CHAPTER II
THEORETICAL BACKGROUD AND LITERATURE REVIEW

2.1 Surfactants

Surfactants are wetting agents that lower the surface tension of a liquid, allowing easier spreading, and lower the interfacial tension between two liquids. The term surfactant is a blend of "surface active agent". Surfactants are usually organic compounds that are amphiphilic, meaning they contain both hydrophobic groups (their "tails") and hydrophilic groups (their "heads"). Therefore, they are soluble in both organic solvents and water. The term surfactant was coined by Antara Products in 1950. A micelle - the lipophilic ends of the surfactant molecules dissolve in the oil, while the hydrophilic charged ends remain outside, shielding the rest of the hydrophobic micelle
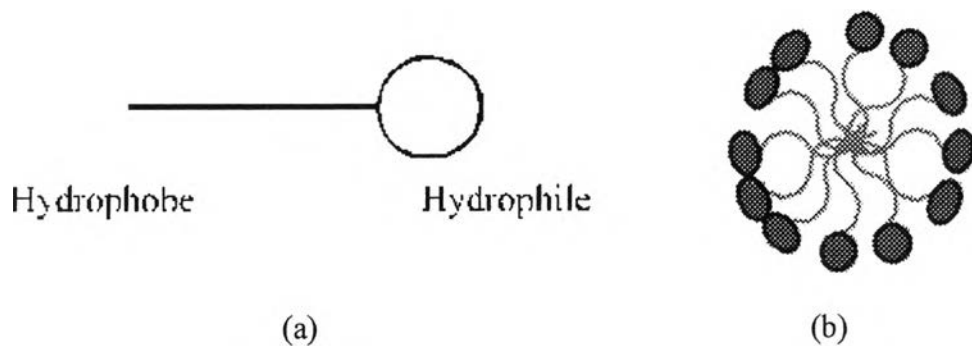

(a)   (b)

Figure 2.1 Schematic of a surfactant molecule (a) and a micelle (b)

2.1.1 Operation and effects of surfactants

Surfactants reduce the surface tension of water by adsorbing at the liquid-gas interface. They also reduce the interfacial tension between oil and water by adsorbing at the liquid-liquid interface. Many surfactants can also assemble in the bulk solution into aggregates. Some of these aggregates are known as micelles. The concentration at which surfactants begin to form micelles is known as the critical micelle concentration or CMC. When micelles form in water, their tails form a core

that can encapsulate an oil droplet, and their (ionic/polar) heads form an outer shell that maintains favorable contact with water. When surfactants assemble in oil, the aggregate is referred to as a reverse micelle. In a reverse micelle, the heads are in the core and the tails maintain favorable contact with oil.

Surfactants are also often classified into four primary groups; anionic, cationic, non-ionic, and zwitterionic (dual charge). Thermodynamics of the surfactant systems are of great importance, theoretically and practically. This is because surfactant systems represent systems between ordered and disordered states of matter. Surfactant solutions may contain an ordered phase (micelles) and a disordered phase (free surfactant molecules and/or ions in the solution).

Ordinary washing up detergent, for example, will promote water penetration in soil, but the effect would only last a few days (although many standard laundry detergent powders contain levels of chemicals such as sodium and boron, which can be damaging to plants, so these should not be applied to soils). Commercial soil wetting agents will continue to work for a considerable period, but they will eventually be degraded by soil micro-organisms. Some can, however, interfere with the life-cycles of some aquatic organisms, so care should be taken to prevent run-off of these products into streams, and excess product should not be washed down gutters.

2.1.2 Classification of surfactants

A surfactant can be classified by the presence of formally charged groups in its head. A nonionic surfactant has no charge groups in its head. The head of an ionic surfactant carries a net charge. If the charge is negative, the surfactant is more specifically called anionic; if the charge is positive, it is called cationic. If a surfactant contains a head with two oppositely charged groups, it is termed zwitterionic.

