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On the Stability of Aqueous Foams and the Effect of Surfactant

Guo, Yinghui

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On the Stability of Aqueous Foams and the Effect of Surfactant

by

Yinghui Guo

A THESIS
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Abstract

A series of experiments were conducted to examine the stability of sodium dodecyl sulfate (SDS) and SDS+NaCl foams in a dynamic foam analyzer where the concentration of the SDS was higher than the critical micelle concentration. A series of tests were done to ensure that the results from the foam analyzer were repeatable and consistent. The results from the experiments demonstrated that the dynamic foam analyzer can produce consistent and repeatable results. As the concentration of SDS increased, the stability of the resulting foams was enhanced. Profiles of the foam height, average bubble size, and bubble count were obtained versus time. The measurements permitted the estimation of the average liquid drainage rate from the foam – this is a novel contribution from the work. Given that the liquid drainage occurs from the liquid films in the foam, this is an important value for evaluating the relative stability of the foam. The SDS and NaCl experiments revealed that the addition of NaCl further stabilized the foam leading to lower average liquid drainage rate from the foam.
Acknowledgements

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Dedication

This paper is dedicated to my mother Hui Huang and my father Chunhai Guo.

They always support me in fulfilling my dream.
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CHAPTER 1 INTRODUCTION

1.1 Background

Foam is a multi-phase dispersion system in which insoluble or slightly soluble gas is dispersed in liquid, gas is the dispersed phase, and liquid is the continuous host phase and dispersion medium (Langevin 1998, Beneventi et al. 2001, Pandey et al. 2003, Tan et al. 2005, Shuixiang et al. 2019, Petkova et al. 2020). Due to interfacial forces and fluid properties (e.g. density and viscosity), in a foam, the gas is separated into bubbles divided by liquid phase films as shown in Figure 1.1; the curved sections of the liquid films are referred to as Plateau boundaries (Plateau 1873, Mingmei et al. 2005, Zhou et al. 2020). The liquid films are typically thin, of order of tens to hundreds of microns, and they arrange themselves so that they achieve a minimal potential energy state.

Figure 1.1: Cross-section schematic of a foam consisting of the gas bubbles, liquid films, and the curved liquid regions where multiple liquid film intersect (referred to as the plateau border).
There are many ways for the gas to enter and be dispersed in the liquid phase, for example, rapid stirring, shaking the container, blowing the gas into the liquid, exsolving the gas from liquid due to a depression of the pressure or increase of the temperature, and having a reaction generate the gas within the liquid phase (Julia and Wiebke 2012). Foams, given the fineness of the bubbles, can have huge interfacial area and thus a large amount of energy associated with the overall interface and its extent (Chao et al. 2020).

In many situations a foam is created in a vertical arrangement where a gas is sparged into the bottom of a liquid layer. Consider the case of a foam filling a column as shown in Figure 1.2. During gas flow into the liquid, the gas forms bubbles in the liquid phase and a foam is established. Given the addition of the gas volume to the liquid volume, the foam reaches heights greater than that of the original liquid. After the gas flow stops, the creation of new gas bubbles stops and the foam undergoes foam destruction (Langevin 2020). This is because foam is naturally unstable – the liquid drains down the liquid films within the film leading to breakage with consequent merging of bubbles or destruction of bubbles at the top layer of the foam. There are three general yet distinct stages of foam destruction. During the first stage of foam liquid drainage, the total height of the foam does not change because even though the liquid content is dropping, the bubbles remain intact and the height of the foam is preserved (Zhigang and Gengdian 2017). In this stage, the topmost liquid films are filling the liquid films in parts of the foam below them and thus, the thinnest films are found at the top of the foam column. In the second stage, the liquid films in the topmost layers of the foam column are now thin enough such that they are rupturing and bubbles are starting to merge and due to the loss of the liquid structure imposed initially, the height of the foam starts to drop (Zhigang and Gengdian 2017). This decline of the height accelerates as the
The topmost bubbles are rupturing and are supplying less and less liquid to the liquid films below them and the lower layers also start to rupture because their films are now too thin to sustain their structure. In the third stage of foam destruction, the foam structure begins to coarsen and the foam height falls at a lower rate than in the second stage.

![Figure 1.2: Stages of foam destruction.](image)

The key to foam stability is the prevention or hindering of the liquid drainage within the liquid films of the foam. If liquid drainage was stopped, then the structure of the foam would be retained.
The focus of the research reported here is on the stability of a water-based foam. Water-based foams have good fluidity (given the low viscosity of water), low density, and strong carrying capacity (Jiaqing et al. 2017).

The bubble diameter of foam can be small but given the number of them, the specific surface area (area per unit volume of the foam) is large. Foam is a soft material. It can not only deform elastically like a solid, but also have fluidity like a liquid (Stefan et al. 2011). Non-toxic, non-polluting, non-flammable, non-explosive and low-cost foams have great advantages for use in household products and industrial processes (Jun et al. 2008). Water-based foams have a wide range of applications: examples include secondary and tertiary exploitation of oil and gas resources, wastewater treatment, soil purification, mineral flotation, cosmetic, foam fire extinguishing, petroleum industry, and brewing industry (Mingmei et al. 2005, Shuixiang et al. 2019, Zhou et al. 2020). These foams can also be used to reduce the resistance to flow for viscous aqueous solutions or raise the effective viscosity of a gas phase since the viscosity of the foam is lower than that of the liquid but higher than that of the gas. In oil exploitation, water-based foams are used to raise the sweep and displacement efficiency for oil recovery (Jiaqing et al. 2017). However, there is a limit on the use of foams – it is the control of the stability of the foam. In some cases, foams are to be avoided e.g. dish-wash machine and front-loader fabric washing machine (Felix 1987). If too much foam is generated, it will be difficult to completely wash off the foam during washing, and the residual foam remains on the items making it impossible to completely clean the items. On the other hand, in other cases, foam stability and preservation are desired e.g. gas foam oil recovery processes, manufacturing processes, and gas viscosification processes. In
other processes, the non-Newtonian nature of the foam’s behaviour makes it desirable e.g. in manufacturing processes.

In most cases, the greater the mass density of the foam, the higher is the effective foam viscosity (Peter and Economides 1992). Peter and Economides (1992) have shown that increased pressure and reduced foam quality leads to lower foam viscosity. Yesenia (2001) have shown that when the shear rate is high, the quality of the foam can be reduced to <80%, and the foam behaves as a pseudoplastic fluid and that foams with quality >80%, they exhibit Newtonian characteristics. These changes of flow behaviour arising from the different quality of the foam can be used to manage the foam’s flow properties (viscosity versus shear rate and viscoelasticity).

Kemin (2013) researched the influence of foam quality on the flow resistance of foamed heavy oil. He found that the effective viscosity of the foam depends on the gas content: the lower the gas content, the higher is the effective viscosity.

1.2 Complexity of Foam: Stability

The complexity of foams arises from their structure which tends to be random and transient with interactions between bubbles involving bubble creation, destruction, and merging (which is linked to liquid film flow). After the foam is generated, the bubbles will merge and the liquid interfaces will re-arrange themselves according to the dynamic of the destruction of the foam. In general, for many foams, during destruction, the surface of the bubbles evolves from a spherical shape to a polyhedron shape, both depicted in Figure 1.3.
The foamability and stability of the foam are two important factors in foam applications because foamability determines the number of bubbles (and their associated size) and speed of foam generation whereas stability determines the rate of foam persistence or destruction (Langevin 1998, Mingmei et al. 2005). Foamability and stability are linked.

Foams composed of high-viscosity solutions often maintain good foam stability (because the liquid drains slowly from the liquid films in the foam), but on the other hand, high-viscosity can impair foamability reducing the total amount of foam produced (since it takes a lot of energy to disperse the gas in a viscous liquid) (Adrian and Regine 2011). Therefore, in general, maximum foamability and maximum stability of a gas-liquid combination is not likely at the same conditions. Thus, for foams, depending on the application, there is a balance to be found between foamability and stability.
The period of time the foam exists in the liquid is the standard to measure the stability of the foam. The foam composite index (FCI) has been used to quantitatively express foam foaming and stability defined as (Jiaqing et al. 2017):

\[
FCI = 0.75V_0t_{1/2}
\]

where \( V_0 \) is the volume of foam and \( t_{1/2} \) is the foam half-life which is the amount of time required for the foam to destabilize and reach half of its original height. The larger the value of the FCI, the better the overall performance of the foam with respect to its foamability and stability. Often, in
may experiments, the main determinant for indexing the stability of one foam versus another foam is the foam half-life.

During the disappearance of the foam, the liquid films separating the bubbles gradually becomes thinner due to drainage under the action of liquid drainage until they rupture and as more and more interfaces rupture and the bubbles merge (Langevin 1998, Denis and Stefan 1999, Langevin 2020), the number of bubbles decreases until they disappear completely (Mingmei et al. 2005). The faster the liquid drainage and due to the surface waves on the liquid films, under the action of the disjoining pressure, the liquid film will thin and break (Langevin 1998, Zhou et al. 2020, Chao et al. 2020). Another mode of instability is referred to as coarsening – in this mechanism, given the higher pressure within smaller bubbles (arising from Young-Laplace pressure), gas dissolution in the liquid films presents a concentration profile that motivates gas transport (in the liquid film) from smaller gas bubbles to larger gas bubbles. The smaller the bubble, the greater the internal pressure of the gas bubble which implies higher concentration of the gas component in the liquid phase (because of thermodynamic equilibrium) and thus gas diffuses from the small bubbles to the large bubbles, causing the small bubble to disappear (Rao et al. 1982). Gas diffusion does not affect the stability of the foam when the foam is created, but when a black film forms, gas diffusion becomes a key mechanism for affecting the stability (Desheng and Xiaoyu 2006). The coarsening mechanism leads to smaller bubbles growing smaller feeding their gas to larger bubbles – eventually the small bubbles disappear. The only way that the films can persist if there are surface active components that have strong repulsive forces that tend to keep the liquid film intact (since they resist movement of water in the liquid film) or if the viscosity of the liquid is high (slows
liquid drainage and also diffusion of gas across the liquid film from smaller bubbles to larger bubbles) (Mingmei et al. 2005; Nurudeen et al. 2017).

When the foam enters the late stage of drainage, the foam film become very thin and sharp black spots appear on the surface of the bubbles – the surface of the foam shows a black interference color. These are referred to as black films. Generally, the thickness of the black film is about 50 nm (Ashok and Joykrishna 2007).

Changes of the surface tension will affect the stability of the foam (Shuixiang et al. 2019; Qiwei et al. 2003). It has been shown that adding surfactants, mineral mud, inorganic salts, or raising the temperature can make foams more stable (Peter and Andrew 1983, Jin and Qicheng 2007, Xueliang et al. 2010, Jiaqing et al. 2017). The lowering of the surface tension means that the energy required to disperse the gas phase in the liquid (and the consequent increase of the interfacial area) drops and thus, it is easier to create the foam. This is why it becomes easier to form foam when soap is added to water.

1.2.1 Description of the Stability of Foam

Currently, there are two common ways to describe the stability of foam: 1. precipitation half-life and 2. foam half-life (Davide et al. 2001). Both methods are good methods for indexing foam stability. The precipitation half-life refers to the time required for the loss of general liquid after foam formation (Rosa et al. 2004). This is directly related to the drainage speed of the liquid in the foam. This method is mainly used in the early stage of foam attenuation and the description of
foam stability during foam drainage. The half-life of the foam refers to the time required for the volume (or height) of the foam to decrease to one-half of its original value (Rosa et al. 2004).

