Foamability and Foam Drainage of Sodium Naphthenate Solutions

BY

WILLIAM H. YANG B.S., Loyola University Chicago, 2009

THESIS

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Defense Committee:

Vivek Sharma, Chair and Advisor Brian P. Chaplin, Chemical Engineering Lewis E. Wedgewood, Chemical Engineering This thesis is dedicated to my girlfriend, Deja Baker, without whom it would never have been accomplished.

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LIST OF ABBREVIATIONS

ASDA	axisymmetric drop shape analysis
cmc	critical micelle concentration
DLVO	Derjaguin, Landau, Verwey, and Overbeek
DSLR	digital single-lens reflex
IDIOM	interferometry digital imaging optical microscopy
MBPT	maximum bubble pressure technique
NaN	sodium naphthenate
RGB	red, green, blue
TAN	total acid number

SUMMARY

Foams that arise during the extraction and processing of crude oil present a challenge in the petroleum industry, particularly in downstream processing during separation and refining, and effect oil recovery and gas production. The stability of crude oil foams are due to commercial surfactants used in enhanced oil recovery, and indigenous surface-active agents found within crude oil. Prominent among such surface species are naphthenic acids that react with salt found in water used during extraction, forming sodium naphthenates. With the depletion of light crude oil reserves and shift towards extracting heavier crude oils that have higher sodium naphthenate fraction, an understanding of how sodium naphthenates influence foam formation and stability is needed. The foamability of sodium naphthenate solution is correlated with its dynamic surface tension, that in turn depends on the mass transfer of surfactants to the fresh interface. As the dynamic adsorption of sodium naphthenate occurs relatively quickly (timescale < 50 ms), we utilize the maximum bubble pressure technique for it allows the necessary time resolution. The dynamic adsorption and dynamic surface tension measurements have not been reported before for aqueous sodium naphthenate solutions. Sodium naphthenates self-aggregate into micelles above a certain concentration called critical micelle concentration (cmc). The equilibrium surface tension of sodium naphthenate aqueous solutions was measured using pendant drop tensiometry and cmc was determined from plotting the equilibrium surface tension for a range of concentrations. Foam drainage and stability are characterized by visualization and analysis of thinning of single foam films of sodium naphthenate aqueous solutions over an extracted concentration range. This drainage by stratification (manifested as stepwise thinning) for sodium naphthenate solutions is shown to manifest as thinner circular domains of progressively darker shades of gray forming and growing

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SUMMARY (continued)

within a thicker film, using the interferometry digital imaging optical microscopy (IDIOM) method developed by Zhang and Sharma.¹

1. INTRODUCTION

In the petroleum industry, foams can be desirable for enhanced oil recovery and undesirable during processing of extracted oil. For example, foams are intentionally used to extract oil in wells and to plug areas where oil had already been recovered during enhanced oil recovery. Undesired foams arise during the refining of oil, damaging processing equipment, and reducing the recovered fraction of the desired petroleum. Foams consist of large volumes of closely packed gas bubbles dispersed within a continuous liquid or solid phase.²⁻⁵ The ability to form and stabilize foams is dependent on the presence of surfactants. Surfactants (short for surface active agent) are organic compounds that have the ability to adsorb at an interface,⁶⁻⁷ lowering the surface or interfacial tension between two phases. Foam formation in the petroleum industry can arise due to commercial surfactants⁸⁻⁹ and indigenous surface active species (see Figure 1¹⁰) found within crude oil, such as naphthenic acids.^{8,11-17} Naphthenic acids possess a hydrophilic carboxylic functional group as well as a hydrophobic aliphatic chain. The ability of naphthenic acids to adsorb at an interface¹⁴ makes them likely candidates for stabilizing foams⁸ and emulsions.^{11-12,15-16} During the transport of crude oil from the reservoir, depressurization causes a release of carbon dioxide and an increase in pH of the water, ^{13,18} for water is coproduced with the oil and gas as a byproduct.^{12-13,18-21} The pH increase causes dissociation of naphthenic acids, converting them into naphthenate anions that can react with salt ions present in water,^{12-13,18-21} thus resulting in the formation of sodium naphthenates. Sodium naphthenates are surface active molecules and get spontaneously adsorbed to liquid-air interfaces, reducing surface tension and aiding in stabilization of foams and emulsions produced during petroleum extraction and processing. The present contribution has two primary motivations: (a) experimental determination of the dynamic adsorption of sodium naphthenate, for it affects



