CHAPTER II
LITERATURE SURVEY

2.1 Surfactants

A surfactant, a contraction of the term SURFace ACTive AgenT, is a substance that, when present at low concentration in a liquid. It tends not only to accumulate at surface but also change the properties of that liquid at a surface or interface.

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 Figure2.1. 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:

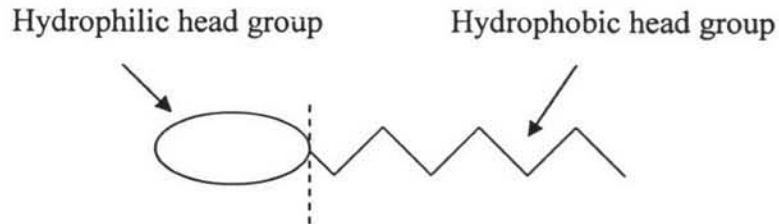Hydrophilic head group   Hydrophobic head group

Figure 2.1 Schematic of a surfactant molecule.

1. Anionic surfactants: The surface-active portion of the molecule bears a negative charge, for example, $RC_6H_4SO_3^-Na^+$ (alkylbenzene sulfonate), $C_{12}H_{25}SO_3^-Na^+$ (sodium dodecyl sulfate).

2. Cationic surfactants: The surface-active portion bears a positive charge, for example, $n\text{-}C_{16}H_{33}N(CH=CH)_2CHCl$ (cetylpyridinium chloride or CPC), $RN(CH_3)^+_3Cl^-$ (quaternary ammonium chloride).

3. Nonionic surfactant: The surface-active portion bears no apparent ionic charge, for example, $C_8H_{17}C_6H_4(OCH_2CH2)_{10}OH$ (polyethylene glycol octylphenyl ether; $OPEO_{10}$), $RCOOCH_2CHOHCCH_2OH$ (monoglyceride of long-chain fatty acid).

4. Zwitterionic surfactants: Both positive and negative charges may be present in the surface-active portion, for example, $RN^+H_2CH_2COO^-$ (long-chain amino acid).

2.2 Foam

2.2.1 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 (Rosen, 1988). The foam are unstable unless there are barriers to prevent coalescence when two gas bubbles touch (Sebba, 1987). The barrier is produced by the presence of a water-soluble surfactant.

The formation of 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 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 the 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 the surfactant carries a charge that is the same sign as that of the surfactant at the water surface, there will be repulsive force by the bubble. If it 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.
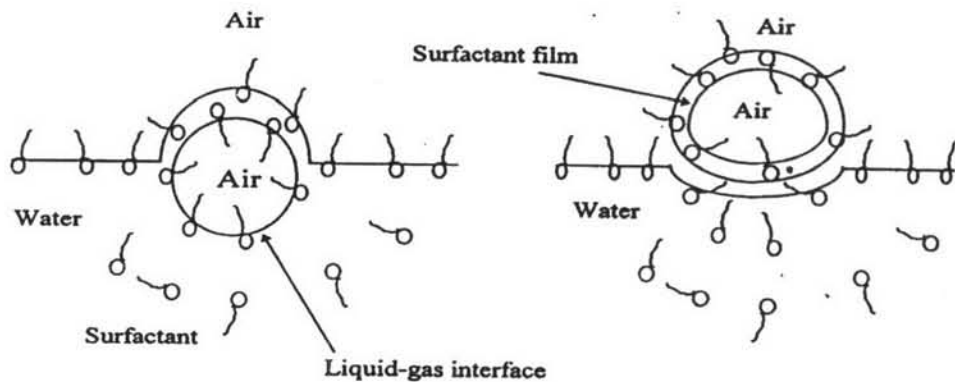
Figure 2.2 Formation of foam (Rosen, 1988).

