CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Structure and Behavior of Surfactants

Surfactants is an abbreviation for surface active agent, which literally means active at a surface (Porter, 1994). A surfactant molecule contains two parts: one is hydrophilic or "water-loving", and the other is hydrophobic or "water-hating". The hydrophilic portion of the molecule (the "head group") is usually an ionic, highly polar group, or nonionic polar group. The hydrophobic "tail group" portion of the molecule is usually a single or double hydrocarbon chain with various degrees of unsaturation or substitution (Lange, 1994). Due to the presence of two structurally dissimilar groups within a single molecule, surfactants or aggregates of molecules called micelles when the concentration of the surfactant solute in the bulk solution exceeds a limiting value, the so-called critical micelle concentration (CMC). Surfactants are usually classified primarily by the chemical type of their hydrophilic part; anionic, cationic, zwitterionic and nonionic surfactants.

Anionic surfactants are surfactant molecules whose polar group is negatively charged such as sodium dodecyl sulfate, $(CH_3(CH_2)_{11}SO_4^-Na^+)$. They are used in practically every type of detergent, the main application of surfactant.

Nonionic surfactants are surfactants that do not have a charged group. Hydrophilicity in nonionic surfactants is provided by hydrogen bonding with water molecule. On heating ethylene oxide derivatives, the biggest group of nonionic surfactants, dehydration takes place and the product comes out of

solution, the temperature at which this takes place is known as the cloud point. Generally, nonionic surfactants are employed as foam stabilisers for anionics, but they can be defoamers when they are practically insoluble (i.e. at or above their cloud point) in the system (Prud'homme, 1996).

In practice, nonionics are usually used in blends with anionics for heavy-duty performance, with the anionics in the larger proportion. More recently, the amount of nonionics has increased relative to the anionics in lower temperature powder detergents. In liquid detergents the nonionics are used at even higher concentrations.

2.2 Mixed Nonionic/Anionic Surfactant Solutions

Most surfactants used in practical applicants are mixtures. Hence, understanding both the structure and properties of mixed micelles containing anionic and nonionic surfactants is essential for many industrial uses of surfactants. Mixtures of surfactants frequently show synergistic interactions in solution (Holland and Rubingh, 1992). This synergy can be manifested as enhanced surface activity, spreading, wetting, foaming, detergency, and many other phenomena (Ogino and Abe, 1993).

Recently, it has been reported that the effect on surface activity of a mixed surfactant system is superior to that of a surfactant alone. Ogino *et al.* (1984) have reported the surface tension measurements of aqueous solutions of a mixed surfactant system: sodium 3, 6, 9 - trioxaicosanoate (ECL, an anionic surfactant which has both nonionic and anionic properties) – hexadecyl polyoxyethylene ether (POE, nonionic surfactant). They found that the composition of mixed micelles changes with the mole ratio of surfactants and the surface charge densities of counterions of mixed micelles decreases with increasing mixed micellar sizes.

Micelle formation by pure nonionic surfactants and their mixtures has been investigated by Abe *et al.* (1985 and 1992). They have found that in the single component nonionic surfactant system, alkyl polyoxyethylene ethers (C_mPOE_n: where m = 12, 14, and 16, at n = 20; n = 10, 20, 30, and 40, at m = 16), the hydrodynamic micellar size increases with an increase in alkyl or poly (oxyethylene) chain lengths. In the case of the $C_{16}POE_{10}$ - $C_{16}POE_{40}$ mixed surfactant system, the hydrodynamic micellar size increases with an increase in the mole fraction of $C_{16}POE_{40}$ and remains constant above a mole fraction of 0.5.

There has been a great deal of recent effort to model and understand these mixed micelles. However, there is an extreme paucity of data on a key parameter of mixed micelle formation: counterion binding. Rathman and Scamehorn (1984 and 1986) suggested fractional counterion binding on mixed micelles of ionic-nonionic surfactants based on the electrostatic model. As a general phenomenon they observed that at low ionic surfactant mole fraction in the mixed micelle the counterion binding fell rapidly with decreasing ionic content.

Further study on the structure and dynamics of mixed micellar systems have been investigated by McCarroll *et al.* (1998). They studied the intramicellar fluidity of mixed micellar solutions containing nonionic surfactants (Igepal CO-630 and Triton X-114) and added sodium dodecyl sulfate by using fluorescence anisotropy of perylene. They found that while the addition of small amounts of SDS significantly increased cloud points, the internal structure of nonionic micelles remained essentially intact. At higher SDS concentrations, the perylene anisotropy decreased smoothly, indicating that the movement of the probe away from the palisade layer of the micelle and/or an increase in the core fluidity.

