LIQUID CONTENT PREDICTORS FOR AQUEOUS FOAMS

by

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Abstract

Historically, foam studies have focused on foamability, foam stability, and foam inhibition as opposed to foam density. Hence, the impact of various factors on foam density is still not well understood. Previous experimental work shows that concentrated surfactant solutions with similar surface tensions produce foams with different liquid fractions. These results contradict the common assumption held that these foams would have near-identical liquid fractions. Therefore, this study probes for correlations between equilibrium and dynamic surfactant adsorption parameters at air-liquid interfaces for aqueous foams made from solutions well above the critical micelle concentration.

A protocol was developed for measuring foam density using a cylindrical foaming apparatus with porous filter plate for gas sparging. The foams were created from aqueous solutions of small-molecule surfactants known to have negligible surface shear viscosity. Equilibrium parameters of the maximum surface concentration, equilibrium adsorption/desorption rate constant, and effectiveness (critical micelle concentration) showed weak evidence of a correlation as quantified by linear and ranked correlation coefficients. The surfactant efficiency (concentration needed to reduce the surface tension 20 mN/m) showed some evidence of linear correlation between the ranking of the variables. In contrast, the time required to reduce the surface tension 35% and 50% of the way from the pure water value to the equilibrium value ($t_{35}$ and $t_{50}$) showed strong evidence of correlation of increasing liquid fraction with faster surfactant adsorption times. The results of this study highlight the influence of dynamics even for highly concentrated surfactant solutions.
Lay Summary

The design of foams for industrial use historically has been achieved using methods of trial and error. This is because the relationship between the physical and chemical properties of the surfactants that cause liquid entrainment into a foam is poorly understood. With simplified systems of aqueous bulk foam solutions comprised of a single surfactant and deionized water, foams were generated to quantify the initial liquid fraction. Weak evidence of correlation was found between the liquid fraction and the parameters that describe the equilibrium between adsorbed, or attached, and desorbed molecules at air-liquid interfaces. In contrast, the liquid fraction in foams showed evidence of correlation to the dynamic surface tension parameters. In addition, extending the correlation of the liquid fraction to other surfactants properties like diffusivity is recommended.
Preface

This thesis is submitted for the degree of the Master of Applied Science at the University of British Columbia. The research described here was conducted under the supervision of Dr. John M. Frostad in the department of Chemical and Biological Engineering at the University of British Columbia. For the current study, I was responsible for conducting the literature review, identifying the research gaps, the greater context of the study with prior work, design of testing protocol and experiments, conducting the experiments, using Python code for data analysis developed in conjunction with Dr. Frostad, and interpretation of results.

Equilibrium surface tension isotherms were gathered in conjunction with Ms. Xiran Li. Her contribution to the experimental data of this thesis is gratefully acknowledged.

Dr. Marek Pawlik and Ms. Sally Finora are gratefully acknowledged for help in coordinating the use of a bubble pressure tensiometer from the Normal B. Kevil Institute of Mining Engineering at UBC.
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<th>Description</th>
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<td>$K_{eq}$</td>
<td>Equilibrium rate constant between adsorption and desorption</td>
</tr>
<tr>
<td>$\Gamma_\infty$</td>
<td>Maximum surface concentration</td>
</tr>
<tr>
<td>$A$</td>
<td>Lateral interactions parameter of adsorbed molecules at interface</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Surface tension</td>
</tr>
<tr>
<td>$\rho_g$</td>
<td>Density of air</td>
</tr>
<tr>
<td>$\rho_l$</td>
<td>Density of water</td>
</tr>
<tr>
<td>$\phi_l$</td>
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<td>Liquid fraction of foam, low gas volume</td>
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<td>$\phi_{l\ mid}$</td>
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</tr>
<tr>
<td>$R$</td>
<td>Ideal gas constant</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
</tr>
<tr>
<td>$t_{35}$</td>
<td>Time needed to reduce surface tension 35 percent from reference solvent value</td>
</tr>
<tr>
<td>$t_{50}$</td>
<td>Time needed to reduce surface tension 50 percent from reference solvent value</td>
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<tr>
<td>$t_{90}$</td>
<td>Time needed to reduce surface tension 90 percent from reference solvent value</td>
</tr>
<tr>
<td>$r$</td>
<td>Pearson product-moment correlation coefficient</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Spearman rank-order correlation coefficient</td>
</tr>
</tbody>
</table>
List of Abbreviations

ASTM American Society for Testing and Materials
C Degrees Celsius
CMC Critical Micelle Concentration
DTAB dodecyltrimethylammonium bromide
EOR Enhanced oil recovery
FAL Foam-assisted lift
HTAB hexadecyltrimethylammonium bromide
K Degrees Kelvin
LPM Liters per minute
MBP Maximum bubble pressure
MFC Mass flow controller
mL milliliters
mm millimeters
mN/m milli-Newton per meter
PB Plateau Borders
Re Reynold’s number
SDBS Sodium dodecylbenzenesulfonate
SDS Sodium dodecyl sulfate
TTAB tetradecyltrimethylammonium bromide
Glossary

Aliphatic  Chemical compounds with saturated or unsaturated carbon bonds in un-conjugated sequences

Amphiphile  Molecule comprised of hydrophobic and hydrophilic portions

Aromatic  Chemical compound that contains conjugated planar double bonds to form a delocalized pi-electron cloud

Bulk solution  Macroscopic liquid solution

Critical micelle concentration (CMC)  Concentration of surface-active molecules at which the air-liquid interface is saturated and surfactants form micelles

Drainage  Passage of a liquid through a foam

Entrainment  Trapping of a physical phase within another (ex: air in liquid, or liquid around gas)

Foamability  Description of total volume of foam that can produced from a given bulk solution; various quantitative definitions

Foam density  Total mass of foam divided by the total volume of foam

Foam stability  Rate of foam volume collapse; usually measured as half-life time for foam films to return to bulk liquid solution and air

Kugelscham  German; qualitative descriptor for the bubbly liquid phase encountered during foam formation

Micelle  Surfactant aggregates in solution that form at above-CMC concentrations

Sparging  Pumping gas (air, nitrogen, etc.) into a liquid solution

Zwitterionic  positive and negative charges in close proximity on ionic head group
Acknowledgements

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Dedication

Dedykacja


Jestem Bogu wdzięczna za taką rodzinne – jesteście wśród najcenniejszi mi ludzie na świecie.
“It was only a mountain, nothing but a big ol’ rock…it ain’t hard if you don’t stop.”

– Dierks Bentley, *The Mountain*

“I have fought a good fight to the end; I have finished my course: I have kept the faith.”

– 2 Timothy 4:7, DRC
Chapter 1: Introduction

A foam is a two-phase dispersion of gas in a liquid that is created by addition of the gas phase as separate bubbles into a bulk liquid solution [1]. The entrainment, or addition of gas, requires an energy input to release, mix, or pump the gas into a bulk liquid solution. In addition, surface-active materials slow liquid drainage and rupture of the liquid films thinning between the gas bubbles in a process known as coalescence. Surfactants enable foam formation and give the foam a lifetime prior to collapse that results from inherent thermodynamic instability [2]. Foam parameters change depending on the type of surfactant. Among these parameters are foamability and foam stability. Foamability is the total volume of foam produced from a liquid solution [3], and foam stability is the ability of a foam to hold a given volume over time [4].

Foam structures, ubiquitous in products such as cosmetics and beverages, have also been exploited in industrial applications [5]. Notable areas include froth flotation [6]–[9], enhanced oil recovery (EOR), as well as petrochemical, personal care, and food industries [10], [11]. Foams are deployed in forests as short-term fire retardants to prevent further wildfire propagation [12]. In addition, foams with high density reduce the blast wave and dissipate energy for blast mitigation [13]–[16]. In exploration and production of oil and gas, one method for increasing production in gas lift wells is to use foam-assisted lift (FAL). In this method, the foam injected into the well-bore relieves liquid flooding and increases crude oil recovery at the ground surface [17], [18]. Different qualities of foams such as foamability, total foam height, foam stability, and foam density alter their performance in these varying applications.

A brief review of foam structures and terms will be described in detail and the relationship of the current study to prior methods of foam characterization.
1.1 Bulk foam types

Bulk foams can be characterized according to the ratio of gas to liquid content, or amount of liquid entrained around the gas bubbles. The two extremes to describe the foam quality are wet and dry foams. These designations are qualitative descriptors that indicate what geometric structure and governing forces are present in the foam structure. Verbist et al. [19] define the dry foam as one with a liquid content less than or equal to 5%. In contrast, a wet foam is defined as having a liquid fraction of greater than 20% [20]. Another foam structure is the “bubbly foam,” referred to by Pugh [21] and others [19], [22] as Kugelscham, where bubbles are well-separated in liquid solution [23]. Figure 1.1 shows the three phases of foam structure over time- first the “bubbly liquid” in a., the wet foam in b., and the dry foam in c. [19], [21], [24], [25]. The bubbly foam is only marginally relevant to the scope of this thesis, and therefore is not described in further detail.

Figure 1.1: a. Bubbly foam (in lower half of column marked by bracket) b. Wet foam c. Dry foam

A bulk foam exhibits different behavior and structure depending on if the foam is in the wet or dry regime. Gas bubbles occur during the foam formation process. Therefore, a wet foam is recognized by the spherical shape of the air bubbles in the initial foam. The size of the bubbles can be mono- or polydisperse depending on the method of generation [2], [24], [26], [27]. After formation, gravity and capillary forces cause drainage out of the liquid films in the foam into a
bulk liquid solution under the foam structure [23], [28]. Liquid drainage around the bubbles results in thinning of the lamellae, or liquid films. The thinning effect changes the bubble shape from spherical to a polyhedral structure, seen in Figure 1.2. [10], [21].

![Dry foam liquid film](image)

**Figure 1.2: Drained foam structure**

Following foam formation and initial drainage, the internal structure is rearranged and distributed by surface tension forces. Until the individual thin films rupture, this drained, or “dry” foam is in a time-dependent state of stability [29].

In addition to a different structure, wet foams are governed by markedly different phenomena than dry foams. With the thinning of the liquid films, inter-molecular effects like Van der Waals forces, electrostatic repulsions, and steric hindrance decelerate the fluid flow and subsequent film thinning in dry foam films [30]. The drainage rates and film stability have been correlated to the dry bulk foam stability, or lifetime, of well-drained dry foams [10], [24], [25] and the foamability of bulk liquid solutions [3], [29]. Numerous studies have been documented in the literature on the use of light interferometry to study thin liquid films from aqueous surfactant solutions; hence the studies included here are by no means exhaustive [3], [31]–[33].

Dry foams have been studied from experimental and modeling perspectives [25], [29]. Because the dry foam must drain to reach a quasi-equilibrium state, the system has a greater
stability. This improved stability provides easier study of the relationship of single film interfaces to the macroscopic foam. Conversely, wet foams are considered a dynamic system because of the simultaneous gas sparging and liquid drainage during and after the foam formation [24], [26], [29]. Thus, the dynamics of foam formation are hypothesized to be significant for understanding the mechanisms of initial foam density [34].

The focus of this study is on freshly formed aqueous foams, and the scope is therefore limited to the physical and physico-chemical factors affecting wet foams. The interested reader is encouraged to review [10], [19], [35], [36] for a detailed understanding of advances in dry foam modeling. Aqueous foams form due to the presence of surface active molecules that adsorb to the air-liquid interfaces created with rising gas bubbles [37]. Mechanisms of surfactant adsorption at interfaces are presented in the subsequent section.

1.2 Surfactant adsorption

By considering gas bubbling in a solution of water, the role of surfactants quickly becomes clear. In a foam, the surfactants from bulk solution adsorb to the air-liquid interfaces as the gas bubbles are rising in the liquid solution during foaming. Surfactants lower the Gibbs free energy of the air-liquid interface with adsorption as seen by a decrease in the surface tension of the air-liquid interface [2]. The adsorbed surfactants also play a role in the stabilization of the liquid foam films to prevent their immediate collapse. Additionally, surfactants decelerate fluid flow and prevent growth or shrinkage of the gas bubbles within the foam, also known as coarsening [38]. Regimes of diffusion-controlled and kinetic-controlled mechanisms have been used to describe the rate and amount of surfactant that adsorbs to the interface prior to saturation. The parameters describing small molecule surfactant adsorption include the following: the ratio of adsorption rate to desorption rate, the maximum surface concentration, the area of the
functional group of the hydrophilic portion of the surfactant, sometimes referred to as the head group, and the lateral interactions of the adsorbed surfactants. These parameters have been used in various adsorption models for small-molecule surfactants that use different physico-chemical properties of each surfactant, such as diffusivity and ionic strength [39]–[41].

Surfactants have varying capacities for surface tension reduction. For water-soluble surfactants, the reduction of surface tension increases with increasing concentration until a critical concentration is reached at which the interface becomes saturated with adsorbed molecules. At this concentration, known as the critical micelle concentration, or CMC, surfactants can no longer adsorb to the saturated interface and start to form micelles in the bulk solution. For surfactants free of any additional surface active impurities, the surface tension has reached a minimum at this concentration [42], [43].

1.2.1 Equilibrium adsorption

The amount of surfactant adsorption at an air-liquid interface depends on the energetic environment of the interface, the valence charge of the molecule, and the surface area of the head group [44]–[46]. Several models relate the quantity of the adsorbed surfactant to the thermodynamic solution activity of the system at a constant temperature. For the case of dilute solutions, the activity is equivalent to the concentration [44]. The bulk concentration of surfactant is distinct from the surface concentration in aqueous surfactant solutions. Surfactant diffusivity, electrostatic repulsions between the molecules, and reorientation of the molecules at the interface may influence the surface concentration as a function of time [17], [44], [47], [48].

The surface concentration, or adsorption, of small-molecule water-soluble surfactants is described by the Gibbs adsorption equation for ideal-dilute capillary systems in Equation 1.1 [2]. The parameter \( n \) represents the ionic charge of the counterions dissociated from the surfactant in
the bulk solution. Therefore, for nonionic surfactants, this parameter is unity. For the case of ionic surfactants with an equal ratio of counterions, \( n \) is equal to 2 [44].

\[
\Gamma_{2,1} = -\frac{C}{nRT} \left( \frac{d\sigma}{dC} \right)_T
\]

(1.1)

Where \( \Gamma_{2,1} \) is the surface concentration for a two-component mixture, \( C \) is the bulk solution concentration, \( R \) is the ideal gas constant, \( T \) is the temperature in Kelvin, and \( \left( \frac{d\sigma}{dC} \right)_T \) is the change in surface tension with concentration at constant temperature \( T \) [2].

Equation 1.2 originally derived by Szyszkowski [49] for surfactant adsorption is an empirical expression that describes the equilibrium surface tension change with concentration for moderately dilute aqueous surfactant solutions.

\[
\sigma_0 - \sigma = RT\Gamma_\infty \ln \left( 1 + \frac{C}{K_{eq}} \right)
\]

(1.2)

Where \( \sigma_0 \) is the surface tension of the reference solvent (deionized water for the current study), \( \sigma \) is the surface tension of the surfactant solution, \( \Gamma_\infty \) is the maximum surface concentration, and \( K_{eq} \) is the ratio of the adsorption and desorption rate constants. Equation 1.2 was used initially to describe the surface tension reduction with increasing concentration curves for homologous series of carboxylic acid surfactants. It has been used in later work to describe the behavior of small-molecule surfactants at concentrations below the CMC [2], [44].

The parameters \( \Gamma_\infty \) and \( K_{eq} \) derived from the Szyszkowski equation can then be applied to the Langmuir adsorption isotherm. The Langmuir isotherm relates surface concentration to bulk solution concentration using assumptions of an energetically uniform interface as well as negligible lateral interactions between adsorbed molecules. While lateral interactions may be present, the total heat of adsorption appears constant as increased surface coverage decreases the heat of adsorption but increases lateral interactions between the molecules [44].
Previous studies on adsorption have used other isotherm models such as the Frumkin isotherm and the reorientation compressibility model that were developed to account for deviations from the Langmuir isotherm adsorption behavior. These deviations in behavior are assumed to be caused by surface ionic charges, compression of the surfactants, and surfactant chain length reorientation at the interface [17]. With the numerous models for surfactant adsorption, no agreement has emerged on the most applicable isotherm model for a small molecule surfactant [42]-[43]. Rather, relationships are proposed based on empirical results. Nonionic surfactants are sometimes well-described by the Langmuir adsorption isotherm [42]; however, the adsorption of ionic surfactants usually carries energetic contributions from the electrostatic repulsions that accumulate with increasing surfactant adsorption. The extent of change in the surface tension measurements from these electrostatic effects is not known a priori for each surfactant.

Elsewhere, the adsorption of ionic surfactants was well-described by the Szyszkowski equation and Langmuir isotherm using the assumption that the activity coefficients were close to one [43]. For non-ionic surfactants, Rosen [43] has stated that the Szyszkowski equation-Langmuir isotherm relationship describes well the adsorption of nonionic surfactants of C18 carbons or less [43]. Therefore, the equilibrium adsorption model used in this study will assume conditions of moderately dilute concentrations where the Szyszkowski equation can be used to predict the maximum surface concentration and the equilibrium rate constant for adsorption/desorption.

