CHAPTER II
HISTORICAL BACKGROUND

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 change the properties of those surfaces (Clint,1992). Surfactant has a characteristic molecular structure consisting of structural group that has very little attraction for solvent, known as a lyophobic group (hydrophobic group for the water or tail group), together with a group that has strong attraction for the solvent, called the lyophillic group (hydrophillic group for the water or head group). This is known as an amphipathic structure. The amphipathic structure of the surfactant 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; the hydrophillic group is an ionic or highly polar group. Depending on the nature of the hydrophilic group (head group) (Rosen,1988), 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 dodecly 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, $RCOOCH_2CHOHCCH_2OH$ (monoglyceride of long-chain fatty acid).

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 film to liquid. So foam is a gas dispersed in a liquid.

The formation of a foam from a bulk involves the expansion of the surface area due to the work acting upon the system. As surface tension is the work involved in creating a new system, then the amount of new area formed will be greater 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 Fig. 2.1.

2.3 Structure of foam

The structure of foam is quite complicated. Foam consists of a thermodynamically unstable two-phase system of gas bubbles in a liquid. The structure of gas cell consists of thin liquid film and there are two-side film which are called the lamellae of the foam. The junction between three or more

gas bubbles is called the Plateau border or Gibbs triangles as seen in Fig. 2.2 (Rosen 1988).
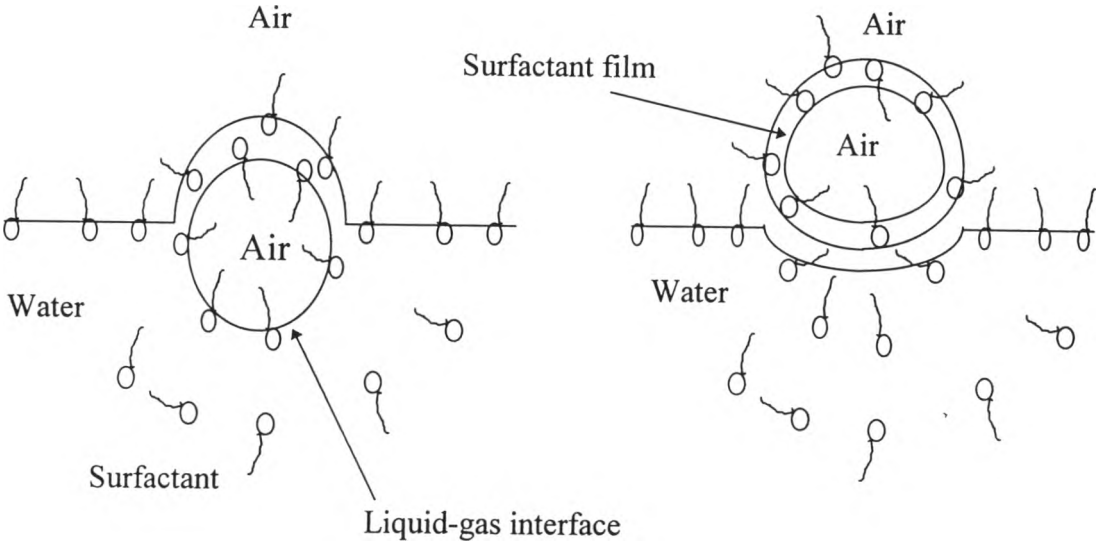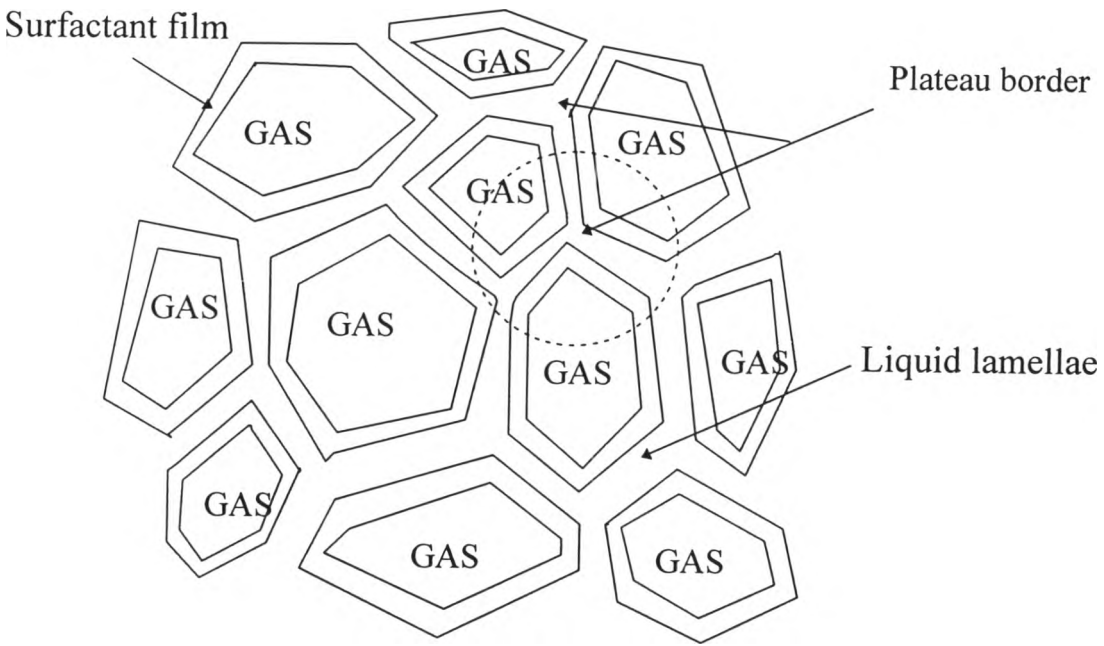