Figure 1. Surface active species indigenous to crude oils. (a) Asphaltenes, (b) resins, and (c) naphthenic acids. Adapted with permission (see Appendix) from Figure 2 in D. Langevin, S. Poteau, I. Hénaut, and J. F. Argillier's paper, "Crude Oil Emulsion Properties and Their Application to Heavy Oil Transportation," *Oil & Gas Science and Technology - Rev. IFP*, Volume 59, Number 5, pages 511-521, September-October 2004.

foamability, and (b) the characterization of thin film drainage to examine the influence of sodium naphthenate on foam drainage and stability.

Light crude oils (API gravity greater than 31.1°)²² extracted from conventional resources are heavily sought out in the industry and return a higher price.²³ Light crude oils tend to be less acidic with lower total acid number (TAN) values (0.05 - 0.60),²² while heavy crude oils (API gravity less than 22.3°) tend to have higher TAN values (0.80 - 8.0).²² This value, used to characterize crude oil, represents the amount of potassium hydroxide needed to neutralize the acidity of one gram of oil. The acidity of crude oil is primarily due to naphthenic acids,^{12-13,16,18,24} which are a major source of equipment corrosion during processing.^{11-13,24-25} With the inevitable decline in conventional oil reserves, the industry has shifted towards seeking out unconventional resources, including heavier crude oils with high naphthenic acid concentrations,^{12,16-17,21-22} which in turn convert to sodium naphthenates. Increasing flow assurance problems are arising in the oil industry due to sodium naphthenate (and other naphthenate forms) formation obstructing pipelines and screens during processing, resulting in expensive production shutdowns.²¹⁻²² Thus, an understanding of foamability and foam stability of sodium naphthenate solution is critical for maximizing the return from heavy crude oils, which return lower percentages of products due to production related challenges.

Additionally, an understanding of how sodium naphthenates influence foam stability is also relevant from an environmental standpoint. For example, the BP oil spill that leaked 4.9 million barrels (210 million gallons) worth of light crudes into the Gulf of Mexico was disastrous from both economic and environmental standpoints.²⁶⁻²⁸ The spill resulted in the formation of brownish stable emulsions, known as a "mousse."²⁷ Initial efforts of cleanup involved the use of a dispersant known as Corexit 9500,²⁹ which has been shown to be toxic.³⁰⁻³¹ It is believed in the aftermath that a large amount of oil remains in the Gulf of Mexico,³²⁻³³ with an estimate of one million barrels of oil unaccounted for.³⁴ Even though the emulsions formed by leaked oil contain asphaltenes as well as additional surface active species that are not naphthenic acid based, the study of naphthenic acid adsorption kinetics and foam drainage is important as it could provide insight into their influence on emulsions and could prove useful to improving oil spill cleanup efforts.

1.1 Background

1.1.1 Sodium Naphthenate in Petroleum Industry

Sodium naphthenates are white-yellow crystalline in appearance. Sodium naphthenates act as anionic head-tail surfactants, with a carboxylic functional group as the hydrophilic head group and hydrophobic aliphatic chain with a ring as the tail. Mass transfer of anionic surfactants from the bulk solution to the interface is influenced by shape and size of the surfactant as well as its charge dependent interactions. The ability of sodium naphthenate (and all head-tail surfactants) to lower interfacial tension and to stabilize emulsions or foams, is due to interfacially adsorbed surfactants. Ortiz *et al.*³⁵ studied the influence of surfactants on the interfacial tension and stability of water-in-oil emulsion systems stabilized by asphaltenes, and reported a decrease in interfacial tension after the addition of sodium naphthenates at small and high concentrations in emulsions consisting of heptane-toluene mixtures with added asphaltenes, and aqueous solutions.