The quality of the foam is expressed by the gas-to-foam ratio (Benjamin, 1999; Argillier & Herzhaft, 1998) given by:

\[
\Gamma = \frac{V_g}{V_g + V_L} \times 100\%
\]

where \(\Gamma\) is the quality of the foam, \(V_g\) and \(V_L\) are the volume of the gas and liquid, respectively (Argillier and Herzhaft 1998). Rand and Kraynik (Rand and Kraynik 1983) have shown the smaller the bubbles, the more stable is the foam. Furthermore, the quality of the foam changes with pressure. The higher the foam quality, the denser is the foam structure (Duane, 1994).

1.2.2 Effect of Additives on the Stability of Foam

The addition of surfactant to water reduces the surface tension (surface energy) of the solution making it easier to produce bubbles. The surfactants adsorb on the surface of liquid films making the liquid films stronger and enhancing the stability of the foam (Jun et al., 2008; Boos et al. 2012; Alireza et al. 2020; Petkova et al. 2020; Qiwei et al. 2003). In the case of surfactants, when the liquid film is locally expanded, the liquid film will become thinner, and the surfactant concentration on the thinned zone will drop leading to a concentration difference which motivates both surfactant and water molecules moving towards the thinned zone. This yields an action that increases the thickness of the film. This self-repairing behavior is due to the interfacial tension gradient that induces flow and is referred to as the Marangoni effect (Jin & Qicheng, 2007; Qiwei
et al. 2003). A commonly used surfactant is sodium dodecyl sulfate (SDS) which is beneficial to the stability of the water-based foams. Surfactants can automatically adsorb on the surface of the liquid film in the form of a monolayer, thereby reducing the surface-associated free energy of the foam (Shuixiang et al. 2019). The Gibbs film elasticity, as well as surface diffusion, can homogeneously distribute the surfactant on the liquid surfaces which in turn can influence the Marangoni effect (Qiwei et al. 2003). Surfactant adsorption forces on the foam surface and foam drainage rate are the two influencing factors that balance as the foam coalesces (Qiwei et al. 2003).

The concentration of the surfactant has an important influence on foaming properties and foam stability. When the surfactant concentration is lower than critical micelle concentration (CMC), the surfactant is distributed in the liquid phase as individual molecules. When the concentration is larger than the CMC, the surfactant forms micelles – structured arrangements of the surfactant molecules (Tan et al. 2005, Hammouda 2013, Petkova et al. 2020). The micelles can have different shapes including spherical or planar bilayer structures. As shown in Figure 1.4, when the concentration is less than the CMC, the surface tension of the solution depends on the surfactant concentration (Tan et al. 2005). Beyond the CMC, the surface tension remains relatively constant. Despite the impact of surface tension on a foam’s foamability, above the CMC where the surface tension is effectively constant, a relatively stable foam can occur (Wang et al. 2009; Ashok and Joykrishna, 2007).
If a salt is added to an aqueous surfactant solution, the salt changes the absorbability of the surfactant on the interfaces and also changes the charge structure of the interface (Alireza et al. 2020). The addition of salt also affects the diffusion of surfactants in the liquid films as well as gives rise to osmotic pressure effects that motivate liquid movement (Felix, 1987). Different cations and anions all have different effects on foam stability (Hirasaki & Lawson, 1985); for example, aqueous foam stability has been found to follow the following order: $\text{Li}^+ < \text{Na}^+ < \text{Cs}^+ < \text{Mg}^{2+}$, and $\text{Al}^{3+} < \text{Ca}^{2+} < \text{Na}^+$. The addition of salt also changes the size of bubbles: the size of the bubbles decreases as the concentration of salt increases (Felix, 1987). Argillier added 5 g/l of NaCl aqueous solution and 200 g of surfactant to a 3-litre glass beaker with a pH of 9 and stirred for 2 minutes at 2000 rpm. They found that the resulting quality of the foam is between 0.85-0.95 (Jiaqiang et al. 2013). However, the quality depends on the conditions of the formation of the foam.
It can not only increase the stability of the foam, but also can improve the defoaming speed. There are many ways to speed up the disappearance of foam: (1) Physical method, such as increase temperature, ultrasonic vibration; (2) Chemical method (add defoamer), such as Polysiloxane, Hydrophobic solid particles, Polyether modified silicone oil etc.

1.3 Problem Statement

At present, there is a lack of systematic research on the influence of salt and surfactant concentrations on foam stability especially for systems that are above the CMC for the surfactant. The main questions being addressed in the research documented in this thesis are as follows:

1. Are foam experiments in a dynamic foam analyzer repeatable?
2. How does surfactant concentration, when above the CMC, affect the stability of an aqueous foam?
3. How does salt concentration, in the presence of a surfactant that is above the CMC influence the stability of an aqueous foam?

1.4 Organization of Thesis

The thrust of the research proposed here is to investigate the effects of salt and surfactant concentration (with concentration above the CMC) on the stability of foam. This thesis is organized as follows. **Chapter 2** provides a literature review on the subject matter of the thesis. **Chapter 3** describes research conducted by using a dynamic foam analyzer to understand the impact of surfactant concentration (>CMC) on the stability of aqueous foams. **Chapter 4** presents
and investigation of the effects of both salt and surfactant concentrations (>CMC) on the stability of the foam. **Chapter 5** summarizes the major conclusions from the studies in this thesis and provides recommendations for the future work.
CHAPTER 2 LITERATURE REVIEW

2.1 Background

Foam is a multi-phase dispersed system in which insoluble or slightly soluble gas is dispersed in liquid: gas is the dispersed phase and liquid is the continuous phase and dispersion medium (Shuixiang et al. 2019). Because of the density difference and instabilities as the gas penetrates or mixes with the liquid, the gas is divided into multiple bubbles in the liquid which are bounded by liquid films. Relative to the size of the bubbles, the liquid films between the bubbles can be very thin. In most foams, the volume fraction of the gas in the foam is significantly greater than that of the liquid.

All liquid is capable of foaming – this includes water and oil and even rock (molten lava and other rocks form foams when gas exsolves from the liquid phase – these get frozen in place when the rock solidifies). As shown in Figure 2.1, foams are seen in nature e.g. seaside foams, rock as well as human-made products e.g. shaving cream, mattresses, and rubber seals. For many products, the liquid phase of the foam is solidified to make the final product (a solid foam is created).
As described in the Introduction, foamability and stability of the foam are two key factors for the application of foams. Foamability determines the number of bubbles (and their size) and speed of foam generation whereas stability determines the effective time that the foam exists (Mingmei et al. 2005). These two factors appear to compete with each other. For example, a high viscosity solution will maintain good foam stability but given its viscosity, it would have been difficult to create the foam in the viscous liquid which could limit the total amount of foam produced (Adrian & Regine, 2011). Thus, for most foamable solutions, the foamability and stability of the foam cannot reach their maxima under the same conditions. Thus, for applications, often the focus is on finding the balance between foamability and stability.

The focus of the research documented here is on aqueous solutions – given the low viscosity of water, the foamability is high and the key issue becomes the stability of the foam. In some applications, the foam is to be avoided (meaning that it is destroyed quickly) and in other
applications, the foam is to preserve (meaning it holds its form for as long as possible). The foam composite index (FCI) is often used to quantitatively express the stability of the foam (Jiaqing et al. 2017):

$$\text{FCI} = 0.75V_0t_{1/2}$$

where $V_0$ is the volume of foam, and $t_{1/2}$ is the foam drainage half-life. In this formula, the key measure of the stability of the foam is the half-life (the time it takes for the foam’s volume to drop to half its original value). The greater the half-life, the longer the foam persists, and the more stable is the foam.

After the foam is produced, it will gradually disappear. Under normal circumstances, the period of time the foam exists in the liquid is the standard to measure the stability of the foam.

Water-based foam has good fluidity (due to low liquid phase viscosity), relatively low density (due to high gas content), and strong carrying capacity (Chao et al. 2020). In many cases, the bubble diameter of aqueous foams can be small with the overall foam having very large surface area. Aqueous foams can maintain their shape (before they suffer critical destruction of the liquid films) but are also deformable and can be pumped. Thus, they can behave both elastically as well as a liquid (Stefan et al. 2011). In many applications, the target is to create non-toxic, non-polluting, non-flammable, non-explosive and low-cost foams (Jun et al. 2008). Therefore, water-based foam has a wide range of applications and is used in many household and industrial settings including secondary and tertiary exploitation of oil and gas resources, wastewater treatment, soil purification, mineral flotation, cosmetics, foam fire extinguishing, detergents and cleaning materials, and brewing industry (Shuixiang et al. 2019; Mingmei et al. 2005; Jiaqing et al. 2017).
1.1 Water-base foam composition

Foam is composed of gas and liquid. The gas can be air, natural gas, nitrogen, carbon dioxide, etc. Due to safety considerations, in some applications, air and natural gas are not used for example in oil extraction where combustible and explosive gases present hazards, and nitrogen or carbon dioxide is generally used. In the research reported here, the system consists of deionized water and air.

As described by Sebba (Felix, 1987), the liquid film of water-based foam consists of three layers: two interfaces sandwiching an aqueous solution layer (Felix, 1987). If surfactant is present, the surfactant will be present on interfaces (as well as the bulk). The quality of the foam is the ratio of the gas volume and foam volume (Alireza et al. 2020); for most foams, this ratio is usually high (Benjamin, 1999). The quality is given by:

\[ \Gamma = \frac{V_g}{(V_g+V_l)} \times 100\% \]

where \( \Gamma \) is the quality of the foam, \( V_g \) is the volume of the gas in the foam, and \( V_l \) is the volume of the liquid in the foam (Benjamin, 1999). The quality of the foam changes with pressure. Generally, when the foam quality is higher than 70%, the structure of the foam will change greatly. The lower the foam quality, the denser the foam structure. A dense foam structure will sharply increase the foam viscosity (since the liquid volume content in the foam is relatively large) (Jiaqing et al. 2013; Peter et al. 1992). When the shear rate is high, in some cases, the quality of the foam will drop to less than 80% and for some, they exhibit pseudoplastic behaviour. Above a quality of 80%, some foams demonstrate Newtonian characteristics (Yesenia et al. 2001).
In one practical application, Kemin researched the influence of foam quality on the flow resistance of THCO1 and THCO2 heavy oils (Kemin, 2013). When the gas content of the foam is greater than 74%, Kemin showed that the density of the foam is less than that of the THCO1 oil (due to the presence of gas) and the foam floats on the viscous oil in the horizontal pipeline with stratification between the liquid heavy oil phase and the foam. Therefore, in this case, the creation of foam does not help much to reduce the flow resistance of the viscous oil. On the other hand, when the gas content of the foam is 30% (and the density of the foam is closer to the THCO1 heavy oil), the foam aids in lowering the overall effective viscosity of the liquid reducing the resistance to flow. Kemin showed that if the quality drops below 10%, then the effective amount of foam is not sufficient to help reduce the flow resistance of the heavy oil. The situation is quite different in vertical pipes. At 74% gas content, the foam reduces the resistance to flow in the pipe by 70% thus helping the flow of the THCO2 heavy oil. Thus, for this application, the foam quality and physical system which uses the foam are both important.