Fig. 2.1 Formation of foam.

Fig. 2.2 The structure of foam.

2.4 Foam stability

The stability of foam can be split into two factors, film elasticity and film drainage (Rosen,1988). 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. Both theories can be explained the foam formation because gravity causes liquid to drain out of the thin lamellae, and hence 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 Fig. 2.3.

The film drainage is the second factor that shows 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 foaming 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 also high therefore the drainage rate in the lamellae decreased with the amount of surfactant in the lamellae increased.
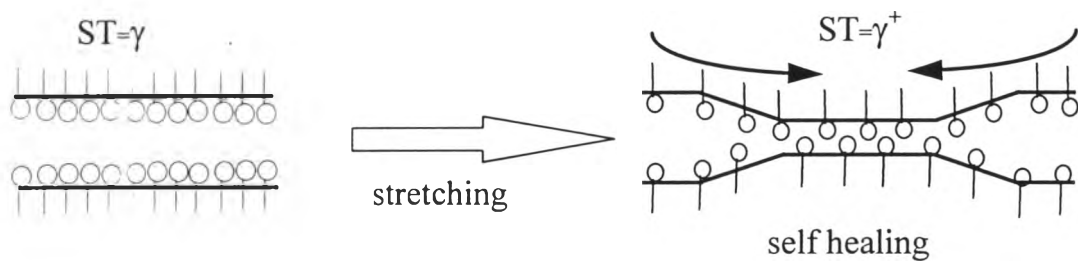
Drainage by surface tension difference depends on the existence of pressure difference at the various point in the lamellae because of the difference in curvature at the surface of the lamellae. The pressure difference (dP) quantified by Laplace is as follows:

$$dP = ST(\ 1/R_1 + 1/R_2)$$

where ST is surface tension and, R_1 and R_2 are the radii of the curvature of the liquid surface.
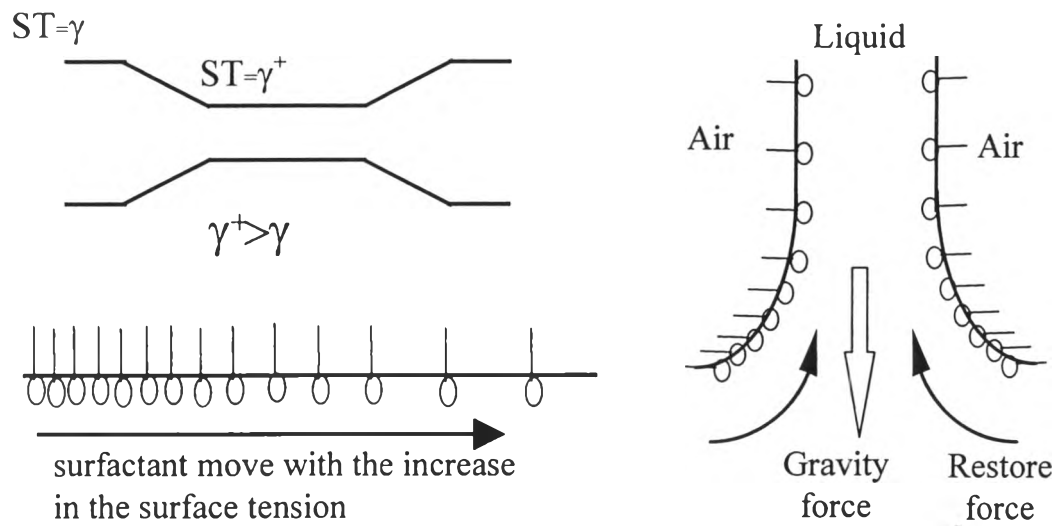
a) Marangoni effect