Naphthenates are not the only indigenous species found in crude oil to stabilize foams and emulsions. Other indigenous species in crude oil found to stabilize foams include asphaltenes and resins. Asphaltenes and resins are similar in that they are polar species with high molecular weight.³⁶ Structurally, they are polycyclic compounds with heteroatoms found within the cyclic network.^{8,35} Asphaltenes are a fraction of crude oil soluble in aromatic solvents and insoluble in paraffinic solvents.³⁵ Conversely, resins are soluble in paraffinic solvents and insoluble in aromatic solvents.³⁶ Understanding the effects of these species within a system provides insight regarding how much influence sodium naphthenates have in stabilizing foams and emulsions. For example, sodium naphthenates have been shown to competitively adsorb with asphaltenes and dominate the interface at higher sodium naphthenate concentrations in which molecular self-aggregates (micelles and liquid crystals) appear within the bulk.^{35,37} However, in the present thesis we focus on sodium naphthenates only, to determine their behavior in aqueous dispersions.

According to Horváth-Szabó *et al.*, aqueous sodium naphthenate solutions form an isotropic phase for concentrations less than 41.8 wt.% and for temperatures between $30 - 50^{\circ}$ C, indicating a lone liquid phase existing.³⁸ A lamellar liquid crystal and gel phase coexist with the isotropic phase³⁸ for concentrations between 41.8 – 74.5 wt.%. Observing the liquid crystal phase under a polarizing microscope, Horváth-Szabó *et al.* observed defect structures, postulated to be screw dislocations that form surface protrusions.³⁸ These surface protrusions have been shown to produce a flexible oil-water interface in water-diluted bitumen systems, susceptible to flocculation.³⁷ The flexible interface was observed by contracting the volume of a water droplet within a heptol-diluted bitumen solution and quantified using a "crumpling ratio".^{35,37} A rigid skin was observed for interfaces dominated by asphaltenes, whereas a droplet remained spherical for interfaces dominated by asphaltenes, whereas a droplet remained spherical for interfaces dominated by asphaltenes, whereas a droplet remained spherical for interfaces dominated by asphaltenes, whereas a droplet remained spherical for interfaces dominated by asphaltenes, whereas a droplet remained spherical for interfaces dominated by sodium naphthenates.³⁷ From these observations, Moran and Czarnecki³⁷ postulated that asphaltenes were displaced or blocked from the interface when high concentrations of sodium naphthenates, the crumpling ratio and interfacial tension decreased.

Poindexter *et al.* showed that asphaltene concentration correlates well with collapse slope (the rate of foam collapse in the absence of sparge gas),³⁹ a parameter that characterizes foam stability. Two crude oils examined in the study have low collapse slopes compared to two light crude oils that have steep collapse slopes.³⁹ The crude oils with low collapse slopes are characterized as having moderate asphaltene and resin concentrations. These indigenous species contribute to higher bulk viscosities, which also contribute to increased foam stability.³⁹ Despite

the ability to produce stable foams, these heavier crude oils did not produce high foam volumes, suggesting that other factors contribute to the ability of crude oil to form foam. Furthermore, non-asphaltenic crudes were shown to produce higher foams.³⁹ These crudes were characterized as having higher densities, viscosities, and resin concentrations. Asphaltenes precipitate out of crude oils during extraction due to depressurization and injection of aromatic solvents, which are used to promote recovery. Yang and Czarnecki found that sodium naphthenates do not co-precipitate with asphaltenes in the presence of heptane solvent.¹⁷ Rather, within a system that included DI water added to a mixture of diluted bitumen and a sodium naphthenate-heptane solution, it was observed that sodium naphthenate preferentially dissolved in water.¹⁷ This system best simulates what occurs in industrial practices,¹⁷ where sodium naphthenates arise during recovery of bitumen under alkaline conditions.^{17,40}