Some commonly encountered surfactants of each type include:

- <u>Ionic</u>
  - o Anionic (based on sulfate, sulfonate or carboxylate anions)
    - Sodium dodecyl sulfate (SDS), ammonium lauryl sulfate, and other alkyl sulfate salts
    - Sodium laureth sulfate, also known as sodium lauryl ether sulfate (SLES)
    - Alkyl benzene sulfonate
    - Soaps, or fatty acid salts
  - o Cationic (based on quaternary ammonium cations)
    - Cetyl trimethylammonium bromide (CTAB) a.k.a. hexadecyl trimethyl ammonium bromide, and other alkyltrimethylammonium salts
    - Cetylpyridinium chloride (CPC)
    - Polyethoxylated tallow amine (POEA)
  - o Zwitterionic (amphoteric)
    - Dodecyl betaine
    - Dodecyl dimethylamine oxide
    - Cocamidopropyl betaine
    - Coco ampho glycinate
- <u>Nonionic</u>
  - o Alkyl poly(ethylene oxide)
  - o Copolymers of poly(ethylene oxide) and poly(propylene oxide) (commercially called Poloxamers or Poloxamines)
  - o Alkyl polyglucosides, including:
    - Octyl glucoside
    - Decyl maltoside
  - o Fatty alcohols
    - Cetyl alcohol
    - Oleyl alcohol

2.2 Foam

2.2.1 Foam formations

Foam is produced when air or some other gas is introduced beneath the surfactant of a liquid that expands to enclose the gas is the film to liquid. Foam is a gas dispersed in a liquid (Rosen, 1988). The foam is unstable unless there are barriers to prevent coalescence when two gas bubble touch (Sebba, 1987). The barrier is produced by the present of a water-soluble of surfactant.

The formation of the foam from a bulk involves the expansion of the surfactant area due to the work acting upon the system. As surface tension is this work involved in creating a new system, then the amount of new area formed will be grater the low surface tension. Therefore, the surfactant is required for foam formation because it can reduce the surface tension of new surface area.

In accordance with Gibbs adsorption equation, surfactant will be adsorbed at this surface to produce an expanded monolayer. The gas will rise to the upper surface of water that also has a similar monolayer of surfactant on it. Because the head group of surfactant carries a charge that is the same sign as that of surfactant at the surfactant at the water surface, there will be repulsive force by the bubble. If in has enough momentum, it will penetrate the surface by lifting up a thin film of water and floating on the water as shown in Figure 2.2
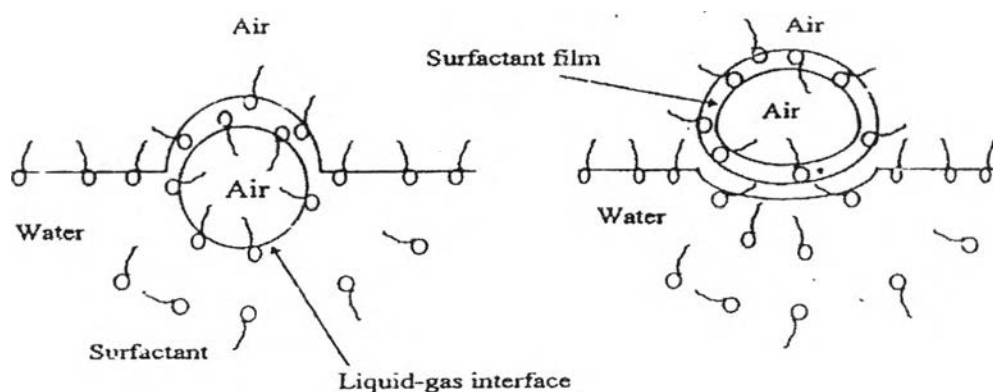

Figure2.2 formation of foam (Rosen, 1988)

2.2.2 Structure of foam

Two main types of foams may be distinguished: (1) spherical foam ("Kugel Schaum"), consisting of gas bubbles separated by thick films of viscous liquid produced in freshly prepared systems. This may be considered as a temporary dilute dispersion of bubbles in the liquid. (2) Polyhedral gas cells produced on aging; thin flat "walls" are produced with junction points of the interconnecting channels (plateau borders). Due to the interfacial curvature, the pressure is lower and the film is thicker in the plateau border. A capillary suction effect of the liquid occurs from the centre of the film to its periphery.

