

CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Physical Chemistry of Surfactants

The chemical composition, physical structure, and key physical properties of foam, namely its stability and rheology, are all closely interrelated. Since there is a large interfacial area of contact between liquid and vapor inside a foam, the physical chemistry of liquid-vapor interface and its modification by surface-active molecules plays a primary role underlying these interrelationships.

For aqueous solutions, the chemical constituents most commonly responsible for foaming are surfactants, in which each molecule has a hydrophobic and hydrophilic region. A typical example is the anionic surfactant, sodium dodecyl sulfate [151-21-3] (SDS). In spite of its hydrophobic hydrocarbon chain, SDS is readily soluble in water due to its polar head group. At concentration higher than 8 mM, the so-called critical micelle concentration (CMC), SDS molecules form spherical micelles where the hydrophobic tail of approximately 64 molecules clump together so that only their hydrophilic head are exposed to water. At still high concentration, even more exotic structures are formed in the bulk solution.

Just as surfactants self organize in the bulk solution as a result of their hydrophilic and hydrophobic segments, they also preferentially adsorb and organize at the solution-vapor interface. For aqueous surfactant solution, the hydrophobic tails protrude into the vapor and leave only the hydrophilic head groups in contact with the solution. The energetically more favorable of this arrangement can be seen by the reduction in the interfacial free energy per unit

area, or surface tension, σ . However, the reduction is not in itself responsible for foaming; the primary benefit is that less mechanical energy needed to be supplied to create the large interfacial area in foam.

The reduction of surface tension with increasing surfactant adsorption gives rise to a nonequilibrium effect that can promote foaming. A sudden increase in the interfacial area by mechanical perturbation or thermal fluctuation results in a locally higher surface tension because the number of surfactant molecules per unit area simultaneously decreases. The Gibbs elasticity, E , is often used to quantify the instantaneous change in surface tension, σ , with area A . If the film of liquid separating two neighboring bubbles in a foam develops a thin spot, the surface tension gradient in the vicinity of the thin spot will induce a Marangoni flow of liquid toward the direction of higher σ . This flow of liquid toward the thin spot helps heal the fluctuation and thus keeps the neighboring bubbles from coalescing.

2.2 Foam Description

Foam is a nonequilibrium dispersion of gas bubbles in a relatively smaller volume of liquid. An essential ingredient in liquid-based foam is a surface-active molecule. These reside at the interfaces and are responsible for both tendency of a liquid to foam and the stability of the resulting dispersion of bubbles. For instance, it is common experience that a relatively stable foam can be made by bubbling gas through soapy water, but not through pure water. Observed from a distance, foam made from a clear liquid appears homogeneous and white. When observed more closely the intricate structure formed by the close packing of distinct gas bubbles becomes apparent. Figure 2.1 illustrates several features of this so-called microstructure which are common to many foams. Near the top of the sample, most of the liquid has

drained away leaving a dry foam consisting of nearly polyhedral gas bubbles separated by thin liquid films of uniform thickness. Near the bottom of the sample, by contrast, the foam is relatively wet and consists of bubbles that are more nearly spherical. Whether the bubbles are spherical, polyhedral, or in between, they typically have a distribution of sizes and pack together into a disordered, aperiodic structure. The average bubble diameter is varied from 10 μ m to 1 cm. In practice, the average bubble size and shape in foam can be altered for a given liquid according to the production method, the surface-active ingredients and other chemical additives such as viscosity modifiers or polymeric stabilizers.

The nonequilibrium nature of foams is revealed by the time evolution of their structures. From Figure 2.1 the sample has evolved by the gravitational segregation of liquid downward and bubble upward. In addition to drainage, two other mechanisms by which foams evolve are direct coalescence of neighboring bubbles via film rupture and by the diffusion of gas molecules through the liquid from small bubbles to large bubbles. No matter which of these three processes dominates for a given foam, the liquid and vapor portions invariably consolidate and separate with time; in equilibrium there is no foam, only one region of liquid and one of vapor. The physical chemistry of the interfaces and the foam structure primarily determine the relative rates of the three aging mechanisms.