2.3 Foam Formation

Foam is a gas dispersed in a continuous liquid phase. The dispersed phase is sometimes referred to as the internal (dispersed) phase, and the continuous phase as the external phase (Michael and Irene, 1993; Pugh, 1996).

As a general rule, a foam is not generated in a pure liquid phase. A surfactant that strongly adsorbs at the air interface is necessary in order to produce a foam in aqueous solution. Foam consists of a thermodynamically unstable two-phase system of gas bubbles in a liquid. Foam is generated by air forming spheres in the liquid (spherical foam) but this then forms honeycomb foam with relatively thick lamellae between the cells as shown in Figure 2.1.
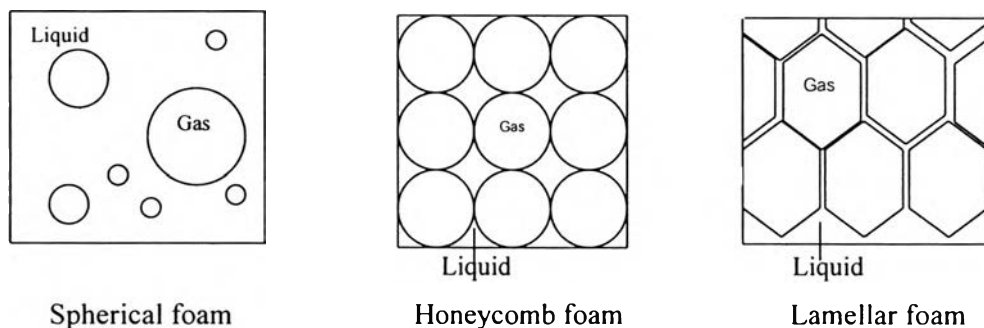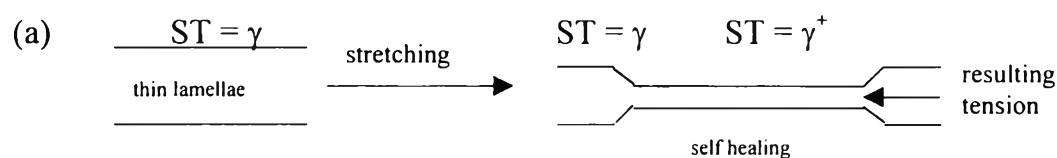

| Spherical foam | Honeycomb foam | Lamellar foam |

Figure 2.1 Different kinds of foam.

The formation of a foam from a bulk liquid involves the expansion of the surface area due to the work acting upon the system. Since surface tension is the work involved in creating a new surface, the amount of new area formed (i.e. the foam) will be greater the lower the surface tension. Thus, the reduction of surface tension by the surfactant is the primary requirement of foam formation (Porter, 1994; Schick, 1966).

The Gibbs surface elasticity and the Marangoni effect are two mechanisms responsible for the operation of the film elasticity. Gibbs effect is

due to the increase in surface tension with the decrease in the surfactant concentration below CMC. Marangoni effect depends on the time required for surface tension to obtain its equilibrium because the initial surface tension of a new surface is always greater than the equilibrium as shown in Figure 2.2. The two theories are dependent on concentration for maximum foaming but only operate in dilute solution. Therefore, there have been many studies to show that foam is at a maximum at about the CMC (Rosen, 1989).
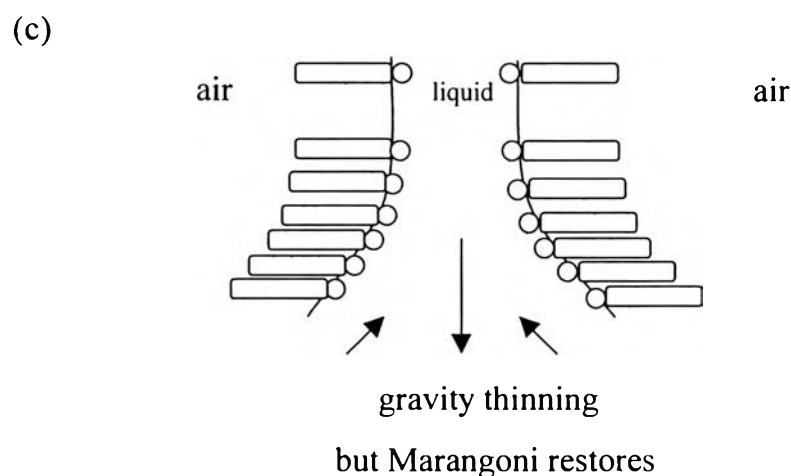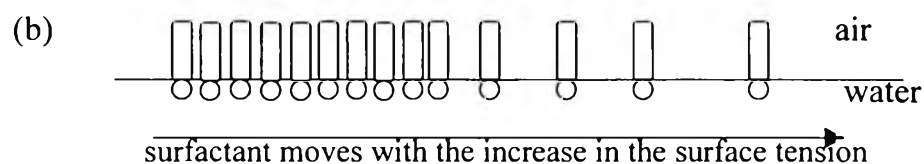
Gibbs film elasticity