The pressure difference between neighboring cells, ΔP, is related to the radius of curvature (r) of the plateau border by,

$$\Delta p = \frac{2\gamma}{r}$$

In a foam column, several transitional structures may be distinguished (Figure 2.3). Near the surface, high gas content (polyhedral foam) is formed, with a much lower gas content structure near the base of the column (bubble zone). A transition state may be distinguished between the upper and bottom layers.
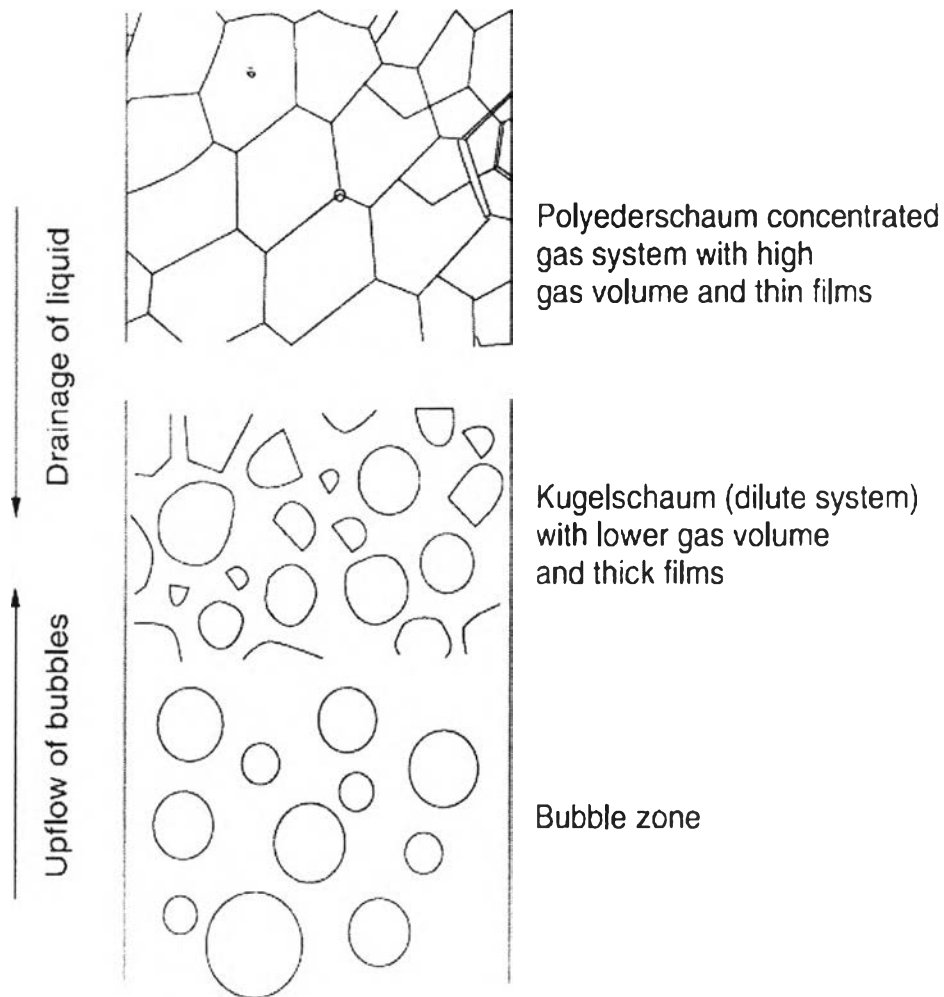
Polyederschaum concentrated
gas system with high
gas volume and thin films

Kugelschaum (dilute system)
with lower gas volume
and thick films

Bubble zone

Fig. 2.3 Schematic of foam structure in a column. (Tadros, 2005)