1.2 Stability of Foams

As described in Chapter 1, after a foam is created, it starts to disappear. During the disappearance of the foam, the liquid film separating the bubbles gradually becomes thinner until the films burst which merges the bubbles together, and the number of bubbles decreases until they disappear completely (Mingmei et al. 2005; Chao et al. 2020, Rio et al. 2014). The liquid, given gravity drainage due to the density difference between the liquid and gas, will drain through the liquid films to the base of the foam (where a liquid pool accumulates). Generally, there are five main reasons for the foam to disappear, described in the following.
(1) The liquid film between adjacent bubbles thins and destabilizes, causing the bubbles to merge together, forming a coalesced new larger bubble (Jin & Qicheng, 2007). This thinning can occur due to liquid drainage or due to fluctuations of the interfaces themselves (waves) that propagate through the system due to the destruction of bubbles. Raising the viscosity of the solution can hinder gravity drainage and thus yield a more stable foam (Zhigang & Gengdian, 2017). Given the volume of liquid in the films, the amount of liquid drainage is small but does contribute to foam destruction. This mechanism is referred to as drainage.

(2) The smaller the bubble, the greater the pressure within the bubble due to Young-Laplace capillary effects which creates a higher concentration of the gas molecules in the liquid film on the side of the smaller bubble. This causes the gas to diffuse within the liquid film from the smaller bubble to larger bubbles (where the pressure is lower and consequent concentration in the liquid film is lower) leading to the disappearance of the smaller bubbles (Denis & Stefan, 1999). This mechanism is referred to as coarsening. The presence of surfactants adsorbed on the surface of the liquid films can slow down diffusive transport of the gas molecules through the liquid films.

(3) Evaporation of the liquid can occur from the liquid films to the gas phase (whether at the top of the foam or within the foam to the bubbles interiors). This can lead to the rupture of the liquid layers. For a water-air system, increasing the air humidity can well reduce the evaporation of water in the foam, reduce the discharge rate, and increase the stability of the foam (Barnes 1986, Li et al. 2012, Xueliang et al. 2010). This mechanism is referred to as evaporation. The presence of surfactants adsorbed on the surface of the liquid films can hinder the ability of the water to evaporate.
(4) As the liquid film thins, in the presence of surfactants or other charged molecules, there are several forces (arising from electrostatic double layer, Van der Waals, and short-range steric forces), displayed in Figure 2.2, that act across the film which are described as the Derjaguin and Landau, Verwey and Overbeek (DVLO) theory. When the film gets thinner past the maximum, the sum of potentials becomes negative and attractive forces start to dominate the system. This means that the film tends to thin further. Thereafter, the sum rapidly evolves positive and the film then stops thinning and further thinning of the film requires externally applied work on the system (or evaporation). Thus, the repulsion forces, referred to as the disjoining pressure, tend to resist the further thinning of the film. The disjoining pressure is defined as the difference between the pressure in the thin film relative to that in the bulk phase from which the thin film emerged.

![Diagram of DVLO potentials](image)

**Figure 2.2: DVLO potentials for a thin film.** The attractive forces are Van der Waals forces. The double layer repulsion is caused by the electrostatic repulsion arising from the double layer. The short-range forces are the repulsive steric forces.
(5) Liquid flow within the films associated with capillary pressure differences can lead to flow from the film to the border plateaus as shown in Figure 2.3. A pressure gradient is created in the liquid film associated with the capillary pressure within the liquid film that moves liquid from the liquid film flat regions to the curved regions. This mechanism can be a major contributor to the destruction of foam and is referred to as capillary flow.

![Diagram of liquid film flow](image)

**Figure 2.3: Flow induced from capillary pressure gradient in liquid film.**

The instability of the foam arises as soon as foam creation stops. In the early stages of liquid drainage, the number of bubbles remains the same and the height stays relatively unchanged as the liquid films thin but the foam largely remains in place. After sufficient liquid drainage and thinning of the liquid films, the films in the foam at the top of the foam start to rupture and the height of the foam starts to drop. Also, any films within the foam volume will rupture if too thin causing bubbles to merge. Furthermore, coarsening is occurring throughout the foam volume leading to the disappearance of smaller bubbles. In most foams, coarsening is a slower process than that of liquid...
drainage. Evaporation at the top of the foam depends on the concentration of the liquid in the ambient environment whereas in the bubbles, it will depend on the local humidity of the gas in the bubble. When a bubble ruptures to the ambient environment, the liquid vapour that was in the bubble will be released to the environment.

2.1.1 Influence of Temperature and Pressure

Temperature can change the stability of foams and its behaviour is complex. First, the viscosity of the liquid phase will increase the cooler the temperature and as a consequence, the liquid drainage rate drops and thus the stability is enhanced (Jun et al. 2008; Desheng & Xiaoyu, 2006). Second, the lower the temperature, the higher is the density of the liquid and thus the effect of gravity drainage rises and thus the stability is diminished. Third, the lowering of temperature raises the surface tension and as a consequence it is harder to create the foam (the foamability is enhanced). However, the lower the temperature and the greater the surface tension, the more prone are the interfaces to deform so they can minimize their surface area to minimize their energy state which would tend to lead to a less stable system. Fourth, the lower the temperature, the lower is the evaporation rate of the liquid from the films and thus the films would tend to last longer thus stabilizing the foam (Nurudeen et al. 2017). Fifth, the lower the temperature, the thinner is the electrostatic double layer (EDL) and thus, the lower is its influence on impeding water movement in the liquid films (Zuo et al. 2012, Alizadeh and Wang 2020). Thus, this would tend to destabilize the foam.
Jiaqiang explored by experiment foams produced by 3 g/l AOS, 1 g/l AES, 4 g/l HEC and 3 g/l XG aqueous solution (Hirasaki & Lawson, 1985). He showed that as the temperature increased, the apparent foam viscosity also increases. At about 30°C, a maximum appears, and then the apparent foam viscosity begins to decrease as the temperature rises. At low temperatures, as the temperature increases, the bubble volume expands and the surface area of the bubble increases, resulting in an increase in surface tension and an increase in apparent viscosity (Jiaqing et al. 2017; Hirasaki & Lawson, 1985).

The smaller the bubble radius in the foam, the more uniform the bubble radius value, and the better the stability of the foam. Rand and Kraynik applied a pressure of 1 to 20 bar to a foam in an autoclave and observed the changes of the foam. As the pressure increases, the bubbles in the foam formed have a tendency to become smaller, the drainage time also becomes longer, the rate of foam bursting becomes slower, and the stability of the foam increases (Peter & Andrew, 1983).

2.1.2 Measurement of Stability

There are many commonly used methods to study foam stability, such as Ross-Miles’ method, Bikerman’s method, to detect changes in foam diameter, Plateau boundary, electrical conductivity and foam liquid content (Shuixiang et al. 2019). The generation of foam is divided into two stages: (1) The initial of foaming; (2) Foam accumulation. They have different rates, so the analysis methods should also be different (Petkova et al. 2020).
With respect to the measurement of the stability of foam, the method used in the research documented in this thesis is the half-life. It is defined as the time it takes for the foam to reach half its original height. In many experimental approaches, the height of a foam is monitored through time using a transparent column. We use the same approach with a dynamic foam analyzer, the DFA100, displayed in Figure 2.4.

![DFA100 Dynamic Foam Analyzer](image)

**Figure 2.4: The DFA100 Dynamic Foam Analyzer.**

The DFA100 (Krüss Scientific Inc.) is a professional electronic instrument for measuring foam foamability and stability. It analyzes the properties of the foam by measuring the volume, liquid content, foam density, bubble size and bubble size distribution of the bubble generated by the
solution. In addition, The DFA100 assists in the optimization of foam-forming products or, in the case of unwanted foam formation, helps with specific foam prevention and help in the effective prevention of foam in areas where it is undesirable. The advantage of DFA100 is that it can measure foam characteristics repeatedly and accurately by using an electronic gas flow control system in an accurately controlled foaming process. At the same time, the DFA100 instrument also uses an optical sensor to measure the quantity of foam generated by the solution and the foam attenuation characteristics, even if the life of the foam is very short, clear and accurate measurement data can be obtained. As a result, the DFA100 is a reliable instrument for analyzing the whole spectrum from slow to very fast decaying foams.

The DFA100 can generate foam in two ways: (1) blowing gas into the liquid and (2) stirring with temperature up to 90°C. In addition, DFA100 can also use externally connected gases such as carbon dioxide.

2.2 Additives for Enhancing the Stability of Foams

Pure liquid cannot form stable foam. For example, the time scale over which a pure water foam disintegrates is of order of microseconds and as such, a foam cannot be created with pure water. To form a stable aqueous foam, surface active chemicals must be added to the water that enable easier foam formation (foamability) and the preservation, as best that can be done, of the foam after it is created. Surfactants are used as foaming agents or stabilizers to reduce the difficulty of foam formation, increase the number of bubbles, increase foam stability, and extend the time of foam decay (Jiaqing et al. 2017). Surfactants can be divided into four types: (1) anionic surfactants,
(2) cationic surfactants, (3) non-ionic surfactants, and (4) amphoteric surfactants (Jiaqing et al. 2017).

Anionic surfactants can dissociate surface-active anions in water. There are many commonly used anionic surfactants, such as Sodium Dodecyl Sulfate (SDS, also referred to as sodium lauryl sulfate), sodium dodecyl benzene sulfonate, fatty acid soap, coconut oil alkyl sulfate, fatty alcohol ether sodium sulfate, and so on (Julia & Wiebke, 2012). Anionic surfactants have high foaming ability, are available from a wide range of sources, and are reasonably priced. However, it should be noted that anionic surfactants have poor anti-electrolyte ability. If there are other ions in the solution, care should be taken to avoid precipitation (Stefan et al. 2011).

Cationic surfactants carry a positive charge and are generally salts derived from organic amines and can dissociate surface active cations in water (Adrian & Regine, 2011). The foamability of cationic surfactants is worse than that of anionic surfactants, and the price is higher, and options are less than that of anionic surfactants (Jun et al. 2008). Therefore, cationic surfactants are rarely used as foaming agents.

Non-ionic surfactants do not dissociate ions in water but exist in the liquid as molecules or micelles. The lipophilic group side can be a hydrocarbon chain or a polyoxypropylene chain, and the hydrophilic group side can be a hydroxyl group or ether bond, for example CP and AEO (Song et al. 2011).
Amphoteric surfactants have both anions and cations in the ions dissociated from water (Tcholakova et al. 2008). The pH value has a great influence on this zwitterion (Peter et al. 1992). In an acidic environment, zwitterion presents cationic characteristics whereas in an alkaline environment, zwitterions present anionic characteristics, and when they are electrically neutral, they present non-ionic characteristics (Alireza et al. 2020). Betaine is a typical amphoteric surfactant (Jiaqiang et al. 2013). Due to the high price of amphoteric surfactants and poor economic benefits, they are rarely used in industrial processes.

