



CHAPTER II

THEORETICAL BACKGROUNDS AND LITERATURE SURVEY

2.1 Surfactants

Surfactants are a diminutive form of the phrase SURFace ACTIVE AgeNTs. When they are added to a liquid at low concentrations, the properties of that liquid at a surface or interface can be altered significantly (Porter, 1994).

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 the concentration of the surfactant at the surface and reduction of the surface tension of the water but also the orientation of the molecules at the water surface with its hydrophilic group in the aqueous phase and its hydrophobic group oriented away from it, leading to a significant reduction in the surface tension (Rosen, 1988).

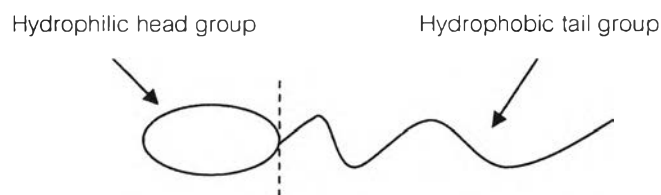


Figure 2.1 Schematic of a surfactant molecule.

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 cleaning and detergent formulation, including surface tension modification, foam, and separation (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:

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 are 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

are 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 involving in creation a new surface; the amount of new area formed will be greater with the lower surface tension. Therefore a surfactant is required for foam formation because it can reduce the surface tension of the new surface area, as shown in Figure 2.2.

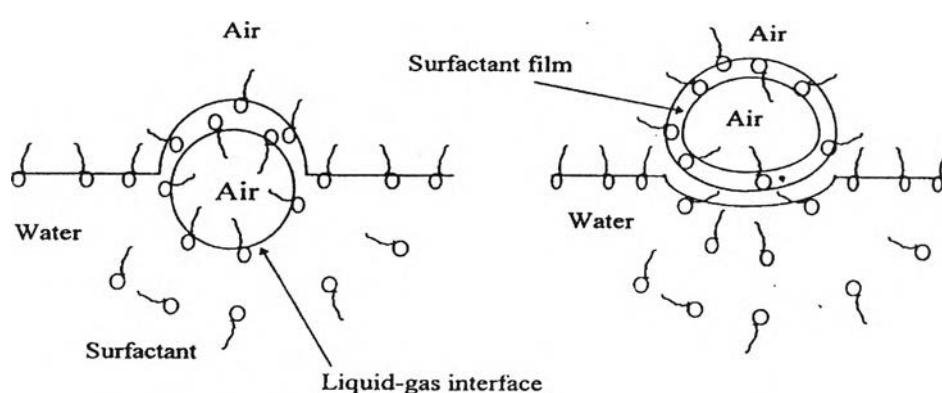


Figure 2.2 Formation of foam (Rosen, 1988).

2.2.2 Structure of Foam

Foam consists of a high-volume fraction of gas dispersed in a liquid. 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 bubbles generally meet. The joining area of the bubbles is called the Plateau border or Gibbs triangle as shown in Figure 2.3. Most of the water in the foam is found in the plateau border. Thus, the plateau border will play an important role in the drainage of water (Rosen, 1988; Adamson, 1990). Foam can be categorized into two types as follows:

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, known as wet foam.
2. Polyederschaums: Foam contains mostly gas phase separated by

thin films or lamellar, as shown in Figure 2.4b. Bubbles form polyhedrons, known as older foams, and dryer foams.

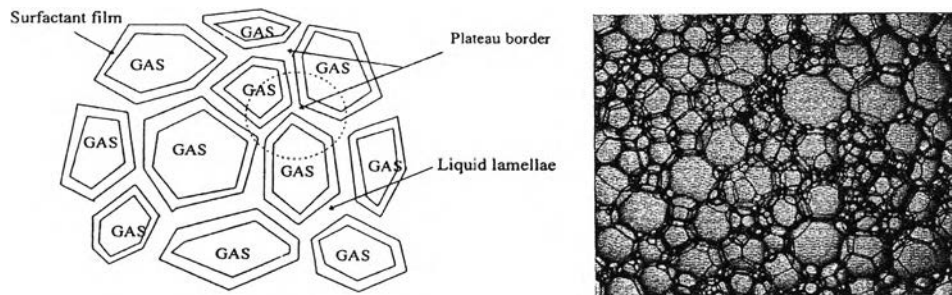


Figure 2.3 The structure of liquid foam (Rosen, 1988, Weaire, 2002).