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. There are two major affecting factors the stability of the foam.
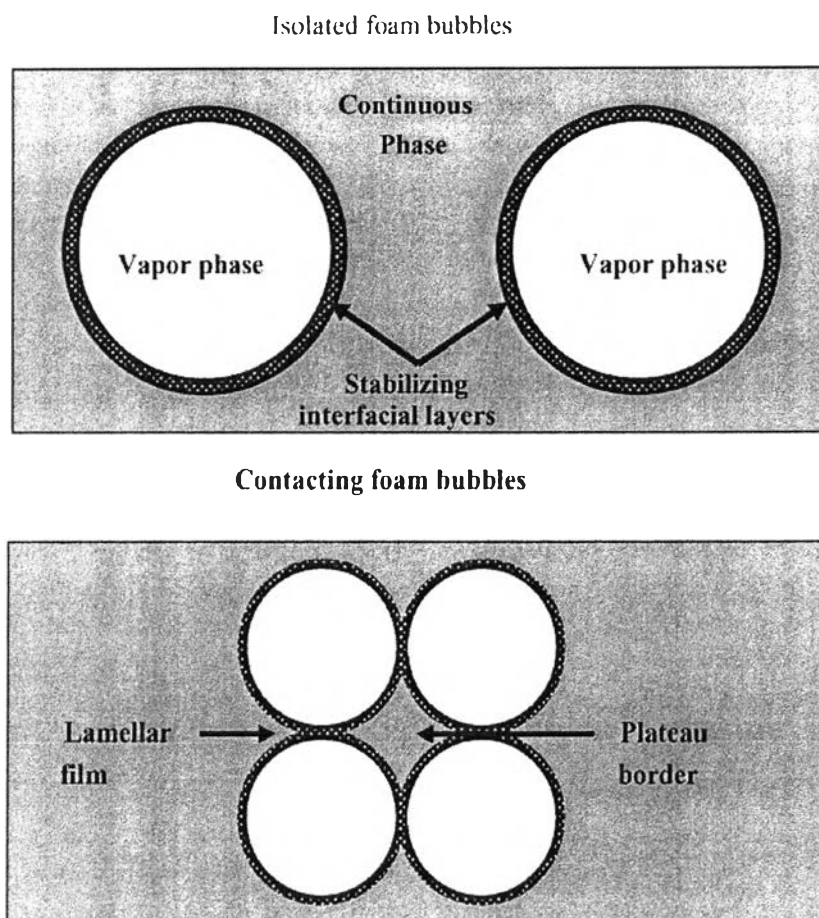
Isolated foam bubbles

Contacting foam bubbles

Figure 2.4 The basic anatomy of a foam structure. (Myers, 2006)

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 based on the change in surface tension with changing concentration of the surface-active solute. The other is the Marangoni effect based on the changing the surface tension with time. Both film elasticity theories postulate that elasticity 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 thin spot from the thicker portion 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 help heal and thicken the thinned spot by a surface transport mechanism (Rosen, 1988).Both theories can be

