CHAPTER II

BACKGROUND AND LITERATURE SURVEY

2.1 Surfactants

Surfactants, an abbreviation for surface active agents, are one which acts preferentially at surfaces of the dissolved solution. This characteristic may give such agents one or more of these properties in solution: detergency (cleaning ability), defoaming (ability to break bubbles), emulsifying (ability to suspend an insoluble material in liquid), film forming (ability to form bubbles), reduction of surface tension and wetting.

Surfactants, when present at low concentration in a system, can adsorb onto the surface or interface of the system and alter the surface or interfacial energies in marked degree of those surfaces or interfaces. This is because a polar compound consisting of an amphipathic molecule, *i.e.* a molecule with a hydrophilic head attached to a long hydrophobic tail. At a particular concentration (known as the critical micelle concentration, CMC) surfactant molecules become more favorable to form aggregates call micelles as shown in Figure 2.1.

In general, the hydrophobic group consists of a hydrocarbon chain containing 10-20 carbon atoms. Oxygen atoms, a benzene ring, amides, esters, other functional groups, and/or double bonds may interrupt the chain. The hydrophilic group is usually referred to as the head group which is either strongly polar or charged.

Surfactants are classified by the charge of the hydrophilic group. In anionic surfactants, the hydrophilic groups can be phosphates, sulfonates, sulfates, and carboxylates, $C_{17}H_{35}CO_2^-Na^+$. Cationic surfactants are typically amine and/or ammonium groups, as in $(C_{18}H_{37})_2N^+(CH_3)_2Cl^-$. In nonionic surfactant, as the name implies, there is no charge on the molecule. The solubilizing contribution can be supplied by a chain of ethylene oxide groups, $C_{15}H_{31}O(CH_2CH_2O)_7H$. Finally, amphoteric surfactants are provided by the presence of positive and negative charges in the molecule, as in $C_{12}H_{25}N^+(CH_3).2CH_2CO^-$.

Commercially, Anionic surfactants are manufactured and used in greater volume than all other types of surfactants. The reason is the ease and low cost of manufacture, and they are practically used in every type of detergent, the main application of surfactants.
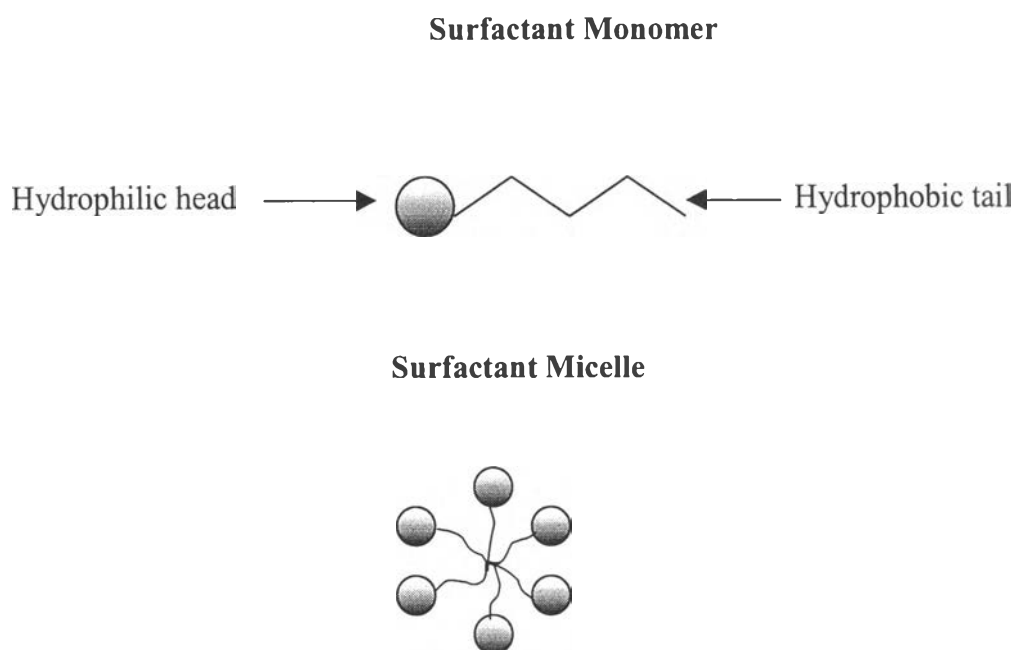
Surfactant Monomer

Hydrophilic head ⟶ ◯⌣⌣ ⟵ Hydrophobic tail

Surfactant Micelle

Figure 2.1 A surfactant molecule and a surfactant micelle

2.2 Foam

Foam is a nonequilibrium dispersion of gas bubbles in a relatively small volume of liquid. An essential ingredient in a liquid-based foam is surface-active molecules. 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 2.2.