1.2.2 Dynamic adsorption

For surfactant adsorption at “fresh,” or newly created air-liquid interfaces, the amount adsorbed increases until an equilibrium between the adsorbed and desorbed amount of surfactant...
is reached. Experimentally, the equilibrium is seen in a stabilization of the value of the surface tension measured [2].

Surfactants reduce surface tension at new interfaces at rates that depend on a characteristic diffusion time, a kinetic barrier to adsorption, or a combination of the two parameters [2], [47], [52], [53]. Several studies have focused on whether the characteristic diffusion rate or a kinetic barrier to adsorption is the governing mechanism for adsorption [39], [47], [54], [55]. However, there is currently lack of agreement about the best adsorption mechanism to describe a wider sampling of surfactants. In addition, the surface tension reduction of above-CMC solutions is expected to have faster adsorption due to the micelles of surfactants that provide a large supply of surfactants near the air-liquid interface [2]. Currently, semi-empirical models have been proposed to describe the rate of reduction of surface tension. A dynamic model for the limit of long and short times has been derived from the Ward and Tordai equation [56] that is the primary expression for dynamic surface concentration. Equation 1.3 shows the short timescale expression for time-dependent surface tension and Equation 1.4 shows the long-term asymptotic expression for surface tension reduction [19], [56]- [57].

\[
\sigma = \sigma_0 - 2RTC_0 \left( \frac{D}{\pi t} \right)^{\frac{1}{2}} \\
\sigma = \sigma_e + \frac{RT\Gamma^2}{2C_0} \left( \frac{\pi}{Dt} \right)^{\frac{1}{2}}
\]

Where \(\sigma\) is the time-dependent surface tension, \(\sigma_0\) is the reference surface tension, \(R\) is the ideal gas constant, \(T\) is the temperature in Kelvin, \(C_0\) is the initial bulk solution concentration, \(t\) is the time, and \(D\) is the diffusivity. The term \(\Gamma\) in Equation 1.4 represents the surface concentration, while the term \(\sigma_e\) is the equilibrium surface tension.
Another model of adsorption was developed by Rosen and Hua [52] based on the theory of molecular relaxation time and used as a correlation to foam density [17], [52], [59]. This model, shown in Equation 1.5, uses a two-parameter empirical equation to describe the time-dependent surfactant adsorption.

\[
\frac{\gamma_0 - \gamma_t}{\gamma_t - \gamma_m} = \left( \frac{t}{t^*} \right)^n
\]  

(1.5)

Where \(\gamma_0\) is the reference surface tension (i.e. that of the solvent), \(\gamma_t\) is the surface tension at time \(t\), \(\gamma_m\) is the meso-equilibrium surface tension of the surfactant solution, \(t\) is the time, \(t^*\) (also known as \(t_{1/2}\)) is the time needed to reduce the surface tension \(\gamma_t\) from \(\gamma_0\) to a value one-half of the meso-equilibrium value \(\gamma_m\), and \(n\) is a fitting parameter. Meso-equilibrium is observed to be the final equilibrium surface tension for many surfactants and has been used interchangeably in [17]. As seen in Figure 1.4, [52] \(\gamma\) is used in place of \(\sigma\) for surface tension [52].
Figure 1.3: Generalized dynamic surface tension curve. Curve- I. induction region.; II.- rapid fall region; III.- meso-equilibrium region IV.- final equilibrium. Reprinted with permission from Rosen and Hua [52].

Previous work has shown for small-molecule surfactants, the meso-equilibrium surface tension is equivalent to the final equilibrium surface tension [17], [18], [59]. Thus, for similar small-molecule surfactants in this study, the characteristic time $t^*$ can elucidate the speed of adsorption of the surfactants. Because the existence of local surface tension gradients is assumed for the air-liquid interfaces being created in the foam, this parameter is important for understanding the mechanisms of time-dependent adsorption and its role in enhancing or suppressing Marangoni flows, described in the next section.

1.3 Gibbs-Marangoni effects

Bubbles rising in fluids at low concentrations exhibit conditions of non-equilibrium surface coverage [8], [60]–[63]. A bubble’s fresh interface is in motion, and its velocity is decelerated as surfactants adsorb. In addition, the bubble’s rising causes perturbation of the
surfactant-laden interface. Thus, a bubble’s surface exhibits localized areas of surfactant
depletion that increases the surface tension locally in the depleted regions [24], [26]. Therefore,
the driving force towards equilibrium surface coverage of the surfactant causes fluid to move
towards the depleted areas. This phenomenon, known as the Gibbs-Marangoni effect, causes an
increase in fluid flow around the interface to re-establish equilibrium [15], [52]-[53].

Recovery from surface tension gradients is related to the rate at which surfactants can
adsorb to the interface to change the non-equilibrium surface coverage to an equilibrium state.
Liquid entrainment in foams involves fluid flow around the bubbles. Thus, any parameter that
enhances or suppresses fluid flow is of interest to liquid content prediction in foams. Parameters
of dynamic adsorption are therefore expected to have a significant effect on the initial liquid
content within a foam [18], [59].

Due to the competing theories on the mechanisms of surfactant adsorption, experimental
parameters directly from dynamic surface tension curves have been used in this thesis. The time
points used as parameters in this study are \( t_{35} \), \( t_{50} \), and \( t_{90} \), which represent 35, 50, and 90
percent of the total time needed to reach the equilibrium surface tension value.

1.4 **Foam density in relation to stability, drainage, and foamability**

Foam density is a parameter that is calculated directly from the liquid content profile in a
freshly formed wet foam [10], [19], [34]. Because the density of water is three orders of
magnitude greater than that of air, the liquid fraction present within the foam is the experimental
parameter of focus for determining the foam density. The liquid fraction, shown in Equation 1.6,
is the ratio of the volume of liquid entrained in the foam over the total foam volume [25]. The
foam density is described by the expression in Equation 1.7.
\[
\phi_l = \frac{V_{\text{liquid}}}{V_{\text{foam}}}
\]

(1.6)

\[
\rho_f = \rho_l \phi_l + \rho_g (1 - \phi_l) \approx \rho_l \phi_l
\]

(1.7)

Where \( V_{\text{liquid}} \) is the volume of liquid entrained in the foam, \( V_{\text{foam}} \) is the total foam volume, \( \rho_f \) is the foam density, \( \rho_l \) is the liquid density, \( \rho_g \) is the density of the gas, and \( \phi_l \) is the liquid fraction.

Few predictive models exist for the initial liquid fraction of a foam, and they depend upon highly controlled methods of generation [21]-[22], [53]-[54]. The liquid entrainment and drainage of single films has been used to make correlations to the entrainment and drainage in bulk aqueous foams [3], [34], [68]. A longer timescale for the gravitational drainage of planar thin films has been correlated to increased foamability in the bulk foams of the same surfactants [3]. In addition, a film drainage study was done using laser reflectivity for aqueous films at concentrations above and below the CMC [68]. The results of this study showed a lower exponent than expected for a power-law fit to the data. The differences in fluid drainage rates out of single bubble films are hypothesized to be a result of fluid flow along thin film interfaces that are neither fully mobile or immobile [34]. Mathematical modeling of this drainage out of the films would therefore require a modification of the fluid flow boundary conditions. Further investigation is required into the parameters that may govern the degree of surface mobility and thus change the total liquid entrainment in a freshly formed foam.

Wet foams have been investigated for simultaneous drainage effects for applications like froth flotation and mineral processing. In dynamic foams, or foams with continual gas supply, the force of gravity that causes liquid drainage is coupled with the buoyancy of the rising foam until a steady-state is reached [37], [65]. Dynamic foam studies with an end goal application in mineral studies frequently use a foaming vessel of length scales where drainage effects in the
bulk foam are non-negligible [6], [69]. Foams produced in a 84 centimeter cylindrical foaming column showed a correlation to the rate of surface tension reduction $R_{1/2}$ [52], [59]. The extent to which this analysis can be extended to foams produced on a length scale where drainage effects can be minimized to a near-negligible level is not evident in the current literature and thus presents a central focus for the current study.

1.5 Surfactant properties

Surfactants with different ionic charge, chain length, and chemical functional group were chosen for this study to capture a range of small molecule surfactants. Previous work has shown these molecules exhibit negligible surface shear viscosity [70]. Viscosity at the surface is thus hypothesized to have a negligible effect on the liquid entrainment in the air-liquid interfaces. Surfactants of similar molecular weight, surface tension at the CMC, and negligible interfacial shear viscosity are expected to modify hydrodynamic boundary conditions for liquid drainage out of films depending on surfactant type and concentration. The extent or nature of these modifications remains unknown. Initially, three well-studied surfactants – TritonX-100, HTAB, and SDS, which are a nonionic, cationic, and anionic molecule, respectively – were used in the initial research in this area [34]. In the current study these three surfactants were used for method development and initial indication of trends. The initial results in this study suggested a possible correlation with the dynamic adsorption parameters. Therefore, five additional surfactants with varied time scales of adsorption reported in the literature were chosen for testing.

1.6 Research hypotheses and objectives

Fundamental mechanisms that account for the differences in bulk foam density for freshly formed wet foams with a finite gas volume are not fully understood. Previous research
on initial foam density of these static foams suggests that molecular-level surfactant properties affect the initial liquid fraction in foams [4], [34], [59]. Variations in individual surfactant adsorption parameters are hypothesized to change the bulk fluid flow in a freshly created foam and thus the initial liquid volume entrained within the foam. Therefore, the objective of this study is to investigate bulk foam liquid fractions of simplified systems consisting of a single surfactant in aqueous solution used to create a foam.

The research questions motivating this study are the following:

1. To what extent do the equilibrium and dynamic surfactant adsorption parameters show evidence of correlation to a trend of liquid fraction in aqueous foams?

2. Does the density of aqueous foams show identifiable trends based on the presence or absence of valence charge?

It is well-established that the maximum foamability should be achieved at or above the CMC for a given aqueous surfactant solution [71]. Therefore, the focus of this study is on the behavior of foams produced from solutions at concentrations well above the CMC of the surfactant studied. A protocol for investigating the initial liquid fraction is developed as part of this study as a standard experimental testing method is not established. Finally, the relationships between the adsorption parameters and the initial liquid fractions will be quantified using statistical correlations that test for linear relationships between the variables as well as between the rankings of the variables.

1.7 Outline of thesis

The remaining structure of this thesis is divided into a section for the review of previous experimental and modeling research and the gaps left in the field in chapter 2. Chapter 3 gives an outline of the materials and instrumentation used in this work. The measurement of the liquid
fraction is not a well-established procedure, therefore Chapter 4 focuses on the development of an initial liquid fraction measurement protocol. The remaining chapters describe the results, conclusions, and recommendations for future work.
Chapter 2: Review of Previous Research

Relevant theories, previous work, and background information are given to familiarize the reader with the current state of the art, and the knowledge gaps that motivate the current study. Previous theories and experimental methods of bulk foams, foam modeling, surfactant adsorption, and chemical functionalities are reviewed.

2.1 Foaming studies

2.1.1 Vessel variations

A Ross-Miles test, where a cylindrical vessel is used for foaming, is the current recommended foam testing method from ASTM D 1173-07 [72]. Several industrial agencies have also adopted this geometry for foaming tests [59], [73]. However, various vessel sizes and shapes have been proposed to tailor the foaming test to the final application [37]. Foam production into a vessel of varied cross-sectional area, such as a conical shape, has been proposed both from practical and fundamental considerations. For practical considerations, an increasingly larger volume of foam is produced from a conical vessel for the same change in height.

In the analysis of Ross and Suzin [74], the foam volume produced for dynamic foams was different in experiments where the only change between experiments was the shape of the foam vessel used. Per the researchers, the cylindrical vessel over- or under-represents the foamability for dynamic foams due to the fixed surface area for gas loss [74]. Analytical solutions for the change in the liquid fraction were found for containers with increasing cross-sectional surface area in the direction of the bottom of the foaming vessel. This increasing cross-sectional area created a liquid fraction that was uniformly distributed across the height of the
section of foam being modeled. The main force affecting fluid flow therefore was gravity, and the change to the liquid fraction due to capillary effects could be neglected [75].

In a more recent study, foam volume suppression or foam volume enhancement was also observed as a function of increasing or decreasing superficial gas velocity in cylindrical vessels. In contrast, the foam volume showed a near-uniform increase with increasing superficial gas velocity in conical vessels [22].

The wettability of the surface of the containers has also been studied for the effect it may have on gravity-driven drainage in foams with inconclusive results [76]. Moreover, the effect of the vessel surface properties on foam formation is expected to be minimal in a turbulent foaming environment where the ratio of the bubble diameter to the vessel diameter $S$ is less than or equal to 0.12 and the Reynold’s number Re is greater than 100 [37], [77]. Malysa [37] states in a review on the subject that the foaming experiment should be designed so that the vessel best represents the final application of the foaming test [37]. The geometry and the relative dimensions of the foaming column used should be noted prior to cross-referencing various foaming studies. For example, a dynamic foam in a column 1 m in height, a dimension seen in froth flotation studies [6], can produce a different picture of foam properties than seen with foaming vessels on the height scale of 240-300 centimeters [4], [44], [65].
2.1.2 Defining foamability

Empirical and theoretical models are used for characterizing foam formation. Properties of the foam such as foam height, foaminess (defined below), and retention time of gas are dependent on diverse empirical parameters. These parameters range from the superficial gas velocity used for foam production [22], [78], effective film elasticity of the individual thin films within a partially drained foam, or the HLB number [79].

Common methods of foam formation involve gas sparging either through a single orifice, such as a capillary tube, or through a sintered filter plate [35], [37], [78]. Additional methods use mechanical mixing, shaking, or turbulent gas flow to produce foams for various tests [37], [78], [80].

The foamability of a surfactant solution is its ability to entrain gas and produce a foam. Sett et al. [3] defined foamability as the total volume of foam generated in a fixed time period of gas injection. The foamability can depend on the method of generation used for the foam. However, Bikerman [81] developed a metric of foaminess $\Sigma$ defined in Equation 2.1 to
characterize foaminess as a fundamental property of the foam. This relationship is based on the average foam volume and the volumetric gas flow rate into the foam, and has been used to describe the average lifetime of a bubble in a foam [37].

\[ \Sigma = \frac{V_f t}{V_g} = \frac{V_f}{u_g} \]  \hspace{1cm} (2.1)

Where \( \Sigma \) is the foaminess parameter defined in units of time, \( V_f \) is the average volume of the foam, \( V_g \) is the total volume of gas sparged into the foam, \( t \) is the experimental time, and \( u_g \) is the volumetric flow rate.

Bikerman found that the ratio \( \frac{V_f t}{V_g} \) stopped changing with changes in the bulk solution volume as well as a middle range of gas velocities. The unit of foaminess was postulated to be a parameter of the foam independent of experimental conditions such as the gas flow rate, the size distribution of the pores in a sintered plate, and the dimensions of the foam generation vessel. However, the assumptions of no coalescence between the gas bubbles as well as a negligible liquid fraction within the foam do not always hold true for wet foams [37]. The relationship of the superficial gas velocity, the total foam height, and the resulting foam stability was investigated by Neethling et al [28], where a foam height equilibrium was found for lower gas velocities, but not found for increased gas velocities within given the testing parameters [28].

An extension of the Bikerman’s foamability unit called retention time was derived by Malysa [37], [79] for dynamic, steady-state foams. The unit was derived from experimental observations of the dependence of the total gas volume in both solution and foam on increases in the gas flow rate. The retention time describes the partitioning of gas and liquid between the bulk liquid and bulk foam phases according to Equation 2.2.

\[ rt = \Sigma + \frac{\Delta V_l}{\Delta u_g} \]  \hspace{1cm} (2.2)
Where \( rt \) is the retention time, \( \Sigma \) is the Bikerman parameter, \( \Delta V_l \) is the change in the volume of the bulk solution phase with a change in flow rate, and \( \Delta u_g \) is the change in flow rate.

Physically, the \( rt \) parameter describes the time needed for a volumetric unit of gas to move through both the bulk solution and the foam. Thus, the retention time can be considered as a residence time parameter for the gas injected in creating a foam. The \( rt \) parameter is independent of the flow rate and the vessel geometry. The variations in the gas retention in a foam point to different fundamental properties of the surfactants that cause the differences in fluid behavior and the gas retention time. For the seven surfactants used in the study of Malysa et al. [79] the retention time increased with increasing surfactant concentration. However, it is currently not fully understood what other parameters of surfactants cause the variations in gas hold-up times [37].

2.1.3 Pre-micellar and micellar regimes

Below the CMC, the foamability of a surfactant solution increases with increasing concentration until an equilibrium height has been reached. Previous experimental and theoretical studies show that the maximum foam height possible for an aqueous surfactant solution is at the CMC or near this concentration [3], [71]. Surfactants adsorb on the newly created interfaces during foam formation which in turn decreases the bulk solution concentration. The decrease in concentration leads to a depletion of surfactant in the bulk solution and decreases the foamability of the solution during gas sparging. The extent to which a solution can become depleted depends on the surfactant type and bulk concentration [34]. Therefore, the maximum liquid fraction for a given surfactant is expected to occur at concentrations above the CMC [34]. At this time point, the bulk surfactant solution provides a reservoir supply of
surfactant for adsorption to the rising gas bubbles. In addition, significant drainage of fluid out of the foam has not yet occurred.