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 that are celled 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 will play an important role in the drainage of water in foams (Rosen, 1988; Adamson, 1990).
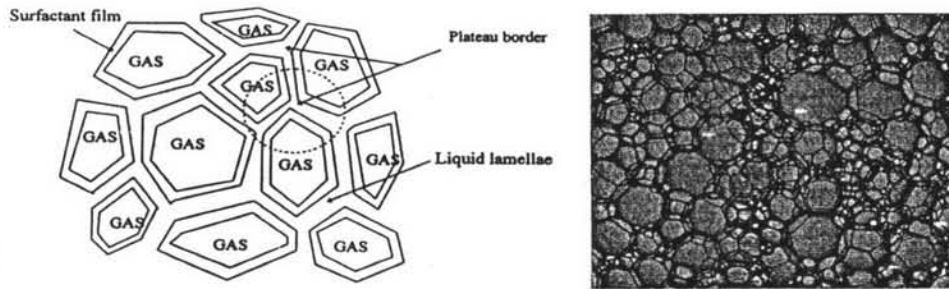
Figure 2.3 The structure of liquid foam (Rosen, 1988, Weaire, 2002).

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.
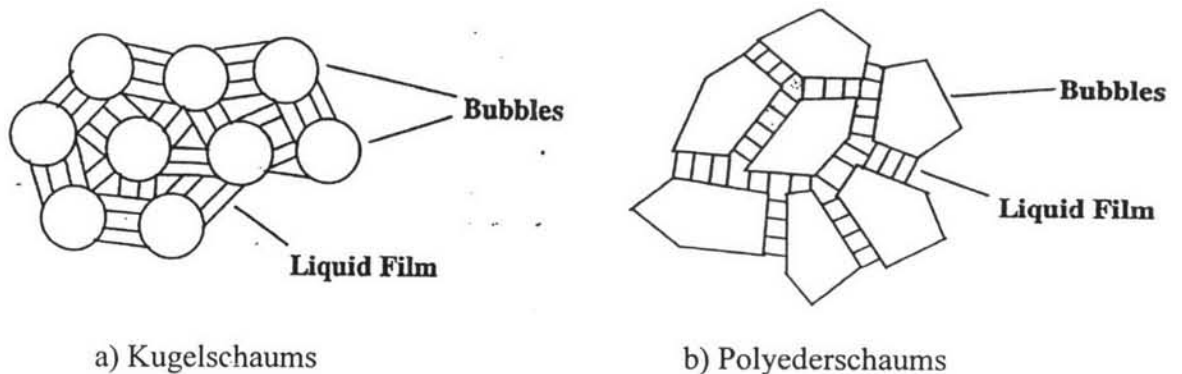

a) Kugelschaums

b) Polyederschaums

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.
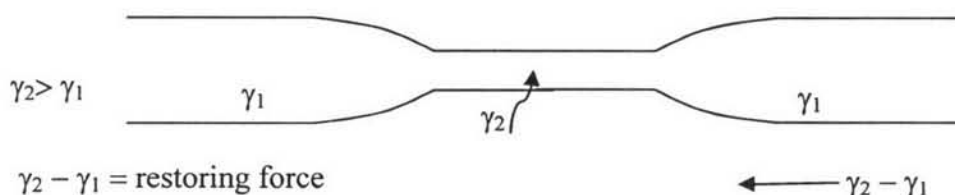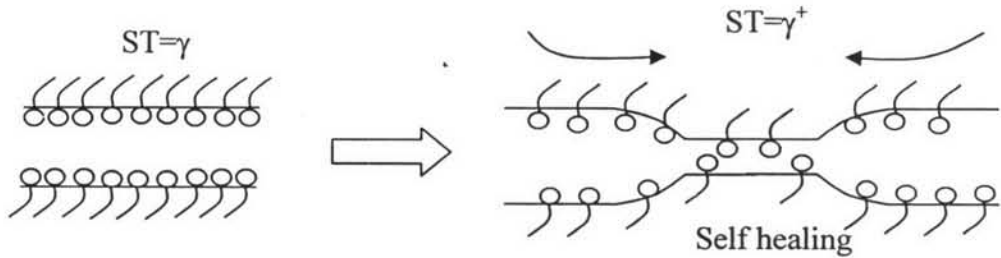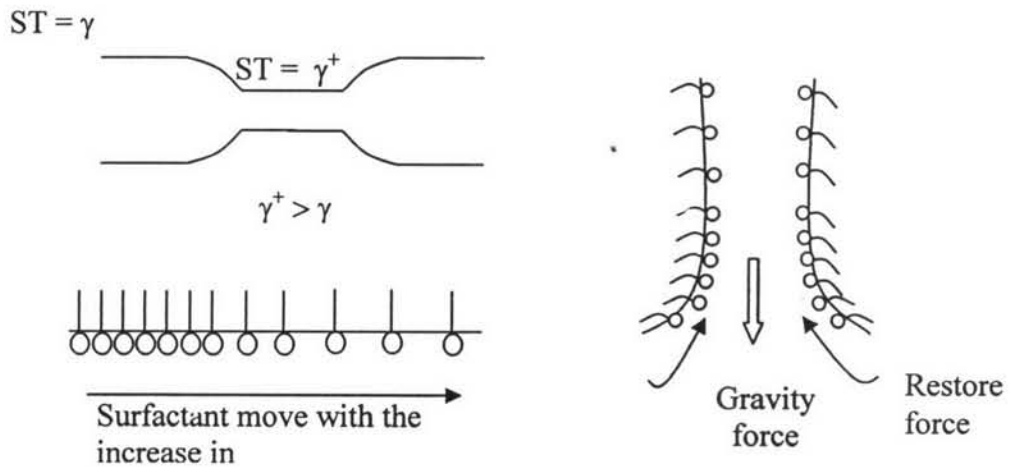

