

CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Surfactant

A surfactant or a surface-active agent is a substance that, when present at low concentration in a system, has the property of adsorbing onto the surfaces or interfaces of the system and of altering to marked degree the surface or interfacial free energies of those surfaces or interfaces (Rosen, 1989). Surfactant has an amphipathic structure. In aqueous phase, it is composed of two parts, hydrophobic group (water-disliking) and hydrophilic group (water-liking). By the polarity of hydrophilic group, surfactant is classified into 4 types:

Anionic: The surface-active portion of the molecule bears a negative charge, for example, $\text{RCOO}^- \text{Na}^+$ (soap), $\text{RC}_6\text{H}_4\text{SO}_3^- \text{Na}^+$ (alkylbenzene sulfonate).

Cationic: The surface-active portion bears a positive charge, for example, $\text{RNH}_3^+ \text{Cl}^-$ (salt of a long-chain amine).

Zwitterionic: Both positive and negative charges may be present in the surface-active portion, for example, $\text{RN}^+\text{H}_2\text{CH}_2\text{COO}^-$ (long-chain amino acid).

Nonionic: The surface-active portion bears no apparent ionic charge, for example, $\text{RC}_6\text{H}_4(\text{OC}_2\text{H}_4)_x\text{OH}$ (polyoxyethylenated alkylphenol).

Due to the presence of two structurally dissimilar groups within a single molecule, surfactants form aggregates of molecules called micelles when the concentration of the surfactant solute in the bulk solution exceeds a limiting value or critical micelle concentration (CMC).

2.2 Foam

Initially, it is important to stress that absolutely pure liquid cannot foam unless a surface-active material is present. Foam is a non-equilibrium dispersion of gas bubbles in a relatively smaller volume of 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. The structure of a typical foam formed is shown schematically in Figure 2.1. In the lower part of the foam, bubbles are spherical (so-called kugelschaum) and of small size with a relatively low gas volume fraction. As the liquid drains out of the foam, the bubbles distort to form polyhedra. This polyhedral foam (polyederschaum) consists of plane-parallel films joined by channels called Plateau borders or Gibbs triangles (Figure 2.2). The gas volume fraction is here relatively high and the density low so that polyhedra first form at the top of the foam column.

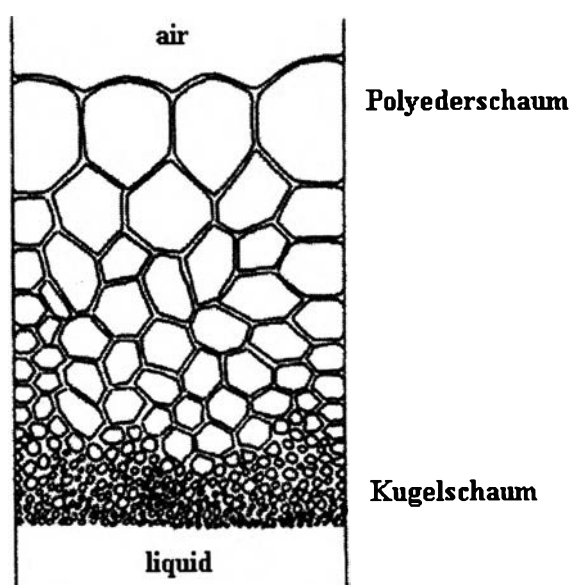


Figure 2.1 Foam structure of a surfactant solution in a cylindrical vessel generated by shaking method (Garrett, 1992).

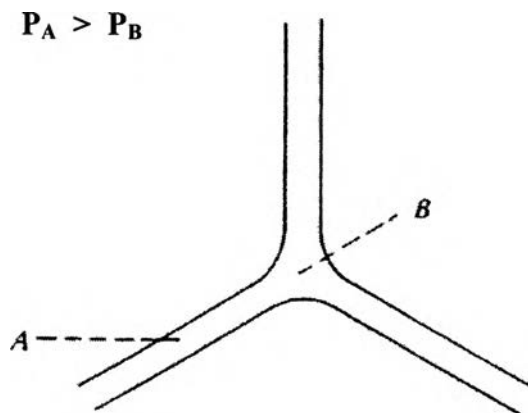


Figure 2.2 Plateau border at point of meeting of three bubbles.