2.2.1 Influence of Surfactant

The addition of surfactant to the liquid reduces the surface tension of the solution making it easier to produce bubbles (Peter & Andrew, 1983) Surfactants are adsorbed on the surface of the liquid film making the liquid film stronger and prolonging the life of the foam (Jun et al. 2008). Due to the high surface tension of water, surfactants are easily adsorbed on the surface of the liquid film enabling practical manufacturing and other processes that take advantage of water-based foam (Duane, 1994; Boos et al. 2012; Alireza et al. 2020; Petkova et al. 2020). The addition of surfactant helps to increase spreading of a solution on a solid (Boos et al. 2012). The Marangoni effect (where flow occurs under a gradient of the surface tension) can reduce the rate of thinning of a foam film thereby affecting the dynamic stability of the foam film (Petkova et al. 2020). Surfactants can automatically adsorb on the surface of the bubble liquid film in the form of a monolayer, thereby reducing the surface free energy of the foam (Shuixiang et al. 2019). At low concentrations, surfactants adsorbed at air-water interfaces form monolayers on the surface as shown in Figure 2.5. The monolayer of surfactant molecules imparts a resistance to the film to extension, thus
providing a stabilizing mechanism for the thin liquid film. If the film extends, the local lowering of the surfactant surface concentration raises the local surface tension which induces a surface tension gradient which in turn promotes flow to the extended (depleted) part of the film. This behaviour can be thought of as elastic behaviour of the interface.

![Diagram of surfactant adsorption on foam surface](image)

**Figure 2.5: Surfactant (SDS, head group is negatively charged) adsorbed on surface of thin liquid (water) film.**

Surfactant adsorption on the foam surface and the foam drainage rate are two influencing factors that balance of the foam coalesces (Petkova et al. 2020). When the bubble is covered with a sufficient number of adsorbed molecules, the adsorption rate is greater than the repulsive force of the bubble and the gas-liquid interface, it prevents the foam from coalescing. Otherwise, the foam film will quickly become thinner and rupture, causing bubbles to merge (Petkova et al. 2020).

For the research that is documented here, the surfactant used is Sodium dodecyl sulfate (SDS, CH$_3$(CH$_2$)$_{11}$SO$_4$Na) has good foaming properties and has a rich amount of data in the published literature. SDS consists of a 12 carbon chain attached to a sulphate group. Given that it has a hydrophilic head group (the sulphate group) and a lipophilic tail, it exhibits amphiphilic properties.
enabling it to form micelles. In pure water at 25°C, its critical micelle concentration (CMC) is equal to 0.0082 mol/litre (Cifuentes et al. 1997; Bergeron, 1999; Markarian et al. 2005; Hammouda, 2013; Fauser et al. 2015). Solutions of SDS in pure water are easy to prepare and it has low cost. These advantages make SDS a good surfactant and thus, it is commonly used in many cleaning products e.g. soap, detergents, and toothpastes (Qiwei et al. 2003).

2.2.2 Influence of Surfactant Molecular Structure

It has been found that the molecular mass of the surfactant can increase its surface activity (thus leading to greater resistance of the liquid film to deformation), but on the other hand, it can result in a decrease of foamability (Tan et al. 2005). When the chain length of the alkyl group does not change, the foamability can be improved by increasing the hydrophilicity of the molecule (Wang et al. 2009). The length and number of the hydrophobic tail of the alkyl group are other important factors that affect the foamability (Wang et al. 2009; Song et al. 2011).

In the molecular structure of the surfactant, the longer the hydrophobic chain, the slower the gas diffusion rate through the liquid film and thus, the smaller is the impact of coarsening and as a result, the foam is more stable (Kofi et al. 2015). To some extent, increasing the length of the alkyl chain can improve the stability of the foam, but above a certain length, due to a lower diffusion coefficient (due to its greater molecular weight), the surfactant molecules take longer to reach the interface between the gas and liquid, thereby reducing the stability of the foam (Davide et al. 2001). Multiple experimental results have proved that increasing the degree of esterification of surfactant molecules can increase the elasticity of the molecules, thereby raising the viscosity of the liquid,
improving the stability of the liquid film, reducing the speed of liquid drainage, and the foam can last longer (Rosa et al. 2004; Ashok & Joykrishna, 2007).

2.2.3 Influence of Surfactant Concentration

The concentration of the surfactant has an important influence on foaming properties and foam stability and whether the concentration is greater than the critical micelle concentration (CMC) or less than the CMC, different behaviours occur (Yesenia et al. 2001). When the concentration is less than the CMC, the increase in the concentration of surfactant will increase the surface activity of the solution decreasing the surface tension of the solution. This has a direct impact on the foamability and stability of the solution. First, it will improve the foamability of the solution (Mingmei et al. 2005). However, if the surfactant concentration is relatively small on the liquid films, its impact there as a stabilizer might be limited. It has been found that relatively stable foams occur when the concentration of surfactant is higher than the CMC (Anh et al. 2003; Nicoleas et al. 2005).

2.2.4 Influence of Combination of Surfactants

In industrial processes, normally more than one surfactant is used as a foaming agent (Shuixiang et al. 2019). On the one hand, the purification of surfactants increase costs and thus impure mixtures are less costly and the compounding of multiple surfactants increases the foamability of the solution over that of the individual surfactants (Nicoleas et al. 2005, Bera et al. 2013). For example, it is possible to use a combination of a lot of low-priced surfactants and a small amount
of high-priced surfactants to increase foaming properties while reducing costs (Stubenrauch et al. 2009). The compounding of surfactants can improve the stability of the foam, and usually can extend the half-life of the foam significantly (Stubenrauch et al. 2009). For example, xanthan gum (XG) and hydroxyethyl cellulose (HEC) are individually good foam stabilizers but together, they can effectively improve the stability of the foam and increase the half-life and FCI of the foam (Stubenrauch et al. 2009).

In some operations, the blowing agent (e.g. air) is added at the same time as the surfactant mixture (foaming agent) to the liquid (Chao et al. 2020). It has been found that doing this reduces the total amount of foam generated but the half-life of the foam is raised significantly with higher value of FCI obtained (Jiaqing et al. 2017). Thus, this suggests that it is not only the chemical make-up of the surfactant package that is important but so too is the method used for creating the foam.

However, some surfactant mixtures demonstrate the dominance of a single component. Petkova et al. (2020) used the automated Bartsch test to evaluate the foamability of the foam and tried to find the effect of a mixture of various surfactants on foamability. The surfactants included one anionic – sodium dodecyl sulphate (SDS), two cationic – dodecyltrimethylammonium bromide (DTAB) and cetyltrimethylammonium bromide (CTAB), and four non-ionic – polyoxyethylene-23 lauryl ether (Brij 35); polyoxyethylene-20 cetyl ether (Brij 58); polyoxyethylene sorbitan monolaurate (Tween 20); and polyoxyethylene sorbitanmonopalmitate (Tween 40). Thus, this is a complex mixture of surfactants. They evaluated the foam volume generated at 20°C. The results show that the performance of Brij 35 for reducing the surface tension was not affected by other surfactants and that a single surfactant behaviour was evident. The experiment shows that the instantaneous
surface elasticity, surface coverage and absorptivity of surfactant decrease with time as the foam evolved – this demonstrates the dynamics of surfactant transport in the system as the foam is generated especially for a system where each component has a different diffusion coefficient. Surfactants change the surface force of the foam which affects the rate of thinning of the liquid films in the foam. By changing the adsorption time of the surfactant, the thinning speed of the liquid film is reduced.

Results in the literature show that ionic surfactants and non-ionic surfactants have different effects on foam stability. The principle of non-ionic surfactants in solution is via steric repulsion to maintain the stability of foam (Ivanov et al. 1970). However, to prevent bubbles from coalescing, it needs at least 95% CMC surface coverage (Ivanov et al. 1970; Khr et al. 2002). Ionic surfactants and non-ionic surfactants also have different surface diffusion and Gibbs elasticity characteristics, because of electrostatic repulsion effects caused by ionic surfactants. Electrostatic repulsion can also enhance the stability of the foam creation process (Khr et al. 2002). At lower surface coverage and Gibbs elasticity, ionic surfactant can help produce a lot of foams (Ivanov et al. 1970).

The relationship between the surfactant concentration and the foaminess of the surfactant solution is more complicated. Jun’s experiment proved that both dodecanol alcohol and cetyl alcohol have good compounding properties with SDS (the combination of cetyl alcohol is better than dodecanol alcohol). The foam produced with this mixture has a dense surface and the average size of the bubbles are smaller with more uniform size. Higher alcohol can effectively improve the stability of foam because alcohol molecules can make surfactant micelles easier to form (effectively reducing the CMC) (Jun et al. 2008). This is also a process of free energy reduction (Jun et al.
But as the mass fraction of SDS increases in the surfactant mixture, foamability first increases and then decreases. When the concentration of surfactant exceeds the CMC, the surface tension of the solution for this mixture does not continue to decrease but actually increase slightly (Jun et al. 2008). As a result, there is a decrease of the liquid content and stability of the foam. Experiments show that the combination of 2.0% SDS and 1.5% cetyl alcohol has a half-life of about 21 hours. A combination of 2.0% SDS and 2.0% dodecanol alcohol has a half-life of 29 hours.

Julia studied the effect of bubble size on foam foamability and stability (Julia & Wiebke, 2012). In the experiment, nitrogen was used to bubble through the porous glass disk into the solution to generate bubbles, and the size of the bubbles was changed by changing the gas flow rate and the size of the pore of the disk. The surfactant mixture concentration is 10 times the CMC with component ratios of C_{12}E_6, β-C_{12}G_2 and C_{12}E_6 : β-C_{12}G_2 = 1:1. Julia measured the foaming ability by measuring the time required to generate 80 ml volume of foam at different gas flow rates (20-200 ml/min). When the gas flow rate is higher than 100 ml/min, the foamability of the three liquids are basically the same. When the gas flow rate is less than 100 ml/min, the foamability of C_{12}E_6 begins to deviate from the theoretical value and the other two surfactant mixtures. When the gas flow rate is less than 20 ml/min, it was not possible to generate 80 ml of foam because the rate of generating new foam does not exceed the rate of foam collapse. Also, the foamability of the C_{12}E_6 : β-C_{12}G_2 = 1:1 mixture is less than that of β-C_{12}G_2. Therefore, the foamability of the surfactant solution follows the following order: β-C_{12}G_2 > C_{12}E_6 : β-C_{12}G_2 = 1:1 mixture > C_{12}E_6. They also noted a critical gas flow rate phenomenon. When the gas flow rate exceeds the critical value, the bubbles burst instantaneously due to the shear stress exerted on them when the gas flows
preventing the formation of the foam – this implies that the adsorption rate of surfactants is not sufficient to support foam formation. They also found that the amount of liquid contained in the foam did not affect the measurement of foam stability and foamability. In terms of foam stability, the order of most stable to least is as follows: $\beta$-C$_{12}$G$_2 >$ C$_{12}$E$_6 : \beta$-C$_{12}$G$_2 = 1:1$ mixture $>>$ C$_{12}$E$_6$, but the results of $\beta$-C$_{12}$G$_2$ and C$_{12}$E$_6 : \beta$-C$_{12}$G$_2 = 1:1$ mixture is close and only formed intact foam when the gas flow rate is lower than 20 ml/min. Due to the different stability of the foam formed by the three surfactant solutions, the initial amount of liquid contained in the foam is also different. Poor foam stability causes more bubbles to burst and more liquid to drain, leading to worst foam stability. In the first 100 s after foaming, the volume of foam produced by solution $\beta$-C$_{12}$G$_2$ was almost unchanged and remained stable, but the volume of foam produced by solution C$_{12}$E$_6 : \beta$-C$_{12}$G$_2 = 1:1$ mixture decreased and collapsed, whereas the foam produced by solution C$_{12}$E$_6$ disappeared completely. The measurement shows that the surface rigidity and surface elasticity of the foam produced by $\beta$-C$_{12}$G$_2$ solution is the best, which shows that good surface rigidity and surface elasticity helps to produce more stable foam. The bubble radius of the three surfactant solutions was basically the same when the foam was first generated, and the polydispersity index (PI) was also very similar. During the 400 seconds of the experiment, the bubble radius produced by solution $\beta$-C$_{12}$G$_2$ did not change significantly and PI only slightly increased. Foam drainage is the main reason for this change process.

