structure of gas cell consists of thin liquid film and there are two-side films which are called the lamellae of the foam where three or more 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. Most of the water in the continuous phase will be found in the plateau border. Thus, the plateau border will play an important role in the drainage of water in foams (Rosen, 1988; Adamson, 1990).

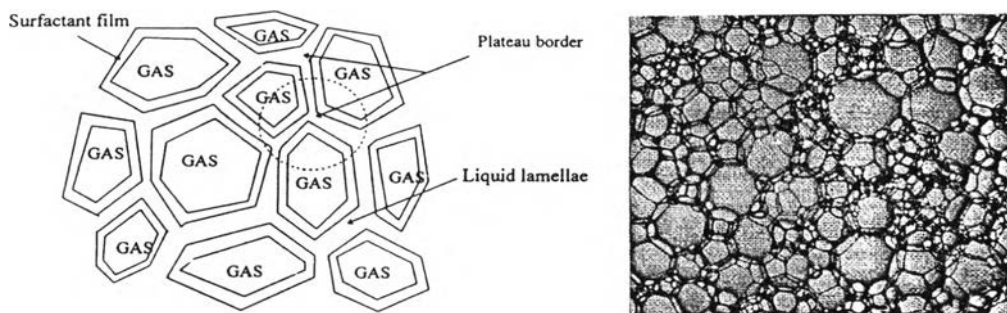


Figure 2.3 The structure of liquid foam (Rosen, 1988, Weaire, 2002).

Foam can be classified into two general categories:

1. Kugelschaums: In this case, foam consists of nearly spherical Bubbles separated by rather thick liquid films as shown in Figure 2.4a. Bubbles are fresh made, wet foam.
2. Polyederschaums: Foam contains mostly gas phase separated by thin films or lamimar as shown in Figure 2.4b. Bubbles form polyhedrons, older foams, and dryer foams.

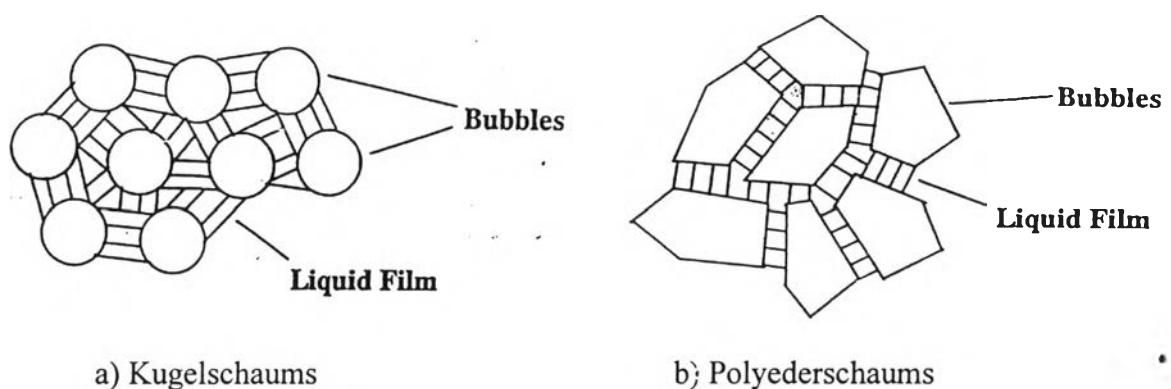


Figure 2.4 Schematic of foam (Rosen, 1988).

2.2.3 Foam Stability

Foam is destroyed when the 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 will burst. The stability of the film will depend on many factors. These are two major affecting factors the stability of foam.

1. Film elasticity: Film elasticity indicates how easily the foam is formed that can be explained by two theories. One is the Gibbs effect that is based on the change in surface tension with changing concentration of the surface-active solute. The other is the Marangoni effect based on the change in surface tension with time. Both film elasticity theories postulate that elasticity is due to the local increase in surface tension with extension of the film. As a local spot in the film thins and stretches and the area of the film in that region (Figure 2.5) increases, its surface tension increases and a gradient of tension is set up that causes liquid to flow toward the thinned spot from the thicker portions around it. The thinning spot thereby automatically draws liquid from its perimeter and prevents further thinning of the film. In addition, the movement of surface material carries with it underlying material that helps heal and thicken the thinned spot by a surface transport mechanism (Rosen, 1988). Both theories can be explained that the surface tension increases in the thin lamellae. There is now a restoring force from the Gibbs elasticity and the Marangoni effect bringing surfactant molecules back into the region of high surface tension (Porter, 1994), as shown in Figure 2.6.