Foams that are relatively stable on experimentally accessible time scales can be considered a form of matter but defy classification as either solid, liquid, or vapor. They are solid-like in being able to support shear elastically; they are liquid-like in being highly compressible. The rheology of foams is thus both complex and unique, and makes possible a variety of important applications.

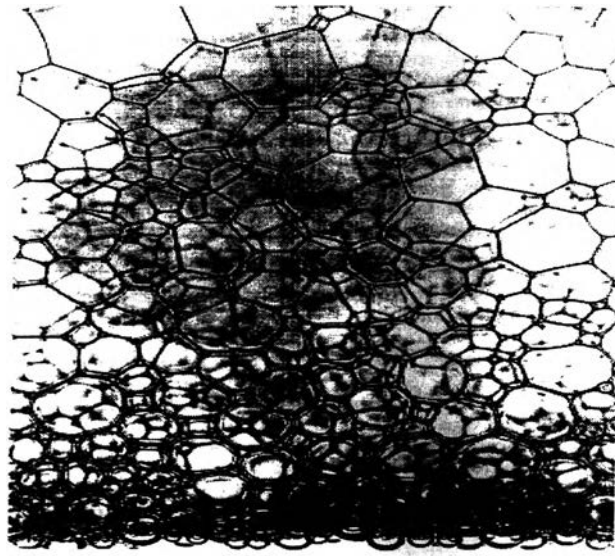


Figure 2.1 Photograph illustrating the microstructure of the foam which still persists two hours after shaking in aqueous solution containing 5% SDS (Prud'homme, 1996)

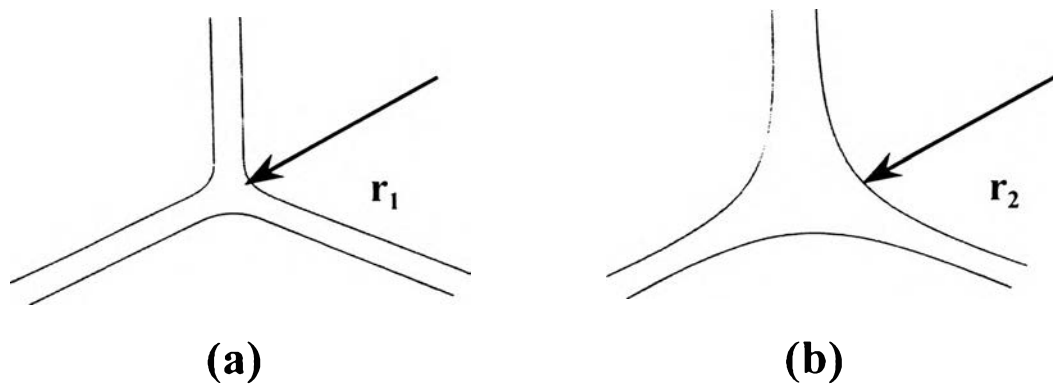


Figure 2.2 Two-dimensional schematic illustrating the distribution of liquid between the Plateau border and the films separating three adjacent gas bubbles. (a) Flat films and highly curved borders occur for dry foams with strong interfacial forces. (b) Nearly spherical bubbles occur for wet foams where the surface tension dominates the interfacial forces. (Prud'homme, 1996)

2.3 Foam Structure

Foam structure is characterized by the wetness of the system. Three types of system can be classified.

Very Wet Foam: Froth. Foam with arbitrarily large liquid to gas ratio can be generated by excessive agitation or by intentionally bubbling gas through a fluid. If the liquid content is sufficiently great, the foam consists of well-separated spherical bubbles that rapidly rise upwards displacing the heavier liquid. Such a system is usually called a froth, or bubbly liquid, rather than a foam. When the bubbles in a froth reach the surface, they may instantly burst, they may seethe and gradually burst, or they may collect together and form a more proper foam, all according to the quantity and nature of the surface-active components in the former, and hence there are no interfacial forces or Marangoni effects to hinder the direct coalescence of bubbles.