After 134 seconds of foam generation, the average value of the radius of the bubbles in the C$_{12}$E$_6$ solution increased significantly, the radius value distribution range was wider, and the PI value also increased significantly. At the same time, the volume of the foam has also become smaller. The foam produced by solution C$_{12}$E$_6 : \beta$-C$_{12}$G$_2 = 1:1$ mixture will also show this change, but it
takes longer than that of C_{12}E_6. Foam drainage and foam coalescence work together in this process of change. It takes at least 10 minutes or even several hours for the foam to coarsen, so no foam coarsening was observed within 7 minutes of the experiment. It takes a longer experiment time to observe the coarsening of the foam. When the experiment lasted for about 200 seconds, the foam produced by C_{12}E_6 solution collapsed. Different surfactants will cause the foam to exhibit different surface rigidity and surface elasticity. One of the influencing factors is the different packing and orientation of the surfactant on the foam surface. In the early stage of the experiments, the foams produced by solution C_{12}E_6 : \beta-C_{12}G_2 = 1:1 and solution \beta-C_{12}G_2 showed similar states, and the characteristics of the early foam were mainly controlled by drainage. The foams produced by the C_{12}E_6 : \beta-C_{12}G_2 = 1:1 mixture solution and the C_{12}E_6 solution in the mid-term of foam death exhibit similar behavior, and the characteristics of the mid-term foam are mainly controlled by foam coalescence. The characteristics of the foam in the late period of the foam are mainly controlled by the coarsening of the bubbles.

Jiaqiang et al. (2013) studied the effects of eight different foaming agents on the foamability of solutions. The four anionic surfactants that was used included sodium dodecyl sulfate (SDS), sodium alpha-olefin sulfonate (AOS), sodium benzenesulfonate (ABS) and sodium lauryl polyoxyethylene ether sulfate (AES). All showed reasonable foamability. However, the results showed that the foamability of ABS and AES are better than that of SDS and AOS. The concentration at which the surfactant has the largest amount of foaming and the longest half-life is called the optimal concentration. The optimal concentration of ABS and AES is 2 g/l, and the optimal concentration of SDS and AOS is 3 g/l. The half-life of the ABS and AES solutions exceeded 8.8 minutes. However, the performance of another set of non-ionic surfactants, including
coconut methyl monoethanolamide (CMMEA), octylphenol ethoxylate (OP-10), cocamidopropyl hydroxy sulfobetaine (CHSB) and disodium lauroamphodiacetate (LAD-40), are much lower than the above four anionic surfactants. CMMEA has a very low hydrophile-lipophile balance (HLB) value. The lower the value of HLB, the worse the foamability of the surfactant. When the concentration of the surfactant solution increases to 4 g/l, OP-10 still cannot produce a stable foam. Although CHSB and LAD-40 produce stable foams, they require a high concentration of surfactants. The price of amphoteric surfactants is much higher than that of non-ionic surfactants so in most applications non-ionic surfactants are chosen as foaming agent for products (Jiaqiang et al. 2013). Non-ionic surfactants are more efficient and economical (Jiaqiang et al. 2013). In this experiment, it was found that AES and AOS can produce the largest FCI value when added to the solution at the same time. AES and AOS are the best combination in this experiment. The size distribution of the bubbles conforms to a partial normal distribution.

Jiaqiang et al. (2013) studied the effects of the combination of six surfactants on solution foamability and foam stability. These 6 surfactants include sodium dodecyl sulfate (SDS), sodium dodecylbenzene sulfonate (ABS), 3# foaming agent, cetyltrimethylammonium bromide (CTAB), oil Sodium (SO) and polyacrylamide (PAM). Among these surfactants, there are four types of surfactant solutions that produce foams with good foaming properties and stability, include SDS, 3#, SO and CATB. When the two surfactants are compounded together, the foam can get higher foamability and stability. When SDS is compounded with 3# in a mass ratio of 1:1, the foam has the largest FCI value. And the foamability and stability of the foam are much better than other combinations. Name this combination of surfactants AFS-1. As the combined concentration of surfactants increases, the foamability and stability of the foam increase first and then decrease.
Constantly increasing the concentration of surfactants cannot always improve the foamability and stability of the foam. When the concentration of the surfactant is 2 g/L, the foamability and stability of the foam have both peaks. Three different types of foam stabilizers were also selected in the experiment, including dodecanol, acrylate copolymer SF-1 and polyacrylamide PAM. Dodecanol is a higher fatty alcohol, which can reduce the repulsive force between surfactant molecules. SF-1 is a suspension stabilizer used to maintain the balance of solution viscosity. The characteristic of SF-1 is that it can be compounded with many middle surface-active agents. PAM can increase the viscosity of the solution and reduce the rate of foam drainage and gas diffusion. These three foam stabilizers have a good effect of increasing foam stability and are often used in compounding with other foaming agents. Three different foam stabilizers were added to AFS-1. By adjusting the mass ratio of each foam stabilizer and AFS-1, the experiment obtained the best combination of surfactants: 1 g/L SDS + 1 g/L 3# + 3 g/L dodecanol + 3 g/L SF + 3 g/L PAM. This combination of surfactants can produce 380 mL of foam, with a foam half-life of 6050 min and an FCI of $1.7 \times 10^6$. This was found to be a super foam microns), uniform distribution, and a smooth surface. The shape of the bubbles is spherical. Through the XP-300C image analyzer, Jiaqiang observed that the foam produced by the solution has a thick liquid film, which ensure the high stability of the foam. The strong liquid film has a good anti-interference ability to prevent the bubble from bursting.

2.2.5 Influence of Tackifier

With the loss of liquid in the films, the liquid film of the foam becomes fragile and easily ruptures. The pressure difference between the inside and outside of the liquid film and the effect of gravity
are the main reasons for the liquid to flow out of the liquid film (Adrian & Regine, 2011). Adding a tackifier can effectively reduce the speed of the liquid flowing out of the liquid film and can also reduce the solubility of the gas in the liquid film (Adrian & Regine, 2011). Because the tackifier can form hydrogen bonds with the surrounding water molecules thus crowding the space for water molecules to move, thereby preserving the liquid film (Cosima et al. 2017). However, adding too much tackifier will make the viscosity of the liquid phase too high, making it difficult for the liquid to foam (Stefan et al. 2011). Therefore, tackifiers tend to reduce the foamability and foaming volume of the liquid (Felix, 1987).

Carboxymethyl cellulose, pectin and gelatin are good tackifiers (Jun et al. 2008). When they are compounded with surfactants, they can effectively improve the stability of the foam (Jun et al. 2008). With a combination of the mass fraction of 2.0% Carboxymethyl cellulose, 2.0% SDS and 1.5% cetyl alcohol, the half-time of the foam reaches 67 hours (Jun et al. 2008). With mass fraction of 1.2% Carboxymethyl cellulose, 2.0% SDS and 2.0% dodecanol alcohol, the half-time enlarges to 80 h (Feng, 2008).

2.2.6 Influence of Film Former

Although a thickener or tackifier can help the liquid film retain water molecules, it can change the chemical properties of the water film. Therefore, the addition of tackifier is typically used as an auxiliary method to delay bubble rupturing (Jiaqing et al. 2017). Experiments have proven that for some applications the foam with only the tackifier, foaming agent and foam stabilizer is not good enough to resist external forces, and the shape of the foam after drying is sparse and easily deformed. Therefore, it is necessary to increase the force between surfactants to form a stronger
liquid film (Qiwei et al. 2003). Generally, polymer emulsions are selected as film-forming agents – they enlarge the viscosity of the liquid phase. After the liquid is added to the film former, it can form a mixed film with the liquid film formed by the surfactant (Qiwei et al. 2003). The new liquid film has higher viscosity, stronger interaction between surfactant molecules, and higher foam stability (Jun et al. 2008). Because the polymer particles in the emulsion will be close to each other and aggregate, the aggregation of the particle state develops the aggregation of the molecular state, thereby forming a new and more stable liquid film (Jun et al. 2008).

In one example, after adding the mass fraction of 5.0% soluble glass, 3.0% Styrene acrylic emulsion, 2.0% Carboxymethyl cellulose, 2.0% SDS and 1.5% cetyl alcohol to water, the half-time of the foam reached 96 hours. The foam formed under this condition has a smooth and dense surface, certain anti-interference ability, and self-repair ability (Jun et al. 2008). Moreover, the foam can still maintain a good shape after a period of time (Jun et al. 2008).

2.2.7 Influence of Ions

Inorganic salts salt out or dissolve the hydrophobic groups of surfactants through hydration, change the original charge effect, or produce ionic reactions, which affect the formation of micelles (Pendy et al. 2003). Inorganic salt is usually added to the solution together with various foaming agents (Pendy et al. 2003). The impact of inorganic salt on foam formation and stability is complex (Thomas et al. 2006). Inorganic salts may increase the stability of the foam or may decrease the stability of the foam (Pandey et al. 2003; Nurudeenn et al. 2017). Even if only one kind of inorganic salt is added to the solution, as the concentration of the salt continues to rise, the stability of the
foam will first decrease, then increase, and then decrease (Jianbing et al. 2015). Combination of different metal ions also affect the stability of the inorganic salt to the foam (Thomas et al. 2006). It shows that shielding electrostatic repulsion is not the only factor which can affect the stability of the foam. The influence of metal ions on the adhesion of surfactants can also change the stability of foam (Thomas et al. 2006).

Mixing a variety of different salt ions will have a greater impact on the foam (Jiaqing et al. 2017). Because too much salt ions compress the double adsorption layer of surfactant on the foam film, and at the same time cause the surfactant to aggregate and precipitate, this will reduce the surface tension of the foam and reduce the viscosity of the foam (Jiaqing et al. 2017). Experiments have proved that both NaCl and CaCl₂ will reduce the foamability of the solution, and the inhibitory effect on the foamability of the solution will increase as the ion concentration increases (Jiaqing et al. 2017). The main effect of Ca²⁺ and Mg²⁺ on the foamability and stability of the solution is to react with the surfactant to form a precipitate.

2.2.8 Influence of pH

The pH of the solution does not influence non-ionic surfactants but it has a significant effect on ionic surfactants (Kathrin et al. 2015). Generally, there is a critical pH value, and the foamability and stability of the solution increase before reaching the critical value, and then decrease after reaching the critical value (Günseli et al. 2004). Normally, this critical value tends to be a neutral solution with a pH of 7. It is worth noting that although the foamability and stability of the foam are reduced in an alkaline environment, the result is still better than in an acidic environment. A
strong acid environment can make the foam extremely unstable (Feng, 2008). In one example, at 22°C, in a solution consisting of 1.2% Carboxymethyl cellulose, 2.0% SDS, 2.0% dodecanol alcohol and 100 mL water, the half-life about 50 hours to lose half of the liquid in foam (Feng, 2008).