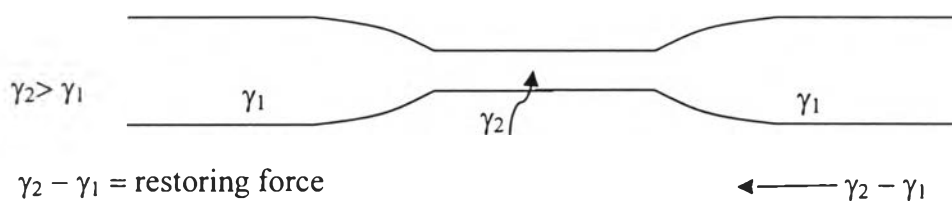
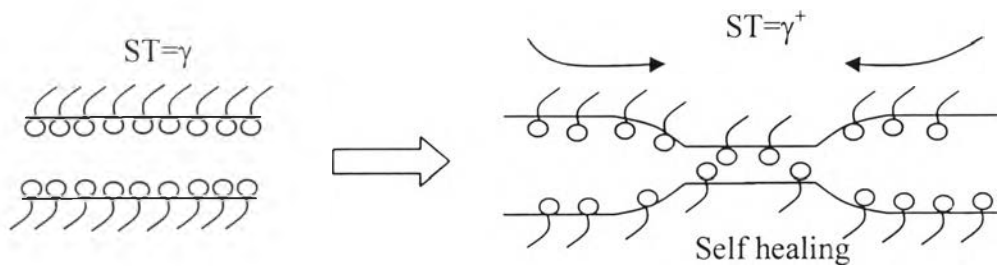
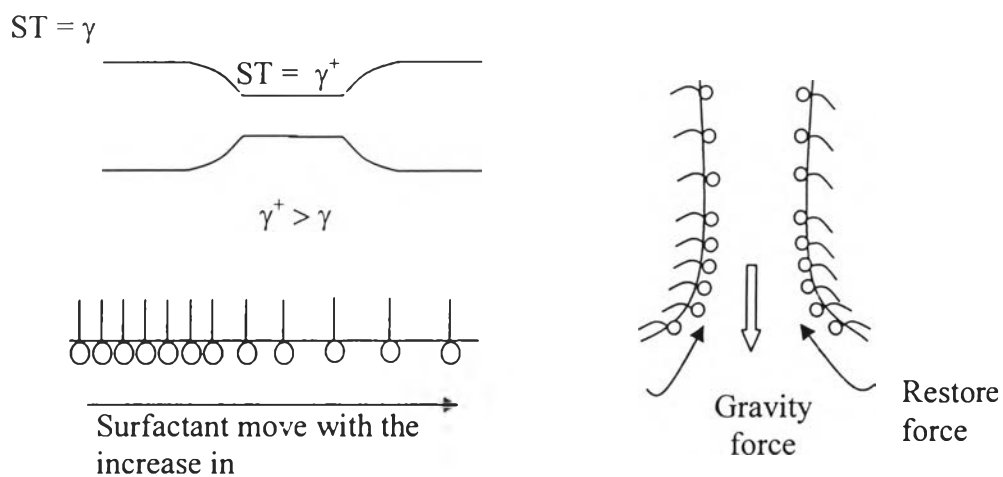


Figure 2.5 Stretch portion of foam lamella, illustrating mechanism of film elasticity.



a) Gibbs Film Elasticity



b) Marangoni Effect

Figure 2.6 Marangoni Effect and Gibbs Film Elasticity.

2. Film drainage: Film drainage is the factor that indicates how rapidly the foam breaks once formed. Drainage of the film occurs under two influences. The first is drainage by gravity that is important mainly in very thick lamellae, such as is present when the foam is first formed. The bulk viscosity of the foaming solution is a major factor affecting the rate of drainage by gravity in thick lamellae. Thickeners are often added to increase the bulk viscosity when very stable foams are desired. At a high concentration of surfactant the viscosity of the bulk solution is also high therefore the drainage rate in the lamellae is decreased with the amount of surfactant in the lamellae is increased.

The second is drainage by surface tension difference that is more important when the lamella is thin. Since the curvature in the lamellae is greatest in

the plateau borders, there is a greater pressure across the interface in these regions than elsewhere in the foam. Since the gas pressure inside on individual gas cell is everywhere the same, the liquid pressure inside the lamellae at the highly curved Plateau Border (point A) must be lower than in the adjacent, less curved regions (point B) of the plateau area. Thus, the continuous phase liquid drains from the thin film (point B) to the adjoining Plateau Borders (point A) as shown in Figure 2.7. The difference pressure (ΔP) can be calculated by the following equation;

$$\Delta P = \gamma \left(\frac{1}{R_A} + \frac{1}{R_B} \right) \quad (1)$$

where γ is surface tension

R_A and R_B are the radii of the curvature of the lamellae at point A and B, respectively.