Wet Foam: Spherical Bubbles. If there are sufficiently strong repulsive interactions, such as from the electric double-layer force, then the gas bubbles at the top of a froth collect together without bursting. Furthermore, their interfaces can come as close to each other as allowed by the repulsive forces; typically on the order of 100 nm. Thus bubbles on top of a froth can pack together very closely and still allow most of the liquid to escape downward under the influence of gravity while maintaining their spherical shape. Given sufficient liquid, such a foam can resemble the random close-packed structure formed by hard spheres. With less liquid, depending on the distribution of bubble sizes, the bubble must distort from their spherical shapes. Spheres of identical size can pack to fill at most 0.74 of space; this occurs if they are packed into a crystalline lattice. A foam with a monodisperse size distribution but less than 26% liquid is thus composed of bubbles which are not spherical but are noticeably squashed together. Typical foams as in Figure 2.1 have a

fairly broad distribution of bubble sizes and can therefore maintain spherical bubbles with significantly less liquid. Empirically, foams with greater than about 5% liquid tend to have bubbles that are still approximately spherical, and are referred to as wet foams. Such is the case for the bubbles toward the bottom of the foam shown in Figure 1. Nevertheless, it is important to note that even in the case of these wet foams, some of the bubbles are deformed, if only by a small amount.

Dry Foam: Polyhedral bubbles. A dry foam, by contrast, is one with so little liquid that the bubbles are severely distorted into approximately polyhedral shapes. Typically this occurs in foams with less than 1% liquid by volume, as is the case for the bubbles toward the top of the foam shown in Figure 2.1 The structure of polyhedral foams is more appropriately described in terms of the liquid films separating neighboring bubbles rather than in terms of the packing of bubbles as individual units. Most of the interfacial area in polyhedral foam is in the form of polygonal liquid films having uniform thickness and separating two adjacent gas bubbles. The structure formed by these films is seemingly random, but nevertheless possesses a certain regularity which follows from mechanical constraints. The first of these is that only three films can mutually intersect, and they must meet at an angle of 120° . The intersection of four films is unstable and breaks up into two sets of three because the surface tension of the film exerts a force which acts to minimize the total interfacial area. The region of intersection formed by three films is known as Plateau border. It is the Plateau border, rather than the thin liquid films, which is apparent in the polyhedral foam shown toward the top of Figure 2.1.

A real foam has further degree of freedom available for establishing local mechanical equilibrium: the films and Plateau borders may curve. In fact, curvature can be readily seen in the border of Figure 2.1. In order to maintain

such curvature, there must be a pressure between adjacent bubbles given by Laplace's law according to the surface free energy of the film and the principal radii of curvature of the film. The Laplace pressure is determined by the region of greatest curvature. Thus, at the facets of the bubble where the surface is nearly flattened and the curvature is decreased, force is maintained by the effects of the disjoining pressure, which must balance the Laplace pressure in the regions of high curvature.

Even though pressure difference can exist between adjacent bubbles, and between the gas and the liquid, the pressure throughout the continuous liquid structure of films, borders and vertices must be constant; otherwise, liquid flows until all pressure gradient vanish. Figure 2.2 shows cross section of three films meeting in a Plateau border, and illustrates how pressure balance is achieved between liquid residing in a film and liquid residing in a border. Since the films are flat and opposite faces are parallel away from the border, the pressure inside the film equals the pressure in the gas minus the disjoining pressure. In the border, by contrast, the pressure equals the gas pressure minus the Laplace pressure. The pressure balance is thus achieved by adjusting the distribution of liquid between films and borders until the disjoining pressure equals the Laplace pressure. Figure 2.2 illustrates how flatter films with smaller, more highly curved, Plateau borders are attained when the interfacial forces dominate surface tension. The effect of more liquid being drawn into the Plateau border is called border suction. For similar reasons, vertices are thicker than borders as can also be seen in the Figure 2.1. Thus the distribution of liquid between neighboring bubbles and the corresponding bubble shapes are determined not only by the ratio of gas to liquid, but by the competition between surface tension and interfacial forces as well.