2.3 What is missing in the literature?

Despite the many studies on the impacts of surfactant on foam formation spanning more than 100 years, the impacts of surfactant under different salinities remain unresolved. The research documented in this thesis investigates, using SDS and NaCl, the impact of the concentration of these two materials on the stability of an aqueous foam. These results are important for systems where brines are encountered such as petroleum systems.
CHAPTER 3 EFFECT OF SDS CONCENTRATION ON THE STABILITY OF WATER-BASED FOAM

In the research documented here, an investigation on impact of surfactant concentration on the stability of foam. Specifically, the surfactant used in this work is sodium dodecyl sulfate (SDS). Furthermore, repeat tests were conducted with the dynamic foam analyzer to demonstrate that its results are repeatable.

3.1 Introduction

There have been many studies on the impact of surfactant concentrations on foam stability as described in Chapter 2. The key benefits of the addition of surfactant are that it first, lowers the surface tension of the liquid solution which enables greater foamability and second, it enables a charge structure within the liquid films of the foam that help to oppose drainage of flow within the films.

SDS is an organic compound with chemical formula CH$_3$(CH$_2$)$_{11}$SO$_4$Na that comprises a long hydrocarbon tail and a polar headgroup, as show in Figure 3.1. It is an anionic surfactant consisting of a 12 carbon tail which is lipophilic and a sulphate group, a charged headgroup which is hydrophilic (Chao et al. 2020). Since it has lipophilic and hydrophilic parts to the molecule, SDS is amphiphilic and can form micelles in aqueous solution when its concentration is sufficiently high (Jin & Qicheng 2007).
When the concentration of SDS is above the critical micelle concentration (CMC), it exists as micelles (John et al. 2015). Below the CMC, the surfactant is distributed in the liquid as individual molecules – these are referred to as monomers. Above the CMC, the surfactant molecules aggregate together (self-assemble) to form an aggregate of surfactant molecules that are dispersed within the liquid (Vinod et al. 2020). In this form, the micelles within the liquid form a colloidal suspension. Micelles can be varied in shape as shown in Figure 3.2. In many cases spherical micelles form where in the case of a normal-phase micelle, the hydrophobic tails are on the inside and the polar headgroups are in contact with the water. In inverse micelles, as would be the case of micelles in a liquid oil phase, the headgroups are internally facing with the lipophilic tails outwards. In other cases, micelles can have other shapes such as ellipsoids, cylinders, and bilayers (Vinod et al. 2020). The shape of the micelles formed in a solution depend on the concentration and conditions (e.g. temperature, salinity, and pH) of the liquid phase (Vinod et al. 2020).
When the concentration of the surfactant in the liquid phase is above the CMC, all added surfactant to the liquid will form micelles (Rao et al. 1982). This does not mean that there are no more monomers in the solution. In water, the headgroup of SDS interacts with the water molecules (since the water molecules are polar). However, the hydrocarbon tail does not have as much interaction with the water molecules. In a foam, the SDS lowers the surface energy of the liquid interface by two main actions: 1. the surface tension is lowered (energy = interface area x surface tension) and 2. since the headgroups want to interact with the water molecules, the hydrocarbon tail sticks out from the interface thus removing the hydrophobic part of the SDS from the water phase. When a SDS micelle forms within the bulk of the water, the hydrophobic tails are now separated from the bulk water molecules and as such, the system’s free energy is decreased. Hammouda (2013), by using experiment, examined the nanostructure of SDS micelles. He demonstrated that above the CMC, SDS micelles exist in solution as oblate ellipsoid shaped micelles. At 21°C, the lengths of the long and short axes of the ellipsoid were found to be equal to about 21 and 15 Å, respectively.
In the experiments conducted here, the concentration of the SDS in the water phase is greater than the CMC. For SDS in pure water at 25°C, the CMC has been established to be equal to about 0.0082 mol/litre (Cifuentes et al. 1997, Bergeron 1999, Markarian et al. 2005, Hammouda 2013, Fauser et al. 2015). This corresponds to a mass concentration equal to 0.023%. As shown in Figure 3.3, the surface tension of SDS (at 25°C) drops for concentrations below the CMC and then remains about constant above the CMC. For SDS, the surface tension above the CMC is equal to about 38 mN/m (Brady 1948, Fauser et al. 2015). Surface tension measurements obtained by using a TensioCAD semi-automatic tensiometer (Laval Lab Inc.) using a du Nouy ring are listed in Table 3.1 (average of three repeat tests).

**Figure 3.3:** Effect of SDS concentration on surface tension in pure water at 29°C (data from Brady 1948).
For a foam that is created with surfactant concentration above the CMC, the micelles themselves can provide a stabilizing influence on the liquid films contributing to a disjoining pressure effect (Overbeek 1960, Lyklema and Mysels 1965). This is illustrated in Figure 3.4. As the film is being drained of water and its thickness drops, the micelles can be forced from the film by the bounding layers of monomers at the interfaces of the layer (Bergeron 1999). This movement of micelles, given their variable size and motion relative to each other and the water molecules can lead to a ‘stepped’ reduction of the liquid film thickness (Bergeron 1999).

Figure 3.4: Occurrence of micelles in a liquid film in a foam.
3.2 Methods and Materials

The generation of foam (foamability) is divided into two stages: 1. the initialization of foaming and 2. foam accumulation (Petkova et al. 2020). The foamability can be indexed by the total initial height of a foam column given a volume of gas and a gas distribution device.

In the work conducted here, a Dynamic Foam Analyzer (DFA100, Krüss Inc.), shown in Figure 3.5, is an instrument for precisely measuring foam foamability and stability. It analyzes the properties of the foam by measuring the foam volume, liquid content, foam density, bubble size and bubble size distribution of the foam generated. The advantage of DFA100 is that it can measure foam characteristics repeatedly and accurately by with controlled gas flow volume and rate into the liquid repeatedly (camera rate 20 fps, 200 dpi (125 micron) spatial resolution, 216 mm scanning length). The DFA100 instrument also uses an optical sensor to measure the quantity of foam generated by the solution and the foam attenuation characteristics; even if the life of the foam is very short, clear and accurate measurement data can be obtained. Because liquid and gas are both light-transmissive, the instrument uses LED panels and a photodetector to measure the change in light transmittance over time to calculate the height of the liquid column and foam column (Bike et al. 2010). For opaque liquids, infrared light is used for detection.
Initially, the liquid is placed at the base of the glass column. The gas enters the base of the glass column through a finely perforated plate at the base of the column. In the experiments reported here, each perforation in the plate has a diameter equal to 16-40 µm. As the gas flows through the perforated plate, a foam is created and its height grows with continued air injection. As this is happening, the dynamic foam analyzer is recording the height of the foam and starting to collect data on the bubble size distribution within the foam through the side of the glass column. After the target gas volume has been injected into the liquid or the target foam height has been reached, the

Figure 3.5: Dynamic foam analyzer.
gas flow stops. Thereafter, the analyzer records the height and bubble size distribution as the foam column disintegrates.

The gas enters the container from the base of DFA100. The base has many pores, and the diameter of the pores ranges from 40-100 µm. Because liquid and gas are both light-transmissive, the instrument uses LED panels and a photodetector to measure the change in light transmittance over time to calculate the height of the liquid column and foam column. For opaque liquids, infrared light is used for detection. With the continuous generation of foam, the liquid enters the foam, the height of the liquid continues to decrease, and the height of the foam and the height of the entire system continue to increase. When the bubble begins to decay, the data is the opposite.

In the experiments conducted here, de-ionized (DI) water is used. The surfactant is sodium dodecyl sulfate (SDS) supplied by Alfa Aesar (99% purity); the pH is neutral. For each test, the volume of DI water is equal to 30 ml and the gas (air) injection rate into the liquid is equal to 500 ml/min. Note that not all of the liquid is foamed – only a fraction of the liquid in the device is converted into foam. All of the experimental cases are listed in Table 3.1. As shown in the table, at each SDS concentration, three repeat experiments were conducted.
Table 3.1: List of cases examined. The surface tension was measured using a TensioCAD semi-automatic tensiometer (Laval lab Inc.) at 22°C. Three repeats of each case are done. The solubility of SDS in water is equal to about 100 g/litre (10 g/100 ml) thus the SDS concentrations used are below the solubility limit.

<table>
<thead>
<tr>
<th>Tests</th>
<th>SDS (% by mass)</th>
<th>SDS (mmol/litre)</th>
<th>Surface Tension, mN/m</th>
<th>Gas Injection Rate (ml/min)</th>
<th>Initial Liquid Volume (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1, 2-1, 3-1</td>
<td>1</td>
<td>34.68</td>
<td>37.8</td>
<td>500</td>
<td>30</td>
</tr>
<tr>
<td>1-1.5, 2-1.5, 3-1.5</td>
<td>1.5</td>
<td>52.02</td>
<td>38.7</td>
<td>500</td>
<td>30</td>
</tr>
<tr>
<td>1-3, 2-3, 3-3</td>
<td>3</td>
<td>104.0</td>
<td>37.3</td>
<td>500</td>
<td>30</td>
</tr>
</tbody>
</table>

3.3 Results and Discussion

Table 3.2 lists the experimental results from the tests for each of the cases listed in Table 3.1. The time at which the maximum foam height is achieved is similar – this is expected since the gas injection rate is the same for all tests and the height of the foam column in the dynamic foam analyzer is detected until it reaches the maximum foam height of about 137 mm. After the foam has been generated to the targeted height, gas injection stops and the foam height is monitored through time. The time it takes for the foam to reach one-half of its maximum height is the foam half-life and it is listed in Table 3.2. The half-life results show that the higher the concentration of the surfactant, the greater is the half-life of the foam. This implies that the stability of the foam is greater with larger concentration of surfactant. This is consistent with other research (Durga et al. 2005). Table 3.2 also lists the average radius of the gas bubbles after 30 s (about 15 s after the maximum foam height was achieved). The results show that the higher the concentration of the surfactant, the smaller is the average radius of the gas bubbles after 30 s.
Table 3.2: Foam results from SDS experiments. The foam half-life is the time at the foam volume has reduced in volume by 50%.