The greater the difference between R_A and R_B , and the greater the surface tension of the solution in the lamellae, the greater the pressure difference causing drainage (Rosen, 1988).

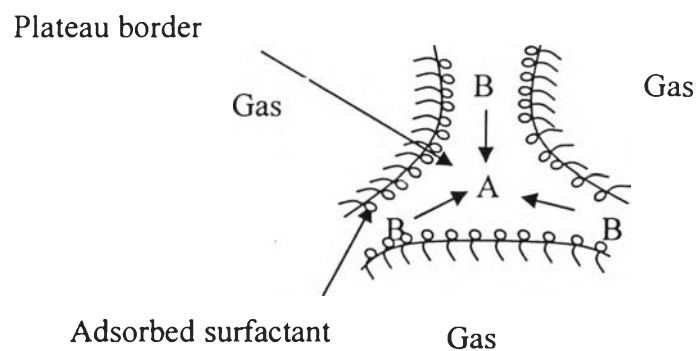


Figure 2.7 Liquid drainage in lamellae by curvature effect.

2.3 Foam Fractionation

2.3.1 Principle of Foam Fractionation

The foam fractionation is an adsorptive bubble separation process that a species of surface active compound is adsorbed at an interface between a dispersed phase (bubbles) and a continuous phase. The dispersed phase with the adsorbed substance is collapsed and collected (Carleson, 1992). The foam separation process can be divided into two types, froth flotation and foam fractionation. Froth flotation separates insoluble materials by frothing, whereas foam fractionation separates soluble species by foams (Carleson, 1992, Okamoto and Chou, 1979).

The foam fractionation, air is sparged to produce bubbles, which rise to the top of liquid column producing foam as shown in Figure 2.8a. As the dispersed phase travels through the continuous phase, mass transfer of the surface-active solute occurs between the two phases. Surfactant adsorbs at the air-liquid interface as illustrated in Figures 2.8b and 2.8c. When the bubble emerges from a solution to form foam with honeycomb structure (Figure 2.8d), the thin liquid film in the foam is stabilized by the adsorbed surfactant (Carleson, 1992, Sebba, 1987). Drainage of liquid in the lamellae due to the gravity, and surface tension difference cause the foam to eventually break or collapse. The collapsed foamate solution that is collected from the top of column has higher concentrations of the surfactant than that in the initial solution (Rosen, 1988).

2.3.2 Foam Fractionation Equipment

Foam fractionation can be classified into two modes: batch mode and continuous mode. In a batch operation, a solution containing a surface-active species is stripped of by introduction of bubbles from a sparger. The rising foam is collected and coalesced to produce the overhead stream as shown in Figure 2.9a. Some of the coalesced foam may be returned to the foam column similar to that in a batch distillation column.

In a continuous operation, the entering liquid may be introduced into the liquid pool or into the foam section of the column. Overhead product is drawn off at the top of the column and underflow from the liquid pool as illustrated in

Figure 2.9b. Some of the overhead may be recycled analogous to a distillation column.

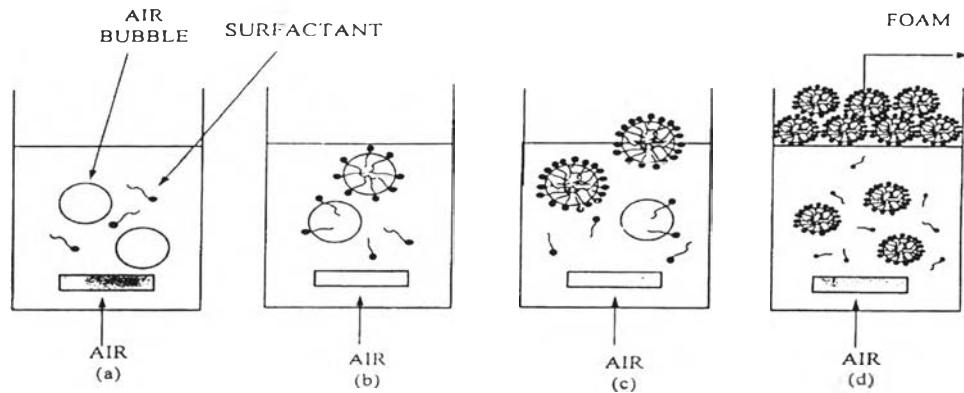


Figure 2.8 Principle of foam formation (Simmler, 1972).

