CHAPTER II
BACKGROUND AND LITERATURE REVIEW

2.1 Structure and Behavior of Surfactants

Surface active agents are materials that accumulate at surfaces and hence they can affect properties of those surfaces. A surfactant molecule usually consists of two main parts, a head group which is a hydrophilic or water liking group, and a tail group which is a hydrophobic or water hating group. In aqueous solution, the hydrophilic part, which is an ionic or highly polarized part, has a very strong interaction with water and tends to adsorb on hydrophilic surface. The hydrophobic part, which is usually a long chain alkyl group $(CH_2)_n$, has very little attraction for water and tends to increase the degree of order in water molecules around its insoluble part. The complex mechanism of the insolubility of the hydrocarbon chain in water involves both enthalpic and entropic contributions resulted from the unique multiple hydrogen-bonding capacity of water. There is a restructuring or re-orientation of water molecules around nonpolar solutes which disrupts the existing water structure and imposes a new and more ordered structure on the surrounding water molecules, giving a decrease in entropy.

The chemical structure of groupings suitable as the hydrophilic and hydrophobic portions of a surfactant molecule varies with the nature of the solvent and the conditions of use.

The classification of surfactants is based on the chemical structure of the hydrophilic group:

- Anionic – the surface-active part of the molecule has a long chain hydrophobe that carries a negative charge;
- Cationic – the surface-active part of the molecule carries a positive charge;

- Nonionic – the surface-active part of the molecule carries no charge;

- Amphoteric – the surface-active part of the molecule may carry a positive or a negative charge or both depending on the conditions of the solutions;

Anionic surfactants are used in greater volume than all other types of surfactants. The reason is the ease and low cost for manufacture of every practical type of detergents, the main application of surfactants. For optimum detergency the hydrophobic group is a linear paraffin chain in the range of C_{12}-C_{16}, and the polar group should be at the end of the chain. Hence the majority of water-soluble anionic surfactants available on a large scale are of the type:

$$CCCCCCCCCCCCC-X$$

X is the hydrophilic group which is ionized and can be:

Carboxylate (soap) $RCOO^-$

Sulphonate RSO_3^-

Sulphate ROS^-

Phosphate $ROPO(OH)O^-$

The sulphates are one of the most important classes of synthetic anionic surfactants. The properties of the sulphates depend upon the properties of the hydrocarbon chain and those of the sulphate group. In term of solubility which is a very important property of surfactant in aqueous solution, the alkali metal salts show good solubility in water. The addition of metal-sulphate salts also shows the "salt effect" that increases the viscosity of dilute solutions but decreases the viscosity of concentrated solutions. The disadvantage of sulphates is their poor hydrolytic stability. Below pH 3.5, sulphates are easily

hydrolyzed and this acid hydrolysis releases sulfuric acid which catalyses the reaction itself (Porter, 1994).

2.2 Foams

Liquid foams are agglomerations of gas bubbles separated from each other by thin liquid films. Foams are not thermodynamically stable but some equilibrium properties of liquid such as surface tension and contact angle can be used for the explanation about foams. In kinetic terms, the concentration of surfactant is a very important factor affecting foam properties by its influence on the foam lifetime. A sharp distinction can be drawn between an unstable foam or transient foam with very short lifetime and a metastable foam or permanent foam with a lifetime of hours or days.

Spherical foams or Kugelschaum with thick films of viscous liquid are generated at the initial state of foam formation. They are later transformed into polyhedral foams or Polyederschaum with thin flat walls by the gravitational force. The polyhedra are mostly regular dodecahedra (Pugh, 1996) and the junction points of the interconnecting channels are known as Plateau border. In terms of foam stability, disproportionation, which is the diffusion of gas from smaller bubbles into bigger bubbles, occurs in a great extent only in Kugelschaum structure (Rosen, 1988). Foam drainage process is strongly associated with the planar thin liquid films and the Plateau border of polyhedral structure. Therefore the difference between properties of these two types of foams should be carefully considered in the experiments about foams.

2.3 Foam Stability

The foam stability is determined by the adsorbed surfactant which controls the mechanical-dynamical properties of the surface layer but this is generally only in the case of thick films (>100 nm). For well drained quasi-foam films, intermolecular forces become dominant and foam stability must be discussed in terms of the common black films and Newton black films.

Two important properties of monolayers, surface viscosity and surface elasticity, are measurable parameters for foam stability. Surface viscosity reflects the speed of the relaxation process which restores the equilibrium in the system (Prud'homme, 1996). Surface viscosity has a close relationship with bulk viscosity that can be expressed as a function of surfactant concentration. At high surfactant concentration, the surface viscosity is high and therefore the drainage rate in the lamellae decreases with the amount of surfactant in the lamellae.