explained that the surface tension increase in the thin lamellae. There is now restoring force from the Gibbs elasticity and the Marongoni effect bringing surfactant molecules back into the region of high surface tension (Porter, 1994), as show in Figure 2.6
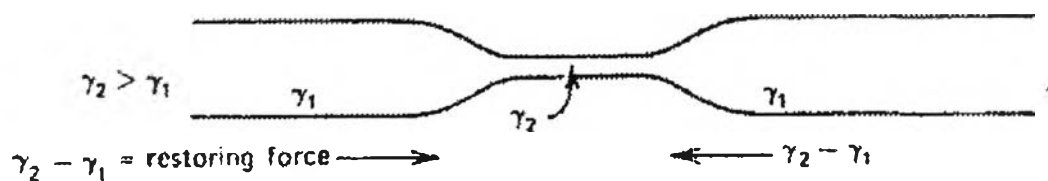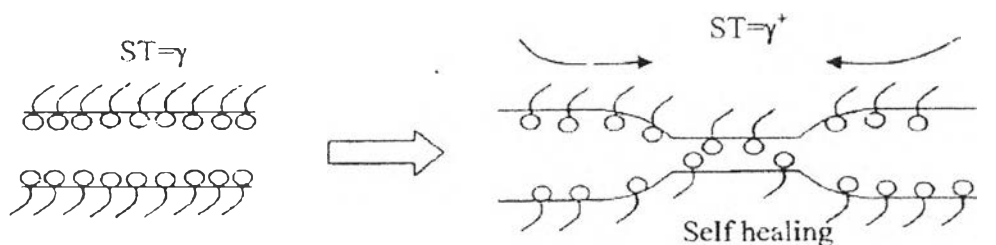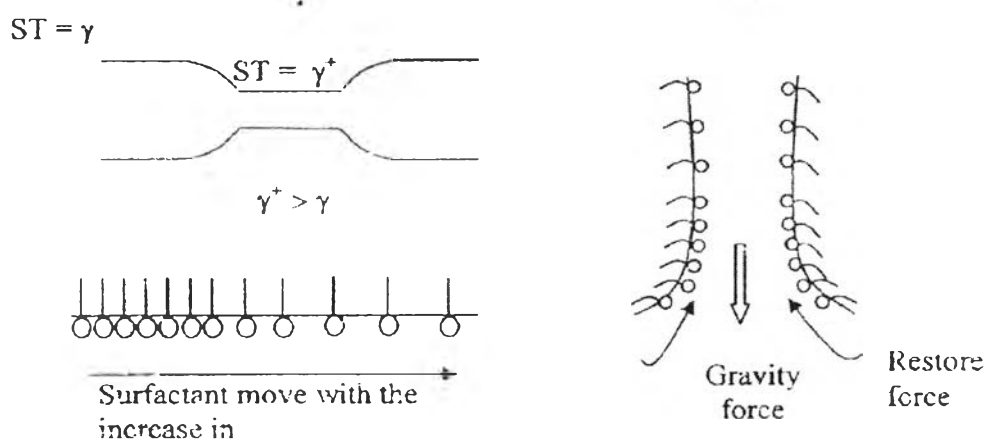

$\gamma_2 > \gamma_1$

γ_1

γ_2

$\gamma_2 - \gamma_1$ = restoring force $\longrightarrow$

γ_1

$\longleftarrow \gamma_2 - \gamma_1$

Figure 2.5 Stretch portions of foam lamellae, illustrating mechanism of film elasticity. (Rosen, 1988)

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 occur under two influences. The first drainage by gravity that is important mainly in very thick lamellae, such as is present when the foam is first formed. The bulk viscosity when very stable foams are desired. At a high concentration of the 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 lamellar is increased.

The second is drainage by surface tension difference that is more important when the lamellae are 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 every-

where the same, the liquid pressure inside the lamellae at the highly curved Plateau Borders (point A) must be lower than in 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;

$$\Delta p = \sigma\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

Where   σ   is the surface tension.