2.4 Foam Stability

Control of foam stability is important in all application. The time evolution of the foam structure provides a natural means of quantifying foam stability. There are three basic mechanisms whereby the structure may change: by the gravitational segregation of liquid and bubbles, by the coalescence of neighboring bubbles via film rupture, and by the diffusion of gas across the liquid between neighboring bubbles.

Drainage. All foams and froths consist of liquid and vapor components that have very different mass densities, making them susceptible to gravitationally induced segregation. In very wet froth the vapor bubbles rapidly move upward while the liquid falls. In longer-lived foams, the gas fraction is higher and the bubbles are tightly packed. Nevertheless, the heavier fluid may still drain downward through the thin films and Plateau borders. In some case, the addition of polymers or micelles in the liquid can increase its viscosity and slow the drainage. In addition to simple laminar flows set by film thickness, liquid viscosity, and the state of the adsorbed surfactant, whole regions of thick film can flow like a plug into the Plateau border and exchange for region of thin film. This process is called marginal regeneration and is believed to be important in foams as a means of bringing liquid from the films into the Plateau borders. Once in the Plateau borders the liquid can more rapidly drain downward. In wet long-lived foams, the bubbles are more nearly spherical so there is no distinction between flow within films and Plateau borders.

Provided there is no rupture of the films, drainage proceeds until there develops a vertical, hydrostatic pressure gradient to offset gravity. The disjoining pressure due to the film thickness being too small to minimize the effective interface potential supports the gradient. Thus individual soap films

in the foam decrease in thickness with increasing height. This results in a nonuniform gas:liquid volume fraction with the foam being more wet near the bottom of the container as in Figure 1.1. The formation of a macroscopic layer of liquid underneath a previously homogeneous foam is called gravitational syneresis, or creaming, and depends not only on the foam composition but also on the size and shape of the container as well.

Film Rupture. Another general mechanism by which foams evolve is the coalescence of neighboring bubbles via film rupture. This occurs if the nature of the surface-active component is such that the repulsive interactions and Marangoni flows are not sufficient to keep neighboring bubbles apart. Bubble coalescence can become more frequent as the foam drains and there is less liquid to separate neighbors. Long-lived foams can be easily formulated in which film rupture is essentially negligible, by ensuring that the surfactants provide a sufficiently large barrier that prevents the two films from approaching each other. Then film rupture is probably a thermally activated process in which a large, rare fluctuation away from equilibrium thickness and over an energy barrier is needed. Film rupture can also be enhanced by mechanical shearing, composition change via evaporation or chemical particulate additives can also greatly affect the rate of film rupture.

Gas Diffusion. For very long-lived foams, film rupture is negligible and drainage slows to a stop as hydrostatic equilibrium is attained. Nevertheless, the foam is still not in thermodynamic equilibrium and continues to evolve with time. This occurs through an entirely different, though very general, means: gas diffusion. Smaller bubbles have a greater interfacial curvature and hence, by Laplace's law, have a higher internal pressure than larger bubbles. This results in a diffusive flux of gas from smaller to larger bubbles. Thus with time small bubbles shrink while large bubbles grow. This process is known as coarsening, or ripening, and results in the net increase in

the average bubble size over time. It is ultimately driven by surface tension and serves to decrease the total interfacial surface area with time.

2.5 Antifoam Mechanisms

Foam formation can create serious problems in some industrial processes, for example, in paper making food processing and fermentation. To control foam formation, chemicals are often added to the foaming liquid.

It is important to distinguish between the two ways of foam controlling: (I) antifoaming where the chemicals are added frequently in dispersed form in order to prevent foaming and (II) defoaming where the chemicals are added to eliminate an existing foam. Their mechanisms can be very different. The defoamers first get into contact with the outer surface of the foam, while antifoams start to act from inside the aqueous phase. Thus for example, alcohols (octanol) are good defoamers but they are very inactive as antifoams.