b) Gibbs film elasticity

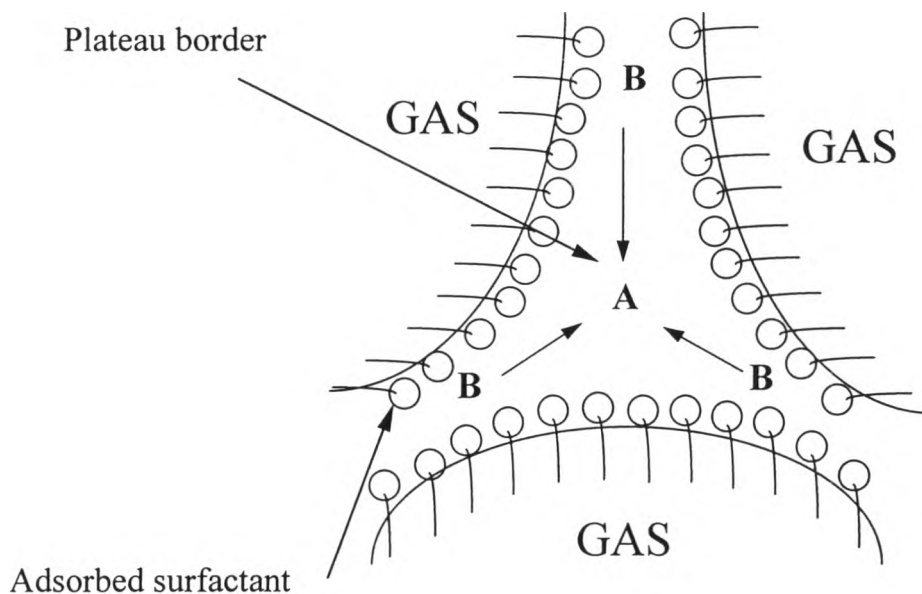Fig.2.3 The Marangoni effect and Gibbs film elasticity.

Plateau border

GAS

GAS

B

A

B   B

GAS

Adsorbed surfactant

Fig.2.4 Gas bubble.

The pressure difference causing drainage of liquid into the Plateau burder at point A from point B (Fig. 2.4). The greater surface tension the greater pressure difference and the greater liquid drainage, the lower stability of foam. Foam are 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. So that the stability of the film will depend on many factor that have effect on the film drainage such as type of surfactant, concentration of surfactant, temperature, etc. (Rosen,1988 and Porter,1994).

2.5 Foam Fractionation

The foam separation process is an adsorptive bubble separation technique that selectively separates surface-active compound in a solution, collects surfactant at the interface between the liquid and gas (Carrleson,

1992). This process is effective especially 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, 1979).

In foam fractionation, air is sparged to produce bubbles which rise to the top of liquid column producing foam as illustrated in Fig. 2.5a. As the bubbles travel through the liquid phase, surfactant adsorbs at the air-liquid interface as shown in Fig. 2.5b and 2.5c. When the air bubble emerges from a cell in the foam honeycomb (Fig. 2.5d), the thin liquid film in the foam (lamellae) is stabilized by the adsorbed surfactant (Sebba, 1987). Drainage of liquid in the lamellae due to the gravity, and surface tension difference cause the foam to eventually break or collapse (Rosen,1988). The collapsed foamate solution that is collected from the top of column has higher concentration of the surfactant than the initial solution. There are two modes of foam fractionation, simple mode (batch wise or continuous), and higher mode with enriching and / or stripping, as shown in Fig. 2.6 (Konduru,1992). In this work, a simple continuous mode of operation is used to recovery the surfactant from water.