r₁   is the radii of the curvature of the liquid surface at the point A

r₂   is the radii of the curvature of the liquid surface at the point B

The greater the difference between r_1 and r_2, and the greater the surface tension of the solution in the lamellae, the greater the pressure difference causing drainage (Rosen, 1988).
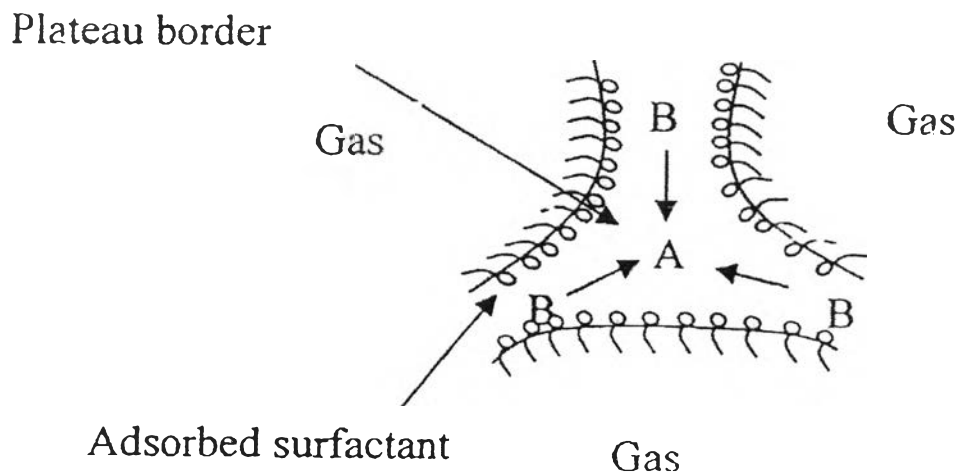

Figure 2.7 Liquid drainage in lamellae by curvature effect.

2.3 Foam Fractionation

2.3.1 Principle of Foam Fractionation

The foam separation process is an adsorptive bubble separation technique that selectively separates surface-active compounds from a solution due to adsorption of surfactant at the interface between the liquid and gas (Carleson, 1989). This process is especially effective for separation of materials at low concentration. Surface-inactive compounds (colligens) can be removed from solution if an appropriate surface-active material (surfactant) is added to the system (Elving, 1982). The foam separation process can be divided into two types, foam fractionation and froth flotation. Foam fractionation separates dissolved material, while froth flotation separates insoluble material (Okamoto and Chou, 1979).
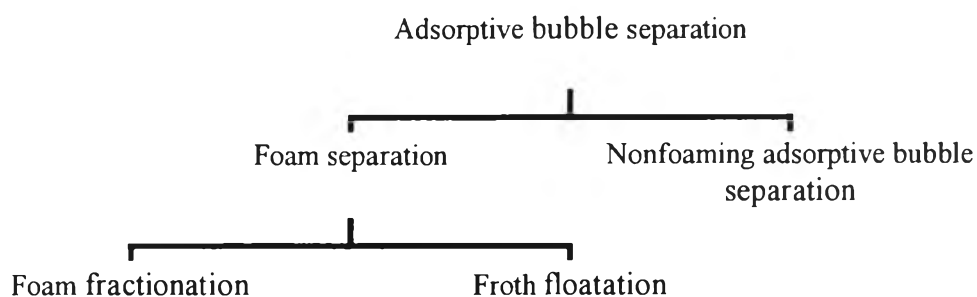
Adsorptive bubble separation

Foam separation   Nonfoaming adsorptive bubble separation

Foam fractionation   Froth floatation

Figure 2.8 Classification of bubble separation techniques.