The antifoaming (or defoaming) agents can be soluble (homogeneous) or insoluble (heterogeneous) in the foam-forming liquid. The heterogeneous antifoaming agents which are used for foam control in aqueous solutions can be classified into three types: (a) nonpolar oils, which are insoluble in the aqueous phase such as alkanes and silicone, oils; (b) hydrophobic solid particles or hydrophobized silica or hydrophobic polymers; (c) mixtures of nonpolar oils and hydrophobic particles. The solid content of the mixture is typically 1-20%. The mixed-type antifoams are much more effective than the oil or the solid particles alone. The synergism between the oil and the hydrophobic solid seems to be a general phenomenon. It occurs with several nonpolar oils (silicone or hydrocarbon oils) and with various types of surfactant solutions (anionic, nonionic, cationic, etc.) However, the

mechanism of antifoaming, especially the synergism between the oil and the solid particles, is still not well understood.

The effect of antifoams strongly depends on their configuration in relation to the surface of the solution. A nonpolar oil is generally dispersed in the aqueous phase in the form of drops (Figure 2.3a). When the drop reaches the solution surface it can enter and form a lens (Figure 2.3c). The oil can spread at the same time as a thin film (probably monolayer) which coexists with the lens. The lens then can slowly spread as a layer (Figure 2.3d) on the aqueous phase under the action of surface forces and gravity. The oil breaks the foam film by spreading as a duplex film on both sides of the foam film, thereby driving out the original film liquid and leaving an oil film which is unstable and break easily. This is known as the spreading mechanism.

The other mechanism is bridging mechanism. According to this mechanism the oil drop inside the foam first enters one of the surfaces of the foam film and form lens, and on further film thinning, the lens enters the other surface and forms an oil bridge (Figure 2.4). The film with the oil bridge is very unstable because the capillary pressure results in local film thinning around the lens and the film pinches off from the drop.

For antifoaming by hydrophobic solid particles alone, the bridging-dewetting mechanism is believed to operate in the foam film. This mechanism is similar to the above bridging mechanism. In this case, the solution forms a convex film at the air/liquid/solid interface, the capillary pressure acts to thin the film and finally the particle dewets and breaking the foam lamella. (Garret, 1992)