However, it is very important to note that the system can exhibit a maximum foaming behavior with increasing surfactant concentration. This behavior can be explained by the understanding in film healing mechanisms. When the foam film is subjected to an external force, a new area is created at the thinning surface leading to an increase in local surface tension. Restoring forces bring the surfactant molecules back to the thinning region with high surface tension. Nevertheless, foam film healing occurs only if the restoring surfactants are brought from the adjacent regions of the film surface (Marangoni effect). In the case of the solution being too concentrated, the differential tension relaxes too rapidly because the available surfactant molecules in the lamella diffuse to the surface and the foam film remains dangerously thin.

In fact, the Marangoni effect, which tends to oppose any rapid displacement of the film surfaces, is superimposed on the Gibbs elasticity or

surface elasticity effect. They both show the effect of surface tension gradient on foam stability by causing the liquid to flow from the thicker section to the thinner section.

2.4 Froth System

The terms foams and froths are often used interchangeably, but it is more usual to refer to the gas-liquid macrocluster systems where the broken structure leaves a homogeneous aqueous phase as foams. Froths usually contain dispersed solid particles, so that the broken structure leaves a heterogeneous system. A froth system cannot be considered as a simple combination of independent aqueous films because it is a much more complex system. The rupture of single froth film can lead to the destruction of an adjacent film, causing local fluctuations in pressure and surface tension. This can lead to a so-called collective effect (Pugh, 1996).

Partially hydrophobic dispersed particles can cause an increase or decrease in foam stability. Providing they are not fully wetted then small particles may become attached to the interface and give some mechanical stability to the lamellae. If they are completely dispersed, they may cause an increase in the bulk viscosity. On the other hand, larger particles having a higher degree of hydrophobicity usually exhibit a finite contact angle (Garrett, 1992) and cause destabilization of froth by creating the penetrated interfaces when adhering to interfaces.

There has been an attempt to emphasize the importance of wetting by showing that an increase in contact angle can cause an increase in defoaming action. However, many experiments have difficulties in measuring contact angles and evaluating the influence of shape, size and roughness of the particles in foaming system because precipitates are often found in the form of amorphous particles.

2.5 Literature Review

Rodriquez *et al.* (1995) studied precipitation in solutions containing mixtures of SDS and sodium octanoate and found that the hardness tolerance of the anionic surfactant increases when the soap is added.

Foaming of detergents having a straight hydrocarbon chain containing 14 or more carbon atoms was found to give stable foam in the presence of small amounts of calcium palmitate by Peper (1958). Bhakta and Ruckenstein (1995) stressed that the method used to generate foams strongly influences the drainage process of standing foams. Ross (1996) stated that foam inhibitors also act as defoamers, but the reverse is not generally true. Angarska *et al.* (1997) studied the effect of magnesium ions on the properties of SDS foam film and found that coions also affect the film properties. Cohen *et al.* (1993) measured foam height and foam stability of LAS solutions according to the Ross-Miles test at a constant temperature. Experiments with varying amount of calcium concentration also show that foam height is almost independent of calcium concentration until a critical calcium concentration is reached. The results show that foam stability does not decrease beyond the CMC in the presence of calcium due to the higher stability of the calcium micelles than that of the sodium micelles. Beyond the CMC, the molecular structures or micelle can form within the thin film and the stepwise drainage mechanism known as stratification was demonstrated by many researchers. The flow of micelles layer into the Plateau borders was given by Ivanov (1988) as the reason of stepwise thinning. Study by Patist *et al.* (1998) shows that low stability micelles give higher stabilizing effect than high stability micelles.

Krustev and Muller (1999) studied the effect of film free energy on the gas permeability of foam films and found that the thicker common black films have higher permeability than the thinner Newton black films. This can

be attributed to the role of surfactant adsorption density at the film surface in the presence of counter ions.

Wang *et al.* (1999) used the sequence of video frames to show that defoamer lenses in the Plateau borders are the active foam-breaking agents causing coalescence between two air bubbles. Koczo *et al.* (1994) found that mixed type antifoams are much more effective than oil drops or solid particles alone because pseudoemulsion films is ore stable without hydrophobic particles. They also found that oil lenses could help the hydrophobic particles to penetrate deeper into the liquid films. Aveyard *et al.* (1994) suggested that in some systems, a contact angle greater than 90° of hydrophobic particles is needed for effective foam reduction. This is the result from the collection of particles in Plateau border regions which reduce the rate of film drainage.