

## **CHAPTER II**

### **BACKGROUND AND LITERATURE SURVEY**

#### **2.1 Surfactants**

Surfactants, a contraction of the phrase SURFace ACTive AgenNTs, are materials that tend not only to accumulate at surfaces but change the properties of those surfaces (Clint, 1992). Surfactants have an amphipathic structure consisting of a structural group that has very little attraction for the solvent, known as a lyophobic group (hydrophobic group in case water is the solvent) or tail group, attached to a group that has strong attraction for a solvent called the lyophilic group (hydrophilic group for water) or head group.

In a highly polar solvent such as water, the hydrophobic group is usually a long-chain hydrocarbon whereas the hydrophilic group is an ionic or highly polar group. Surfactants can be classified in many different ways. By indicating its polarity which depends on the nature of the hydrophilic group, surfactants can be classified as anionic, cationic, zwitterionic, and nonionic surfactants.

#### **2.2 Foam**

##### **2.2.1 Foam Formation**

Foam is a gas dispersed in a liquid. It 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 of liquid. In a foam, gas bubbles are separated from each

other by thin liquid films, the liquid being the continuous phase. Foams would have no stability unless there is a barrier to coalescence when two gas bubbles touch. This barrier is provided by surfactant and the repulsion between surfactant layers sometimes called the disjoining pressure. This may be due to the electrostatic repulsion in ionic surfactant or steric hindrance in nonionic surfactant. Therefore the surfactant is required in foam formation and stabilization because it is adsorbed at the interface between the air bubbles and the thin liquid film as shown in Figure 2.1.

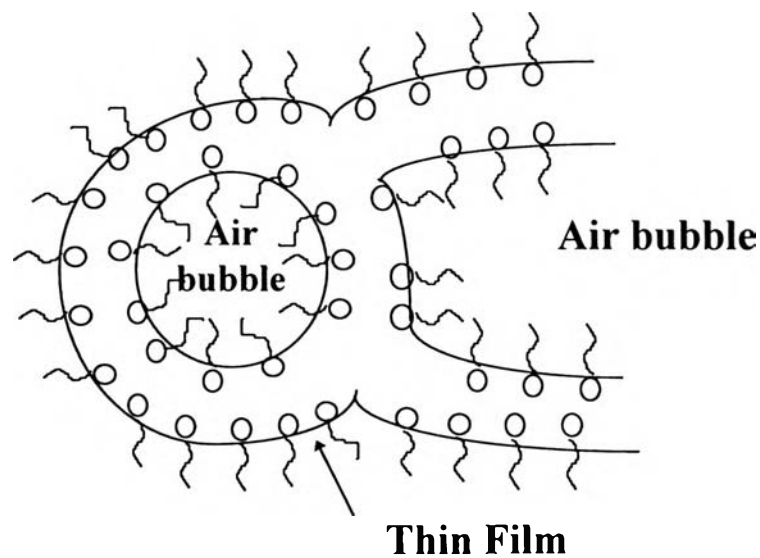


Figure 2.1 Formation of foam.

### 2.2.2 Foam Structure

The structure of foam is quite complicated. Foam consists of a thermodynamically unstable two-phase system of gas bubbles in a liquid. The two-sided liquid films are called the lamellae of the foam. Where three or more gas 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 2.2.