2.2 Mathematical modeling of foams

The bulk of foam modeling studies have focused on dry foam topology and structure evolution [10], [36]. While useful for insight into physical properties of foam systems, the direct applicability to the present study is limited because the foams in this study are in non-equilibrium conditions during their formation.

Leonard and Lemlich [82] laid the theoretical groundwork for modeling of liquid drainage between the Plateau Borders in a foam structure. Verbist et al. [19] use this theory to analyze foam drainage by assuming negligible fluid flow in the film but with flow in the Plateau Borders that has a zero-velocity boundary condition [19], [66]. The network of channels is compared to using Darcy’s Law for porous media and assumes a similar dissipation of stress in the channels. This model has shown good agreement with a dry foam. Drainage experiments that subsequent researchers used included drainage of liquid introduced at the top of the column, called forced drainage [27], or free drainage, where a foam with a uniform flow rate within the structure is formed and allowed to drain. In addition, some of the problems encountered with foam modeling were highlighted, such as the change of the network structure in response to localized pressure drop. Another challenge in creation of the model was how to create a boundary condition that incorporates a condition of having a wetter foam at the bottom experiencing liquid drainage [19].
Koehler et al. analyzed fluid drainage through the channels of the idealized network of a foam that was based on a model governed by viscous dissipation in the nodes, seen in the structure in Figure 2.2b [27]. In this analysis, free and forced drainage experiments were conducted for small molecule surfactants to gather wave front velocity profiles for the drainage of the fluid from the foam. While the model showed agreement for the experimental velocity of the liquid front as it moves through the bulk foam, locally modifying the liquid fraction, the method of generation was tightly controlled to produce a foam of uniform bubble size. Change in bubble size has significant effect on properties of the foam, like stability. Moreover, the bubble size has been correlated to change in the liquid fraction of the foam [65]. However, the control of bubble size is fairly empirical and possible over a small range. Therefore, the applicability of foams of a mono-disperse bubble radius to the more realistic polydisperse foams created in other testing methods and industrial processes is not clear.

In a separate study by Koehler et al. [83] experiments on microscopic films were used to observe the liquid drainage out of an individual Plateau border for aqueous surfactants. The
surface mobility and hence the microscopic drainage rate was found to depend both on the internal foam geometry determined by the liquid fraction (i.e. “wet” or “dry” foam structure) as well as the surfactant chemical parameters. In the study, the bubble interfaces of protein-stabilized foam films and small-molecule surfactant foam films were compared for the effect of surface mobility on fluid velocity. The protein films exhibited rigid interfaces, whereas the surfactant films with SDS-laden interfaces showed non-negligible surface velocity, confirming the results observed in previous single film studies. The surface mobility in this model was based upon the dimensionless parameter \( M \), where the ratio of bulk viscosity to surface viscosity is described as per Equation 2.3 [83].

\[
M = \frac{\mu_a}{\mu_s}
\]  

(2.3)

Where \( \mu \) is the shear viscosity of the bulk solution, \( a \) is the width of the Plateau border, and \( \mu_s \) is the surface shear viscosity [83].

The channel-dominated and the node-dominated models represent two extremes for the viscous dissipation of fluid flow [66]. Neethling et al. [66] used the two models to propose a transitional region where both the nodes and the channels are responsible for viscous dissipation. The analysis was extended in a separate study [28] to include the entire process of growth, drainage, and collapse for both an ideal foam column with and without coalescence. The results of the second work from Neethling et al. show that critical pressures measured to determine the rate of coalescence in the foams is lower than expected from summing the theoretical critical pressures for ruptures of individual bubbles. These results are in agreement with an analysis from Malysa and Lukenheimer [24]. Moreover, the results for the growth rate phase indicate that the liquid fraction inside the foam depends non-trivially on the gas flow rate used. However, the results of this study focus on foam height evolution and contain only a qualitative analysis of
the liquid fraction. Finally, the effects of changing the concentration of the bulk liquid solutions to create the foams are not investigated [28].

Saint-Jalmes et al. [80] created a modified foaming apparatus where a surfactant solution is flowed into a mixing chamber simultaneously with a source of N₂ gas. The mixture exits through a connecting hose line as a foam with uniform liquid fraction. Highly uniform and repeatable foam structures were the objective of the new apparatus for experimental validation of the foam drainage model developed. For the same foam height, a varied drainage profile was tested for changes in the liquid content throughout the entire bulk foam. A single surfactant at a single concentration was used in this study [80]. Therefore, the potential changes in foam structure surface mobility that has been suggested for above-CMC concentrations was not explored [34], [68], [83]. Initial effects of gravity during the foaming process are also not analyzed.

Recently, Yazghur et al. [65] modeled the liquid hold-up in a forming aqueous foam for small molecule surfactants. In the model, semi-empirical estimates of the foam permeability and osmotic pressure in the foam were created and correlated to experimental foam results. The expression developed used a dynamic pressure drop as the basis for liquid drainage during foaming and built upon Darcy’s law for flow through a porous media. A steady-state foaming process was used as opposed to a static foam generation method to achieve a constant liquid fraction. In addition, the liquid profile at different heights was non-dimensionalized with respect to the total initial liquid volume entrained. The results showed that the bubble diameter changes with increasing gas flow rate. Moreover, the model predictions of liquid entrainment changed when using a rigid or mobile interface within the foam. The model with an assumption of surface mobility best predicted the experimental liquid fraction change with foam height.
Discrepancies between free drainage and forced drainage experiments that resulted in different values for the degree of interfacial mobility were discussed. Finally, the modeling shows negligible change in liquid content when using a mono-disperse bubble size distribution as opposed to a polydisperse model. Thus, the results of this study highlight the importance of quantifying surface mobility for liquid content predictors in foams [65].

The theoretical and experimental work done on drainage gives important insights into the governing physical mechanisms in both foam as well as liquid content evolution. However, models to predict the initial liquid entrainment for solutions at above-CMC concentrations are at present not fully developed and verified with systematic testing across various testing conditions.

2.3 Thin film liquid flow

Liquid flow such as in a single thin liquid film has been studied for correlation to bulk foam properties, such as foam stability. Properties of bulk foam stability can be approximated for varying surfactant type, concentration, and temperature, for example, because the conditions of the thin film generated are similar to the conditions in the foam [3]. Foam stability and foamability are two of the bulk foam parameters that have been correlated to the respective thin film liquid velocity, or drainage rate. Analysis of thin film properties is done with use of optical reflectivity [33] [1]. Later work by Berg et al. [68] has used laser reflectivity to track the vertical drainage of soap films in the low capillary number regime. Two distinct drainage behaviors were observed for solutions below or above the CMC. The results highlight that while all solutions tested exhibit Newtonian behavior in the bulk scale, microscopic changes in fluid flow boundary conditions are influenced by changes in solution concentration.

Elsewhere, Sett et al. [3] quantified drainage rates of thin vertical foam films. They also related the drainage rates to foamability and the instantaneous dimensionless liquid fraction of
the foam. The change in film thickness with fluid drainage initially showed a linear decay until the films reached the thickness needed for stabilization due to disjoining pressure effects [3]. Bulk solution foamability increased with addition of a “superspreading” surfactant to SDS, and the bulk foamability correlated to increased disjoining pressure. However, the enhanced single thin film stability did not correlate to the liquid content trends as the liquid content showed little change for either the single-surfactant solutions or the mixed surfactant solutions [3].

The studies on the thin liquid film relationship to bulk foam properties have not resulted in an agreement about the applicability of this correlation. Foam generation, whether a continuous process of gas sparging such as in a dynamic foam or an injection of a finite gas volume for a static foam, is still a dynamic process. In contrast, most thin film studies are allowed to reach an equilibrium that is not necessarily representative of the true interfacial environment at the foam lamellae [24], [26], [37], [84].

Dynamic thin film experiments were done by Frostad et al. [34] to understand the influence of a single surfactant in a bulk foam system. The system used a single bubble created at the tip of a capillary translating in surfactant solution towards the air-liquid interface as seen in the schematics in Figure 2.3a and b.

Figure 2.3: a. Interferometry apparatus used to quantify thin film properties of bubble translating towards interface. b. Film formation of air-liquid-air interfaces. Reprinted with permission from Frostad et al. [34].
The single bubble results were compared to the liquid content of bulk foams produced in a conical vessel. The volume of liquid entrained in the single bubbles varied for the three surfactants. This variation was hypothesized to be related to the tangential stress boundary conditions for each surfactant. The results highlight the need to understand surfactant-specific effects in future hydrodynamic modeling for these systems. The liquid entrainment of the single bubble films was different for each surfactant and bulk foam produced. However, the surfactants with the greatest liquid volume entrained were different for the thin films and the bulk foams. These results indicate that further work on the single-interface level is required to understand the causes of the liquid entrainment trends in both the single films and in the bulk foams [34].

2.4 Previous research on foam density

Foaming experiments in the study of Frostad et al. [34] were done using a conical vessel. The liquid fraction trend in this study showed different results than for that of the study of Kawale et al. [59], where a cylindrical vessel was used. Finally, Acharya et al. [4] correlated the foam density and stability of foams produced in a cylindrical vessel for SDS and a “gemini” surfactant to the foam volume stability and foam liquid stability to other surfactant properties such as wet foam film elasticity and dynamic surface tension [4].

Kawale et al. and Acharya et al. separately related equilibrium and dynamic properties of surfactants to foam density with varying conclusions about the parameters’ overall effects on the initial liquid fraction. In the study of Acharya et al. a decreasing bubble size in the foam produced via a smaller fritted filter porosity yielded lower liquid fractions in the foams [4]. In contrast, the study of Kawale et al. found good correlation of increasing liquid fraction with decreasing bubble size radius [59].
2.5 Summary

The review of the current state of the art highlights the current gaps in the understanding of the initial liquid entrainment in bulk foams. Varying degrees of surface mobility have been identified for liquid velocity in the spherical bubbles that comprise the foams. Thus, a greater understanding of the equilibrium and dynamic adsorption of surfactant in bulk foams is investigated and correlated to the initial bulk foam liquid fraction in the experimental results described in this thesis in Chapter 5.
Chapter 3: Methods and Materials

This chapter outlines the experimental protocols adopted and developed for this study. A brief background on the method will be given, followed by the details of the methods and measurement.

3.1 Surfactants

Nonionic and ionic surfactants were used in this study to characterize the liquid entrainment behavior across a wide variety of surfactant types. The nonionic surfactants were from the Triton series as TritonX-100, TritonX-45, and TritonX-165. These nonionic surfactants vary only in terms of the degree of ethoxylation in the polymeric portion. The cationic surfactants were comprised of trimethylammonium salts HTAB, TTAB, and DTAB which allowed for comparison of the liquid fraction across structurally similar surfactants. The anionic surfactants were surfactants with a sulphate group for SDS and sulphonate functional group for SDBS. The chemical structures of the surfactants are shown in Figure 3.1. All surfactants were used as received without further purification.
Figure 3.1: Chemical structure of surfactants: a. TritonX-100; b. TritonX-45; c. HTAB; d. TritonX-165; e. SDS; f. SDBS; g. DTAB; h. TTAB

3.2 Equilibrium surface tension

Measurement of equilibrium surface tension was accomplished using a Wilhelmy method, where the primary assumption is that a zero-degree contact angle is made between the fluid of interest and the measuring apparatus. The most common apparatus uses a platinum plate to dip into the liquid. For this study, a metal alloy rod with a mixed metal-oxide coating was used with the wetted perimeter equal to the circumference of the rod [85]. As seen in Figure
3.2b the rod is positioned just at the interface to allow for isolation of the downward force resulting from the surface tension of the air-liquid interface.

The Wilhelmy method was used with the force tensiometer in the MicroTrough G4 trough-tensiometer apparatus from Kibron. The temperature of the solutions used was at ambient conditions in the range of 22 °C to 25 °C. Prior to use, the probe was flamed cleaned and activated by passing the probe through a Bunsen burner flame. The probe was then mounted on a force transducer with a resolution accurate to 0.1 mN/m. The probe was tared in air prior to sample measurement.

To capture the full range of surface tension change, 12-20 different concentrations were used at levels below the expected CMC. In addition, 1-5 concentrations were used above the CMC to capture the plateau seen in the surface tension curve. To verify the tensiometer readings, a sample of deionized water with a surface tension of 72.5- 73.0 mN/m was used in testing as expected from results reported in literature. The variations reflect changes in temperature and humidity conditions [2], [86]. For this study, the target surface tension to verify the purity of deionized water was 72.8 +/- 0.5 mN/m. For surface tension readings outside of the range specified above, the test solution was discarded and glassware re-purified. Calibration and glassware cleaning protocols are described in detail in Appendix A.1 and A.2, respectively.
Surface tension readings were taken before and after the addition of a stir bar to verify the surface purity of the liquid. The surfactant concentration was varied by sequential addition of a stock solution. To shorten the time of diffusion of surfactant to the interface, the solution was gently stirred for 30 seconds after addition of surfactant to the water, and the reading was taken directly after stirring was stopped. Additionally, to ensure the probe was fully wetted and a zero-contact angle created, the probe was displaced 3 mm into the solution and brought back to the initial height.

To validate the experimental results, generation of the isotherms was done twice for each surfactant. The surfactant HTAB exhibited the lowest solubility in the concentration range of interest and was measured three times for validation.

### 3.2.1 Szyszkowski equation fitting routine

The maximum surface concentration $\Gamma_\infty$ and equilibrium adsorption-desorption rate constant ratio $K_{eq}$ were calculated using the Szyszkowski Equation (1.2) reviewed in section 1.2.1. A curve-fitting routine using a Nelder-Mead method in Python was written for this purpose. The experimental values obtained from the fitting routines were on the same order of magnitude as the literature values and will be discussed in the subsequent chapter. The code used for this fitting routine is included in Appendix B.1.

### 3.3 Foaming measurements

Bulk foam properties were generated and analyzed with a dynamic foam analyzer from Krüss. The DFA100™, or Dynamic Foam Analyzer, measures the parameters of foam formation and foam stability for a given solvent-surfactant system. The apparatus is similar to a Bikerman foaming column as it uses a sintered filter disk through which to pass air to create a foam and provides control over the gas flow rate. The total height of the respective parts of foam and
liquid are detected and recorded based on the amount of light transmitted through the column to a one-dimensional camera (Figure 3.3a). The images are then processed and plotted in real-time in the user interface as shown in Figure 3.3b.

![Figure 3.3: a. DFA method of detection (Krüss) b. Example of ADVANCE image analysis data](image)

3.3.1 **DFA100 column: loading and cleaning**

To ensure the correct identification of the initial bulk liquid height in the foam column, the initial volume in the column must be known and provided to the software. Bulk solutions were made at the desired concentration and a precise volume of solution transferred to the column via serontological pipette. The column base was then placed in the DFA for foaming tests.

After completion of the test, the column was sparged via a compressed air supply until the entire bulk solution and foam was ejected from the column. The column was then filled with three sequential washes of deionized water and sparged during each wash to remove any surfactants adhering to the fritted filter plate. The inside of the column was gently wiped with surfactant-free wipes and reloaded with bulk solution for a subsequent foaming test.

3.3.2 **Height resolution in DFA100**

Initial testing showed some discrepancy in the height detection capability of the DFA100 compared to the technical specifications. To further understand the equipment capability, a
foaming test was completed where a small volume of gas was injected into the column in subsequent steps. Based on the change in liquid height detection, the actual height resolution detection by the line sensor was 0.6mm. Moreover, the detection capabilities of the instrument show greater discrepancy at the high and low extrema of the column volume. While this does not have direct impact on this study, the observed values are larger than the 0.125 mm capability specified by the manufacturers, but the reasons for the detection discrepancies are not fully understood.

3.3.3 Initial foam density method development

Stock solutions of each surfactant were made according to the concentrations in Table 3.1. To avoid reducing the bulk concentration below the CMC during foaming, a concentration of ten times the CMC concentration was used. However, TritonX-45 appeared dispersed in solution versus fully solubilized at higher concentrations. Solutions at higher concentrations would show separation after about an hour. Therefore, a lower concentration of nine times the CMC was used for TritonX-45 to ensure solution stability during the foam test repeats. Few foam studies exist on micellar solutions at concentrations multiple levels above the CMC. Hence, foaming tests at this concentration add to the body of knowledge of surfactant foaming behavior.
Table 3.1: Surfactant concentrations

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>10*CMC</th>
<th>Stock solution (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TritonX-100</td>
<td>3.0</td>
<td>100</td>
</tr>
<tr>
<td>HTAB</td>
<td>10.0</td>
<td>50</td>
</tr>
<tr>
<td>SDS</td>
<td>70.0</td>
<td>500</td>
</tr>
<tr>
<td>TritonX-45</td>
<td>0.9</td>
<td>20</td>
</tr>
<tr>
<td>TritonX-165</td>
<td>4.0</td>
<td>100</td>
</tr>
<tr>
<td>SDBS</td>
<td>9.0</td>
<td>100</td>
</tr>
<tr>
<td>TTAB</td>
<td>37.0</td>
<td>-</td>
</tr>
<tr>
<td>DTAB</td>
<td>160.0</td>
<td>-</td>
</tr>
</tbody>
</table>

3.4 Dynamic surface tension

Air-liquid interfaces of surfactant solutions show a time-dependent adsorption until reaching an equilibrium surface tension value. The rate of change of the surface tension is characterized by an induction time, a rapid decay time, and the final attainment of the equilibrium value, or meso-equilibrium for surfactants with significantly slower adsorption. Maximum bubble pressure tensiometry (MBP) is the current state-of-the-art method for measuring dynamic surface tension. Instruments utilizing this method can achieve sub-millisecond time scales [87].