Figure 2.5 Stretch portion of foam lamella, illustrating mechanism of film elasticity.

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 occur 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;

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

where γ is surface tension.

R_A is the radii of the curvature of the liquid surface at point A.

R_B is the radii of the curvature of the liquid surface at point B.

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).
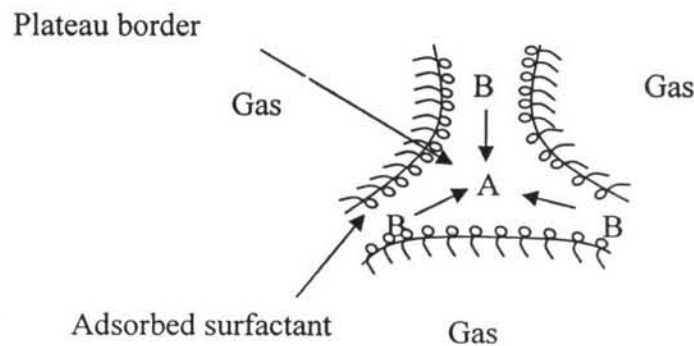

Figure 2.7 Liquid drainage in lamellae by curvature effect.

2.3 Foam Fractionation

2.3.1 Principle of Foam Fractionation

The foam separation process is an adsorptive bubble separation that describes a process where a species is adsorbed at an interface between a dispersed

phase (bubble) and a continuous phase. The dispersed phase with the adsorbed substance is collected (Carleson, 1992). The foam separation process can be divided into two types, froth flotation and foam fractionation as shown in Figure 2.8. Froth flotation separates insoluble materials by frothing, whereas foam fractionation separates soluble species by foams (Carleson, 1992; Okamoto and Chou, 1979).
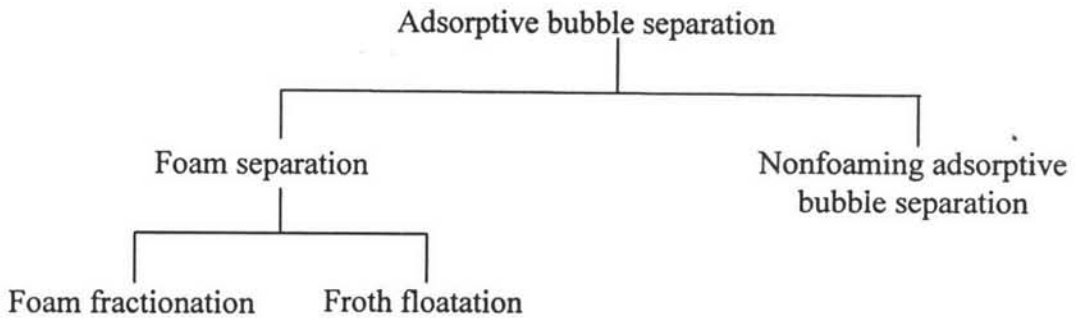
Adsorptive bubble separation

Foam separation

Nonfoaming adsorptive bubble separation

Foam fractionation   Froth floatation

Figure 2.8 Classification of bubble separation techniques.