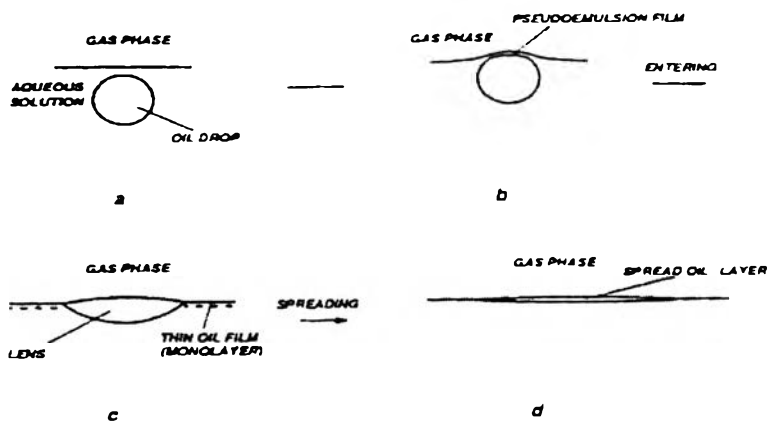


Figure 2.3 Schematic of the spreading antifoam mechanism

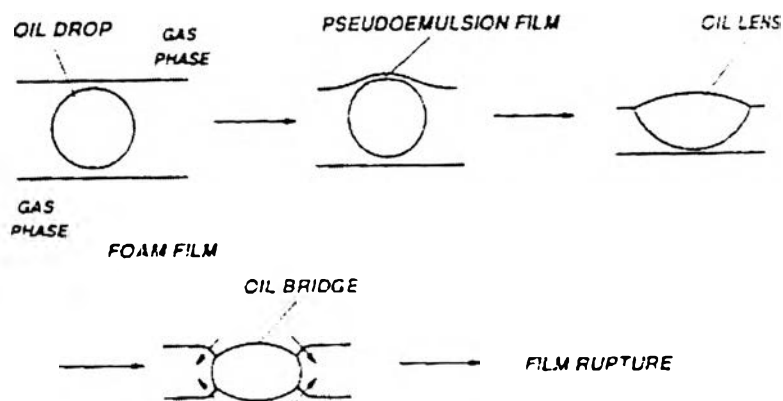


Figure 2.4 Schematic of the bridging-dewetting antifoam mechanism

2.6 Literature Review

Peper (1958) found that calcium salts of long chain fatty acid (stearic and palmitic) replaced parts of surface film of sodium dodecyl benzene sulfonate or sodium lauryl to form a “solid” brittle film having no elasticity. This calcium soap film consequently produced unstable foam but if the calcium soap formed a true mixed film with the surfactant, the foam was not destroyed by calcium soap.

Wang *et al.* (1999) investigated the role of hydrophobic particles in mineral oil-based defoamer by using fluorescent labeling and microscopy. Defoamer emulsion droplets in water was found to adhere to the air/water interface to become lenses that nucleated bubble coalescence. Fluorescent label was covalently bonded to silica and confocal laser scanning microscopy showed that the hydrophobic silica particles concentrated in the oil/water interface near the three-phase contact line. Furthermore surfactants added to defoamers to facilitate emulsification were required for the transport of the silica to the water/oil interface. Removal of excess silicone oil from the emulsification process lowered defoamer performance.

Angarska *et al.* (1997) investigated unstable and equilibrium foam films and foams formed from solutions of sodium dodecyl sulfate and bivalent electrolyte. It was found that at low ionic strength and low surfactant concentration the films with magnesium ions were more stable than the film with sodium ions. At higher surfactant concentration the film containing $MgCl_2$ became stable while the films with $MgSO_4$ remained unstable. The unstable films exhibited at least five types of rupture, which were documented by photographs and frequently, distribution curves of the film lifetimes. In the case when magnesium ions were present the formation of lenses inside the film was observed; the lenses contributed to a longer lifetime of the films. With the

stable film the transition from common to Newton black film occurred at magnesium concentration between 0.01 and 0.015 M.

Aveyard *et al.* (1993) studied foaming behavior of aqueous solution of three surfactants (SDS, CTAB, and AOT) in the presence and absence of hydrophobic particles (paraffin wax, PTFE, and ethylenebis (stearamide)) and dodecane. They have found that dodecane alone was an effective foam breaker for CTAB solutions. The hydrophobic particles studied were all effective in reducing initial foam volumes, the percent foam reduction achieved depending on surfactant concentration. Foam reduction by particles alone or in the presence of dodecane varied smoothly with the contact angle (θ_1) of the surfactant solution with solid in air. The presence of dodecane reduced the value of θ_1 required for effective foam breaking. Contact angles were used in conjunction with interfacial tension to estimate the extent of adsorption of surfactant on the particles. Adsorption at the solid/aqueous solution interface was very similar to that at the air/solution interface and a little less than that at the oil/solution interface.

Aveyard *et al.* (1994) studied the relation of the contact angles of solid on film and foam stability. He found that spherical glass beads and cylindrical rods with contact angles more than 90° rapidly ruptured single soap films. The stabilizing effect was attributed to collection of particles in the Plateau border regions of the foams and the concomitant reduction in the rate of film drainage.

Mata and Joseph (1999) fluidized hydrophobic and hydrophilic versions of two different sands in a slit bubble reactor. They found that the hydrophobic sands suppressed the foam substantially better than their hydrophilic counterparts. They also observed that, for a fix solid volume fraction, the 500-600 μm hydrophobic particles were more effective in destroying foam than the 600-850 μm . This was because the smaller particles

could penetrate the foam more easily than large particles. For a fixed particle size, the greater the volume fraction of hydrophobic particles, the more effective their foam suppression.