The foam formation from a bulk liquid involves the expansion of the surface area due to the work acting upon the system. Since the surface tension is the work involved in creating a new surface, the amount of new interfacial area or foam will

typically be greater in the case of lower surface tension. Hence, the reduction of surface tension by the surfactant is the primary requirement of foam formation.

A two-dimensional illustration of a foam system is depicted in Figure 2.3. The general foam structure is contained on the bottom by the bulk liquid and on the upper side by a second bulk phase, in this case, gas. Within the magnified region, the various parts of the foam structure are clarified. The gas phase is separated from the thin liquid film, by a two dimensional interface. However, a sharp dividing surface does not exist in reality between gas and liquid. Dictated by mathematical convenience, the physical behavior of this interfacial region is approximated by a two dimensional surface phase (the Gibbs surface). A lamella is defined as the region that encompasses the thin film, the two interfaces on either side of the thin film, and part of the junction to other lamellae. The connection of three lamellae, at an angle of 120°, is referred to as the Plateau border.

The pressure difference across a curved interface due to the surface or interfacial tension of the solution is given by the Laplace equation,

$$\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \tag{2.1}$$

where γ is the surface tension, and R_1 and R_2 are the radii of curvature of interface. Since the curvature in the lamellae is greatest in the Plateau borders, therefore the pressure across the interface in these Plateau is greater regions than elsewhere in the foam. However the gas pressure inside an individual gas cell is equal everywhere. As a result, the liquid pressure inside the lamella at the highly curved Plateau border (B) must be lower than in the adjacent, less curved regions (A) of the Plateau area as shown in Figure 2.4. This causes drainage of the liquid from the lamellae into the Plateau borders. In a column of foam, liquid also drains as a result of hydrostatic pressure, with the result that lamellae are thinnest in the upper region of the column and thickest in the lower region. Foam can be destroyed when the liquid drains out from between the two parallel surfaces of the lamella, causing it to get a critical thickness (50-100 A°), the film will collapse and the bubble will burst.
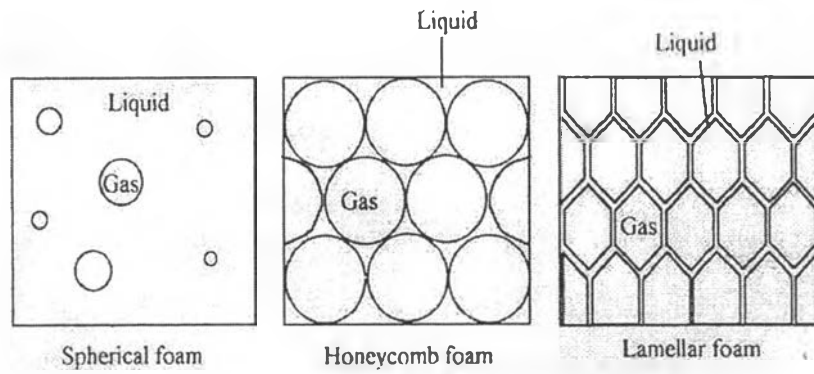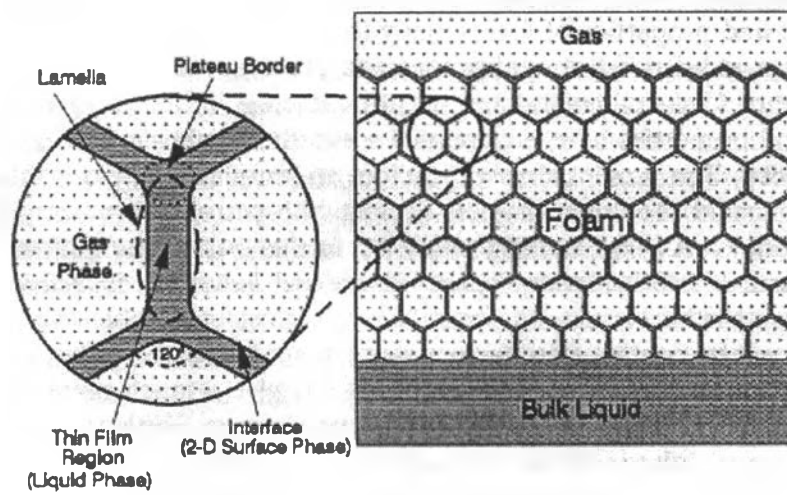
Figure 2.2 Different kinds of foam (Porter, 1994)