All foams are thermodynamically unstable, due to their high interfacial free energy. For convenience, the instability has been expressed according to the kinetics and has been classified into two extreme types. (Pugh, 1996)

- *Unstable* or transient foams with lifetimes of seconds
- *Metastable* or so-called permanent foams with lifetimes which may be measured in days

2.3 The Drainage and Thinning of Foams

The extent and rate of drainage of solution from the interior of the foam film is one of the important factors determining foam stability, since drainage causes thinning of the films and when the film reaches a critical thickness (50-100 Å), the film may rupture spontaneously (Rosen, 1989). Initially the liquid will drain due to gravity and flow downward through the network, the polyhedral bubbles will be produced and the capillary forces can then come into play. The pressure differences in the thin films (resulting from difference in curvature) will cause further thinning. Restoring forces resulting from the Gibbs-Marangoni effect can restore the thickness and prevent further

thinning. Gravity is therefore the main driving force for drainage, and can act directly on the film and indirectly through capillary suction in the Plateau borders, but can be opposed by the surface tension gradient along the air-water interface.

However, as a general rule, the drainage rate of foams may be decreased by increasing the bulk viscosity of the liquid. This may be achieved in aqueous systems by simply adding a solute such as glycerol, liquid paraffin, or polyoxyethylene (high molecular weight) to the aqueous phase.

An alternative method to decrease the foam drainage is by increasing the surface viscosity and surface elasticity. Generally, packing a high concentration of surfactant or particles in the surface causing high adhesive or cohesive bonding can increase the surface viscosity and elasticity. This type of mechanism is illustrated in Figure 2.3.

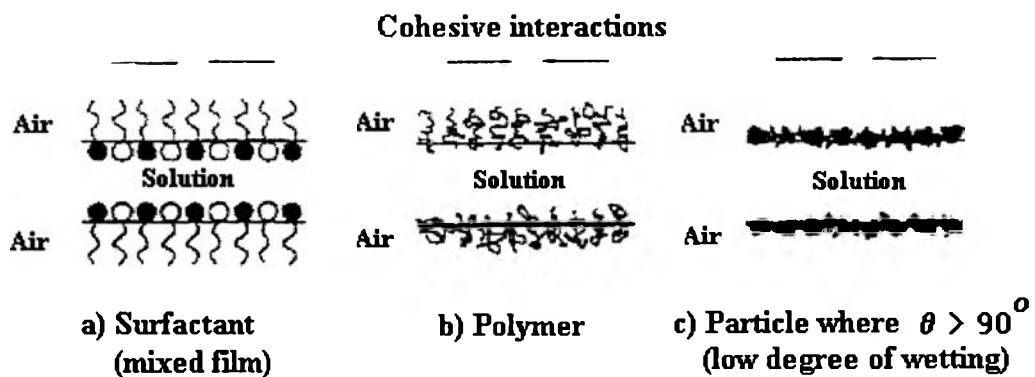


Figure 2.3 An increase in surface viscosity can be achieved by the presence of a high packing density of certain types of surfactant species which can cause strong cohesive interactions. For example: (a) mixed surfactant system, (b) polymers, and (c) particles with high contact angle attached to the air-solution interface (Pugh, 1996).

2.4 Foaming Properties

The study of foaming properties must be represented by two terms, foamability and foam stability. The amount of foam formed under a given condition is a measure of the foamability. On the other hand, the decay rate of a foam volume is a measure of foam stability.

There are many researchers who studied the foaming properties. These are some examples:

Iglesias *et al.* (1995) presented the experiment method and processing techniques, which allowed the monitoring of two characteristic parameters, half decay time ($t_{1/2}$) and the original height (H_0), to estimate foamability and foam stability for short life foams.

Laheja *et al.* (1997) studied the stability of foams generated with ionic and nonionic surfactant solutions at concentrations higher than the critical micelle concentration and the influence of water-soluble polymer and organic phase addition on the stability of these foams. Addition of polymer increases stability of the foam, but addition of organic phase decreases the stability.