For dynamic measurements, a range of bubble flow rates is programmed to capture the change in maximum bubble pressure due to varied surface tension values for various surface ages. Faster sparging rates produce lower surface ages. Therefore, a sequence of flow rates must be programmed to capture the entire surface activity of the induction, rapid fall, and equilibration. The maximum pressure occurs when the bubble is a hemisphere and the surface tension can be calculated using the Young-Laplace equation shown in Equation 3.1 [52], [88].
\[ P_{\text{max}} = P - P_0 = \frac{2\gamma}{R} + \rho gh \]  

(3.1)

Where \( P_{\text{max}} \) is the pressure in the bubble when the radius of the bubble reaches the radius \( R \) of the orifice, \( P \) is the gas pressure, \( \gamma \) is the surface tension, \( \rho \) is the density of the liquid, \( g \) the acceleration of gravity, and \( h \) the depth of immersion of the orifice.

3.4.1 Instrument installation

A SensaDyne maximum bubble pressure tensiometer model PC-500L from Chem-Dyne Research Corporation was used initially to attempt to measure the dynamic surface tension for the surfactants in this study as seen in Figure 3.4a and b.

![Sensadyne PC-500L MBP tensiometer](image1)

![Dual probes of tensiometer](image2)

**Figure 3.4:** a. Sensadyne PC-500L MBP tensiometer b. Dual probes of tensiometer

After installation, the instrument was calibrated with deionized water and ethanol according to the surface tension values shown in Table 3.2. A gas supply of 50 psi was fed into the instrument and then split into two streams by a pressure regulator to two mass flow controllers, MFC A and MFC B.
Table 3.2: SensaDyne calibration solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Surface Tension (mN/m)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized water</td>
<td>72.6</td>
<td>22.1</td>
</tr>
<tr>
<td>Ethanol</td>
<td>21.8</td>
<td>22.1</td>
</tr>
</tbody>
</table>

3.4.2 Method development

The surface tension values in Table 3.2 were used for calibration of the flow rate sequences used to produce dynamic surface tension from the surfactant solutions. An example of the flow rate sequence and corresponding values for the TritonX-100 surfactant at a well-above CMC concentration of 3.0 mM is shown in Table 3.3. Note that some of the discrepancies occurring in the instrument were higher bubble frequencies than expected within the percentage sequence, as seen in the bubble frequency increase reported with the decrease to 10 percent cross-sectional area opened in the MFCs.

Table 3.3: Flow rate program for dynamic surface tension of 3.0 mM TritonX-100

<table>
<thead>
<tr>
<th>MFC A (%)</th>
<th>MFC B (%)</th>
<th>Surface tension (mN/m)</th>
<th>Temperature (°C)</th>
<th>Surface Age (s)</th>
<th>Bubble Frequency (bubble/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>40</td>
<td>45.25</td>
<td>21.7</td>
<td>0.387</td>
<td>2.315</td>
</tr>
<tr>
<td>35</td>
<td>35</td>
<td>45.2</td>
<td>21.7</td>
<td>0.417</td>
<td>2.194</td>
</tr>
<tr>
<td>30</td>
<td>30</td>
<td>43.84</td>
<td>21.6</td>
<td>0.43</td>
<td>1.914</td>
</tr>
<tr>
<td>25</td>
<td>25</td>
<td>42.44</td>
<td>21.7</td>
<td>0.456</td>
<td>1.867</td>
</tr>
<tr>
<td>20</td>
<td>20</td>
<td>41.29</td>
<td>21.8</td>
<td>0.554</td>
<td>1.649</td>
</tr>
<tr>
<td>15</td>
<td>15</td>
<td>40.08</td>
<td>21.8</td>
<td>0.559</td>
<td>1.509</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>39.07</td>
<td>21.7</td>
<td>0.224</td>
<td>4.114</td>
</tr>
</tbody>
</table>

The test results in Table 3.3 were completed with a reduced external flow rate into the MFCs. After adjustment, higher bubble rates were accessible. The higher flow rates resulted in decreased surface times; however, the surface tension values did not follow the expected
decrease from the solvent value of 72 mN/m to the equilibrium value. The surface tension values recorded were near the equilibrium value even with faster bubble frequencies and the lower surface age results, as seen in Table 3.4. For example, the surface tension appears to be near the equilibrium value even at surface ages as low as 0.031s.

Table 3.4: Increased flow rates for dynamic surface tension of 3.0 mM TritonX-100

<table>
<thead>
<tr>
<th>MFC A (%)</th>
<th>MFC B (%)</th>
<th>Surface tension (mN/m)</th>
<th>Temperature (° C)</th>
<th>Surface Age (s)</th>
<th>Bubble Frequency (bubble/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>40</td>
<td>31.31</td>
<td>21.8</td>
<td>0.031</td>
<td>20.367</td>
</tr>
<tr>
<td>35</td>
<td>35</td>
<td>29.08</td>
<td>21.9</td>
<td>0.033</td>
<td>19.427</td>
</tr>
<tr>
<td>30</td>
<td>30</td>
<td>29.88</td>
<td>21.8</td>
<td>0.037</td>
<td>17.986</td>
</tr>
<tr>
<td>25</td>
<td>25</td>
<td>29.53</td>
<td>21.8</td>
<td>0.042</td>
<td>16.273</td>
</tr>
<tr>
<td>20</td>
<td>20</td>
<td>30.48</td>
<td>21.8</td>
<td>0.046</td>
<td>15.175</td>
</tr>
<tr>
<td>15</td>
<td>15</td>
<td>31.3</td>
<td>21.8</td>
<td>0.052</td>
<td>13.966</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>30.11</td>
<td>21.8</td>
<td>0.062</td>
<td>12.255</td>
</tr>
</tbody>
</table>

Previous work by Fainerman et al. (2006 [87]; 2009 [89]) showed values in the range of 42 mN/m for the same time point. Data found in the literature reports some issues with using bubble frequencies higher than 8 bubbles/second [90]. Literature existing on use with the instrument from SensaDyne reports the lowest surface ages for surface tension curves at frequencies lower than 20 bubbles/second. Finally, the effects of modifying the potentiometers in the instrument to increase the sensitivity of the pressure-induced changes in the voltage were in the process of being analyzed when the instrument at UBC experienced a malfunction. Further experimental work was not possible for this thesis.

3.4.3 Literature values for dynamic surface tension

In place of measurements, literature data was used for the dynamic surface tension for the correlation analysis to the initial foam liquid fraction. The values of interest are the time points
$t_{35}$, $t_{50}$, and $t_{90}$ corresponding to the time at which the surface tension has decreased 35, 50, and 90 percent from the original solvent surface tension value, respectively.
Chapter 4: Foam Density Measurement Development

Liquid entrainment is a property of aqueous foams for which no unified standard measurement method exists. Moreover, measuring the foam density has previously been tailored to the instrumental set-up being used [4], [18], [34], [59]. This chapter outlines the steps taken to develop a protocol to measure foam density by tracking the change in the total liquid content of the initial bulk solution.

4.1 Time point of initial density

The liquid volume in the foam was determined based on the change in liquid height at the time of foaming completion. This point was chosen to avoid the onset of drainage effects or coalescence of the lamellae in the foam. An algorithm written in Python was used to detect this time point in the data and if needed was manually corrected in the post-processed results.

4.2 Effect of varied gas volume injected

With the DFA, the column height is 0.24 meters and thus the foams were expected to show minimal effects of drainage when foaming at a constant flow rate. In addition, the bulk solution volume was chosen to maximize foam visualization by the one-dimensional line sensor which is at 19 mm, or 50 mL above the bottom of the column. A range of flow rates was tested to verify adequate liquid height detection.

Initial testing was completed at 0.2-0.5 LPM for a range of gas volumes injected using a G1 filter plate of 100-160 µm pore size from Krüss. The lower flow rate was initially chosen to minimize effects of backpressure at the internal flow meter. However, the lower flow rate resulted in noticeable effects of drainage. Therefore, a flow rate of 0.5 LPM was chosen for the initial DFA tests.
Lower gas volumes injected resulted in a lower repeatability of the liquid fraction, as shown in Figure 4.1. The data suggests practical limitations for gas volumes in the range of less than 50 mL. Figure 4.1 shows a decrease in the liquid entrained with increasing gas volume in the foam across all three surfactants used for method development. One possible reason for these results is that non-negligible drainage of liquid out of the foam is occurring with increasing foaming time. However, the rank order for the volume of liquid entrained for the surfactants remains consistent across three out of the four gas volumes.

Further verification of the trend for liquid content was completed using a G2 fritted filter plate with pore size 40-100 µm. Three gas volumes were used with the finer filter as seen in Figure 4.2.
From this initial testing, two important results were determined. First, the trend for liquid entrainment shows that HTAB entrains the least liquid, while SDS entrains the most liquid, and only slightly more than TritonX-100. These results vary from the study of Frostad et al. [34], where the trend for liquid entrainment from least to greatest was SDS followed by TritonX-100 followed by HTAB. A conical vessel was used for bulk foams generation in this study, preventing a direct comparison to the current study. The results of the current study show agreement with the work of Kawale et al. [59], where SDS was found to have the largest liquid entrainment, followed by HTAB. Unfortunately, TritonX-100 was not used in the study of Kawale et al.

The differences in the liquid entrainment can be attributed to several factors, most notably the effect of using non-uniform vessels for foam generation. In addition, the foams produced in the previous work from Kawale et al. [59] were at both below-CMC and above-
CMC concentrations. However, the highest concentration used in the study of Frostad et al. [34] was fixed at 10mM instead of a multiple above the CMC.

4.3 Drainage rate

Because the drainage rate of the fluid out of the foam did not correspond to a common time decay function, such as logarithmic decay, the time for half of the total liquid volume in the foam to drain back into a bulk liquid solution was used to estimate the timescale for drainage. The drainage time was then compared to the theoretical foaming time for a uniform volumetric flow rate, where the foaming time is the quotient of the theoretical gas volume and the volumetric flow rate, i.e. $t_{foaming} = \frac{V_{gas}}{u_{gas}}$. For a gas volume of 80 mL, and effective flow rate of 0.96 LPM, the total foaming time was 5.0 seconds. In contrast, the drainage time scale of this flow rate and gas volume was 5.5 to 6.0 seconds. Thus, the middle gas volume of 80 mL should have fast enough foam formation to limit effects of fluid drainage on the initial liquid content.

4.4 Flow rate variance

After collecting the initial data, inconsistencies were observed for the gas flow rate. Therefore, a comparison test of the programmed flow rate and true flow rate was completed using both internal and external gas supplies. The change in flow rate between the internal and external gas supplies are shown in Figure 4.3a. Figure 4.3b shows the true gas volume achieved, calculated based on the known volume of liquid loaded and the total volume of the column as detected by the DFA line sensor.
Figure 4.3: Internal and external flow rate comparison for TritonX-100 foams. a. Percent change in flow rate. b. Percent deviation from gas volume set-point

4.5 Final testing parameters

Initial foaming tests showed that the gas flow meter produced a decreasingly accurate flow rate with lower gas volumes, lower programmed flow rates, and decreasing fritted filter size. Therefore, the procedure developed for the bulk foam tests was designed to use high flow rates to minimize the onset of drainage effects during foam formation. The parameters used are listed in the table below.

Table 4.1: Optimized testing parameters for DFA-100 foaming tests

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution volume (ml)</td>
<td>80</td>
</tr>
<tr>
<td>Solution concentration</td>
<td>10 times CMC</td>
</tr>
<tr>
<td>Gas flow rate target (LPM)</td>
<td>0.96</td>
</tr>
<tr>
<td>Foaming fps</td>
<td>20</td>
</tr>
<tr>
<td>Gas volume set-points (mL)</td>
<td>40, 80, 160</td>
</tr>
</tbody>
</table>
The set points and the average true flow rates and true gas volumes obtained with the DFA100 foaming tests with the updated experimental settings are summarized in Table 4.2. As outlined above, the true target flow rate is achieved with a programmed flow rate set-point that is 15-20% lower than the target.

Table 4.2: Results for true flow rate and gas volumes in DFA100 Foaming tests

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Programmed set-point</th>
<th>Mean values with standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow rate</td>
<td>0.80 LPM</td>
<td>0.98 ± 0.03 LPM</td>
</tr>
<tr>
<td>Low gas volume</td>
<td>34.0 mL</td>
<td>47.0 ± 1.4 mL</td>
</tr>
<tr>
<td>Middle gas volume</td>
<td>67.0 mL</td>
<td>86.0 ± 7.8 mL</td>
</tr>
<tr>
<td>High gas volume</td>
<td>134.0 mL</td>
<td>171.0 ± 3.1 mL</td>
</tr>
</tbody>
</table>

4.6 Summary

A method for measuring the liquid fraction in a freshly formed foam was developed using a commercially available foaming apparatus called the DFA100. The surfactant solutions used for the method development tests were TritonX-100, HTAB, and SDS that are a nonionic, cationic, and anionic surfactant, respectively. The optimized testing parameters presented in Table 4.1 were used to gather the liquid fraction data for all foams produced and reported in Chapter 5. The standard deviations of the gas volumes and flow rate for all foaming tests using these optimized parameters are shown in Table 4.2.
Chapter 5: Foam Density Correlations

In this chapter, the plots showing the results of equilibrium surface tension, dynamic surface tension, and the bulk foam densities are presented based on the experimental set-ups described in Chapter 3 and Chapter 4. Equilibrium and dynamic surfactant adsorption parameters are correlated to the bulk foam liquid fractions, followed by a discussion of the trends for the liquid fraction in foams.

5.1 Equilibrium surface tension isotherms

The results of the data collection of equilibrium surface tension are shown in Figures 5.1a and b. The points represent experimental values while the black lines are calculated from the best fit of the Szyszkowski surface tension equation using the method outlined in Section 3.1.2. A summary of these experimental values is included in section 5.6.

![Surface tension isotherms with Szyszkowski equation curve fit](image1)

Figure 5.1: a. and b. Surface tension isotherms with Szyszkowski equation curve fit

5.2 Dynamic surface tension

The concentrations chosen were the CMC or near the CMC of each surfactant studied. While for many of the surfactants, dynamic surface tension values were possible for the above-
CMC concentrations of interest, such as the Triton surfactants, the remaining surfactants did not have data points at these concentrations. In addition, the time scales of adsorption for micellar solutions is predicted to be near the resolution capability of many commercial bubble pressure tensiometers, making data collection with CMC or above-CMC concentrations difficult. Dynamic surface tension plots for TritonX-100, TritonX-45, and TritonX-165, SDS, and HTAB were found at the CMC, whereas dynamic surface tension curves for SDBS, TTAB, and DTAB at concentrations just below the CMC were used. The plots for the dynamic surface tension data taken from literature are shown in Figure 5.2-5.9 below. The abbreviation of DST is used for dynamic surface tension. For figures containing curves at various concentrations, a red arrow with the designation of “CMC curve” points to the data points from which the time points were extracted.

**Nonionic surfactants**

![Figure 5.2: DST curve for TritonX-100. The red arrow indicates the curve used for analysis. The symbols used for the concentrations are as follows: △ = 0.2 mM (CMC); □ = 0.5 mM (reported from [87]); ■ = 0.5 mM; ◇ = 1.0 mM; ♦ = 2.0 mM. Reprinted and adapted with permission from Fainerman et al. [91].](image)
Figure 5.3: DST curve for TritonX-45. The red arrow indicates the curve used for analysis. The symbols used for the concentrations are as follows: ♦ = 0.1 mM (CMC); □ = 0.2 mM; ▲ = 0.5 mM; △ = 1.0 mM (CMC); Reprinted and adapted with permission from Fainerman et al. [91].

Figure 5.4: DST curve- TritonX-165. The red arrow indicates the curve used for analysis. The symbols used for the concentrations are as follows: ■ = 0.4 mM (CMC); ◇ = 1.0 mM; ▲ = 2.0 mM; □ = 5.0 mM. Reprinted and adapted with permission from Fainerman et al. [91].
Anionic surfactants

Figure 5.5: DST curve for SDS. The concentration used was 8mM, indicated by the red arrow. Figure reprinted with permission from Kawale [17].

Figure 5.6: DST curve for SDBS. Figure reprinted with permission from Phan et al. [92].
Cationic surfactants

Figure 5.7: DST curve for HTAB. Adapted with permission from [93]. Copyright 2005 American Chemical Society.