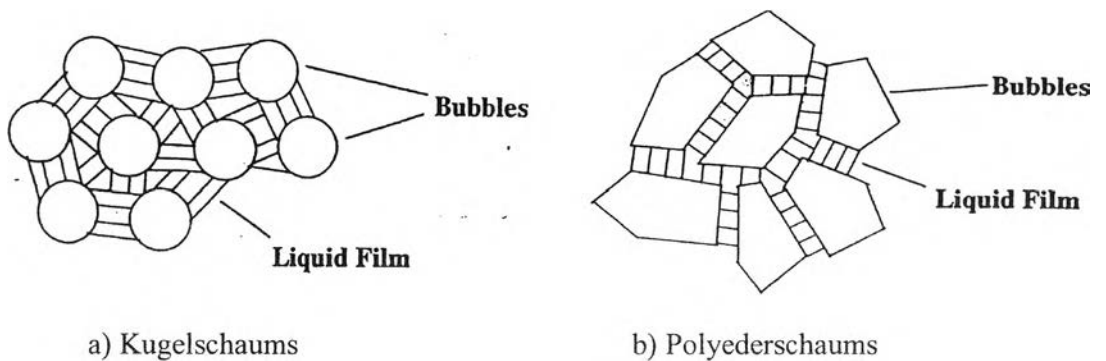


Figure 2.4 Schematic of foam (Rosen, 1988).

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 too thin. 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 factors, affecting the stability of foam.

1. Film elasticity: Film elasticity indicates how easily the foam can form which 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 surfacetension with time. Both film elasticity theories postulate that elasticity is due to the local increase in surface tension with the extension of the film, as shown in Figure 2.5. As a local spot in the film thins and stretches and the area of the film in that region increases, its surface tension increases and a gradient of tension is set up that causes surfactant molecules to flow toward the thinner spot from the thicker zone. The thinning spot thereby automatically drag some water molecules with them, resulting in thickening the thinner zone. As a result, the thinner zone becomes thicker, known as healing effect. Both theories can be explained that the surface tension increases in the thin lamellae. There is 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.

2. Film drainage: Film drainage is the factor that can cause the foam to break. Drainage of the film occurs under two influences. The first is the drainage by gravity that is important mainly in very thick lamellae, 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 desirable. At a high concentration of surfactant, the viscosity of the bulk solution is also high and, therefore, the drainage rate in the lamellae decreases.

The second is the drainage by pressure difference that is more important when the lamella is thin. Since the curvature in the lamellae is the 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). 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 expressed by the following equation :

$$\Delta P = \gamma [1/R_A + 1/R_B] \quad (1)$$

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 , the greater the pressure difference causing drainages (Rosen, 1988).

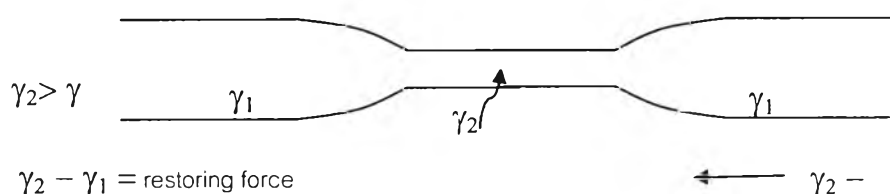
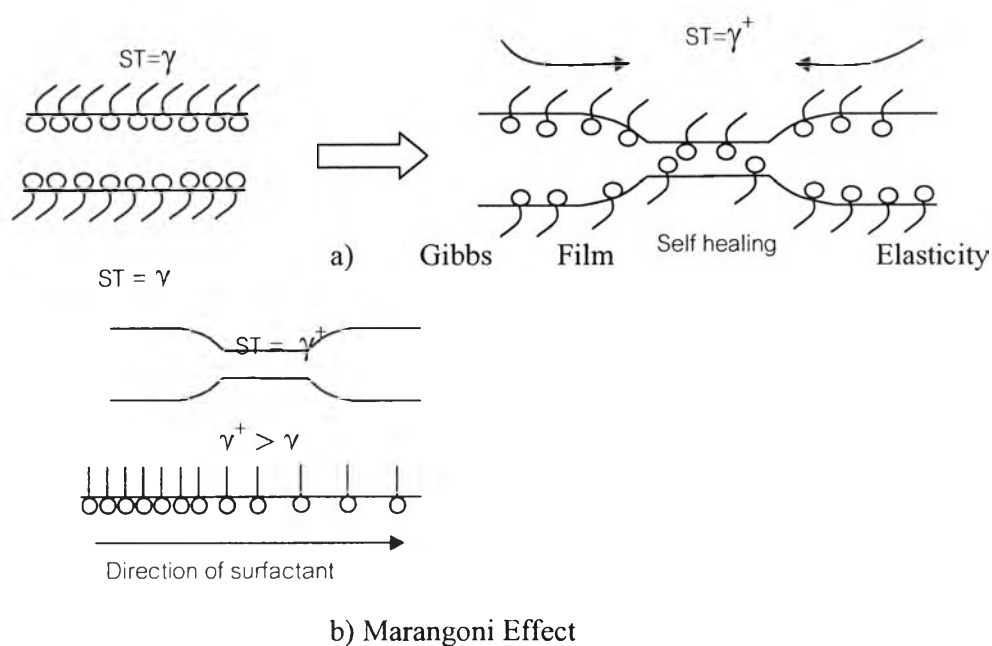


Figure 2.5 Stretch portion of foam lamella, illustrating mechanism of film elasticity.



b) Marangoni Effect

Figure 2.6 Marangoni effect and Gibbs film elasticity.