The effect of tetraalkylammonium chloride on the micellar stability of sodium dodecyl sulfate (SDS) solutions was investigated by Patist *et al.* (1998). They related this effect to the dynamic interfacial properties, such as foamability and foam stability as well as surface viscosity and surface tension. They found that the addition of tetraalkylammonium salt to SDS solutions as antifoaming agent shows two opposing effects depending on its concentration.

Jha *et al.* (1999) continued the study on the effect of antifoaming agents (2-ethylhexanol, tributyl phosphate, and tetrabutylammonium chloride) to sodium dodecyl sulfate and proposed the correlation of the stability of micelles and antifoaming efficiency. They found that 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, which begins to improve the foamability of SDS solutions.

2.5 Antifoaming

When undesirable foaming of a solution cannot be reduced sufficiently by replacing the surfactant with a lower foaming one, or when the foam is caused partially or entirely by nonsurfactant components of the solution, then antifoaming agents are used to reduce the foam.

There are two terms relating to the foam controlling:

- *Antifoamers* are usually added to the aqueous phase, prior to foam formation, and act to prevent or inhibit foam formation.
- *Defoamers* or foam breakers are added to eliminate an existing foam and usually act on the outer surface of the foam.

Antifoaming (or defoaming) agents must be present as undissolved particles (or droplets) in the liquid. They can be classified into three types: (a) nonpolar oils such as alkyl phosphates, alcohol (diols), polydimethylsiloxane, (b) hydrophobic particles, for example, polytetrafluorethylene particles, hydrophobic silica particles, and (c) mixtures of nonpolar oils and hydrophobic particles such as the mixture of silicone oil and hydrophobic silica particles.

2.6 Antifoaming Mechanism

The antifoaming mechanisms of insoluble particles in aqueous solution of surfactant have been proposed over the years. These are some well-known mechanisms:

– *Replacement-destabilization antifoaming mechanism*

In this mechanism, the antifoamer must be very surface active so that it can adsorb at the air-liquid interface, displace some of the surfactant molecules, and form a mixed monolayer that cannot stabilize the foam. This mechanism can be shown by Figure 2.4.

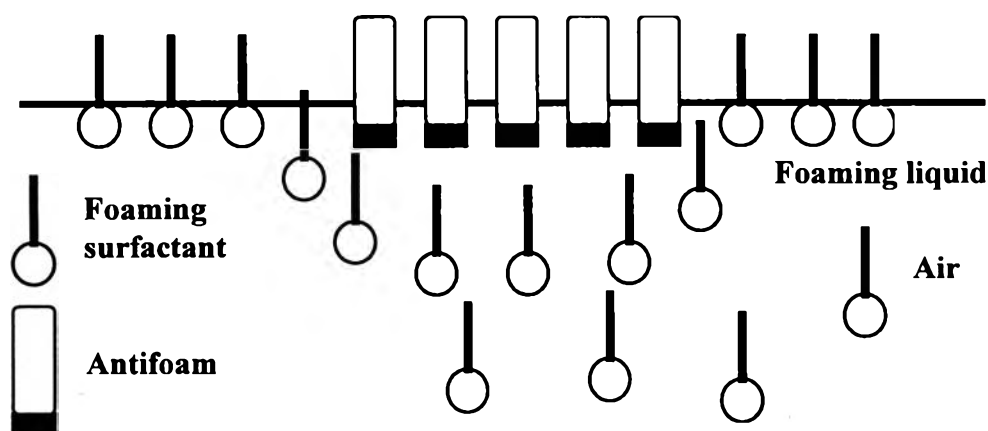


Figure 2.4 Replacement-destabilization antifoaming mechanism.

Pepper (1958) studied the defoaming of synthetic detergent solution by soaps and fatty acids, and concluded that the defoaming is due to the formation of islands of solid calcium soap film which replace part of the surfactant-stabilized foam film making the film unstable because of their inflexible brittle nature. This is so-called replacement-destabilization mechanism.