Figure 5.8: DST curve- TTAB. Adapted with permission from [93]. Copyright 2005 American Chemical Society.
5.3 Initial foam density

Using the DFA testing parameters outlined in section 4.4, the foam densities of eight surfactants were collected at a low, middle, and high gas volumes to capture the impact of potential drainage effect. The initial liquid fraction for three gas volumes of all the surfactants is shown in Figure 5.10a. The error bars represent the liquid fraction and gas volume standard deviations on the y- and x-axis, respectively. Note the legend is omitted in Figure 5.10a but follows the same convention as the legend in Figure 5.10b. In addition, the drainage half-life of the foams is shown in Figure 5.10b. The data set of drainage times of TritonX-45 had significant outliers which caused the large standard deviation seen in the error bars for the first data point.
5.3.1 Liquid fraction trends

Different trends are observed in the liquid fraction results from Figure 5.10a. Most of the surfactants show a near-constant liquid fraction with increasing gas volumes. The greatest variance is seen with the TTAB and DTAB surfactants, respectively. The anionic surfactant SDBS entrains the largest volume of liquid and produces the largest liquid fraction for two out of three of the gas volumes.

The surfactants SDBS and DTAB showed similarly high liquid fractions as compared to the rest of the surfactants. SDS, TritonX-100, TritonX-165, and TTAB follow next in the order of greatest liquid fraction. These surfactants show a near-identical liquid fraction for the 80 mL and 160 mL gas volume targets, respectively. The liquid fraction at the 40mL gas volume, however, deviates away from the trend seen with the larger gas volumes. SDS, TritonX-100, TritonX-165 liquid fractions show more scatter at this gas volume. In addition, the surfactant TTAB has a lower liquid fraction than HTAB at the 40 mL gas volume as opposed to the trend for the 80 and 160 mL gas volumes.
The ionic or nonionic property of the surfactant does not appear to change the liquid fraction results based on any identifiable trend. For example, the nonionic Triton surfactants are among the highest and the lowest liquid fractions obtained. In addition, the two highest liquid fractions correspond to an anionic and cationic surfactant (i.e. SDBS and DTAB, respectively). The final trend for the liquid fraction of the surfactants using the middle gas volume is as follows: $\phi_{\text{initial SDBS}} \geq \phi_{\text{initial DTAB}} > \phi_{\text{initial SDS}} \approx \phi_{\text{initial TritonX-100}} \approx \phi_{\text{initial TritonX-165}} \geq \phi_{\text{initial TritonX-45}}$.

### 5.3.2 Drainage half-life trends

In contrast to the results at 0.5 LPM from Figure 4.1, the results in Figure 5.10b suggest that drainage of liquid out of the foam is mitigated with a higher flow rate. The liquid fractions for three increasing gas volumes with 1.0 LPM show only slight fluctuation for each surfactant. The higher gas flow rate counteracts the apparent effect of gravity on fluid flow out of the foam. In addition, the drainage half-life trends are also similar for the same gas volume. Figure 5.10b shows the drainage half-life of liquid out of the foam column as an average of the 6 repeat runs collected at each gas volume. Three distinct drainage times emerge corresponding to the gas volumes used with each surfactant. The high gas volume (160mL target) drainage time is longer than that of the lower gas volumes as can be expected for the generation of a larger volume of foam.

Interestingly, the drainage times for each surfactant in Figure 5.10b are nearly uniform across the average time calculated for the high gas volume, as is highlighted for the data points around 9.0 seconds. These surfactants produce different liquid fractions and hence entrain different volumes of liquid during formation. However, the rates of fluid flow out of the foam after formation are similar. The reason for this deviation in fluid flow behavior during formation
and drainage after formation is not well understood. However, the results suggest that the overall influence of surfactant properties on fluid flow within the foam significantly changes between the foam formation period and the drainage period after the foam has been formed.

### 5.4 Equilibrium correlations

Maximum surface concentration $\Gamma_\infty$ and the equilibrium adsorption-desorption constant $K_{eq}$ are plotted with respect to the liquid fraction in Figure 5.11a and b. Surfactant efficiency (i.e. pC$_{20}$) and surfactant effectiveness (i.e. CMC) data points versus liquid fraction are shown in Figure 5.12a and b. The Pearson product-moment correlation coefficient $r$ and the Spearman correlation coefficient $\rho$ were calculated for each of the surfactant parameters and are listed in Table 5.1.

![Figure 5.11](image)

**Figure 5.11** a. Maximum surface concentration $\Gamma_\infty$ and b. $K_{eq}$ relationship versus liquid fraction
Figure 5.12 a. Surfactant effectiveness and b. surfactant efficiency versus liquid fraction

Table 5.1: Correlation coefficients for equilibrium parameters

<table>
<thead>
<tr>
<th>Liquid fraction</th>
<th>Parameter</th>
<th>Pearson r</th>
<th>p-value</th>
<th>Spearman ρ</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\phi_l) low</td>
<td>(\Gamma_\infty)</td>
<td>0.300</td>
<td>0.471</td>
<td>0.323</td>
<td>0.435</td>
</tr>
<tr>
<td></td>
<td>(K_{eq})</td>
<td>0.463</td>
<td>0.248</td>
<td>0.299</td>
<td>0.471</td>
</tr>
<tr>
<td></td>
<td>CMC</td>
<td>0.506</td>
<td>0.201</td>
<td>0.571</td>
<td>0.139</td>
</tr>
<tr>
<td></td>
<td>pC_{20}</td>
<td>-0.642</td>
<td>0.086</td>
<td>-0.714</td>
<td>0.047</td>
</tr>
<tr>
<td>(\phi_l) mid</td>
<td>(\Gamma_\infty)</td>
<td>0.220</td>
<td>0.601</td>
<td>0.048</td>
<td>0.910</td>
</tr>
<tr>
<td></td>
<td>(K_{eq})</td>
<td>0.362</td>
<td>0.379</td>
<td>0.072</td>
<td>0.866</td>
</tr>
<tr>
<td></td>
<td>CMC</td>
<td>0.446</td>
<td>0.268</td>
<td>0.405</td>
<td>0.320</td>
</tr>
<tr>
<td></td>
<td>pC_{20}</td>
<td>-0.616</td>
<td>0.104</td>
<td>-0.524</td>
<td>0.183</td>
</tr>
<tr>
<td>(\phi_l) high</td>
<td>(\Gamma_\infty)</td>
<td>0.234</td>
<td>0.577</td>
<td>0.299</td>
<td>0.471</td>
</tr>
<tr>
<td></td>
<td>(K_{eq})</td>
<td>0.316</td>
<td>0.445</td>
<td>0.323</td>
<td>0.435</td>
</tr>
<tr>
<td></td>
<td>CMC</td>
<td>0.388</td>
<td>0.342</td>
<td>0.619</td>
<td>0.102</td>
</tr>
<tr>
<td></td>
<td>pC_{20}</td>
<td>-0.620</td>
<td>0.101</td>
<td>-0.738</td>
<td>0.037</td>
</tr>
</tbody>
</table>
The anionic surfactant SDBS entrains the most liquid in the initial foams. However, DTAB has the highest maximum surface concentration $\Gamma_\infty$ as well as the highest adsorption-desorption rate ratio $K_{eq}$. In addition, SDS has the second highest $\Gamma_\infty$ and $K_{eq}$. TritonX-45 has the lowest liquid fraction and the lowest $K_{eq}$. However, TritonX-165 has the lowest $\Gamma_\infty$ yet produces a liquid fraction larger than over half of the surfactants. Moreover, the second and third lowest values for $K_{eq}$ were produced by TritonX-165 and SDBS, respectively. As can be seen in Figure 5.1a. and b., these two surfactants produce higher liquid fractions across the entire surfactant group.

Initially, it was hypothesized that an increase in the maximum surface concentration results in an increased liquid fraction. However, the results of 5.11a. do not support this hypothesis. SDBS has the highest liquid fraction, yet only the fifth-highest $\Gamma_\infty$. DTAB has the highest surface concentration and second-largest liquid fraction. Finally, TritonX-165 has the lowest $\Gamma_\infty$, but the second or third highest liquid fraction across the different gas volumes. The same trends occur with the $K_{eq}$ parameter in that SDBS has the fifth highest value for this parameter. TritonX-165 again has the lowest $K_{eq}$ and the second or third largest liquid fraction in the foam. The correlations were classified as weak if the coefficients for $r$ and $\rho$ were below a value of 0.5. The p-value was also calculated, and the correlations were considered to be strong with a p-value of 0.1 or lower.

The data in Figure 5.11a. and b. suggests that the equilibrium adsorption parameters correlate weakly to the initial liquid fraction within the foams. Moreover, the correlation coefficient results support this with $r$ less than 0.5 and p-values above 0.1. One consideration for the weak correlation is that the timescales for obtaining these parameters is much longer than the time scale of a bubble forming and rising in the foams. Moreover, previous analyses have
suggested that direct correlation of equilibrium parameters is not applicable for wet foams that are inherently dynamic systems [24]. The foams produced here are classified as static foams [22]; hence the direct applicability of the analysis of dynamic wet foams to static foams was not well-delineated. Elsewhere, it was suggested that using parameters $\Gamma_\infty$ and $K_{eq}$ derived from sub-CMC adsorption behavior no longer describes adsorption behavior above the CMC. Therefore, the parameters are not applicable as a factor in foam liquid fraction at surfactant solutions above the CMC [17]. However, this theory was not well-described in other literature sources. The correlation results in this study suggest that these Szyszkowski constants are minimally related to the liquid fraction. From these results of liquid fraction, it is not clear whether the interfaces within the foam have equilibrium surface coverage at the surface. In addition, while all surfactants used in this study are water-soluble, qualitative observation of the surfactants during experiments showed that TritonX-45 and HTAB were the least soluble in deionized water and crystallized (HTAB) or became cloudy (TritonX-45) after one day.

A surfactant’s effectiveness is inversely proportional to the CMC, whereas the efficiency in reducing the surface tension is proportional to the pC$_{20}$. The results for surfactant effectiveness (CMC) and surfactant efficiency (pC$_{20}$) in Figure 5.1a and b suggest that at high values for the effectiveness, the liquid fraction will also be at a lower value among various surfactants. However, a strong correlation between the effectiveness and the liquid fraction is not possible as demonstrated by the results for the effectiveness of the Triton surfactants. While these three nonionic surfactants have the highest effectiveness, the liquid fractions of the surfactants are scattered in terms of the trend. TritonX-45 has the lowest liquid fraction, the highest effectiveness, and the highest efficiency. The correlation coefficients also show a weak correlation of effectiveness to the liquid fraction. Notably, the $r$ coefficients range from 0.388 to
0.506, with p-values above 0.1, with a similar range seen for the ρ coefficients. Out of the four equilibrium parameters tested, the surfactant efficiency shows the strongest evidence for correlation to the liquid fraction with correlation coefficients around -0.6 to -0.7.

### 5.5 Dynamic correlations

Dynamic surface tension data points were gathered from literature sources based on the percent reduction from the surface tension of deionized water. The values represent $t_{35}$, $t_{50}$, and $t_{90}$ time points as described in section 3.4.3. The values are plotted with the liquid fraction results for each gas volume per surfactant. Lack of resolution in the data available for the DTAB surfactant prevented determination of the $t_{35}$ and $t_{50}$ time points. The liquid fraction of DTAB is therefore omitted for the $t_{35}$ and $t_{50}$ plots in Figure 5.13a. and b. The $t_{90}$ versus initial liquid fraction plot is shown in Figure 5.13c., with legend omitted for figure clarity. Table 5.2 shows the results of the correlations coefficients $r$ and $ρ$ to the liquid fractions with respective p-values.
Figure 5.13: Dynamic adsorption correlations for a. $t_{35}$ time points for 7 of 8 surfactants; b. $t_{50}$ time points 7 of 8 surfactants; c. $t_{90}$ time points versus liquid fraction plot for all surfactants

Table 5.2: Correlation coefficients for dynamic parameters and liquid fraction

<table>
<thead>
<tr>
<th>Liquid fraction</th>
<th>Parameter</th>
<th>Pearson r</th>
<th>p-value</th>
<th>Spearman $\rho$</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\phi_l$ low</td>
<td>$t_{35}$</td>
<td>-0.853</td>
<td>0.015</td>
<td>-0.321</td>
<td>0.482</td>
</tr>
<tr>
<td></td>
<td>$t_{50}$</td>
<td>-0.849</td>
<td>0.016</td>
<td>-0.25</td>
<td>0.589</td>
</tr>
<tr>
<td></td>
<td>$t_{90}$</td>
<td>-0.360</td>
<td>0.381</td>
<td>-0.395</td>
<td>0.333</td>
</tr>
<tr>
<td>$\phi_l$ mid</td>
<td>$t_{35}$</td>
<td>-0.883</td>
<td>0.008</td>
<td>-0.143</td>
<td>0.760</td>
</tr>
<tr>
<td></td>
<td>$t_{50}$</td>
<td>-0.879</td>
<td>0.009</td>
<td>0</td>
<td>1.000</td>
</tr>
<tr>
<td></td>
<td>$t_{90}$</td>
<td>-0.355</td>
<td>0.389</td>
<td>-0.180</td>
<td>0.670</td>
</tr>
<tr>
<td>$\phi_l$ high</td>
<td>$t_{35}$</td>
<td>-0.908</td>
<td>0.005</td>
<td>-0.393</td>
<td>0.383</td>
</tr>
<tr>
<td></td>
<td>$t_{50}$</td>
<td>-0.905</td>
<td>0.005</td>
<td>-0.286</td>
<td>0.535</td>
</tr>
<tr>
<td></td>
<td>$t_{90}$</td>
<td>-0.355</td>
<td>0.388</td>
<td>-0.443</td>
<td>0.272</td>
</tr>
</tbody>
</table>

The correlations in Figure 5.13 give a qualitative understanding of the surface tension reduction capabilities of surfactants at saturated or near-saturated interfaces. Moreover, the strength of the linear correlations to the initial liquid fraction is larger for the $t_{35}$ and the $t_{50}$
times compared to the $t_{90}$ times, as evidenced by p-values two orders of magnitude smaller than the p-value of the linear relationship of $t_{90}$ to the liquid fraction. In contrast, very weak evidence is seen for a correlation between the ranking of the $t_{35}$ variable, with values in in the range of -0.32 to -0.14.

The surfactant SDBS produces the highest liquid fraction and is one order of magnitude slower than SDS for the dynamic adsorption. This result appears to contradict the conclusion that decreasing adsorption times lead to higher liquid fractions in foams. However, this may be partially accounted for by the fact that the dynamic data used was not taken exactly at the CMC for all surfactants.

The $t_{90}$ versus liquid fraction results in Figure 5.12c deviate from the trend shown by the $t_{35}$ and $t_{50}$ timescale. Moreover, the coefficients for the linear and the ranking relationship show weak evidence of correlation with $r$ greater than -0.5, with p-values above 0.1 for both relationships. The TritonX-100 results highlight this point in that the surfactant has a long timescale to reach a near-equilibrium surface tension value in comparison with the rest of the surfactants. A longer timescale poorly represents the liquid fraction in foams as seen from the plot here. This result points to the influence of the dynamics of disequilibrium of coverage at the surface on the fluid flow in foams, in contrast to any equilibrium adsorption characteristics.