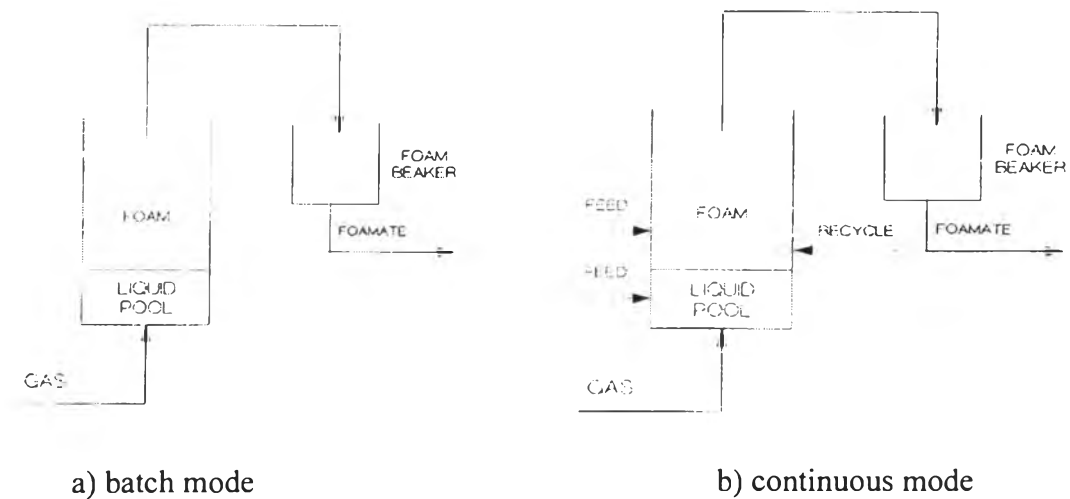


Figure 2.9 Experimental configurations for foam separation (Carleson, 1992).

2.3.3 Applications of Foam Fractionation Process

Possible applications of foam fractionation process are in the fields of wastewater treatment and, recovery of components such as protein or surfactants from solution. Some of the research works on these fields are described here.

For the batch mode, the recovery of gold (III) by foam fractionation with nonionic surfactant: polyoxyethylene nonyl phenyl ether (PONPE20) was studied. The surfactant showed a strong affinity to Au (III) and played a double role of foam producer and metal collector. The effect of concentration of the surfactant and the metal, air flow rate and solution temperature were investigated and discussed in terms of the recovery and the enrichment of Au (III). The recovery increased with an increase in either the concentration of surfactant or air flow rate whereas the enrichment ratio improved with decreasing air flow rate (Kinoshita, 2003). The effect of external reflux and temperature on foam fractionation of Poly(vinyl alcohol) (PVA) were investigated. The results showed that the enrichment ratio and separation factor increased with increasing temperature. The external foamate reflux was found to be essential for foam fractionation when treating a highly foaming solution (Yamagiwa *et al.*, 2001). Grieves and Wood (1964) studied the effects of temperature and liquid residence time of the ethylhexadecyldimethyl ammoniumbromide-water system. They found that the drain rate and enrichment ratio increased with increasing temperature. The variation in liquid residence time and the solution height had no influence upon the separation. Changes in feed rate and air rate causing variation of the volume of air employed per unit volume of feed treated was pointed out to be a prime variable affecting the separation. Tharapiwattananon (1995) investigated the recovery of surfactant from water by using foam fractionation in continuous mode. One cationic (CPC) and two anionic (DADS and SDS) surfactants were used in this work. Effects of experimental parameters, such as concentration of liquid feed surfactant, airflow rate, foam height and liquid height were investigated. From the results, it showed that this cationic surfactant was easier to remove from water by foam fractionation than anionic surfactant. The enrichment ratio decreased with increasing in the air flow rate and surfactant concentration. Kumpabooth (1997) studied further on the effects of temperature and salinity. Increasing temperature resulted in a increase in the enrichment ratio for all these surfactants while the rate of surfactant recovery stayed approximately constant for CPC and DADS and mildly decreased for SDS. As salinity was increased, the foam wetness increased resulting in decreasing

enrichment ratio. Since generally a higher volume of a less concentrated solution is formed overhead, a slightly increase in foam recovery rate was found.

For multistage mode, Boonyasuwat *et al.* (2002) studied the recovery of cationic (CPC) and anionic (SDS) surfactant from water by using multistage foam fractionation with one to four stages. They found that the enrichment ratio increased with decreasing air flow rate, increasing foam height per tray, increasing feed liquid flow rate, increasing feed surfactant concentration, and increasing number of stages. Liquid height in the trays was found to have a little effect on the multistage foam fractionation process. Chuyingsakultip (2003) continued the work by studying further the effect of several variables such as tray spacing, feed position and recycle ratio. The results showed that the values of both enrichment ratio and %surfactant recovery did not change significantly when increasing the recycle ratio but the highest enrichment ratio was obtained when the feed was fed to higher trays.