(a)

$$ST = \gamma$$

thin lamellae

stretching

$$ST = \gamma \qquad ST = \gamma^{+}$$

resulting tension

self healing

Marangoni

(b)

air

water

surfactant moves with the increase in the surface tension

(c)

air   liquid   air

gravity thinning
but Marangoni restores

Figure 2.2 Gibbs film elasticity and the Marangoni effect.

2.4 Foaming Properties

It is well known that the persistence of foam films is promoted by the presence of surfactants in the foaming solution. In foaming, correlation between surfactant structure and foaming in aqueous solution requires a distinction between the efficiency of the surfactant, its bulk phase concentration, and its effectiveness. Therefore, in comparing the foaming properties of different surfactants, the terms foamability and foam stability must be clearly defined. The amount of foam formed under a given condition is a measure of the foamability, and the decay rate of a foam volume is a measure of foam stability. Since most of the foaming data have been obtained by the use of Ross-Miles method (Ross, 1953), the correlation discussed here is based mainly on data obtained by that method. The general concept that anionic surfactants are better foamers than nonionic surfactants is limited to specific conditions, i.e. household detergency process. A major difference between the concentration dependence of foam properties of nonionic surfactants and ionic ones is that, with the latter, the electrolyte concentration increases with the surfactant concentration because the surfactant is itself an electrolyte. Hence, the electrostatic repulsion will decrease rapidly with increasing surfactant concentration and film thinning will also increase. In contrast, with nonionic surfactants, the electrolyte concentration will be negligible over the entire concentration range (Schick and Schmolka, 1987).

Koczo and Racz (1991); Koczo et al. (1994) studied the foaming properties of liquids by characterizing their foamability which was defined as the foam volume obtained from a unit volume of liquid. They investigated the relations between the different parameters of foam beating and the properties of the foams formed by measuring the expansion ratio and drainage rate of the foams formed. The surfactant concentration was measured by high-

performance liquid chromatography (HPLC). They found that the beater did not destroy the foam when its speed was increased up to a certain limit, but it redispersed the bubbles. A new method to estimate the stability of short-life foams was studied by Iglesias et al. (1995). It was found that, under certain starting conditions, short-life foam decay exhibited a linear variation in the foam column height with the logarithm of the elapsed time. Raymundo et al. (1998) reported a methodology to evaluate foaming capacity and stability. The initial overrun value [(foam volume – volume of solution)/volume of solution*100] is taken as the measure of foamability. The foam stability can be evaluated from the plot of overrun versus time.

The stability of aqueous foams can be significantly enhanced by the addition of a small amount of water-soluble polymer. Sita Ram Sarma et al. (1988) reported that the addition of water-soluble agent increases the bulk viscosity and thereby decreases the rate of drainage. It is also found that the decrease in drainage half-life and the increase in initial drainage rate are gradual with the increase in temperature, Pradhan et al. (1990). Further studies have been reported by Pradhan and Khilar (1994). It was found that, without an additive, the foam stability increased significantly with the increase of generation pressure due to the decrease of bubble size of foam, the foam was produced in a packed bed. However, it changed weakly with the change in generation pressure for foams with polymer additives.

The foaming properties of modified nonionic surfactant have been studied by Colin et al. (1997). They have shown that small chemical modifications of the molecule have huge effects on the foaming properties of the solution. In the concentrated solutions, the reduction of the foamability of nonionic surfactants is related to the existence of the cloud point. For dilute solutions, a long conformational rearrangement at the surface is responsible for the decrease of the foaming ability.