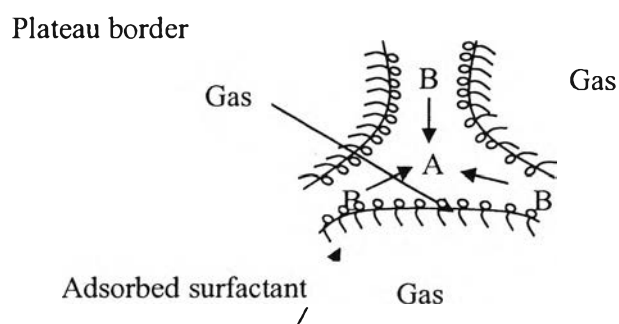


Figure 2.7 Liquid drainage in lamellae by curvature effect.

2.3 Foam Fractionation

2.3.1 Principle of Foam Fractionation

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 (liquid). The dispersed phase with the adsorbed substance is collapsed and collected (Carleson, 1989). 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, 1989, Okamoto and Chou, 1979).

Foam fractionation, air is sparged to produce bubbles, which rise to the top of liquid column producing foam, as shown in Figure 1.1. As the dispersed phase travels through the continuous phase, the mass transfer of the surface-active solute occurs between the two phases. Surfactant adsorbs preferentially at the air-liquid interface. When the bubbles emerge from a solution to form foam with honeycomb structure, the thin liquid film in the foam is stabilized by the adsorbed surfactant (Carleson, 1989, Sebba, 1987). Because of drainage of liquid in the lamellae, the foam eventually breaks or collapses. The collapsed foamate solution that is collected from the top of column has a higher concentration of the surfactant than that in the initial solution (Rosen, 1988).

2.3.2 Factors affecting Foam Fractionation

Many factors affect the performance and efficiency of a foam fractionation system and the relative importance of each depends on the specific conditions.

1. Surfactant Concentration

At surfactant concentrations much lower than its CMC, an increase in surfactant concentration results in an increase in the excess surface concentration of the surfactant, leading to a decrease in the surface tension. The former effect tends to increase the enrichment ratio, whereas the latter effect results in lower rates of drainage and higher rates of foam production and foam wetness, thus leading to lower enrichment ratios (Thrarapiwattananon, 1996).

2. Gas Flow Rate

Gas flow rate strongly affects the rate of removal of dissolved substances. The removal of dissolved substances involves their distribution or partition between gaseous and aqueous phases. An increase in interfacial area, as occurs with increasing gas flow rate, causes an increase in removal at any given time. However, a low gas flow rate is in general beneficial for separation in terms of high enrichment. There must be sufficient gas flow to maintain the foam height that is essential for good separation (Tharapiwattananon, 1996, Kumpabooth, 1996). To operate foam fractionation, an optimum air flow rate is required to obtain both high removal and high enrichment ratio.

3. Foam Drainage

Foam drainage is commonly carried out by passing the foam upward through a length of column of expanded diameter. The drainage of foam results from competition between gravitational forces and the capillary pressure in channels separating adjacent bubbles. The drainage-capillary effects imply that top of the foam becomes dry while the bottom of the foam remains wet. The dryer foam corresponds to a longer residence time for drainage to reduce the water content of the foam. The higher the foam drainage, the higher the enrichment ratio of surfactant but the lower the removal of surfactant.

4. Other Physical Variables

Among the other physical variables, bubble-size distribution, agitation, column length, etc., do not cause any primary effects on the ultimate separation of materials. However, it was reported that the foam height had a significant effect on the separation of albumin, and the effect was very pronounced near the foam-liquid interface (Ahmad, 1975). A change in foam height produced a drastic change in the separation efficiency.

2.3.3 Related Work

Possible applications of foam fractionation process are in the fields of wastewater treatment, and the recoveries 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 effects of the concentrations of the surfactant and the metal ion, air flow rate and solution temperature were investigated and discussed in terms of the recovery and the enrichment ratio 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 *et al.*, 2003). The effect of external reflux and temperature on the removal efficiency of poly(vinyl alcohol) (PVA) in foam fractionation were investigated. The results showed that the enrichment ratio and separation efficiency increased with increasing temperature. The use of 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 flow rate and air flow rate were pointed out to be prime variables affecting the separation efficiency of foam fractionation. Tharapiwattananon (1996) investigated the recovery of surfactant from water by using foam fractionation in continuous mode. One cationic (cetyl pyridinium chloride, CPC) and two anionic (Polyoxyethylene (20) sorbitan monolaurate, DADS and Sodium dodecyl sulfate, SDS) surfactants were used in this work. The effects of operating parameters, such as concentration of liquid feed surfactant, air flow rate, foam height and liquid height were investigated. From the results, the cationic surfactant was easier to be removed from water by foam fractionation than the anionic surfactants. The enrichment ratio decreased with increasing the air flow rate and surfactant concentration. Kumpabooth (1996) further studied the effects of temperature and salinity. Increasing temperature resulted in an increase in the enrichment ratio for all these studied surfactants while the rate of surfactant recovery stayed approximately constant for CPC and DADS and mildly

decreased for SDS. As salinity increased, the foam wetness increased resulting in decreasing enrichment ratio but a slightly increase in foam recovery rate was found.