### 5.6 Summary of data results

A consolidation of the liquid fraction results and correlation parameters discussed in section 5.3 to 5.5 is presented in Table 5.1. The Triton surfactants are named using a “TX” and number abbreviation for conciseness. For example, TritonX-100 is abbreviated as TX-100. The standard deviation for the liquid fraction calculated from six different repeat tests is abbreviated as st.dev. In addition, the shading scheme in the surfactant title row indicates the valence charge
description of the surfactants. No shading indicates the nonionic surfactants, light gray indicates anionic surfactants, and darker gray indicates the cationic surfactants. Finally, the abbreviation “Lit.” is an abbreviation for a literature source.
Table 5.3: Surfactant liquid content, equilibrium and dynamic parameters

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>TX-100</th>
<th>TX-45</th>
<th>TX-165</th>
<th>SDS</th>
<th>SDBS</th>
<th>HTAB</th>
<th>TTAB</th>
<th>DTAB</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\varphi_l) low gas volume</td>
<td>0.105</td>
<td>0.021</td>
<td>0.107</td>
<td>0.119</td>
<td>0.131</td>
<td>0.088</td>
<td>0.078</td>
<td>0.131</td>
</tr>
<tr>
<td>(\varphi_l) low gas st. dev.</td>
<td>0.003</td>
<td>0.026</td>
<td>0.003</td>
<td>0.008</td>
<td>0.016</td>
<td>0.011</td>
<td>0.023</td>
<td>0.010</td>
</tr>
<tr>
<td>(\varphi_l) mid gas volume</td>
<td>0.116</td>
<td>0.025</td>
<td>0.121</td>
<td>0.115</td>
<td>0.148</td>
<td>0.091</td>
<td>0.108</td>
<td>0.141</td>
</tr>
<tr>
<td>(\varphi_l) mid gas st. dev.</td>
<td>0.002</td>
<td>0.015</td>
<td>0.013</td>
<td>0.008</td>
<td>0.009</td>
<td>0.007</td>
<td>0.030</td>
<td>0.013</td>
</tr>
<tr>
<td>(\varphi_l) high gas volume</td>
<td>0.117</td>
<td>0.019</td>
<td>0.125</td>
<td>0.129</td>
<td>0.145</td>
<td>0.090</td>
<td>0.115</td>
<td>0.131</td>
</tr>
<tr>
<td>(\varphi_l) high gas st. dev.</td>
<td>0.005</td>
<td>0.003</td>
<td>0.003</td>
<td>0.003</td>
<td>0.010</td>
<td>0.004</td>
<td>0.019</td>
<td>0.012</td>
</tr>
<tr>
<td>(\Gamma^\infty_{\text{exp}}) ((10^6 \text{mol} \cdot \text{m}^{-2}))</td>
<td>3.0</td>
<td>3.0</td>
<td>1.1</td>
<td>11.0</td>
<td>7.76</td>
<td>9.0</td>
<td>8.0</td>
<td>11.3</td>
</tr>
<tr>
<td>(K_{\text{eq}}) ((10^3 \text{m}^3 \cdot \text{mol}^{-1}))</td>
<td>0.001</td>
<td>0.001</td>
<td>5.0(\times)10^{-3}</td>
<td>2.216</td>
<td>0.362</td>
<td>0.230</td>
<td>0.301</td>
<td>3.892</td>
</tr>
<tr>
<td>CMC_{\text{exp}} (mM)</td>
<td>0.3</td>
<td>0.15</td>
<td>0.7</td>
<td>7.0</td>
<td>2.0</td>
<td>1.0</td>
<td>3.0</td>
<td>14.23</td>
</tr>
<tr>
<td>CMC_{\text{lit}} (mM)</td>
<td>0.29</td>
<td>0.1</td>
<td>0.4</td>
<td>6.8</td>
<td>0.9</td>
<td>0.9</td>
<td>3.6</td>
<td>16.0</td>
</tr>
<tr>
<td>(t_{35}) (s)</td>
<td>1.08</td>
<td>6.176</td>
<td>0.0199</td>
<td>0.00089</td>
<td>0.05</td>
<td>0.0371</td>
<td>0.004</td>
<td>-</td>
</tr>
<tr>
<td>(t_{50}) (s)</td>
<td>2.0</td>
<td>10.0</td>
<td>0.08</td>
<td>0.0024</td>
<td>0.1</td>
<td>0.07</td>
<td>0.01</td>
<td>-</td>
</tr>
<tr>
<td>(t_{90}) (s)</td>
<td>100</td>
<td>80</td>
<td>100</td>
<td>0.17</td>
<td>2.5</td>
<td>5.0</td>
<td>1.5</td>
<td>0.01</td>
</tr>
<tr>
<td>Lit. source, dynamic data</td>
<td>[89]</td>
<td>[89]</td>
<td>[89]</td>
<td>[17]</td>
<td>[92]</td>
<td>[17]</td>
<td>[93]</td>
<td>[94]</td>
</tr>
</tbody>
</table>
5.7 Summary of liquid fraction correlations

The liquid fractions of eight surfactants were analyzed for correlations to various parameters in sections 5.2 to 5.5. These correlations included the equilibrium surfactant adsorption constants, surfactant properties of efficiency (pC₂₀) and effectiveness (CMC), and dynamic surface tension time points. Pearson’s product moment $r$ and Spearman rank-order $\rho$ correlation coefficients were used to describe the linear relationship between the adsorption parameters and liquid fractions at the respective low, medium, and high gas volumes. The parameter values used for analysis were tabulated from experimental and literature sources into table 5.3 in section 5.6.

Equilibrium constants of maximum surface concentration $\Gamma_{\infty}$ and the adsorption-desorption rate ratio $K_{eq}$ showed poor correlation to the liquid fraction, as seen by the lack of a trend for the surfactants tested. The surfactant effectiveness shown by CMC values also did not result in a predictive trend for the liquid fraction. The surfactant efficiency, or pC₂₀, results show some evidence of a trend.

In contrast to the equilibrium parameters, the dynamic surface tension parameters describing the initial stages of adsorption $t_{35}$, and $t_{50}$ show evidence of a negative linear correlation to the liquid fraction, as seen by the $r$ correlation coefficient approaching -1 across the low, middle, and high gas volume liquid fractions. Moreover, the evidence is strengthened by the p-values less than 0.01 for two out of three liquid fractions. A trend of increasing liquid fraction with faster initial surfactant adsorption time is therefore suggested from these results. This trend is especially seen in the surfactants with dynamic surface tension data taken from concentrations right at the CMC. The results suggest that trends in the liquid fraction can be
predicted based on the times of initial adsorption and surface tension reduction, such as from timescales of $t_{50}$ or lower, though further work is needed to verify the trends.
Chapter 6: Research Summary and Recommendations

The foam density characterization protocol developed in this project lays the groundwork for systematic study of foams in relation to their interfacial and molecular characteristics. With this protocol, potential extensions to this project and further applications are highlighted in this chapter. These recommendations include varying the vessel geometry, varying DFA experimental parameters, and investigation of additional surfactants.

6.1 Gas supply in DFA

Previous work has used both atmospheric air as well as a single-component gas source such as N\textsubscript{2} [59] or C\textsubscript{2}F\textsubscript{6} [27] in foaming experiments. Given that atmospheric lab air contains a higher relative humidity than compressed air or commercial gas sources, using a more controlled gas supply could help further improve the liquid fraction results repeatability.

6.2 Varying bubble size

The effect of changing the filter plate porosity on the average bubble size distribution as the bubbles are being generated at the filter is not fully understood. Initial work completed in this study used three surfactants and two different filter plate porosities. A larger liquid fraction across all surfactants was seen when using a smaller size porosity. This change in filter plate resulted in a larger foam volume created that limited the range of gas volumes that could be injected. Possible routes for optimization are to limit testing to a single gas volume and increasing the initial bulk solution volume when using increasingly smaller pore size filter plates.

Previous studies have observed that a greater control over the bubble size distribution is obtained when the foam is formed by bubbling air into a single-sized orifice, such as in the modeling studies of Koehler et al. [27] or Neethling et al. [28], [66] reviewed in section 2.2. Therefore, it is recommended to use one size of capillary tip similar to the apparatus used by
Kawale et al. [59] or single-diameter tubing similar to the method used by Saint-Jalmes et al. [80] to generate foams for the study of the initial liquid fraction. A comparison of the liquid content in foams generated with a single tip versus with a porous filter plate is therefore a possible extension of this work.

6.3 Vessel geometry

Use of a cylindrical foaming apparatus enables direct comparison with previous research such as in the studies of [4], [28], [59]. However, previous studies such as those reviewed in section 2.1 have suggested that the foamability of the surfactant solutions is better elucidated using non-uniform surface area geometry for the foam generation vessel. A comparative study on liquid entrainment in foams produced in conical, rectangular, and cylindrical vessels for the same bulk surfactant solution is a possible extension of the work done in this study for greater understanding of the factors affecting the liquid content in foams. Descriptions of the apparatuses can be found in the studies of Frostad et al. [34], Kawale et al. [59], Cunningham [22], and Yazghur et al. [65].

6.4 Molecular characteristics of surfactants

In this study, the correlation between the equilibrium adsorption parameters from the Szyszkowski surface tension equation was investigated per the motivation described in chapters 1 and 2. Extending the correlation between the initial liquid entrainment and equilibrium molecular parameters like the diffusivity and the HLB number is recommended. The HLB number, or hydrophile-lipophile balance, is a designation of the ratio of hydrophobic portion to hydrophilic portion of the surfactant molecule [2], [43].

Molecular diffusivity is considered the governing parameter of surfactant adsorption for surfactants without energetic barriers at the interface [47]. This diffusion-limited adsorption has
been used to accurately describe adsorption for a significant number of nonionic surfactants [39], [47]. Thus, it is hypothesized that the relative diffusivities of surfactants can determine how fast a surfactant can adsorb to the interface.

6.5 Dynamic surface tension experiments

Hardware malfunction during the method development experiments prevented collection of experimental data for the dynamic surface tension of the surfactants studied in this project. Reported data and analysis in the literature show that the accuracy of the SensaDyne PC500-L is not guaranteed at bubble frequencies higher than 8 bubbles/second [90]. While the full surface tension curve may not be possible for fast acting surfactants such as TritonX-165, using an instrument with a faster time resolution will still enable insight into the speed of adsorption of the surfactants.

6.6 Additional surfactants

This study set out to delineate foam density effects and subsequent correlations due to surfactant adsorption using eight model surfactants from ionic and non-ionic categories. In addition, the ionic surfactants used were limited to a valence charge of +1 or -1. A preliminary list of surfactants envisioned for future testing use is shown in Table 6.1 below, with literature values for the surfactant parameters listed along with the sources. Dynamic surface tension data was not prevalent in the literature for the surfactants other than those studied in this thesis. Therefore, the list of parameters is limited to equilibrium adsorption parameters. To distinguish between ionic and nonionic surfactants, shading is used in the first column following the convention from Table 5.3. Lighter shading indicates the anionic surfactants, while darker shading indicates the cationic surfactants.
Table 6.1: Equilibrium properties of surfactants from literature

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Γ∞ (10^6 mol*m^-2)</th>
<th>pC20</th>
<th>CMC</th>
<th>Mol. Weight (g/mole)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brij 30</td>
<td>93.26</td>
<td>0.06 mM</td>
<td>362.54</td>
<td>[59]</td>
<td></td>
</tr>
<tr>
<td>Tween 20</td>
<td></td>
<td>0.059 mM</td>
<td>1227.54</td>
<td>[95]</td>
<td></td>
</tr>
<tr>
<td>Span 20</td>
<td></td>
<td>0.024 mM</td>
<td>346.46</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Triton DF-12*</td>
<td></td>
<td>290 ppm</td>
<td>proprietary</td>
<td>[95]</td>
<td></td>
</tr>
<tr>
<td>(C_2H_5)_2CHCH_2(OC_2H_4)_6OH</td>
<td></td>
<td>0.1 M</td>
<td>337.43</td>
<td>[43]</td>
<td></td>
</tr>
<tr>
<td>C_{12}H_{25}(OC_2H_4)_7OH</td>
<td>2.9</td>
<td>5.2</td>
<td>8.2 * 10^-5 M</td>
<td>494.7</td>
<td>[43]</td>
</tr>
<tr>
<td>C_{12}H_{25}(OC_2H_4)_{12}OH</td>
<td></td>
<td></td>
<td>14.0 * 10^-5 M</td>
<td>714.96</td>
<td>[43]</td>
</tr>
<tr>
<td>n-Decyl-α- D-glucoside</td>
<td>3.7</td>
<td></td>
<td>8.5 * 10^-4 M</td>
<td>320.426</td>
<td>[43]</td>
</tr>
<tr>
<td>Ecosurf SA-7</td>
<td></td>
<td>17 ppm</td>
<td>proprietary</td>
<td>[95]</td>
<td></td>
</tr>
<tr>
<td>C_{16}H_{33}N^+(CH_3)_3Cl^-</td>
<td></td>
<td></td>
<td>1.3 * 10^-3 M</td>
<td>320.0008</td>
<td>[43]</td>
</tr>
<tr>
<td>C_{16}H_{33}Pyr^+Br^-</td>
<td></td>
<td></td>
<td>6.4 * 10^-4 M</td>
<td>384.446</td>
<td>[43]</td>
</tr>
<tr>
<td>C_{12}H_{25}N^+(C_4H_9)(CH_3)_2Br^-</td>
<td></td>
<td></td>
<td>7.5 * 10^-3 M</td>
<td>350.42</td>
<td>[43]</td>
</tr>
<tr>
<td>Sodium 1-dodecane sulfonate</td>
<td>2.9</td>
<td>2.3</td>
<td>1.2 * 10^-2 M</td>
<td>272.38</td>
<td>[43], [95]</td>
</tr>
<tr>
<td>Sodium dodecyl benzenesulfonate (SDBS), 70 °C</td>
<td>3.7</td>
<td>3.1</td>
<td>348.48</td>
<td>[43]</td>
<td></td>
</tr>
<tr>
<td>Linear alkyl benzene sulfonic acid (LABSA)</td>
<td></td>
<td></td>
<td>180.16</td>
<td>[95]</td>
<td></td>
</tr>
<tr>
<td>Linear alkyl benzene sulfonic acid (LABSA)</td>
<td></td>
<td></td>
<td>180.16</td>
<td>[95]</td>
<td></td>
</tr>
<tr>
<td>Branched SDS</td>
<td>1.7</td>
<td>2.9</td>
<td>7-10 mM</td>
<td>288.372</td>
<td>[43]</td>
</tr>
<tr>
<td>Brij L23 (polymeric)</td>
<td></td>
<td>0.09mM</td>
<td>1199.54</td>
<td>[108]</td>
<td></td>
</tr>
<tr>
<td>C_{3}H_{17}N^+(CH_3)_2COO^- (zwitterionic)</td>
<td>2.8</td>
<td></td>
<td>2.5 * 10^-1 M</td>
<td>201.3</td>
<td>[42]</td>
</tr>
</tbody>
</table>
Chapter 7: Conclusions

In this thesis, a protocol for measuring initial foam density for aqueous surfactant solutions of small-molecule surfactants was developed. Bulk solutions composed of one surfactant in deionized water were used to allow for direct comparison of surfactant adsorption in foams. This study used different equilibrium and dynamic surface tension parameters to correlate to the liquid fraction trends produced from eight different surfactant solutions. The surfactants used were composed of commonly studied nonionic, cationic, and anionic surfactants.

The results of the foam density experiments showed that the anionic surfactant SDBS produces the highest liquid fraction with the cationic DTAB surfactant closely following, whereas the nonionic TritonX-45 and the cationic HTAB has the lowest and second lowest liquid fractions, respectively. These results point to a lack of identifiable trend for the liquid fraction based on the surfactant ionic charge. In addition, the results for the adsorption parameters $\Gamma_\infty$ and $K_{eq}$ did not correlate strongly to the liquid fractions of the surfactants. The evidence for weak correlation is supported via correlation coefficients and p-values.

Surfactant properties of efficiency, or $pC_{20}$, and effectiveness, or CMC, were compared to the liquid fraction from equilibrium surface tension isotherm data. The CMC showed weak evidence of correlation for a linear relationship to the liquid fraction, whereas a mild correlation was observed between the $pC_{20}$ and liquid fraction.

Dynamic surface tension data was initially gathered using a SensaDyne maximum bubble pressure tensiometer PC-500L to get time points of 35, 50 and 90 percent reduction from the reference solvent surface tension. Difficulty with accessing timescales short enough for the adsorption of well-above CMC solutions prevented conclusive results from being gathered from experimental data prior to a hardware malfunction of the tensiometer. Literature data for $t_{35}$, $t_{50}$,
were used from CMC or near-CMC concentrations for the dynamic surface tension correlations to the liquid fractions.

The results of the correlations to the dynamic surface tension time points \( t_{35} \) and \( t_{50} \) showed strong evidence for a trend in increasing liquid fraction with faster surfactant adsorption. However, the \( t_{90} \) timepoints did not follow the same correlations for the liquid fraction as the \( t_{35} \) and \( t_{50} \) time points. The correlation between the liquid fraction and the \( t_{50} \) time point shows agreement with previous studies where a faster adsorption rate correlated to an increase in the liquid fraction in a foam [18], [59].

The protocol developed in this work lays groundwork for future investigations into the mechanisms surrounding liquid entrainment in bulk foams. Because no model currently exists to explain the relationship of surfactant adsorption and the initial liquid fraction in foams, this study has helped to highlight the knowledge gaps surrounding the impact of surfactants on fluid flow in foams during formation and initial drainage. The effect of vessel choice for foam formation has been shown to be significant for relating results of different studies. Certain studies have concluded that using a conical vessel better represents the true foamability of an aqueous surfactant solution [22], [74]. However, the use of cylindrical vessel simplifies the direction of fluid flow during formation and enables comparison to several other prior studies as well as industrially relevant metrics.

The results of this work are limited by the experimental protocols developed. A specific set of surfactants and foaming properties has been identified, whereas the number of surfactants that could be tested is numerous. In addition, certain groups of surfactants, such as zwitterionic surfactants, were not included in this study. Furthermore, the specifics of surfactant-micelle kinetics were not a topic of focus in this work. However, further understanding into the rate of
micelle formation as well as the equilibrium ratio of micelle to monomer in the bulk solution are expected to be a factor in liquid entrainment. Further analysis of the work done on micellization kinetics following the methods and theories from Fainerman et al. [57], [87], [89], [96] is recommended to develop methods for incorporating micellization parameters for comparison with initial liquid fraction.

Future work recommendations include a comparative study of foam density in various vessels geometries. Systematic variation of diffusions times with respect to foam densities produced for nonionic surfactants is a regime yet to be fully explored.
Bibliography


[64] G. Elfring and et al., “Surface viscosity and Marangoni stresses at surfactant laden interfaces.”


Appendices

Appendix A  Cleaning and Calibration Procedure: Experimental work

A.1 Calibration: MicroTrough G4

The MicroTrough tensiometer was initially calibrated using the surface tension of various solvents. Deionized water is a commonly used solvent but is highly prone to surface-active species contamination. Therefore, the solvents IPA, toluene, and ethanol were used to calibrate the tensiometer, with the literature values for surface tension shown in Table A.1 below.