<table>
<thead>
<tr>
<th>Test</th>
<th>Time at which maximum foam height achieved (s)</th>
<th>Maximum foam volume achieved (ml)</th>
<th>Maximum foam height achieved (mm)</th>
<th>Gas volume in foam (ml)</th>
<th>Liquid volume in foam (ml)</th>
<th>Time at which 25% liquid drained from foam (s)</th>
<th>Time at which 50% liquid drained from foam (s)</th>
<th>Foam Half-life (s)</th>
<th>Average Radius after 30 s (µm)</th>
<th>Average Foam Half-life (s)</th>
<th>Average of Average Radius after 30 s (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>14.87</td>
<td>172.3</td>
<td>137.1</td>
<td>110.6</td>
<td>6.1</td>
<td>39.9</td>
<td>57.9</td>
<td>183.9</td>
<td>218.0</td>
<td>181.9</td>
<td>203.6</td>
</tr>
<tr>
<td>2-1</td>
<td>15.41</td>
<td>172.6</td>
<td>137.3</td>
<td>110.4</td>
<td>6.1</td>
<td>50.9</td>
<td>78.9</td>
<td>193.4</td>
<td>200.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-1</td>
<td>14.92</td>
<td>171.1</td>
<td>136.1</td>
<td>110.2</td>
<td>6.1</td>
<td>31.4</td>
<td>42.4</td>
<td>168.4</td>
<td>192.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-1.5</td>
<td>15.00</td>
<td>172.3</td>
<td>137.1</td>
<td>112.6</td>
<td>6.1</td>
<td>167.0</td>
<td>301.0</td>
<td>394.5</td>
<td>69.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-1.5</td>
<td>14.91</td>
<td>170.3</td>
<td>135.5</td>
<td>111.7</td>
<td>6.1</td>
<td>171.9</td>
<td>344.9</td>
<td>502.4</td>
<td>64.0</td>
<td>452.2</td>
<td>64.0</td>
</tr>
<tr>
<td>3-1.5</td>
<td>14.83</td>
<td>169.6</td>
<td>135.0</td>
<td>111.0</td>
<td>6.1</td>
<td>161.8</td>
<td>332.3</td>
<td>459.8</td>
<td>59.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-3</td>
<td>14.90</td>
<td>172.3</td>
<td>137.1</td>
<td>112.7</td>
<td>6.1</td>
<td>181.9</td>
<td>363.9</td>
<td>638.4</td>
<td>56.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-3</td>
<td>14.88</td>
<td>172.3</td>
<td>137.1</td>
<td>111.8</td>
<td>6.1</td>
<td>160.9</td>
<td>307.4</td>
<td>731.9</td>
<td>50.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-3</td>
<td>14.96</td>
<td>172.3</td>
<td>137.1</td>
<td>112.2</td>
<td>6.1</td>
<td>182.0</td>
<td>324.5</td>
<td>545.0</td>
<td>55.0</td>
<td>638.3</td>
<td>53.7</td>
</tr>
</tbody>
</table>
Table 3.3 lists the average drainage rates for the liquid after 25% and 50% of the original liquid in the foam has drained from the foam. The results show that the higher the SDS concentration, the slower is the drainage of the liquid from the foam, or in other words, the greater the ability of the liquid films to resist drainage.

Table 3.3: Average Drainage rates for 25% and 50% of the liquid in the foam to drain from the foam.

<table>
<thead>
<tr>
<th>Test</th>
<th>Average Drainage Rate after 25% liquid drained from foam (ml/s)</th>
<th>Average Drainage Rate after 25% liquid drained from foam (ml/s)</th>
<th>Average Drainage Rate after 50% liquid drained from foam (ml/s)</th>
<th>Average Drainage Rate after 50% liquid drained from foam (ml/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>0.1529</td>
<td>0.1557</td>
<td>0.1054</td>
<td>0.1088</td>
</tr>
<tr>
<td>2-1</td>
<td>0.1198</td>
<td></td>
<td>0.0773</td>
<td></td>
</tr>
<tr>
<td>3-1</td>
<td>0.1943</td>
<td></td>
<td>0.1439</td>
<td></td>
</tr>
<tr>
<td>1-1.5</td>
<td>0.0365</td>
<td>0.0366</td>
<td>0.0203</td>
<td>0.0188</td>
</tr>
<tr>
<td>2-1.5</td>
<td>0.0355</td>
<td></td>
<td>0.0177</td>
<td></td>
</tr>
<tr>
<td>3-1.5</td>
<td>0.0377</td>
<td></td>
<td>0.0184</td>
<td></td>
</tr>
<tr>
<td>1-3</td>
<td>0.0335</td>
<td>0.0350</td>
<td>0.0168</td>
<td></td>
</tr>
<tr>
<td>2-3</td>
<td>0.0379</td>
<td></td>
<td>0.0198</td>
<td></td>
</tr>
<tr>
<td>3-3</td>
<td>0.0335</td>
<td></td>
<td>0.0188</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3.6 displays the height of the foam versus time for the tests. The profiles demonstrate that the experiments are largely repeatable and although there are deviations between the profiles of the foam height versus time, they are consistent with each other. A comparison of the profiles reveals that the greatest change of the height occurs with the lowest concentration solution reflecting the greater instability of the lower concentration foam. The slope of the height versus time for the 1% SDS solution is largely constant throughout its measurement. For the 1.5% case, the profile is distinctly different in shape – there are two regions that are evident in the profile each
with its own slope. The first region has low slope and exists up to about 130 s. The second region has higher slope and exists from about 130 s until the end of the experiment (most evident by looking at Tests 2 and 3 for the SDS 1.5% case). For the 3% case, the profiles have a small plateau up to about 50 s and thereafter drops smoothly with greater slope.
Figure 3.6: Foam height versus time for SDS 1, 1.5, and 3 mass percent.
Figure 3.7 displays the average bubble radius versus time for the SDS 1, 1.5, and 3 mass percent cases after the maximum foam height has been achieved (after about 15 s). The results show that the initial radius of the bubbles is similar for the 1.5 and 3 mass percent cases at about 50 microns but are higher for the 1 mass percent case where it is equal to about 80 microns. This difference is likely due to the rapid destruction of the foam as it is being created which occurs at the lower surfactant concentration. During the foam accumulation process, bubbles are created but at the same time, the created bubbles are merging to create larger ones. This process is quite fast as seen by the rapid increase of the average bubble radius in the 1.0 mass percent case – the average bubble radius rises from about 80 to above 200 microns in about 10 s.

In general, the results in Figure 3.7 reveal that the greater the concentration of the SDS solution, the smaller is the average radius of the bubbles (values listed in Table 3.2). For the 1 mass percent SDS case, in the first 20 s of the process after the foam height was established, the bubbles rapidly merge creating larger bubbles. For this case, after about 25 s, the average radius of the bubbles remains roughly the same with no significant increase. The results for the 1 mass percent case suggest that as time proceeds, smaller bubbles are no longer merging together to form larger bubbles. From Figure 3.6, we know that the column height is falling, which given the average bubble remains about the same implies that the bubbles are being destroyed within the column, likely from the top with relatively little bubble merging occurring due to internal liquid films rupturing.

For the 1.5 and 3 mass percent SDS cases, the average bubble size grows with time revealing that the bubbles are merging together to form larger bubbles. For the 1.5 mass percent case, the average
bubble size grows until about 330 s after which the bubble sizes remain constant (with the exception of the Test 3 results). This suggests that for some tests that at some point, the bubbles stop merging and the average bubble size remains roughly constant. In the 3 mass percent case, the results of Tests 1 and 2 show that the average bubble size grows significantly. Test 3 for this case shows a flatter profile starting about 450 s.

The results from the repeat tests demonstrates that the average bubbles size profiles are largely consistent with each other although there are deviations especially towards the later time of the test. Furthermore, the comparison of the 1.5 and 3 mass percent cases shows that their profiles are very similar up to about 300 s. Beyond this point of the time, the 1.5 and 3 mass percent case profiles deviate from each other demonstrating the impact of the concentration of the SDS on the longer term behaviour of the generated foams.

Figures 3.8, 3.9, and 3.10 display examples of the views of the bubbles morphologies for all of the cases and tests through time. The colors indicate bubbles of similar dimensions. In the 1.0 mass percent SDS case, the results show that the bubbles tend to stay the same size with limited merging occurring. This is different than the 1.5 and 3 mass percent cases shown in Figures 3.8 ad 3.9 which show larger and larger dimension bubbles evolving through time as the bubbles merge together. The images in Figures 3.7 to 3.9 show that the bubbles evolve from spherical small bubbles to larger bubbles with multiple border plateaus with smaller bubbles sitting within the spaces between the larger bubbles. Eventually, these smaller bubbles merge or through coarsening, feed the larger bubbles growing them further.
Figure 3.7: Average bubble radius versus time for SDS 1, 1.5, and 3 mass percent.
Figures 3.8: Bubble size comparisons for SDS 1 mass percent for small section of bubble column imaged.
Figures 3.9: Bubble size comparisons for SDS 1.5 mass percent for small section of bubble column imaged.
Figures 3.10: Bubble size comparisons for SDS 3 mass percent for small section of bubble column imaged.
Figure 3.11 displays the bubble count per unit area (bubble areal density) and the mean bubble area (in square microns) for selected tests for each of the SDS concentration cases. The results show that the bubble areal density decreases and mean bubble area increases as each of the foam systems evolve through time reflecting the merging of bubbles. After the foam is established at its maximum initial foam height, the number of bubbles drops rapidly within the first few seconds. Thereafter, the bubble areal density drops less quickly – for the 1.5 SDS mass percent case, the bubble areal density evolves quickly to a nearly flat profile with density oscillating between 4 and 5 bubbles/mm². In the 1.5 and 3.0 SDS mass percent cases, the bubble areal density drops less rapidly than that of the 1.0% case, reaching lower limits of about 4 and 3 bubbles/mm², respectively. The mean bubble area follows the same trend as that of the bubble size.
Figure 3.11: Bubble count per mm² and mean bubble area (µm²) versus time for SDS 1, 1.5, and 3 mass percent.
The results show that the greater the surfactant concentration, the longer is the persistence of the foam thus demonstrating its greater stability. The concentrations of SDS used in this work are all above the SDS critical micellar concentration (CMC) and thus, as a consequence, the surface tension of the solutions examined here are constant and equal to about 38 mN/m (Brady 1948). The literature has shown that a foam is more likely to occur if the surface tension of the aqueous phase (in air) is lower and that stability is greater with a greater amount of surfactant (Jiaqiang et al. 2013). However, above the CMC, given that the surface tension of the liquid remains largely constant, the ability for the solution to create more stable foams as the surfactant concentration rises speaks to the action of the surfactant in the liquid films. The surfactant micelles that were in the bulk liquid phase are now distributed amongst the thin liquid films that create the foam. This usually takes the form of micelle layering or ordered microstructure formation within the films themselves and these structures can impact the liquid drainage within the films thus controlling the stability of the foam. It is likely that the micelles are being ‘squeezed’ from the liquid films as liquid drainage and flow occurs but this is resisted by the presence of the micelles. The higher the concentration of SDS, the greater is the number of micelles, and the higher is the difficulty for the liquid films to empty themselves of water.

In all the experimental data, the quality of the foam is maintained at about 0.964. The foam quality is very stable, and the influence of surfactants and salt is small. When a fixed volume of foam is produced, the volume of gas used will decrease in a small range as the stability of the foam decreases. Foam Capacity ($V_{\text{foam}}/V_{\text{gas used for foaming}}$) is from 1.4 to 1.5.
3.4 Conclusions

A series of tests were done to evaluate the repeatability of the dynamic foam analyzer and to examine the impact of SDS concentration in pure water on the stability of the created foam when the concentration of the SDS is substantially above its critical micelle concentration (CMC). The results show that the dynamic foam analyzer is repeatable and provides results that are consistent with each other in repeat tests. The results also reveal that the greater the surfactant concentration, the greater is the half-life of the foam suggesting that the foams are more stable. However, given that the SDS concentration is greater than the CMC, the surface tension is largely constant despite the concentration of the SDS and thus the enhanced stability is due to the presence of the micelles in the liquid which likely create a ‘disjoining’ pressure that resists the rupturing of the liquid films.
CHAPTER 4 EFFECT OF SDS AND SALT ON FOAM STABILITY

This chapter presents the results of experiments to examine the combined effects of SDS and NaCl on the stability of an aqueous foam.

4.1 Introduction

Camp and Durham (1955) examined the half-life of foams created from sodium laurate (a soap) solutions and electrolytes at high pH (pH=10). The results show that the foam stability, as measured by the half-life, was enhanced when the concentration of sodium ions rises. Zhang et al. (2015) describes how they added NaCl to SDS aqueous solutions and how the combination of the two can lead to ultrastable foams. However, their concentrations of the two materials are sufficiently high such that they observed solid precipitation from the solutions as the foams aged. This could be case for lower concentration bulk aqueous solutions where in the foam liquid films, the loss of water from the films leads to a local increase of the concentrations to the solubility limits of the additives.