– *Adsorption-destabilization antifoaming mechanism*

Kulkarni *et al.* (1977) proposed the so-called adsorption-destabilization mechanism in which bubbles rupture through depletion of surface surfactant as a result of rapid local adsorption of surfactant on hydrophobic particles. This leads to weak spots on the foam film where film ruptures.

– *Bridging-dewetting antifoaming mechanism* (Figure 2.5)

In this mechanism, the particle first penetrates the air-liquid interface, and once the foam film thins down to the size of the particle through liquid drainage, a particle bridge will be formed in the film. For hydrophobic particles, the curvature of the film at the particle is convex ($\theta > 90^\circ$), the capillary pressure in this case will act to thin the film. Finally, the particle dewets and the film ruptures. On the other hand, for hydrophilic particle which has the contact angle less than 90° , the capillary will act to oppose drainage resulting in foam stabilizing.

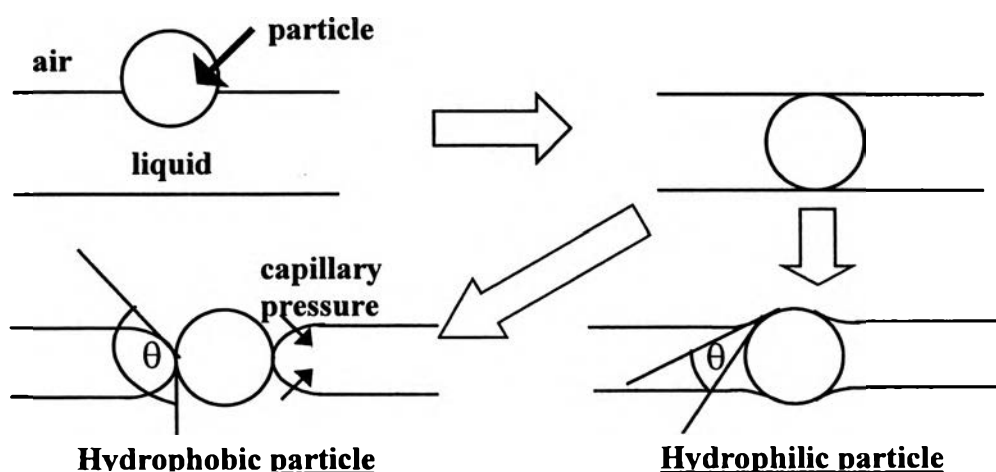


Figure 2.5 Bridging-dewetting antifoaming mechanism.

Garrett (1979) carried out a series of shaking test experiments with finely divided ($\sim 5\mu\text{m}$) polytetrafluorethylene (PTFE) particles as antifoam

material. A correlation between foam volume destroyed and receding contact angle was found from this study.

- In the case of large smooth particles (large enough to touch both surface and with contact angles $\theta > 90^\circ$), dewetting occurs.
- In the case of $\theta < 90^\circ$, this can cause a stabilizing effect.

Johansson and Pugh (1992) studied the stability of foams in the presence of finely ground quartz particles of different size fractions and hydrophobicities. Particles in the more hydrophilic range did not appear to influence the froth properties, but more hydrophobic particles destabilized the froth.

Aveyard *et al.* (1994) confirmed the concept of maximum of enhanced foam stability, which corresponded to a critical surface hydrophobicity for smooth spherical particles (45 μm diameter) and cylindrical rods. From their experiments the maximum foam stability was reported to occur at 90° (static advancing contact angle) but the effect of particle size was not taken into consideration.

The mechanism of film collapse by single spherical particles has been studied by cinematographic experiments by Dippennar (1982a) and generally confirmed Garrett's dewetting mechanism. In addition, Dippennar (1982b) emphasized the dynamic contact angle rather than the equilibrium situation. This study appears to indicate that with large particles and high contact angles, the film easily destabilized. Further experiments with galena (cubic shaped particles) also show that with contact angles $< 90^\circ$, then the froth was destabilized and this was explained by ease of the movement of the three-phase boundary across the smooth regular surface.