1.1.2 Foams: Structure, Stability and Lifetime

Understanding the complex properties of foams is desirable due to their wide application to different industries^{2,4,41-43} and presence in everyday items such as foods, shaving cream, and detergents.⁴⁴ Within the petroleum industry, foams are often used in enhanced oil recovery of petroleum remaining in depleted oil wells, which are trapped due to capillary and viscous forces.⁴⁵ Foams are injected into wells to plug areas where oil has already been recovered, due to their ability to decrease gas mobility in highly-permeable areas.^{9,44-45} Furthermore, foams improve the ability for a fluid to push out (sweep) the oil in wells^{9,44-45} by increasing the viscosity of the displacing medium, thus making it more effective in its ability to be in contact with the desired flow pathways.⁴⁵ A generalization of the process used for oil recovery is as follows: A slug is injected to displace mud in the well and a driving fluid follows to displace the oil into highly-permeable areas, allowing the oil to be recovered in the production well.⁴⁵ Then a

slug with a foaming agent is injected with a gas to create foam that plugs the highly-permeable areas, followed by the first step to recover the remaining oil.⁴⁵ Conversely, the foams that arise during the refining of oil are generally undesirable;⁹ for example, foams formed in separators due to decrease in pressure, reduce foam production rate and recovered fraction, due to the longer retention time required to allow the foams to destabilize.⁴⁴

Foams can be polydisperse or monodisperse, depending on the size distribution of the bubbles.⁵ Foams contain a large interfacial area and therefore creation of foams requires some form of mechanical energy input, such as bubbling or stirring.^{44,46} Foamability depends on decrease in Laplace pressure correlated with the drop in interfacial tension, and the presence of foaming agents, usually surfactants,^{2,47} as surfactants reduce surface tension (associated work of formation). Foams are intrinsically thermodynamically unstable, and bubbles within the foam coalesce over time and the foam disappears, returning to a separated gas and liquid state. The lifetime of foams can be short or long, with timescales spanning from minutes to years,⁴⁴ and the foam stability depends on the rate of coalescence and disappearance of bubbles.^{3-4,46} Consequently, the stability of foams is dependent on fluxes, forces, and flows that control rate of drainage of the continuous phase found as a thin liquid film between adjacent bubbles. Thus, foamability and foam stability require analysis of adsorption kinetics and drainage kinetics, and the present thesis focuses entirely on foamability and foam stability of sodium naphthenate solutions. As the stability of emulsions also depends on the physicochemical properties of surfactants as well as on the drainage kinetics of dispersed phase,⁴⁴ the discussion included herein on foam formation and forces within thin liquid films is also relevant to such colloidal dispersion systems.

1.1.3 <u>Role of Sodium Naphthenate as Ionic Surfactants</u>

Surfactants, or surface-active agents, are compounds that lower the surface tension (or interfacial tension) between two immiscible phases, as they diffuse to an interface, and influence foamability and foam stability. While the interface can be defined as a boundary between any two immiscible phases,⁷ it will be used interchangeably with surface in this text as a general term to denote the boundary between a liquid and gas phase, unless otherwise mentioned. Oftentimes, surfactants are discussed in terms of their presence in aqueous solutions, and are thus defined as structurally being hydrophilic (water-loving) and hydrophobic (water-hating).⁴⁸⁻⁴⁹ In the most general sense, surfactants are amphiphilic, in that they are composed of a lyophilic (solventloving) polar head group and lyophobic (solvent-hating) non-polar tail.⁶⁻⁷ Surfactants are characterized into four classes based on the nature of the polar head group.^{6-7,44,48,50} In nonionic surfactants the head group possesses no ionic charge; whereas anionic surfactants possess a negative charge, cationic surfactants possess a positive charge at the head, and zwitterionic surfactants possess both negative and positive charges at the head.^{7,48} The latter three surfactants can be generalized as ionic surfactants. Overall, surfactants consist of a polar head group and non-polar tail, exhibit surface activity, and form self-assembled aggregates in liquids.⁶ Sodium naphthenates, with their hydrophilic carboxylic head group and hydrophobic aliphatic tail, are thus an example of a surfactant.