In foam fractionation, air is spared to produce bubbles which rise to the top of a liquid column producing foam as illustrated in Figure 2.9. As the bubbles travel through the liquid phase, surfactant adsorbs at the air–liquid interface. When the air bubbles emerging from solution form a cell in the foam honeycomb, the thin liquid film in the foam (lamellae) is stabilized by the adsorbed surfactant (Sebba, 1987). Drainage of liquid in the lamellae occurs due to gravity, and eventually the foam breaks or collapses (Rosen, 1988). The collapsed foamate solution that is collected from the top of column has a higher concentration of the surfactant than the initial solution. There are two modes of foam fractionation: simple mode (batchwise or continuous) and higher mode with enriching and/or stripping, as shown in Figure 2.10 (Konduru, 1992). In this work a simple continuous mode of operation is used to recover the surfactant from water.
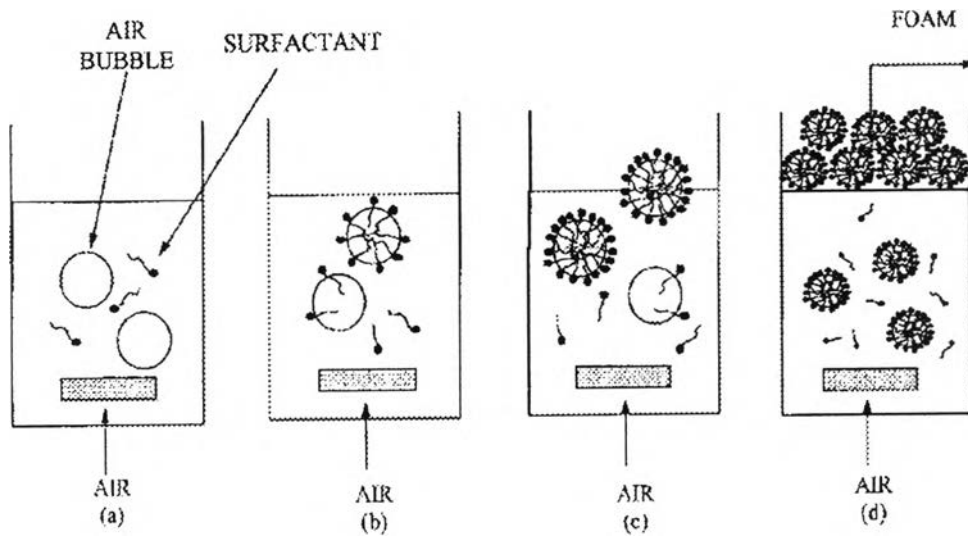
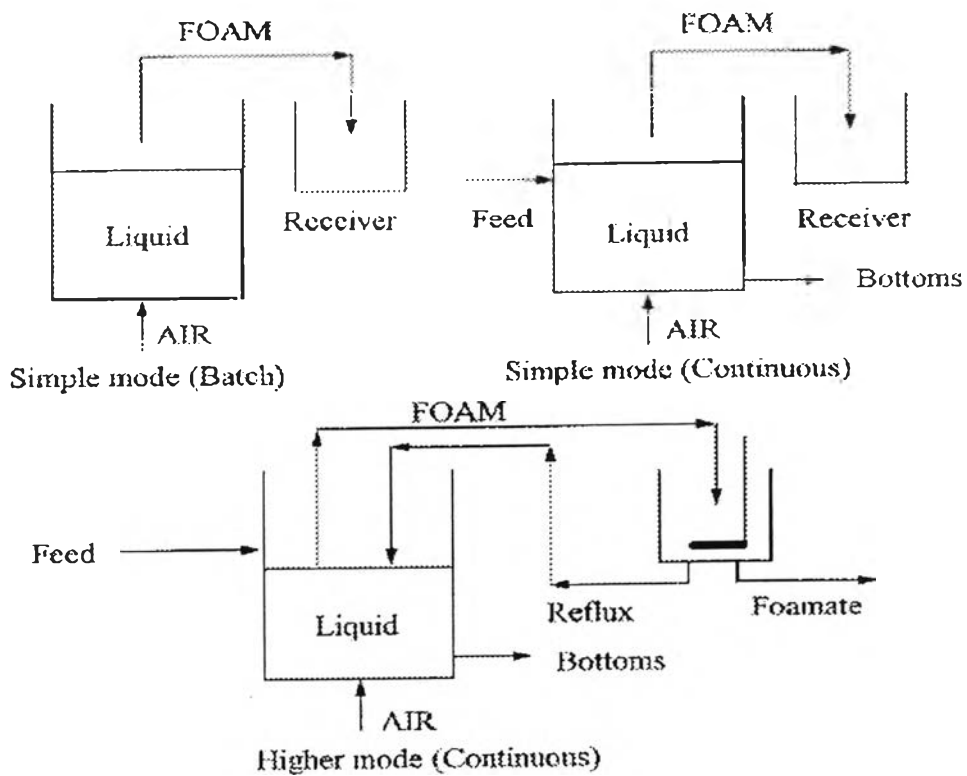**Figure 2.9** Schematic of foam fractionation (Simmler, 1972).

Figure 2.10 Types of foam fractionation (Carleson, 1992).