Wang et al. (2016) examined the stability of SDS-NaCl aqueous foams up to 100 mmol/litre. Their results show that when the concentration of NaCl is low (<1 mmol/litre), the foam half-life increased reflecting an enhancement of the foam stability. However, up to 100 mmol/litre, the foam half-life decreased indicating that the stability of the foam decreased. They ascribed the reasons for the further destabilization of the foams as being due to decreased electrostatic repulsion in the liquid films due to the presence of the ions. This result is not consistent with Wang et al.
(2004) where it was shown that the higher the NaCl concentration (at fixed SDS concentration), the greater is the stability of the foam. In that case, they explained that the greater stability resulted from the promotion of more adsorption of SDS molecules on the gas-water interfaces bounding the liquid films which results from decreased electrostatic double layer repulsion. Thus, this gives rise to an unresolved issue with respect to the impact of NaCl on the stability of SDS aqueous solutions.

Yekeen et al. (2017) examined how mixtures of SDS (up to 1 mass percent) and NaCl affect the stability of foams. Their results showed that below the CMC, the higher the NaCl concentration, the greater is the foam stability. On the other hand, above the CMC, the higher the NaCl concentration, the lower is the foam stability. Yekeen et al. did not examine SDS concentrations greater than 1 mass percent. Thus, at higher SDS concentrations, some of the effects where the salt ions reduce the ability for SDS adsorption at the interface could be avoided and thus, it is possible that at higher SDS concentrations, the foam could be more stable.

Haryanto et al. (2018) examined the stability of SDS aqueous solutions in the presence of cadmium (Cd). Their results show that the greater the concentration of Cd, the greater the amount of foam produced and the longer the foam persists.

Jiang et al. (2020) examined the role of salts in foams stabilized by SDS. They showed that at 26 mmol/litre SDS concentration (about 3 times the CMC), with up to 6 mmol/litre NaCl, the foams are stabilized by the addition of NaCl. However, beyond this NaCl concentration, the stability drops ad achieves a nearly constant value above about 90 mmol/litre NaCl. At 90 mmol/litre SDS
concentration (about 11 times the CMC), the stability of the foam occurs up to about 90 mmol/litre NaCl and beyond this values, the stability of the foam is not enhanced.

Obisesan et al. (2021) examined how the addition of salt (NaCl and CaCl$_2$) affected the stability of foams. In general, they observed that the addition of NaCl reduced the amount of drainage from the foam. However, they stated that trends of foam drainage versus salt concentration are unclear depending on the type of salt and its concentration.

Collins (2004) showed that different ions have different effects on water. For sodium, it is a kosmotrope – an ion that tends to contribute to the order and structure of water molecules. On the other hand, potassium is a chaotrope – it tends to disrupt the structure of water making it more disordered. For the purposes of stabilizing a foam – that is, hindering the drainage of water from the liquid films in a foam – it makes sense that a preferred ion to use would be a kosmotrope. Thus, here, we examine the use of sodium (via the salt NaCl) on the stability of SDS aqueous foams.

Despite the evidence in the literature, the impact of salt on the stability of SDS-foams still remains unresolved. In the research reported here, the stability of higher SDS concentration foams in the presence of NaCl is explored. These high SDS concentrations do not appear to have been examined in the literature.
4.2 Methods and Materials

The methods and materials have been described in Chapter 3. The salt is an additional chemical used in the research reported in this chapter. The salt is 99.99% pure NaCl obtained from VWR International Inc. The concentrations used for the foam experiments are 1 and 2 percent by mass NaCl (far below the solubility limit of NaCl which is equal to about 36g/100g water at 25°C). These mass concentrations correspond to 171.1 and 342.2 mmol/litre, respectively.

With the addition of NaCl to the solutions, it is known that the CMC for the SDS drops (Petkova et al. 2020). When the concentration of NaCl is raised to 100 mmol/litre, the CMC drops to about 2 mmol/litre (from about 8.2 mmol/litre with pure water). Thus, at the concentrations used in the research done here, the solutions are above the CMC of SDS.

4.3 Results and Discussion

Table 4.1 lists the average values of surface tension (three repeats) determined by using a TensioCAD Du Nouy ring apparatus (Laval Labs Inc.). The data shows, in general, that as the NaCl concentration rises, the surface tension of the aqueous solution drops. The decrease on add 10% by mass NaCl to the SDS solutions is between 8 and 20% with the trend that appears to be a minimum in the surface tension between 2 and 5% NaCl. These results are consistent with Jiang et al. (2020).
Table 4.1: Surface tension versus SDS and NaCl concentrations.

<table>
<thead>
<tr>
<th>SDS Concentration, mass percent</th>
<th>NaCl Concentration, mass percent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>1.0%</td>
<td>37.8</td>
</tr>
<tr>
<td>1.5%</td>
<td>38.7</td>
</tr>
<tr>
<td>3.0%</td>
<td>37.3</td>
</tr>
</tbody>
</table>

Figure 4.1 displays the effect of the SDS and NaCl on the foam average half-life (taken from three experiments). The results reveal that the higher the SDS and NaCl concentrations, the greater is the half-life of the foam. At a given SDS concentration, as the NaCl concentration is raised, the half-life increases. Thus, the addition of NaCl introduces greater stability to the foam. In other words, the addition of salt to the aqueous solutions lowers the drainage rate of the water in the liquid films.

Figure 4.1: Effect of SDS and NaCl concentrations on average half-life of foam.
Figure 4.2 displays the time after which 25% of the liquid in the foam has drained from the foam. The lower the time implies that the foam is less stable whereas the higher the time means that the water is having more trouble draining from the liquid films. The results show that the greater is both the SDS and NaCl concentrations, the higher is the time at which 25% of the water is drained from the foam.

![Figure 4.2: Effect of SDS and NaCl concentrations on average time for liquid volume in foam to drop by 25%.](image)

The data plotted in Figure 4.2 can be converted to an average drainage rate, as listed in Table 4.2, for the entire foam. The results show that the enriching of the SDS concentration lowers the liquid drainage rate by up 79% for the 3.0 mass percent case versus the 1.0 mass percent case. As NaCl
is added, this effect is enhanced – the drainage rate drops reaching 93% lower than that of the 1.0% SDS (zero NaCl) case.

Table 4.2: Drainage rates for liquid over the period of time where 25% of the water is drained from the foam. Also listed are the percent reduction of the drainage rate for each case relative to the SDS1.0%-zero NaCl case.

<table>
<thead>
<tr>
<th>SDS Concentration, mass percent</th>
<th>Liquid Drainage Rate from Foam, ml/s (Percent reduction relative to SDS1.0 only case)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0%</td>
<td>0.0428</td>
</tr>
<tr>
<td>1.5%</td>
<td>0.0188 (56%)</td>
</tr>
<tr>
<td>3.0%</td>
<td>0.0089 (79%)</td>
</tr>
</tbody>
</table>

The reason for the behaviour described above is as follows. The presence of sodium from the NaCl, being a kosmotrope, means that the water is more structured in the liquid films. Given that the concentration of SDS is above the CMC, there is a large availability of SDS in the films with micelles present as well as a monolayer at the interfaces of the liquid films. Given more structure (a thicker electrostatic double layer), saturated interface with respect to adsorbed SDS molecules which imparts an enhanced elasticity to the interfaces, and the rich number of micelles in the liquid film which provides resistance to flow leading a disjoining pressure effect, the liquid films are ‘strengthened’ with greater resistance for the flow of water molecules from the films. This enhances the stability of the foam.

Hammouda (2013), in an exhaustive experimental study of the nanostructure of SDS micelles, showed that above the CMC, SDS micelles mostly exist as oblate ellipsoid shaped micelles. From his experiments, at 22°C, he determined that the lengths of the long and short axes of the ellipsoid

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were equal to about 21 and 15 Å, respectively. At 1 mass percent SDS and 1% NaCl, the long and short axes of the ellipsoid change to about 26 and 15 Å, respectively, whereas at 2% NaCl, the long and short axes of the ellipsoid change to about 30 and 15 Å, respectively. This shows that the lengths of the SDS micelles grow as the NaCl concentration increases. Thus, the aspect ratio of the SDS micelles is enlarging as the concentration of NaCl grows. This means that in the thin liquid films in the foam, the larger the salt content, the larger the micelle aspect ratios and it is likely that they experience less shear due to greater alignment of the micelles (Hare and Ghadiri 2013). In this manner, from a flowability point of view, this could aid in ‘squeezing’ the micelles from the liquid film. However, since the stability of the foams are greater with higher salt content, this suggests that the impact of the micelle aspect ratio on the flow in the thin liquid films is small.

4.4 Conclusions

The results demonstrate that at high SDS concentrations, the addition of salt enhances the stability of aqueous foams. The stabilization is likely due to reduced flow of water from the liquid films in the foam due to the presence of the salt – creates more structured water in the thin films – and SDS – adsorbs as a monolayer on the interfaces enhancing their elasticity as well as micelles within the film which provides a tendency to impede water flow. The results from the experiments show that the addition of NaCl to the SDS solutions lowers the average liquid drainage rate from the liquid films.
A series of experiments were conducted to examine the stability of SDS and SDS+NaCl foams in a dynamic foam analyzer. In total, over 100 experiments were done to understand how to use the dynamic foam analyzer and to ensure that the results are repeatable. The concentrations used in the experiments conducted here are higher than that currently found in the literature.

5.1 Conclusions

The following conclusions have been drawn from the research documented in this thesis.

1. The dynamic foam analyzer has repeatable results. This was found for both SDS and SDS+NaCl experiments. The foam height, bubble count, bubble area, and average bubble size versus time were found to be consistent between experiments for the same samples and operating conditions.

2. In the early stage of foam destruction after the foam is formed, the bubbles are small and spherical. As the foam disintegrates, the liquid films bounding the bubbles rupture and the bubbles merge or are destroyed at the top of the bubble column. Liquid drainage from the films makes the topmost bubbles have the thinnest thicknesses and thus, they tend to rupture especially for the lowest SDS concentration experiments conducted in this research. As the bubbles merge, the shape of the bubbles evolves from spherical to polyhedral. In general, the average size of the bubbles increases as the foams disintegrate.

3. The higher the concentration of surfactant, for concentrations above the critical micelle concentration, the more stable is the foam.
4. The results obtained from the SDS experiments show that the average liquid drainage rate from the foam is substantially slowed when the concentration of SDS is raised.

5. The results from the SDS+NaCl experiments reveal that at the SDS and NaCl concentrations examined, the greater the concentrations of the two additives, the more stable is the foam generated. The average liquid drainage rate is significantly lowered when salt is added to the solutions.

6. The reasons for the enhanced stability in the presence of salt is likely due to structuring of water within the liquid films of the foam. This creates lower water drainage rate and thus liquid films that last longer imparting a longer foam life.

5.2 Recommendations

The following recommendations are made as an extension of this thesis.

1. More detailed experiments on the arrangement of SDS and salt within the thin liquid films of the foam are required to understand how the two additives cooperate to enhance the stability of the foam.

2. Modelling is required from a fundamental perspective to understand how SDS monolayers, micelles, and salt ions interact in water and especially at interfaces and thin liquid films bounded by two gas-liquid interfaces. The modelling should be directly linked to the experimental results.

3. A wider range of SDS and NaCl concentrations should be tested. Also, other surfactants and salts should be examined.
REFERENCES


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