In foam fractionation, air is sparged to produce bubbles which rise to the top of liquid column producing foam as illustrated in Figure 2.9a. As the bubbles travel through the liquid phase, surfactant adsorbs at the air-liquid interface as shown in Figure2.9b. and 2.9c. When the air bubble emerges from a cell in the foam honeycomb (Figure 2.9d), the thin 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. Foam fractionation can be classified into two modes: batch mode and continuous mode. In a batch operation, a solution of the surface-active species is stripped of the species by introduction of bubbles from a sparger. The rising foam is collected and coalesced to produce the overhead stream as shown in Figure 2.10a. 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 2.10b. Some of the overhead may be recycled analogous to a distillation column.
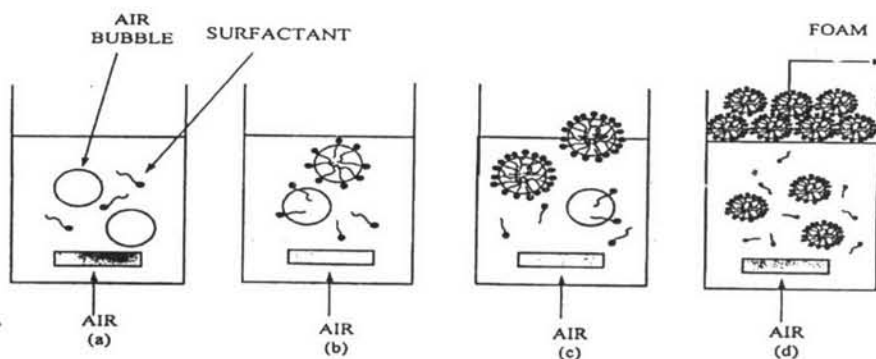

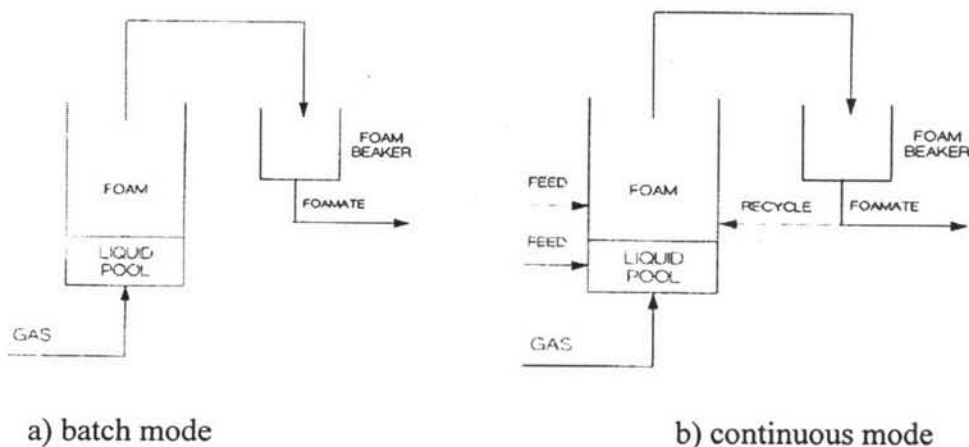**Figure 2.9** Principle of foam formation (Simmler, 1972).

a) batch mode   b) continuous mode

Figure 2.10 Experimental configurations for foam separation (Carleson, 1992).

2.3.2 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, Yamagiwa *et al.*, (2001) investigated the effect of external fomate reflux and temperature on foam fractionation of PVA. With rising temperature, the enrichment and separation factor increases. External foamate reflux

was essential for foam fractionation when treating a 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 contrinuous mode of foam fractionation to remove surfactant from water; two anionic surfactants (DADS and SDS) and one cationic surfactant (CPC) were studied. The effect of air flow rate, foam height, liquid height, surfactant concentration, and sparger 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 height had little effect on the separation process. The enrichment ratio decreases with increasing air flow and surfactant concentration, decreasing pore size of the sparger. Kumpabooth (1997) used the same surfactants as Tharapiwattananon and aiso 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 a 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 in 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 form water by using multistage foam fractionation with one to four stages operated. They found that enrichment ratio increased 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 surfactants from aqueous solution in both single (CPC and $OPEO_{10}$) and mixed systems ($CPC/OPEO_{10}$). 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 the changes in air and liquid flow rates. In single surfactant systems, both surfactant recovery and enrichment ratio obtained in the $OPEO_{10}$ system were higher than in the CPC system. Synergism was observed in the mixed surfactants system, which led to a total recovery of $OPEO_{10}$.