Table A.1: Reference surface tension for various calibration solvents

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Surface tension (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-propanol (IPA)</td>
<td>21.07</td>
</tr>
<tr>
<td>Toluene</td>
<td>28.0</td>
</tr>
<tr>
<td>Ethanol</td>
<td>21.72</td>
</tr>
</tbody>
</table>

A.2 Glassware Cleaning

To ensure the surface purity of both the stock solutions, diluted surfactant solutions, and foaming column, cleaning protocols were developed for each stage of testing. The vessels containing the solutions of surface-active materials were copiously rinsed several times with tap water, and scrubbed with commercial dish soap, then rinsed again with tap water. The vessels were then rinsed 3 times with DI water. Finally, the surface tension of DI water placed in the vessel was tested using the Wilhelmy rod force tensiometer described above. The vessels were cleaned to a surface-active purity within ± 0.5 mN/m of that of the deionized water (72.8mN/m).
Appendix B  Post-processing codes

All of the codes for post-processing of data was written in the Spyder IDE using Python 2.7.10. The codes for analysis of the equilibrium surface tension isotherms as well as the foam density and correlation plots are shown in the subsequent sections.

B.1  Surface tension isotherm code

The functions used for curve fitting are followed by one of the plotting scripts.

Curve Fitting Functions

```python
### Created on Thu Sep 06 15:12:50 2018
@author: Joanna with input from jfrostad

import numpy as np
import csv
import glob as glob
import matplotlib.pyplot as plt
import scipy as sci
from scipy import optimize
import os

# from tempfile import TemporaryFile

# USER-DEFINED INPUTS

This script builds upon the previous script of CSV_reading_Gibbs.py. The objective of this script is to modularize the reading functions of the CSV files, set up an optimization routine for which to fit surface tension versus concentration data to the Szyszkowski equation, and use the fitted parameters in a plot of the surface tension versus concentration.

```
for row in reader:
    tension.append(row[6])
    time.append(row[8])
    temp.append(row[9])

time = np.array(time)
tension = np.array(tension)
tension = tension.astype(float)
print(type(tension))
T = np.array(temp)
Stvalues = tension[startInd:]
AvgST = np.mean(Stvalues)
Stdev = np.std(Stvalues)
print('---------------------------------------------------------
')
return time, tension, T, AvgST, Stdev

def get_conc(fileName):
    truncate = fileName[-4:]
    ind1 = truncate.find('c=')
    ind2 = truncate.find('mM')
    conc = truncate[ind1+2:ind2]
    conc = float(conc.replace(',','.'))
    return conc

def get_conc2(fileName):
    temp = os.path.basename(fileName)
    temp = temp[0:6]
    temp = temp.replace(',','.')
    conc = float(temp)
    return conc

def Szyszkowski(C,B,a):
    T = 298
    y = R*T*B*(np.log(1+(C/a)))
    return y

def Szyszkowski_new(C,B,a,sigma_ref,T):
    sigma = sigma_ref - R*T*B*(np.log(1+(C/a)))
    return sigma

def Langmuir(C,B,a,ionic):
    C: concentration vector
    B: parameter name for maximum surface concentration
    a= parameter name for equilibrium adsorption constant
    ionic= decision based on surfactant charge for monovalent disassociating surfactants
    if ionic==False:
        y=(C*B)/(a+C)
    else:
        y=(C*B)/2*(a+C)
    return y

def FracChange(yi):
    Define fractional change in experimenental y values versus curve fitted values
    Distribute weight equally for fitted curve
    yi= functional values i.e.surface pressure values
    var=np.zeros_like(yi)
for k in range(len(yi)-1):
    var[k] = (yi[k]-yi[k+1])/yi[k]
return var

def obj_fun(params,C,PiData,T):
    """ defining objective function for minimization- using fractional change from fitted surface pressure and actual surface pressure data points """

    """
    B = params[0]
    print 'Beta is ' + str(B)
    a = params[1]
    print 'alpha is ' + str(a)
    t=T
    #setting up physical model function for getting parameters fitted
    PiModel_Fit=R*t*B*np.log(1+(C/a))
    print PiModel_Fit
    print 'The length of PiModel_Fit is ' + str(len(PiModel_Fit))

    #defining minimization of fractional change between model fit and experimental data
    var=np.zeros_like(PiData)
    for k in range(len(var)):
        var[k] = np.abs((PiModel_Fit[k]-PiData[k])/PiData[k])
        print 'Var[k] value is ' + str(var[k])
    return var[k]
import curve_fit as cf
import numpy as np
import csv
import glob as glob
import matplotlib.pyplot as plt
import scipy as sci
from scipy import optimize
import os

#USER-DEFINED INPUTS

This is script to get data plots in a more refined version of data management, plotting, and modular functions to that end. Code first written in September- updated November 2nd

surfactantList= ['TritonX-100', 'SDS', 'HTAB','TritonX-45', 'SDBS']
filepath0= '..\Data\Full Isotherm' + ' ' + surfactantList[0] + ' ' + filepath0
filepath1= '..\Data\Full Isotherm' + ' ' + surfactantList[1] + ' ' + filepath1
filepath2= '..\Data\Full Isotherm' + ' ' + surfactantList[2] + ' ' + filepath2
filepath3= '..\Data\Full Isotherm' + ' ' + surfactantList[3] + ' ' + filepath3
filepath4= '..\Data\Full Isotherm' + ' ' + surfactantList[4] + ' ' + filepath4

#additional surfactants as needed
filepathList= [filepath0,filepath1,filepath2, filepath3, filepath4]
for l in range(len(filepathList)):
    filepath= filepathList[l]
    fileList= glob.glob(filepath + fileString)

fileString = '*mM*.ntb'
#plotting user-defined inputs
surfactantTitle= "Langmuir-Szyszkowski"
markerType= ['bs','ro','g^','mx','y*']
plot_title= "N"
xLabel= 'Concentration (mM)'
yLabel= 'Surface Tension (mN/m)'

startInd = 0

for l in range(len(filepathList)):
    filepath= filepathList[l]
    fileList= glob.glob(filepath + fileString)
print fileList
N = len(fileList)
concNumber = N

#allocate lists/array for storing data
csv_files_reading= []
info= []
data_file= []
data_file_1= []
concentration= np.zeros((concNumber,))
time_data=np.zeros((concNumber,1))
tension_data=np.zeros((concNumber,1))
T_data= np.zeros((concNumber,1))
AvgSTvec= np.zeros_like(concentration)
STavg=[]
Stdev=[]

#read individual files
for i in range(len(fileList)):
    fileName = fileList[i]
    concentration[i]= cf.get_conc(fileName)
time, tension, T, avgST, Std = cf.read_NTB(fileName)
    time_data[i]= time[i]

    #print time_data
    tension_data[i]=tension[i]

    #print tension_data
    T_data[i]=T[i]
    AvgTemp= np.mean(T_data)
    print("%.2f" % round(AvgTemp,2))

    #print T_data
    STavg.append(avgST)
    STavg= np.array(STavg)
    Stdev.append(Std)
    Stdev= np.array(Stdev)
    StartPi=STavg[Ind]
    pi= StartPi-STavg
    T_Kelvin= AvgTemp+273
    T= AvgTemp+273
    mylabel= surfactantList[l]
    plt.figure(1)
    plt.semilogx(concentration,STavg,markerType[l] , label= mylabel)

#load one file list from indicated folder
for j in range(len(filepathfitList)):
    filepath= filepathfitList[j]
    fileList = glob.glob(filepath + fileString)

    print fileList
    N = len(fileList)
    concNumber = N

    #allocate lists/array for storing data
csv_files_reading= []
info= []
data_file = []
data_file_1 = []
concentration = np.zeros((concNumber,))
time_data = np.zeros((concNumber,1))
tension_data = np.zeros((concNumber,1))
T_data = np.zeros((concNumber,1))
AvgSTvec = np.zeros_like(concentration)
STavg = []
Stdev = []

# read individual files
for i in range(len(fileList)):
    fileName = fileList[i]
    concentration[i] = cf.get_conc(fileName)
    time, tension, T, avgST, Std = cf.read_NTB(fileName)
    time_data[i] = time[i]
    tension_data[i] = tension[i]
    T_data[i] = T[i]
    AvgTemp = np.mean(T_data)
    print("%.2f" % round(AvgTemp,2))
    STavg.append(avgST)
    Stdev.append(Std)

# plotting avg surface tension values
STavg = np.array(STavg)
Stdev = np.array(Stdev)
StartPi = STavg[Ind]
pi = StartPi - STavg
T_Kelvin = AvgTemp + 273
T = AvgTemp + 273
plot_1, plot_2 = sci.optimize.curve_fit(cf.Szyszkowski, concentration, pi, sigma=Stdev)
print plot_1, plot_2
Beta = plot_1[0]
alpha = plot_1[1]
plot_1_tuple = tuple(plot_1)
perr = np.sqrt(np.diag(plot_2))
# perr = tuple(perr)
plot_tuple = (plot_1[0], perr[0], plot_1[1], perr[1])

# calling out optimization routine defined by obj function
SurfPresFit = []
InitGuess = [Beta, alpha]
SurfPresFit = sci.optimize.minimize(cf.obj_fun, InitGuess, args=(concentration, pi, T), method='Nelder-Mead', tol=1E-9)
print SurfPresFit
print SurfPresFit.x
Beta_new = SurfPresFit.x[0]
print Beta_new
alpha_new = SurfPresFit.x[1]
print alpha_new
params_tuple = (SurfPresFit.x[0], SurfPresFit.x[1])
plt.figure(1)
if plot_title=="Y":
    plt.title(surfactantTitle, titleFont)
'optimized fit, $\Gamma_\infty$ = %5.3f, $K_\infty$ = %5.3f' % params_tuple
plt.semilogx(concentration,cf.Szyszkowski_new(concentration,Beta_new,alpha_new,StartPi,T), 'k-',linewidth=1)
plt.margins(0.5,0.5)
plt.xticks(fontsize=15)
plt.yticks(fontsize=15)
plt.xlabel(xLabel,fontdict=axesFont)
plt.ylabel(yLabel,fontdict=axesFont)
plt.legend(loc='best' ,handlelength=0.5, fontsize=19, borderpad=0.2)
$\Gamma_\infty$ = %5.3f$\pm$%5.3e, $K_\infty$ =%5.3f$\pm$%5.3e' % plot_tuple)
B.2 Foam density post-processing functions

The script below uses functions to identify the air-liquid interfaces from the post-processed DFA data available from the ADVANCE program in the DFA100. This functions script was the basis for further data extraction and plotting to produce the figures in this thesis.

DFA Functions

import pandas as pd
import numpy as np
import matplotlib.pyplot as plt

def get_profile_data(fileName, visualizeQ=False, visualizeT=False):
    """
    Open a data file from the DFA software (version XX.XX) and extract the raw data of the foam profile (height and volume) as a function of time. Also extract the experimental parameters. Return the data as a dictionary where the values are numpy arrays.
    """
    # Constants and storage variables
dataSheet = 'Height - Raw data'
settingsSheet = 'Settings'
resultsSheet = 'Height - results'
dataKeys = ['t','h_foam','h_liquid','V_foam','V_liquid']
columnNumbers = [0,1,2,4,5]
N = len(dataKeys)
data = {}
data['fileName'] = fileName

    # Check that the sheet names are as expected
    xl = pd.ExcelFile(fileName)
sheets = xl.sheet_names
    if dataSheet not in sheets:
        print 'No data found in %s' % (fileName)
        return

    # Extract data
df = pd.read_excel(fileName,dataSheet)
    values = df.values
    for i in range(N):
        data[dataKeys[i]] = values[:,columnNumbers[i]].astype('float')

    time = data['t']
dt = time[1:] - time[:-1]
timeStep1 = dt[0]
timeStep2 = dt[-1]
if timeStep1 == timeStep2:
    print 'Warning:', fileName, ' does not have a two different time steps.'
ind = np.argwhere(dt > timeStep2*0.9)[0][0]
data['t0'] = t[ind]
data['t'] = t - data['t0']

# Extract experimental parameters
df = pd.read_excel(fileName,settingsSheet)
data['surfactant'] = df.iat[2,1]
data['concentration'] = df.iat[4,1]
temp = df.iat[24,1]
data['Q_setting'] = float(temp[:-5])*1000/60
if type(temp) is float or type(temp) is int:
data['V0'] = temp
else:
data['V0'] = float(temp[:-2])

df = pd.read_excel(fileName,resultsSheet)
data['V_foam_max']= float(df.iat[1,1])
data['V_liquid_foam_max']= float(df.iat[2,1])
data['V_gas'] = float(df.iat[3,1])
data['V_gas_actual'] = data['V_foam'][ind] + data['V_liquid'][ind] - data['V0']
data = compute_foam_metrics(data,visualizeQ,visualizeT)
return data

def find_initial_point(data,method='smoothness',visualize=False,t_start=0,
t_stop=20):
    Use volume of liquid vs time curve to determine the time point that
    corresponds to the initial foam density after the bubbles have all joined
    the foam and a clear liquid-foam interface is visible.
    
    # Parse input
t = data['t']
V = data['V_liquid']

    # Trim data and reshape for curve fitting
ind = np.argwhere((t>t_start) & (t<t_stop))
t = t[ind][:,0]
V = V[ind][:,0]
N = len(t)
tInitial = 0

    if visualize:
plt.figure()

    if method is 'slopes':
        # Constants
smallestGroup = 6

        # Split into two groups and fit each to a line (for all possible groups)
sumResiduals = np.zeros(N-2*smallestGroup)
lowestResidual = 1e10

        for i in range(N-2*smallestGroup):
split = i + smallestGroup

t1 = t[:split]
t2 = t[split:]
V1 = V[:split]
V2 = V[split:]
p1 = np.polyfit(t1,V1,1,full=True)
p2 = np.polyfit(t2,V2,1,full=True)

# Only save the best option
    tInitial = t2[0]
    if visualize:
        if method is 'smoothness':
            # Constants
            sampleSize = 30
            scaleFactor = 4
            minVolChange = 0.2
            stride = 2

            # Quantify the vertical change in the volume data
            t = np.flipud(t)
            V = np.flipud(V)
            dV = np.abs(V[1:] - V[:-1])

            # Locate the first abnormal jump in the data
            maxdV = 0
            increment = 0
            while maxdV < minVolChange:
                maxdV = np.max(dV[:sampleSize + stride*increment])
                increment += 1

            deviations = np.argwhere(dV > scaleFactor*maxdV)
            if len(deviations) == 0:
                split = len(dV) + 1
            else:
                split = deviations[0][0] + 1

            tInitial = t[split-1]

    if visualize:
        t1 = t[:split]
        t2 = t[split:]
        V1 = V[:split]
        V2 = V[split:]
        plt.plot(t1,V1,'go')
        plt.plot(t2,V2,'ro')

        return tInitial

def compute_foam_metrics(data, visualizeQ, visualizeT):
    """
Use the raw foam profile data to compute various properties of interest for analysis and plotting.

```python
# Compute the actual flow rate from the total foam volume vs time
V = data['V_foam'] + data['V_liquid']
t = data['t']
ind = np.argwhere((V>(0.1*np.max(V) + 0.9*V[0])) & (t<0))
x = t[ind][:,0]
y = V[ind][:,0]
p = np.polyfit(x,y,1)
data['Q'] = p[0]
if visualizeQ:
    plt.title('Fit Q')
    plt.plot(x,y,'go')
y = x*p[0] + p[1]
plt.plot(x,y,'r')
plt.plot(t[:ind[0][0]],V[:ind[0][0]],'ro')
```

```python
# Compute the initial liquid fraction of the foam
data['t_initial'] = find_initial_point(data,visualize=visualizeT)
indInitial = np.argwhere(t==data['t_initial'])
data['V_entrained'] = data['V0'] - data['V_liquid']
data['phi'] = data['V_entrained']/data['V_foam']
data['phi_initial'] = float(data['phi'][indInitial])
```

```python
# Compute the time for entrained liquid to fall to half the initial value
V_initial = float(data['V_entrained'][indInitial])
ind = np.argwhere((data['V_entrained'] <= V_initial*0.5) & (data['t']>data['t_initial']))[0]
data['drainageTimeScale'] = float(t[ind] - data['t_initial'])
```

return data

### B.3 Calculation of correlation coefficients

The Python script used to compute the Pearson’s product-moment correlation coefficient as well as the Spearman rank order correlation coefficient is shown in this section.
import dfa_functions_updated as dfa
import plotting_liquid_fraction as plf
import matplotlib.pyplot as plt
import glob
import numpy as np
from matplotlib.patches import Patch
from matplotlib.lines import Line2D
from mpl_toolkits.mplot3d import Axes3D
import scipy as sci
from scipy.stats.stats import pearsonr
from scipy.stats.stats import spearmanr

#user-defined inputs
fileString = '*.xlsx'
folder = '..\Data\DFA data\G1 filter\High flow rate_Ind_0.8LPM\TritonX100\'

fileList = glob.glob(folder + fileString)
plt.close('all')
surfactantList = ['TritonX-100', 'SDS', 'HTAB', 'TritonX-45', 'TritonX-165', 'SDBS', 'TTAB', 'DTAB']
surfactantFolder = ['TritonX100', 'SDS', 'HTAB', 'TritonX-45', 'TritonX-165', 'SDBS', 'TTAB', 'DTAB']
markerList = ['bs', 'ro', 'g^', 'mx', 'kp', 'y*', 'cd', 'k>']
title_all_plot = "Excess surface concentration vs liquid fraction"
plot_title = "N"