Foam fractionation process has been widely studied for the purpose of removing colligends such as organic molecules (Berk et al., 1979), cations (Sil and Tabot, 1977 ; Grieves and Burton, 1987 anf Koutlemani et al., 1994) and anions (Grieves and Bhattacharyya, 1972 and Moussavi, 1994) from the aqueous phase by using surfactant as the collector. Many publications are available on difference modes of operation of a foam fractionation unit such as batch mode (Grieves et al., 1963 and Konduru, 1992), simple continuous mode

(Hsu and Maa, 1985), stripping mode (Grieves and Bhattacharyya, 1972), enriching mode (Lemlich and Lavi, 1961 : Brunner and Lemlich, 1963) and combined mode (Harper and Lemlich, 1965). The effect of such key variables as temperature, feed rate, pH, gas flow rate, feed concentration, foam height, and bubble diameter on the operation of both batch and continuous fractionation have been studied. There are a few publications addressing in surfactant recovery by foam fractionation as this work.
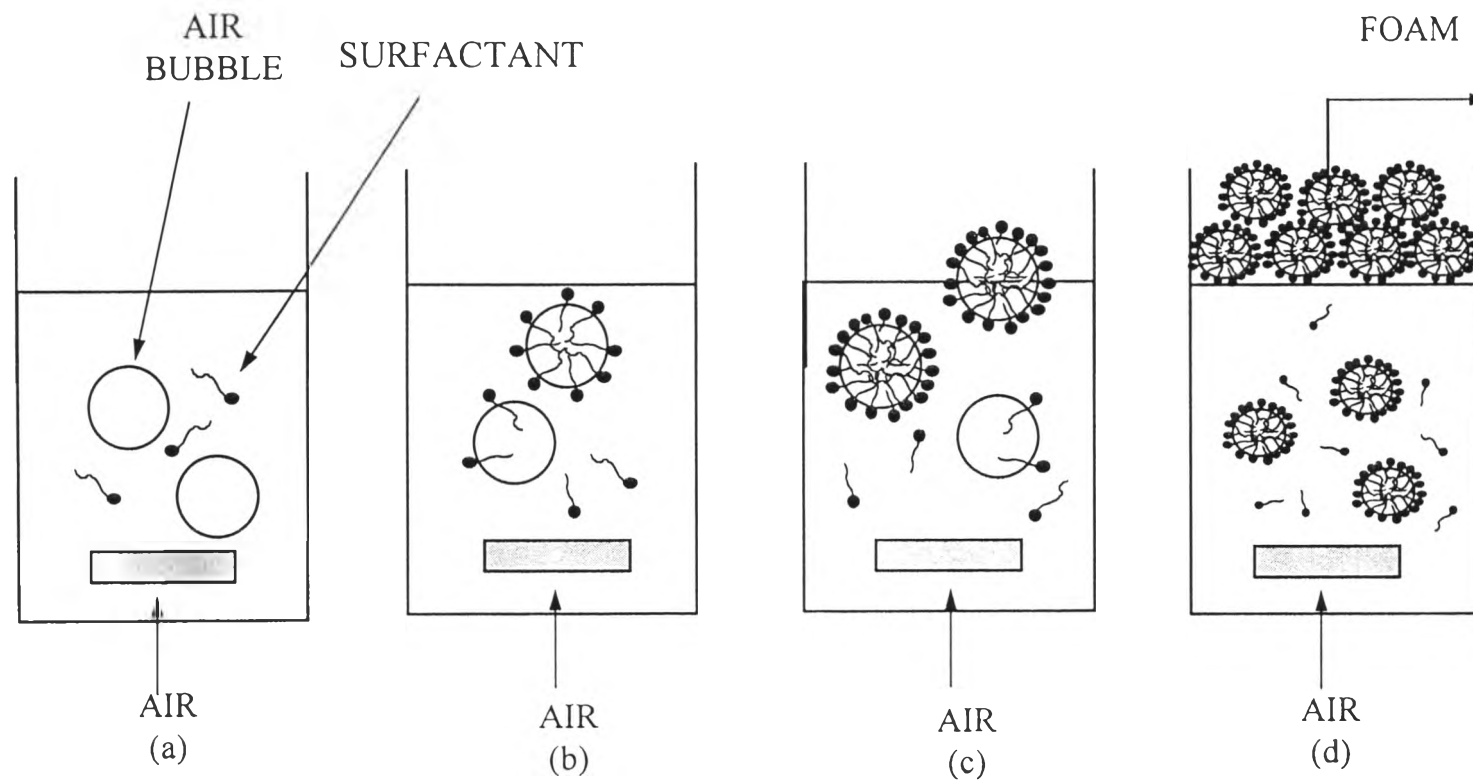
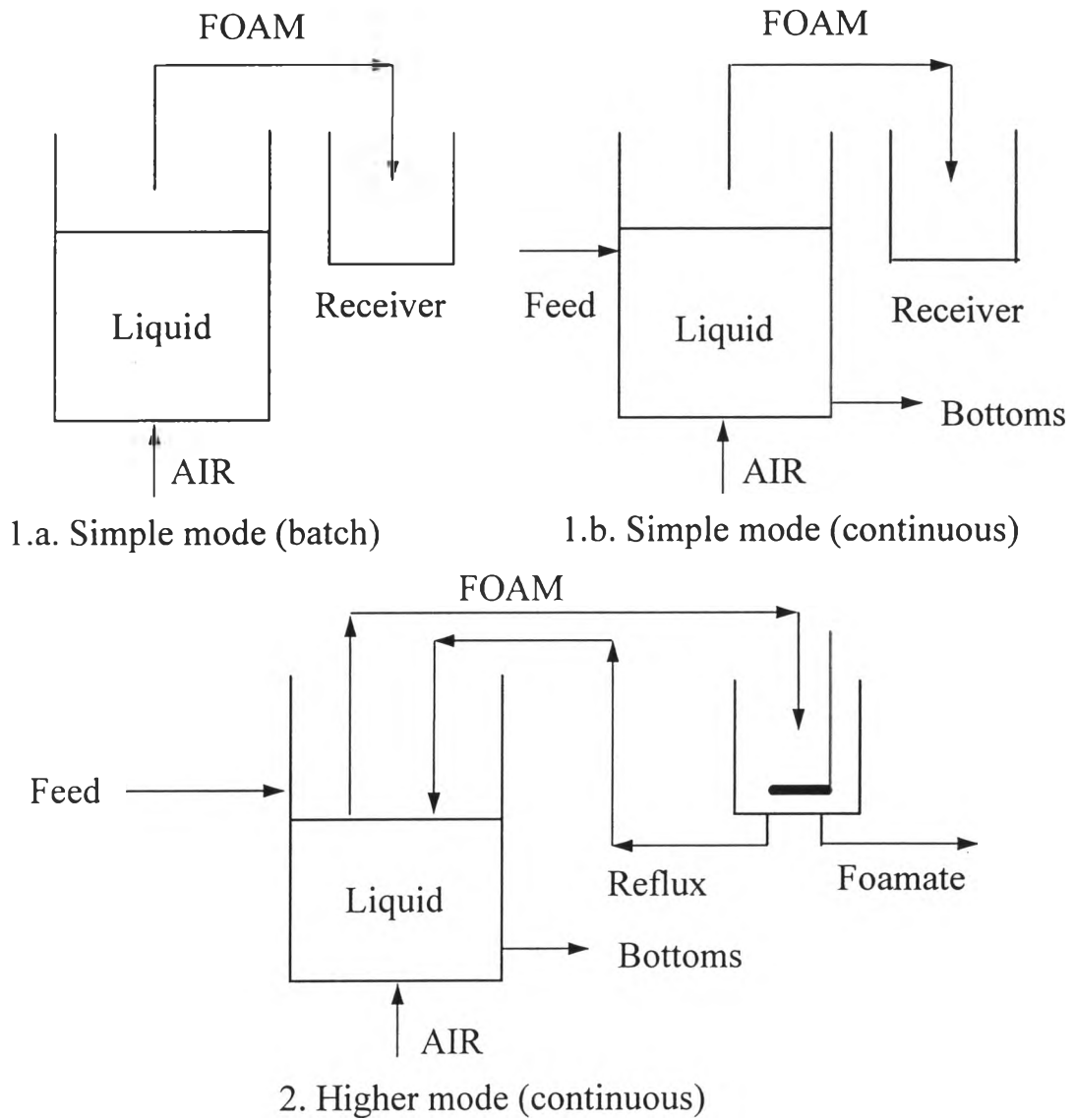Fig.2.5 Principle of foam fractionation.

Fig. 2.6 Types of foam fractionation.

1. Simple mode (batch wise or continuous)
2. Higher mode with enriching and/or stripping