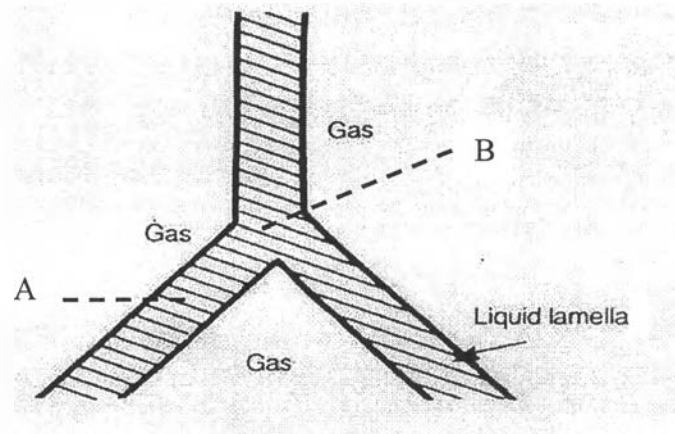**Figure 2.3** A generalized foam system (Schramm, 1994)

Figure 2.4 Plateau border at point of meeting of three bubbles (Rosen, 1989)

2.3 Foam Stability

Control of foam stability is important in all applications, whether degradation of a custom foam is to be minimized or whether excessive foaming is to be prevented. In all cases, the time evolution of the foam structure provides a natural means of quantifying foam stability.

Foam stability can be considered in two different processes, film thinning and coalescence (film rupturing). In film thinning, the liquid films separate two or more bubbles, which approach closely together, and there is no change in total surface area. In coalescence, two or more bubbles fuse together to form a single, larger bubble. In foam termination, the thin liquid films rupture and reduce the total surface area. Because foam is thermodynamically unstable.

A foam film must be slightly elastic in order to be able to withstand deformations without rupturing. The surface-chemical explanation for film elastic comes from Marangoni and Gibbs. If a surfactant-stabilized film undergoes a sudden expansion, then immediately the expanded portion of the film must have a lower

degree of surfactant adsorption than unexpanded portion because the surface area has increased as shown in Figure 2.5. This expansion causes an increased local surface tension that provides increased resistance to further expansions. Then further thinning would ultimately lead to film rupture. A local rise in surface tension produces immediate contraction of the surface. The surface is coupled by viscous forces to the underlying liquid layers. Thus, the contraction of the surface induces liquid flow, in the thin film, from the low-tension region to the high-tension region. The transport of bulk liquid due to surface tension gradients is termed the Gibbs-Marangoni effect and provides the resisting force to film thinning.
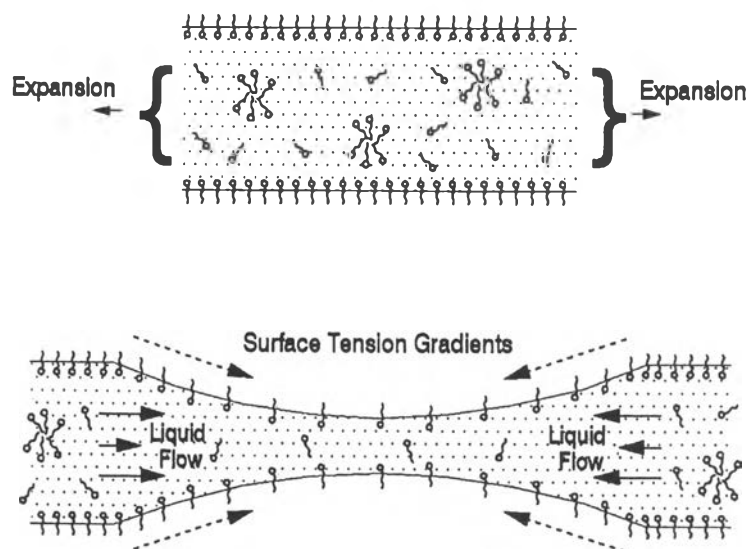