#plotting commands

titleFont = {'family': 'Tahoma', 'weight': 'bold', 'size': 25}
axesFont = {'weight': 'bold', 'size': 20}
title_plot = 'Liquid fraction for 0.8 LPM, external gas'  #yLabel= 'True flow rate, percent change' yLabel= '$\phi_{initial}$'  
xLabel1 = '$\Gamma_{\infty}$ * $10^{6}$ mol/m$^{2}$'
xLabel2 = '$K_{(eq)}$ * $10^{3}$ (m$^{3}$/mol)'
yLabel = '$K_{eq}$ * $10^{3}$ (m$^{3}$/mol)'
xLabel3 = 'CMC (mM)'
xLabel4 = 'pC$_{20}$'
markertype = 'r'
markerSize = 15
markerType = 'ko'
errorbarColor = 'k'
liqFracLowAvg = []
liqFracMidAvg = []
liqFracHighAvg = []
liqFracLowStdAvg = []
liqFracMidStdAvg = []
liqFracHighStdAvg = []
liqFracAvg = []
stDevAvg = []
Pearson_vals = {}
Spearman_vals = {}
P_vals = {}
P_vals1 = {}
legend_elements = [Line2D([0], [0], marker = 's', color='b', markersize=markerSize, label='TritonX-100'),
                   Line2D([0], [0], marker='o', color='w', label='SDS', markerfacecolor='r',
                          markersize=markerSize), Line2D([0], [0], marker = '^', color='g',
                          markersize=markerSize, label='HTAB'),
                   Line2D([0], [0], marker = 'x', color='m', markersize=markerSize,
                          label='TritonX-45'),
                   Line2D([0], [0], marker = 'p', color='k', markersize=markerSize,
                          label='TritonX-165'),
                   Line2D([0], [0], marker = '*', color='y', markersize=markerSize,
                          label='SDBS'),
                   Line2D([0], [0], marker = 'd', color='c', markersize=markerSize,
                          label='TTAB'),
                   Line2D([0], [0], marker = '>', color='k', markersize=markerSize,
                          label='DTAB')]
plot_ADV_phi = "N"
plot_V_gas_setpt = "N"
plot_V_gas_actual = "Y"
V_gas = [34.0, 67.0, 134.0]
annotate_y = "N"

# equilibrium surface tension data
szysz = [3.00, 11.0, 9.0, 3.00, 1.10, 7.76, 8.03, 11.33]
szysz_exp = [3.00E-06, 1.10E-05, 9.00E-06, 3.00E-06, 1.10E-06, 3.90E-06, 8.00E-06, 1.13E-05]
keq = [0.001, 2.216, 0.230, 0.001, 0.0005, 0.004, 0.301, 0.3892]
keq_exp = [1.0, 2216.0, 230.0, 1.0, 0.05, 4.0, 301.0, 3892.0]

# szysz = [3.00, 11.0, 9.0, 3.00, 1.10, 3.88, 8.03, 11.33]
# keq = [0.001, 2.216, 0.230, 0.001, 0.0005, 0.004, 0.301, 0.3892]
cmc = [0.3, 7.0, 1.0, 0.15, 0.7, 2.0, 3.0, 14.23]
T_I_all = [0.065, 0.0004, 0.018, 1.01, 0.006, 0.05, 0.002, np.nan] # array of values < 50% reduction from 72.8 mN/m
T_I_35 = [1.08, 8.89E-04, 0.0371, 6.176, 0.0199, 0.05, 0.004, np.nan] T_I= [1.08, 8.89E-04, 0.0371, 6.176, 0.0199, 0.05, 0.004, np.nan]
T_I_50 = [2.0, 0.0024, 0.07, 10.0, 0.08, 0.1, 0.01, np.nan] # array of values for 50% reduction from 72.8 mN/m
T_I_90 = [100, 0.17, 5.0, 80.0, 100.0, 2.5, 1.5, 0.01] # array of values for 90% reduction from 72.8 mN/m

# function definitions
def liquid_frac_avg(lowLF, midLF, highLF):
    lowGasVol = lowLF
    midGasVol = midLF
    highGasVol = highLF
    liqFracLow = np.mean(lowGasVol)
    stdDevLowGas = np.std(lowGasVol)
    liqFracMid = np.mean(midGasVol)
    stdDevMidGas = np.std(midGasVol)
    liqFracHigh = np.mean(highGasVol)
stdDevHighGas = np.std(highGasVol)

totalLiqFracAvg = np.mean([liqFracLow, liqFracMid, liqFracHigh])

totalStDev = np.std([liqFracLow, liqFracMid, liqFracHigh])

return liqFracLow, liqFracMid, liqFracHigh, stdDevLowGas, stdDevMidGas, stdDevHighGas,
totalLiqFracAvg, totalStDev

def pearson_coefficient(paramX, paramY):
    corCoef =
    sci.stats.pearsonr(paramX, paramY) Pearson = corCoef[0]
    p_val = corCoef[1]
    return Pearson, p_val

def spearman_coefficient(paramX, paramY):
    corCoef =
    sci.stats.spearmanr(paramX, paramY) Spearman = corCoef[0]
    p_val = corCoef[1]
    return Spearman, p_val

def plotting_liquid_frac(lowLF, midLF, highLF, lowG, midG, highG):
    plt.figure(1)
    lowGasVol = lowLF
    lowGas = lowG
    midGasVol = midLF
    midGas = midG
    highGasVol = highLF
    highGas = highG
    liqFracLow = np.mean(lowGasVol)
    stdDevLowGas = np.std(lowGasVol)
    gasLow = np.mean(lowGas)
    stdLowG = np.std(lowGas)
    if plot_V_gas_actual == "N":
        plt.plot(V_gas[0], liqFracLow, markerType, markersize= markerSize)
        plt.errorbar(V_gas[0], liqFracLow, yerr=stdDevLowGas, fmt=''
        , ecolor=erbarColor)
    else:
        plt.plot(gasLow, liqFracLow, markerType, markersize= markerSize) plt.errorbar(gasLow, liqFracLow, xerr= stdLowG, yerr=stdDevLowGas, fmt=''
        , ecolor=erbarColor)
    liqFracMid = np.mean(midGasVol)
stdDevMidGas =np.std(midGasVol)
gasMid= np.mean(midGas)
stdMidG= np.std(midGas)

if plot_V_gas_actual="N":
    plt.plot(V_gas[1],liqFracMid, markerType, markersize= markerSize)
plt.errorbar(V_gas[1],liqFracMid,yerr=stdDevMidGas, fmt='
',ecolor=erbarColor)
else:
    plt.plot(gasMid,liqFracMid, markerType, markersize= markerSize)
    plt.errorbar(gasMid,liqFracMid,xerr= stdMidG, yerr=stdDevMidGas, fmt='
',ecolor=erbarColor)

liqFracHigh=np.mean(highGasVol)
stdDevHighGas =np.std(highGasVol)
gasHigh= np.mean(highGas)
np.std(highGas)

if plot_V_gas_actual="N":
    plt.plot(V_gas[2],liqFracHigh, markerType, markersize= markerSize)
plt.errorbar(V_gas[2],liqFracHigh,yerr=stdDevHighGas, fmt='
',ecolor=erbarColor)
else:
    plt.plot(gasHigh,liqFracHigh, markerType, markersize= markerSize)
    plt.errorbar(gasHigh,liqFracHigh,xerr= stdHighG, yerr=stdDevHighGas, fmt='
',ecolor=erbarColor)

plt.legend(handles= legend_elements,loc='best' ,numpoints=1, handlelength=0.5, fontsize=18, borderpad=0.2)
plt.margins(0.5,0.5)
plt.xticks(fontsize=15)
plt.yticks(fontsize=15)
plt.xlabel(xLabel,fontdict=axesFont)
plt.ylabel(yLabel,fontdict=axesFont)
return plt.show()

#get liquid fraction data
for i in range(len(surfactantList)):
    Folder = "..\Data\DFA data\G1 filter\High flow rate_Ind_0.8LPM\"
    + str(surfactantFolder[i]) + "\"
    #Folder = "..\Data\DFA data\G1 filter\High flow rate_Ind_0.8LPM\TritonX100\"
    plot_gas_decision = plot_V_gas_actual
    leg = []
    Color = 'b'
    markerType = markerList[i]
    markerSize = 13
    lowliqFrac, midliqFrac, highliqFrac, gasLow, gasMid, gasHigh = plf.get_liquid_frac_final(Folder, surfactantList[i], leg, fileString)
    # get average values for liquid fraction and standard deviations LF, MLF, HLF, STDL, STDM, STDH, LFA, LFSTD=
    liquid_frac_avg(lowliqFrac, midliqFrac, highliqFrac)
    liqFracLowAvg.append(LF)
    liqFracMidAvg.append(MLF)
    liqFracHighAvg.append(HLF)
    liqFracLowStdAvg.append(STDL)
    liqFracMidStdAvg.append(STDM)
    liqFracHighStdAvg.append(STDH)
    stDevAvg.append(LFSTD)
    # plotting_liquid_frac(lowliqFrac, midliqFrac, highliqFrac, gasLow, gasMid, gasHigh)
    N = np.ones(3)
    print N
    GammaI = N * szysz[i]
    Keq = N * keq[i]
    pC_20 = N * pC20[i]
    CMC = N * cmc[i]
    # print average and standard deviation
    print liqFracAvg
    print stDevAvg
    # correlation coefficients for surface concentration Gamma_Inf and liquid fraction # placing in dictionary
    Pearson_vals['Gamma_Inf Low'], P_vals['Gamma_inf Low'] = pearson_coefficient(szysz_exp, liqFracLowAvg)
Pearson_vals['Gamma_Inf Mid'], P_vals['Gamma_inf Mid']=pearson_coefficient(szysz_exp,liqFracMidAvg)
Pearson_vals['Gamma_Inf High'], P_vals['Gamma_inf High']=pearson_coefficient(szysz_exp,liqFracHighAvg) #correlation coefficients for Keq and liquid fraction
Pearson_vals['Keq Low'], P_vals['Keq Low']=pearson_coefficient(keq_exp,liqFracLowAvg) Pearson_vals['Keq Mid'], P_vals['Keq Mid']=pearson_coefficient(keq_exp,liqFracMidAvg)
Pearson_vals['Keq High'], P_vals['Keq High']=pearson_coefficient(keq_exp,liqFracHighAvg) #correlation coefficients for pC20 and liquid fraction

Pearson_vals['pC20 Low'], P_vals['pC20 Low']=pearson_coefficient(pC20,liqFracLowAvg)
Pearson_vals['pC20 Mid'], P_vals['pC20 Mid']=pearson_coefficient(pC20,liqFracMidAvg)
Pearson_vals['pC20 High'], P_vals['pC20 High']=pearson_coefficient(pC20,liqFracHighAvg) #correlation coefficients for CMC and liquid fraction

Pearson_vals['CMC Low'], P_vals['CMC Low']=pearson_coefficient(cmc,liqFracLowAvg)
Pearson_vals['CMC Mid'], P_vals['CMC Mid']=pearson_coefficient(cmc,liqFracMidAvg)
Pearson_vals['CMC High'], P_vals['CMC High']=pearson_coefficient(cmc,liqFracHighAvg)

##dynamic correlations

#correlation coefficients for t_i and liquid fraction

T_35_reduced= T_35[0:-1]
liqFracLow_avg_reduced= liqFracLowAvg[0:-1]
liqFracMid_avg_reduced= liqFracMidAvg[0:-1]
liqFracHigh_avg_reduced= liqFracHighAvg[0:-1]

Pearson_vals['t_35 Low'], P_vals['t_35 Low']=pearson_coefficient(T_35_reduced,liqFracLow_avg_reduced)
Pearson_vals['t_35 Mid'], P_vals['t_35 Mid']=pearson_coefficient(T_35_reduced,liqFracMid_avg_reduced)
Pearson_vals['t_35 High'], P_vals['t_35 High']=pearson_coefficient(T_35_reduced,liqFracHigh_avg_reduced)

#correlation coefficients for t_50 and liquid fraction

T_50_reduced= T_50[0:-1]

Pearson_vals['t_50 Low'], P_vals['t_50 Low']=pearson_coefficient(T_50_reduced,liqFracLow_avg_reduced)
Pearson_vals['t_50 Mid'], P_vals['t_50 Mid']=pearson_coefficient(T_50_reduced,liqFracMid_avg_reduced)
Pearson_vals['t_50 High'], P_vals['t_50 High']=pearson_coefficient(T_50_reduced,liqFracHigh_avg_reduced)
High'] = pearson_coefficient(T_50, liqFracHigh_avg)

#Pearson_vals['t_50 Low'], P_vals['t_50 Low'] = pearson_coefficient(T_50, liqFracLowAvg)

#Pearson_vals['t_50 Mid'], P_vals['t_50 Mid'] = pearson_coefficient(T_50, liqFracMidAvg)

#Pearson_vals['t_50 High'], P_vals['t_50 High'] = pearson_coefficient(T_50, liqFracHighAvg)

# correlation coefficients for t_90 and liquid fraction
Pearson_vals['t_90 Low'], P_vals['t_90 Low'] = pearson_coefficient(T_90, liqFracLowAvg)

Pearson_vals['t_90 Mid'], P_vals['t_90 Mid'] = pearson_coefficient(T_90, liqFracMidAvg)

Pearson_vals['t_90 High'], P_vals['t_90 High'] = pearson_coefficient(T_90, liqFracHighAvg)

# Spearman correlation coefficients for Gamma_Inf and liquid fraction
Spearman_vals['Gamma_Inf Low'], P_vals1['Gamma_Inf Low'] = spearman_coefficient(szysz_exp, liqFracLowAvg)

Spearman_vals['Gamma_Inf Mid'], P_vals1['Gamma_Inf Mid'] = spearman_coefficient(szysz_exp, liqFracMidAvg)

Spearman_vals['Gamma_Inf High'], P_vals1['Gamma_Inf High'] = spearman_coefficient(szysz_exp, liqFracHighAvg)

# correlation coefficients for Keq and liquid fraction
Spearman_vals['Keq Low'], P_vals1['Keq Low'] = spearman_coefficient(keq_exp, liqFracLowAvg)

Spearman_vals['Keq Mid'], P_vals1['Keq Mid'] = spearman_coefficient(keq_exp, liqFracMidAvg)

Spearman_vals['Keq High'], P_vals1['Keq High'] = spearman_coefficient(keq_exp, liqFracHighAvg)

# correlation coefficients for pC20 and liquid fraction
Spearman_vals['pC20 Low'], P_vals1['pC20 Low'] = spearman_coefficient(pC20, liqFracLowAvg)

Spearman_vals['pC20 Mid'], P_vals1['pC20 Mid'] = spearman_coefficient(pC20, liqFracMidAvg)

Spearman_vals['pC20 High'], P_vals1['pC20 High'] = spearman_coefficient(pC20, liqFracHighAvg)

# correlation coefficients for CMC and liquid fraction
Spearman_vals['CMC Low'], P_vals1['CMC Low'] = spearman_coefficient(cmc, liqFracLowAvg)

Spearman_vals['CMC Mid'], P_vals1['CMC Mid'] = spearman_coefficient(cmc, liqFracMidAvg)

Spearman_vals['CMC High'], P_vals1['CMC High'] = spearman_coefficient(cmc, liqFracHighAvg)

## dynamic correlations
# correlation coefficients for t_i and liquid fraction

T_35_reduced = T_35[0:-1]

liqFracLow_avg_reduced = liqFracLowAvg[0:-1]

liqFracMid_avg_reduced = liqFracMidAvg[0:-1]

liqFracHigh_avg_reduced = liqFracHighAvg[0:-1]

Spearman_vals['t_35 Low'], P_vals1['t_35 Low'] = spearman_coefficient(T_35_reduced, liqFracLow_avg_reduced)

Spearman_vals['t_35 Mid'], P_vals1['t_35 Mid'] = spearman_coefficient(T_35_reduced, liqFracMid_avg_reduced)
Spearman_vals['t_35 High'], P_vals1['t_35 High']=spearman_coefficient(T_35_reduced,liqFracHigh_avg_reduced)
#correlation coefficients for t_50 and liquid fraction
Spearman_vals['t_50 Low'], P_vals1['t_50 Low']=spearman_coefficient(T_50_reduced,liqFracLow_avg_reduced)
Spearman_vals['t_50 Mid'], P_vals1['t_50 Mid']=spearman_coefficient(T_50_reduced,liqFracMid_avg_reduced)
Spearman_vals['t_50 High'], P_vals1['t_50 High']=spearman_coefficient(T_50_reduced,liqFracHigh_avg_reduced)
#correlation coefficients for t_90 and liquid fraction
Spearman_vals['t_90 Low'], P_vals1['t_90 Low']=spearman_coefficient(T_90,liqFracLowAvg)
Spearman_vals['t_90 Mid'], P_vals1['t_90 Mid']=spearman_coefficient(T_90,liqFracMidAvg)
Spearman_vals['t_90 High'], P_vals1['t_90 High']=spearman_coefficient(T_90,liqFracHighAvg)

print Pearson_vals['Gamma_Inf Low']
print P_vals['Gamma_inf Low']
print Pearson_vals
print len(Pearson_vals)
print P_vals
print len(P_vals)
print Spearman_vals
print len(Spearman_vals)
print P_vals1
print len(P_vals)