Frye and Berg (1989) carried out a hydrodynamic analysis of the mode of action of smooth shaped inert solid hydrophobic particles (spheres, discs, rods, and ellipsoids) on thin films. It was concluded that for dewetting and rupture then contact angle must be $> 90^\circ$ but to achieve rapid film rupture

and high breakdown rates, then an extra 5° or 10° over this critical angle was required.

Wang *et al.* (1998) supported the conclusion of Koczó *et al.* (1994) that defoamer lenses in the plateau borders are the active foam-breaking agents. Hydrophobic silica particles tend to accumulate at the interface between the defoamer oil and the aqueous solution (pseudoemulsion film) to destabilize this area.

Tamura *et al.* (1999) proposed that the antifoaming efficiency of antifoamers strongly depends on the stability of the pseudoemulsion films. For the mixed-type antifoam, the droplets enter the air-solution interface forming a lens with the particles destabilizing the pseudoemulsion film during the early stage of foam breakdown. They found that the film stability was largely affected by surface roughness for both the liquid and the solid antifoamers. From their result, the antifoaming performance was in the order: the mixed-type antifoam > the hydrophobic silica \geq the silicone oil.

2.7 Measurement of the Contact Angle

Contact angles are measured on macroscopic, smooth, nonporous planar substrates by merely placing a droplet of the liquid or solution on the substrate and determining the contact angle by any of a number of techniques. The contact angle can be measured directly by use of a microscope fitted with a goniometer eyepiece or by photographing the droplet. Indirect measurement of the contact angle can be done by measuring the height 'h' and the diameter 'd' of the droplet and assuming a spherical shape, by using the relation, $\tan \theta/2 = 2h/d$ (Rosen, 1989).

Aveyard *et al.* (1993) studied contact angle of surfactant solutions with smooth solid surfaces by using a contact angle microscope. For measurements at the solid-air interface, a drop of liquid was added to the solid

surface using a microsyringe. The volume of the drop was subsequently increased and the drop then left for 10 min before a measurement was made. All experiments were carried out at ambient room temperature.

Garrett *et al.* (1993) determined contact angle by using the sessile drop method. Angle was measured through the aqueous phase directly, using a telescope with a goniometer eyepiece. Particles were compressed to form disc using a press at pressure of about $2 \times 10^8 \text{ N m}^{-2}$.

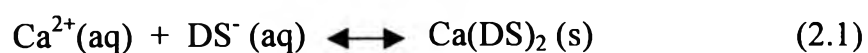
The contact angle was also studied by Tamura *et al.* (1999). Contact angles of the surfactant solution with solid antifoaming agents were measured using a contact angle goniometer. A microsyringe was used to apply solution drops (1 μl) to the sample surfaces at 20°C .

2.8 Precipitate Phase Boundaries

An important characteristic of ionic surfactants is their tendency to precipitate from aqueous solutions. One condition which can cause anionic surfactants to precipitate easily is hard water (water containing multivalent cations). Precipitation of anionic surfactants can inhibit their use in many applications and can affect formulation compositions substantially (Rodriguez, 1997).

Rodriguez *et al.* (1998) studied the effect of sodium octanoate and pH on the precipitation of sodium dodecyl sulfate (SDS) with calcium (hardness tolerance) in water.

From the results, the possible precipitation reaction of SDS occurring in their system is represented by the following equation:



Where DS^- is the dodecyl sulfate ion, Ca^{2+} is calcium ion, and $Ca(DS)_2$ is the calcium dodecyl sulfate precipitate.

Below CMC, all surfactant in the system is present as monomer, and precipitate depends on the total surfactant and total calcium concentrations. Therefore, as the surfactant concentration is increased, the amount of calcium required to cause precipitation decreases as described by the solubility product relationship:

$$K_{SP} = [Ca^{2+}] [DS^-]^2 \gamma_{Ca} \gamma_{DS}^2 \quad (2.2)$$

Where K_{SP} is the activity-based solubility product, $[DS^-]$ is equal to the total SDS concentration, and γ_{Ca} and γ_{DS} are the activity coefficients of calcium and SDS, respectively.