Figure 2.5 The origin of surface elasticity (Schramm, 1994)

2.4 Defoaming

The easiest way to control foam is by the choice of a suitable surfactant. However, in many practical applications there will be severe limitation on the choice of the surfactant with relation to its foaming ability. The primary reason for using a surfactant, *e.g.* detergency, may give high foaming products; the ideal surfactant may be very costly; interaction with other components may change the foam performance. Therefore there can be a need to control the foam by addition of a foam control

agent. Such foam control agents are called antifoams or defoamers. The two terms are not synonymous, as an antifoam is an additive which will prevent foam being formed whilst a defoamer will collapse the already formed foam. The mechanism of the two processes can be very different, although the distinction between them is very vague in practice.

2.5 Defoaming Mechanisms

There are many researches that concern with defoaming mechanism. However, there are not universally accepted. The most likely explanation are a combination of the following:

1.   The formation of an oil/water interface instead of an air/water interface will give a reduced surface tension and hence a reduced Marangoni effect as the surface tension gradient is less.

2.   The hydrophobic oil causes lens which form after the oil drop enters the air-water surface inside the foam film (with or without the formation of duplex oil film), enters the opposite film surface on further film (foam) drainage, and result in the bridge configuration as shown in Figure 2.6. The film then breaks because the capillary forces thin out the film around the bridge and, finally, the film pinches off from the oil.

3.   The surfactant in the defoamer can function as a dispersing agent for the hydrophobic oil. In addition, the defoamer surfactant may replace the foaming surfactant causing the foam at the interface as shown in Figure 2.7.
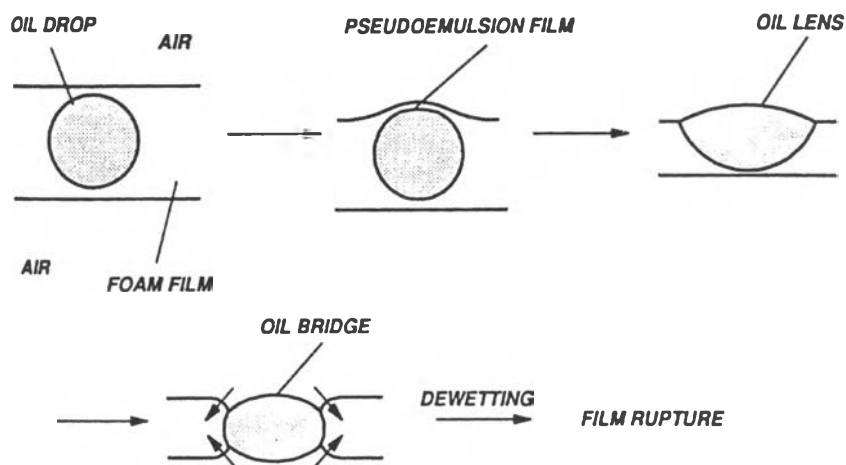
Figure 2.6 Bridging mechanism of antifoaming in foam film by oil (Schramm, 1994)
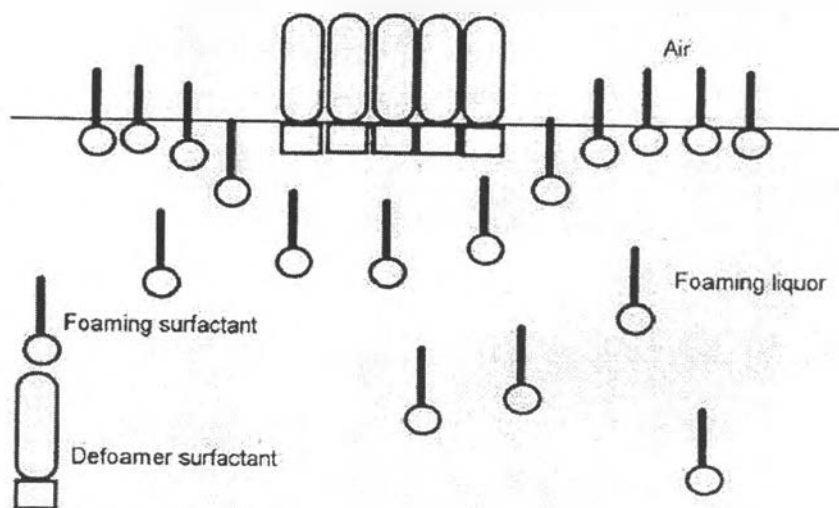