A number of relatively recent studies have shown that the addition of a small amount of certain nonionic surfactants to anionic detergents enhanced foam stability. Schick and Fowkes (1957); and Sawyer and Fowkes (1958) reported that the additives which lowered the CMC the most were in general the most effective for enhancing foam stability by a study of their mixed micelles. Furthermore, it was suggested that the most stable foams were found with detergent additive pairs having 60-90% of additive in the adsorbed monolayers. The requirements for preferential adsorption of additives are the same as that found for foam stability. Solutions of the detergent (without additive) should have a high surface tension, the additive should give water a low surface tension, and should depress the CMC of the detergent.

The stability of micelles with antifoaming efficiency has also been discussed by Jha *et al.* (1999). The addition of antifoaming agents to SDS solutions shows two opposing effects depending on concentration. The antifoaming agents can stabilize the SDS micelles at lower concentrations and in turn act as foam inhibitors. On the other hand, beyond a critical concentration, the antifoaming agents destabilize the micelles (smaller relaxation time), which begin to improve the foamability of SDS solutions. Nikolov and Wasan (1989); and Nikolov *et al.* (1989) have theoretically and experimentally showed that the process of destabilization of foam films by mixed (silica-silicone oil) antifoam drops as observed with a high-speed video camera. The drops formed oil bridges which stretched with time and eventually ruptured the foam films.

2.5 Cloud Point

The sudden onset of turbidity of a nonionic surfactant solution on raising the temperature is called the cloud point. At a somewhat higher

temperature the solution begins to separate into two phases: the surfactant rich phase and the surfactant poor phase. After the phase separation has been completed, the concentration of the surfactant is low in the coexisting water-rich phase because there are few micelles present (Schick, 1966).

The hydration of ether oxygens of the polyoxyethylene group is generally believed to be the main factor in keeping the nonionic surfactant in solution. The increase in temperature causes partial dehydration and finally results in the separation of the surfactant-rich phase. Nonionics having a longer polyoxyethylene group show a higher cloud point by virtue of a greater capacity to hydrate.

The cloud point is rather insensitive to the concentration of the surfactant itself, but is appreciably influenced by the presence of certain additives. Recent investigations by Valaulikar and Manohar (1985), Sadaghiania and Khan (1991) have shown that electrolytes suppress the cloud point in proportion to their concentrations. An electrolyte of lower lyotropic number depresses the cloud point more effectively. Further studies have been carried out by Marszall (1988), the cloud point of mixed ionic-nonionic surfactants (sodium dodecyl sulfate (SDS) – Triton X-100) is drastically lowered by a variety of electrolytes at concentrations that are considerably lower than those affecting the cloud point of nonionic surfactants alone. It is indicated that the factors affecting the clouding phenomena of mixed surfactants at very low concentrations of ionic surfactants and electrolytes are primarily electrostatic in nature. The effect of oilfield chemicals on the cloud point of nonionic surfactants has been reported by Al-Ghamdi and Nasr-El-Din (1997). Alkalis caused a sharp drop in the cloud point of nonionic surfactants. This effect was enhanced in the presence of sodium chloride. Anionic and cationic polymers depressed the cloud point of nonionic surfactant. Sodium dodecyl sulfate (SDS) raised the cloud point of neutral and alkaline solutions

of TX-100 at low sodium chloride concentrations only. Nakama *et al.* (1990) have reported that the liquid-liquid phase separation phenomenon was observed around an equimolar mixture of anionic and cationic surfactants. It can be identified with the cloud point, which is shown by nonionic surfactants.

The ideas on the cloud point phenomena have been extended by Aveyard *et al.* (1990). They have shown that nonionic surfactants above their critical micelle concentration in aqueous solution undergo phase separation at the cloud point as the temperature is raised as a result of concomitant changes in micellar size, shape and interactions.

It is well known that the foamability of nonionic surfactants is reduced above the cloud point temperature. Cohen *et al.* (1993) have proposed that the loss in foam stability of nonionic surfactant solution ($C_{10}E_4$) is due to the antifoam action of the droplets of the surfactant-rich phase which bridge the foam films made from the surfactant-poor phase and produces the rupture of these films.

In addition to exploring a novel cloud point foaming technique to separate nonionic surfactant from aqueous solutions with a wide range of surfactant concentrations, the phase transformation of nonionic surfactant micelles at the cloud point which changed the foaming at room temperature has also been reported by Shen (1997).