Precipitation above CMC depends on the monomeric surfactant concentration and the unbound calcium concentration:

$$K_{SP} = [Ca^{2+}]_u [DS^-]_{mon}^2 \gamma_{Ca} \gamma_{DS}^2 \quad (2.3)$$

The behavior above CMC can be understood by examining the micelle-monomer-precipitate equilibria shown in Figure 2.6.

Figure 2.7 shows precipitation phase boundaries for SDS. For each SDS concentration as the calcium concentration is increased, precipitation first occurs at the precipitation phase boundary where the solution is isotropic. Above the precipitation phase boundary, crystals are present.

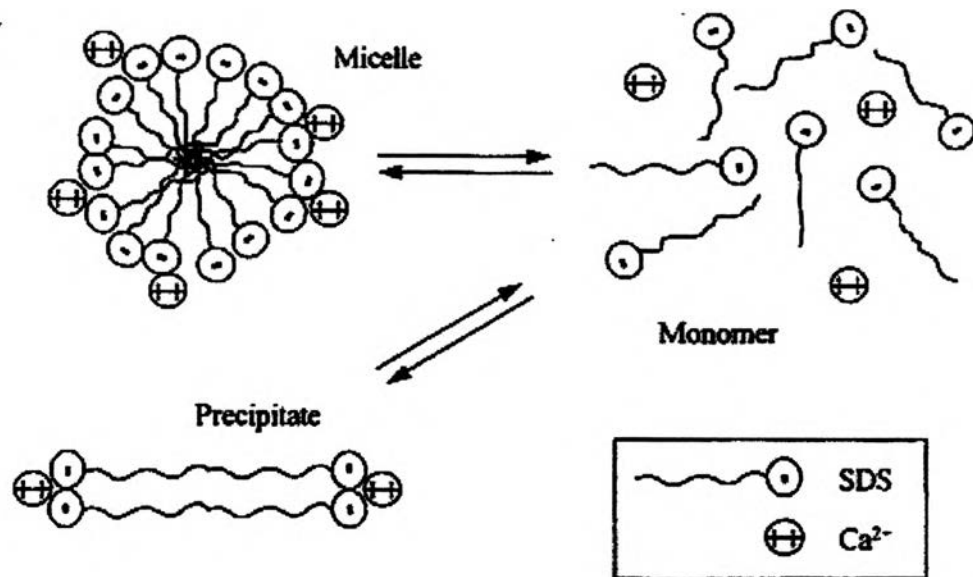


Figure 2.6 Micelle-monomer-precipitate equilibrium diagram for sodium dodecyl sulfate (SDS) in the presence of calcium ions.

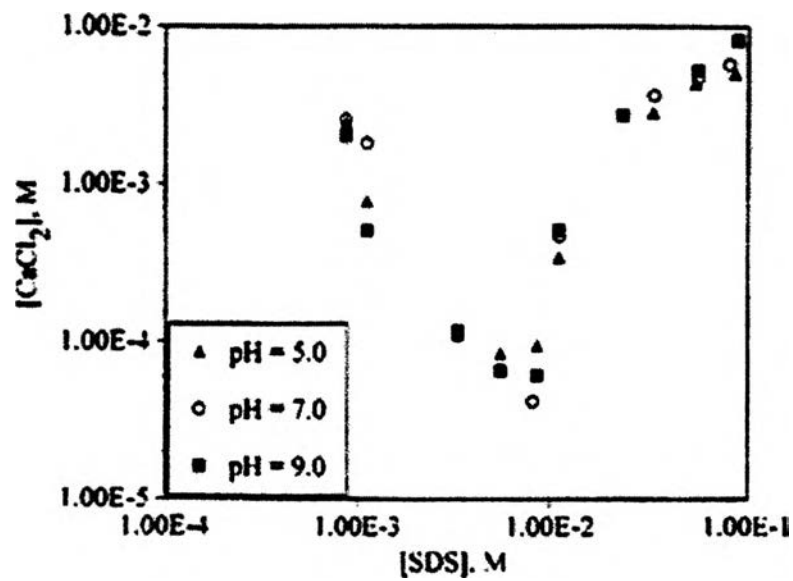


Figure 2.7 Precipitation phase boundaries (hardness tolerance) for SDS.