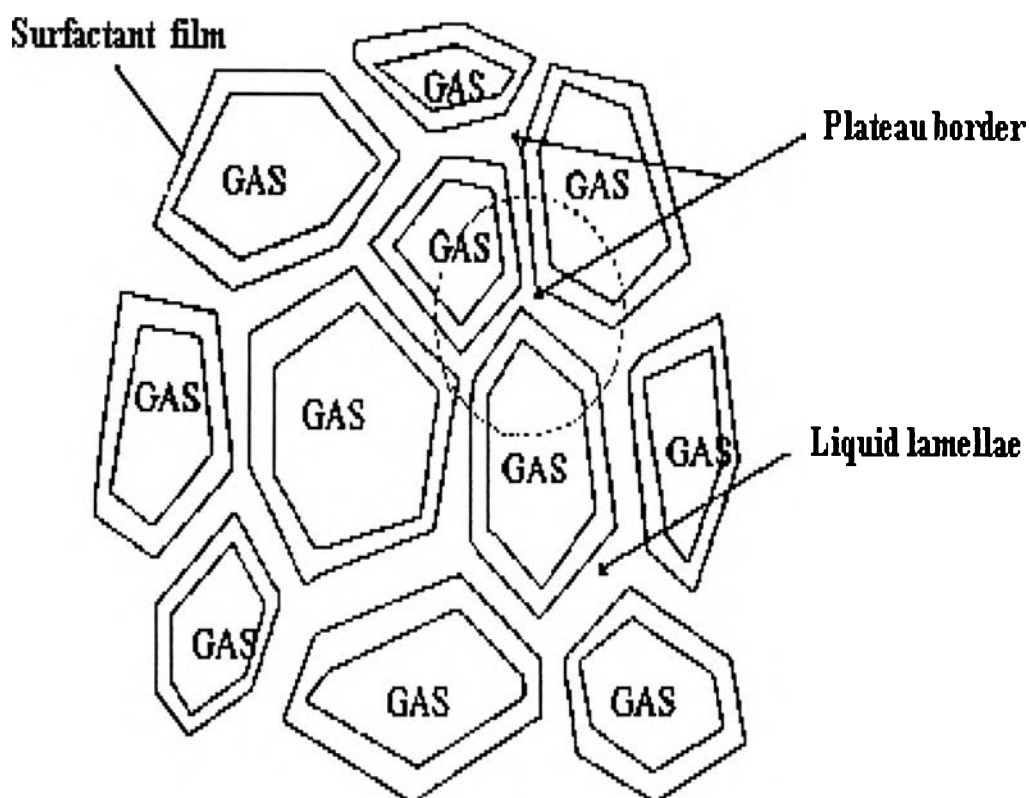


Figure 2.2 The structure of foam.

Foams can be classified into two types, kugelschaum and polyederschaum. The kugelschaum foam has spherical shape and small size with a relatively low gas volume fraction, it has rather thick liquid film. The second type, polyederschaum, contains mostly gas phase separated by thin films or laminas. The foam has polyhedral shape and consists of plane-parallel films joined by channel called plateau border. The two types of foam are shown as Figure 2.3 (Prud'homme, 1996 and Adamson, 1990).

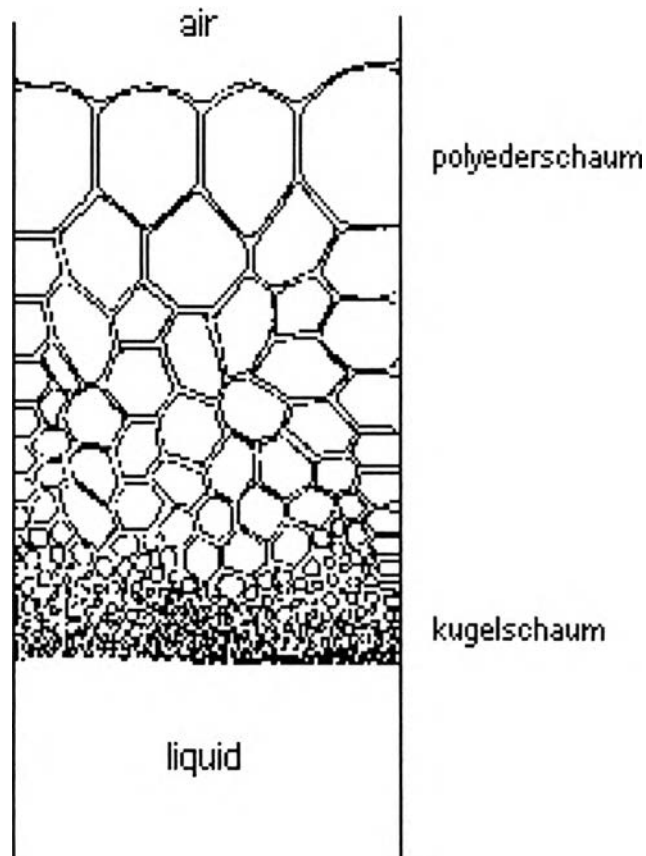


Figure 2.3 The two types of foam : polyederschaum, kugelschaum.

### 2.2.3 Foaming Properties

The foaming properties of liquids are often characterized by their foamability and it is an important characteristic of surfactant solutions. In foaming as in other surface properties, correlation between surfactant structure and foaming in aqueous solution requires a distinction between the efficiency of the surfactant, its bulk phase concentration required to produce a significant amount of foam, and its effectiveness, the maximum foam height obtained with the surfactant solution regardless of its concentration. Distinction must also be made between foam production, measured by the height of the foam initially produced, and foam stability, the height after a given amount of time.

Therefore, in comparing the foaming properties of different surfactants, the term foamability must be clearly defined. In addition, such conditions as the method used to produce the foam, the temperature of the solution, the hardness of the water used, and its electrolyte content must all be specified. Koczo et al., 1990 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.

Schmidt et al, 1997 studied a high-foaming surfactant, AEO-Mild by using the SEN foaming device, which is a useful way of measuring “flash foam”, and the dynamic spray foaming, which is the Shell-designed device for measuring the foam height.

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.