Figure 2.7 Replacement of foaming surfactant by defoamer surfactant (Porter, 1994)

4. Possible interaction between the foaming surfactant and the defoaming surfactant to form mixed micelles and/or mixed monolayers. Mixed micelles and mixed monolayers have the characteristics of being formed at specific ratios of the two component surfactants, with specific surfactant structures giving high synergism in surfactant properties. The highly specific nature of defoamers in paper and paint applications would suggest that mixed micelles and/or mixed surface layers are being formed.

The addition of hydrophobic finely divided solids in hydrophobic oils to high concentrations of high-foaming surfactants gives excellent foam control. In these applications the concentration of defoamer surfactant is very much smaller than the concentration of foaming surfactant. Surfactant interaction is still possible, but is likely to be of low significant. The theory developed by Garrett (1992) has been used to explain the high efficiency of finely divided hydrophobic solids that are used with hydrophobic oils. The overall mechanism proposed by Garrett is illustrated in Figure 2.8. This mechanism can be explained as following (a) the particles rupture the air-water-oil film and the particles are at the surface of the oil droplets (b) the oil droplets adhere to the bubble surface and an oil lens is formed (c) the oil lens then elongates to form a bridge between the air-water-air foam films and (d) capillary pressure in the vicinity of the bridging lens increases the rate of drainage of the foam film.

There is also a large class of defoamers composed of hydrophobic oils, low-solubility surfactants and finely divided solids which are used in applications where the concentration of foaming surfactants can vary from low to high. The mechanism of defoaming will almost certainly involve the formation of mixed adsorption layers and mixed micelles, which could account for the high specificity of such systems.
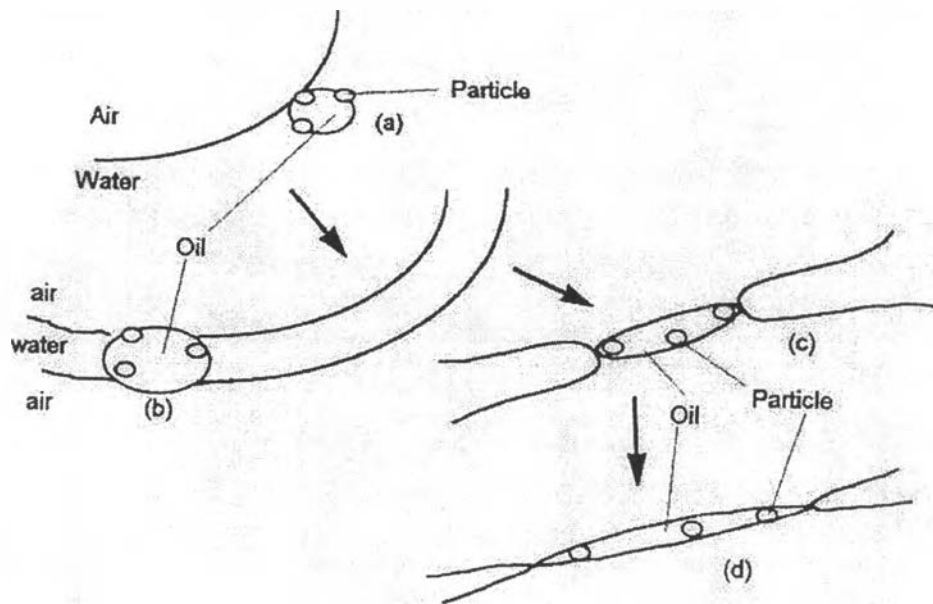
Figure 2.8 Process of film rupture by hydrophobic particle-oil mixtures (Garrett, 1992)

2.6 Literature Review

The widespread importances of foam in general and scientific interest in their formation, stability, and properties have precipitated a wealth of published literature on these subjects.