2.3.2 Application of Foam Fractionation Process

The foam fractionation process has been widely studied for the purpose of removing colligends such as organic molecules, cations, and anions from the aqueous phase by using a surfactant as the collector. Many publications are available on different modes of operation of a foam fractionation unit.

For the batch mode, Yamagiwa *et al.,* (2001) investigated the effect of the external formate reflux and temperature on the foam fractionation of PVA. With rising temperature, the enrichment and separation factor increases. External formate reflux was essential for foam fractionation when treating the highly foaming solution. Grieves and Wood (1964) studied the effect of temperature. They found that temperature had subtle effect on the foam separation process. Tharapiwattananon (1995) investigated a single continuous mode of foam fractionation to remove surfactant from water; two anionic surfactants (DADS and SDS) and cationic surfactant (CPC) were studied. The effect of air flow rate, foam height, liquid height, surfactant concentration, and sprayer porosity were studied. From the result, it shown that the effectiveness of the foam fractionation process in recovering CPC was better than for DADS or SDS. Liquid had little effect on the separation process. The enrichment ratio decreases with increasing air flow and surfactant concentration, decreasing pore size of the sprayer. Kumpabooth (1997) used the same surfactants as Tharapiwattananon and also investigated the effect of temperature and added salt. It was found that the foam flow rate and enrichment ratio increase whereas the foam wetness and the rate of surfactant recovery decrease with increasing temperature. The foam flow rate, foam wetness and the rate of surfactant recovery increase while the enrichment ratio decreases with increasing concentration of salt.

For multistage mode, Darton *et al.* (2004) had developed equipment and process able to supply a number of stages of separation, working with an inert stripping gas. They found that the measured liquid compositions were in good agreement with a model which describes the equilibrium using an adsorption isotherm, and make a mass balance for each stage for the column. The effect of liquid reflux was shown to be important. Boonyasuwat *et al.* (2003) studied the recovery of a cationic (CPC) and anionic (SDS) surfactant from water by using multistage foam fractionation with one to four stages operated. They found that enrichment ratio in-

creased with decreasing air flow rate, increasing foam height of the top tray, increasing feed liquid flow rate, decreasing feed surfactant concentration, and increasing number of stages. The fractional surfactant removal increases with decreasing air flow rate, increasing foam height per tray, increasing feed liquid flow rate, increasing feed surfactant concentration and increasing number of stages. The effectiveness of the foam fractionation process in recovering CPC was better than for SDS. Chuyingsakultip (2004) studied the recovery of a cationic (CPC) form aqueous solution. Effects of several important variables, such as feed position, recycle ratio and tray spacing. The result showed that changing feed position had more impact on the column performance then changing the recycle ratio or tray spacing. Triroj (2005) investigated the recovery surfactant from aqueous solution it both single (CPC and $OPEO_{10}$) and mixed system (CPC/$OPEO_{10}$). From the experimental results, the enrichment ratio increased with decreasing air and liquid feed flow rate, and with increasing foam height. The effect of foam height on the surfactant recovery was not as significant as it was on the enrichment ratio. In contrast, surfactant recovery was strongly affected by changes in air and liquid flow rates. In the single surfactant systems, both surfactant recovery and enrichment ratio obtained in the $OPEO_{10}$ system were higher than thin the CPC system. Synergism was observed in the mixed surfactant system, which led to a total recovery of $OPEO_{10}$. Sripituk (2006) investigated the recovery surfactant from aqueous solution it both single (CPC and $OPEO_{10}$) and mixed system (CPC/$OPEO_{10}$). From the experimental results, the enrichment ratio increased with increasing feed position in CPC system and mixed surfactant system (CPC/$OPEO_{10}$) and decreasing in $OPEO_{10}$, moreover, reflux position or reflux ratio has no effect on the enrichment ratio in all systems. For % surfactant recovery, it increased with increasing feed position in all systems. In addition, reflux position or reflux ratio has no effect on the % surfactant recovery in all systems.