### **2.3 Phase Separation in Nonionic Surfactants and the Cloud Point**

It is well known that phase separation phenomenon is exhibited by some micellar surfactant solutions. There are several situations in which surfactant solutions occur in equilibrium with a separate, predominantly aqueous phase

(Hall and Tiddy, 1981). The phase separation of zwitterionic micelle solutions and concentrated ionic (anionic or cationic) solutions have been reported (Hall and Tiddy, 1981; Rubingh and Holland, 1991). The best known example, however, is the separation of a nonionic micellar phase of polyoxyethylene surfactant solutions (Puvvada and Blankschtein, 1990). The specific applications of such systems and their phase behavior for the extractive preconcentration, separation, and/or purification of metal chelates, biomaterials, and organic compounds have been summarized by Hinze and Pramauro, 1993. The temperature at which the phase separation occurs is known as the cloud point since it involves a drastic increase in turbidity of the solution.

The cloud point temperature is the lowest temperature at which the nonionic surfactant solutions, once above the CMC, become cloudy upon heating (Clint, 1992). The higher the degree of polymerization in the polyoxyethylene surfactant, the higher is the cloud point. The cloud point of nonionic surfactants had been studied by Galera-Gomez and Gu, 1996. The phase separation is shown in Figure 2.4.

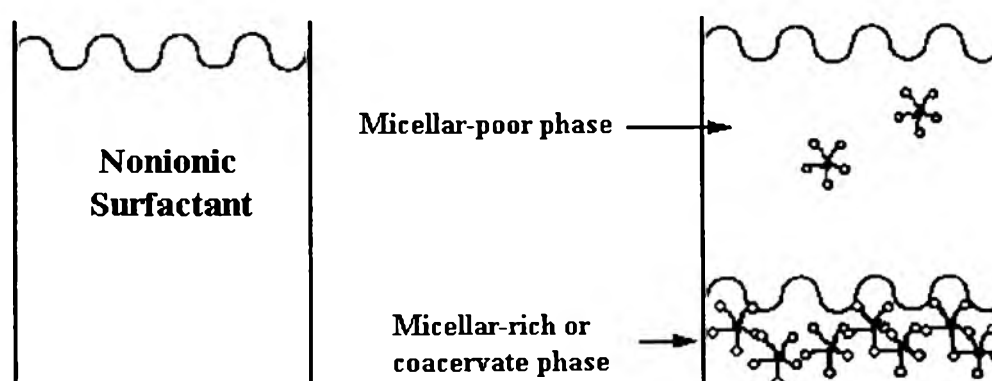


Figure 2.4 Schematic diagram of phase separation in nonionic surfactant.

Above the cloud point, the nonionic surfactant solutions separate into two isotropic phases. The phases consist of a dilute solution of the nonionic surfactant and surfactant-rich micellar phase, or coacervate phase. The concentration of surfactant in the dilute phase is above its CMC at that temperature (Corti et al., 1984).

The origins of such critical phenomena and phase separation behavior of aqueous nonionic surfactant solutions are still the subject of much debate in the literatures. Some researchers (Staples and Tiddy, 1978; Hayter and Zulauf, 1982; Triolo, Magid, Johnson and Child, 1982; Zulauf and Rosenbusch, 1983) have concluded that the micelle size at the critical concentration does not change with temperature. They describe that the phase separation occurs because the attractive pair potential between the micelles increases as the temperature is above the consolution curve. This causes the micelles to come closer and closer, resulting in less hydration of the micelles. The micelles then have the possibility to come into contact with each other and eventually coalesce into bigger micelles. If the density of the bigger micelles is sufficiently different from the bulk solution, then phase separation occurs. Some researchers (Kawaguchi, Hamanaka, and Mitsui, 1983; Ravey, 1983; Corti et al., 1984 ; Kato and Seimiya, 1986; Cummins, Hayter, Panfold, and Staples, 1987), however, infer from their data that there is a substantial growth of the micellar aggregation number with temperature because of the dehydration of the micelles as the temperature is increased, resulting in the difference between the densities of the micellar phase and the bulk solution which causes the phases to separate. Nilsson and Lindman, 1983, determined that the micelles remain strongly hydrated near the cloud point. In summary, it seems useful to ascribe the cause of the phase separation to the dehydration of the micelles.

It is important to emphasize that any factors affecting the dehydration of nonionic micelles can alter the cloud point of a given nonionic surfactant, either increasing it or decreasing it.

It is well-known that the foamability of nonionic surfactants is reduced above the cloud point temperature. Above this temperature, the surfactant aqueous solution separates into two phases, a surfactant-poor phase and a surfactant-rich phase which plays the role of an antifoam. Foaming properties of modified ethoxylated nonionic surfactants was studied by Colin et al, 1997. It was found that, in the concentrated solutions, the reduction of the foamability of nonionic surfactants was related to the existence of the cloud point. The surfactant solution separated into two phases: a dilute micellar phase and a concentrated one, the latter acting as an antifoam. For dilute solution, a long conformational rearrangement at the surface was found to be responsible for decrease in the foamability.