Cohen *et al.* (1993) studied the foaming properties of a commercial-grade linear alkylbenzene sulfonate (LAS) and calcium ion levels by using a LAS-calcium solubility diagram. They found that foam height is almost independent of calcium concentration until a critical calcium concentration is reached, where the amount of precipitated LAS is substantial, and therefore, there is a dramatic decrease of foam height. The critical calcium concentration increases with LAS concentration increase. In addition, foam stability depends on the initial LAS concentration zone. In the premicellar zone, foam stability is independent of calcium concentration, whereas in the postmicellar zone, the higher the calcium concentration, the higher the

whereas in the postmicellar zone, the higher the calcium concentration, the higher the foam stability, until calcium concentration is reached where the foam stability remains constant.

Angarska *et al.* (1997) studied unstable and equilibrium foam films and foams formed from solution of sodium dodecyl sulfate (SDS) and bivalent electrolyte, $MgCl_2$ or $MgSO_4$. They found that at low ionic strength and low surfactant concentration the films with magnesium ions are more stable than films with sodium ions. At higher surfactant concentration the films containing $MgCl_2$ become stable while the films with $MgSO_4$ remain unstable.

Laheja *et al.* (1998) studied the stability of foams generated with ionic and nonionic surfactant solutions at concentrations higher than the critical micelle concentration (CMC). They found that the 80% drainage life, $\tau_{0.8}$, can be used as a parameter for studying the stability of micellar foams from ionic surfactants, such as SDS. The $\tau_{0.8}$ for drainage of foams generated using SDS shows an initial decrease and then increase with an increase in concentration. And both $\tau_{0.5}$ and $\tau_{0.8}$ for foams generated from a nonionic surfactant (TX100) increase with a surfactant concentration beyond the CMC and level off at a higher concentration.

Patist *et al.* (1998) studied the effect of tetraalkylammonium chlorides on the micellar stability of SDS solutions in relation to the slow micellar relaxation time (τ_2) and interfacial properties. They found that upon increasing the concentration of tetraalkylammonium chlorides, the micellar stability increases, due to the ionic interactions between the oppositely charged tetraalkylammonium chlorides and the SDS headgroup. Beyond a critical concentration, the micellar stability decreases again, which is attributed to the disruption of the molecular packing in the micelles as well as at the air/water interface.

Rodriguez *et al.* (1998) studied the effect of sodium octanoate and pH on the precipitation of SDS with calcium (hardness tolerance) in water. Sodium octanoate can exist as octanoate ions (O^-) or as the pronated nonionic fatty acid (HO) with HO/O^- ratio increasing with decreasing pH. At intermediate pH levels, sodium octanoate or sodium octanoate/SDS systems are composed of mixtures of anionic

and nonionic surfactants, resulting in enhancement of micelle formation due to nonideal mixed micelle formation.

Jha et al. (1999) studied the effect of antifoaming agents on the foamability of SDS solutions and correlated the stability of micelles with antifoaming efficiency on the relaxation time (τ_2). The slow relaxation time (τ_2) of SDS micelles, which is directly related to micellar stability. The addition of antifoaming agents to SDS solutions shows two opposing effects depending on concentration. The antifoaming agents can stabilized the SDS micelles at lower micelle 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.

Tamura et al. (1999) studied to clarify the antifoaming mechanism through the use of the six types of antifoaming particles during the defoaming process. They found that the antifoaming efficiency of antifoams strongly depends on the stability of the pseudoemulsion films. Moreover, the film stability was largely affected by surface roughness for both the liquid and the solid antifoams.

Folmer et al. (2000) observed the foaming behavior of the anionic surfactant, sodium dodecyl sulfate or SDS, in the presence and absence of the nonionic polymer, poly(vinylpyrrolidone) or PVP. They found that at very low surfactant concentrations, there is association between surfactants and polymer at the liquid/air interface, giving increased foam and thin film stability as compared to cases for the same surfactant concentrations but without polymer. As the surfactant and polymer associate in the bulk solution, there is desorption of surfactants and polymer from the surface, rendering decreases in foam and thin film stability. At higher surfactant concentrations, the bulk viscosity is significantly increased owing to the presence of both micelles and micelle-polymer complexes. Both the increased surface viscosity and the bulk viscosity contribute to the foam and film stabilities.