The transport of surfactants to a free surface occurs in two stages. In the first stage, the surfactants diffuse from the bulk solution to the subsurface, an imaginary plane between the bulk and surface that is a few molecular diameters thick,⁵¹ due to a concentration gradient. Then in the second stage, the transport occurs from the subsurface to the surface, to bring the hydrophobic tails to the surface and a more favorable state. There are two general models that describe the

transport of surfactant molecules from the bulk to the interface. The diffusion-controlled model accounts for the case involving diffusion from the bulk to the subsurface as the rate-determining step (slow).^{28,51} In this model, it is assumed that the probability of a surfactant arriving to an empty site upon formation of a new interface is high. Conversely, adsorption to the interface is considered to be the rate-determining step in the mixed-kinetic diffusion model.⁵¹ In this model, transport from the subsurface to the interface is limited due to an adsorption barrier, preventing surfactant molecules from adsorbing to the interface.⁵¹ The cause of the barrier can be a result of an increase in surface pressure or due to fewer vacancies at the interface.⁵¹ The latter can also be attributed to steric restraints that may cause the molecules to back-diffuse to the subsurface in order to reorient themselves into a favorable direction to adsorb at the interface.⁵¹

For ionic surfactants, an adsorption barrier also arises in the form of an electrostatic double layer, associated with the presence of excess surface charge due to adsorption of charged surfactant ions and counterions present as a diffuse layer. The net charge at the surface influences a layer of counterion (inner-region), which in turn influences a layer of surfactant ions (outer-region). The combination of surface net charge, inner-region, and outer-region make up the electrostatic double layer.^{7,52-53} The distribution of the oppositely charged counterions is best represented by two regions, following the Guoy-Chapman Stern model. The Guoy-Chapman model⁷ visualized a diffuse distribution of counterions. Due to a screening effect, the concentration of counterions drops off rapidly at first, then gradually as distance from the charged surface increases. The Stern model modifies the Guoy-Chapman model to account for finite ion size effect, important for surfaces with high charge densities, especially at small distances from the charged surface.⁷ The Stern layer,⁷ adjacent to the surface, consists of counterions tightly packed to the surface as a single layer. Adjacent to the Stern layer is the

extended diffuse layer,^{7,52} consisting of co-ions and counterions. The pressure of the diffuse layer results in a repulsive force that retards the adsorption process of incoming surfactants.^{7,52-53} The thickness of the electrostatic double layer is characterized^{7,52} by the Debye length, κ^{-1} . The Debye length can be calculated using the Debye-Huckel theory,⁵⁴

$$\frac{1}{\kappa} = \sqrt{\frac{\varepsilon_0 \varepsilon k_b T}{e^2 N_a \sum Z_i^2 c_i}}$$
(1.1)

where ε is the dielectric constant, k_b is the Boltzmann constant, T is temperature, e is the elementary charge, N_a is Avogadro's number, Z is the valency number, and c is the concentration of ions.

1.1.4 Dynamic Surface Tension

The mass transfer of surfactants to an interface results in a time-dependent variation in interfacial concentration, which manifests as a time-dependent apparent surface tension called dynamic surface tension. Before discussing dynamic surface tension, the thermodynamic basis for surface tension is briefly discussed here. In the scenario of water in contact with air, the water molecules within the bulk are surrounded by each other in such a way that the attractive forces are felt equally in all directions, resulting in a more favorable zero net force.^{6,44,48} Water molecules at the surface interact partially with other molecules within the liquid, and interactions with widely spaced air molecules are minimal. As a result, the net force acting on water molecules at the surface is non-zero.^{6,44,48} The molecules at the surface are pulled towards the bulk as a result of the non-zero net force, and the interface spontaneously contracts in order to minimize the amount of molecules at the interface simultaneously with the surface area.^{6,44} In absence of gravity, contraction and minimization of surface area would result in a spherical drop.^{44,48} This contraction force at the interface accounts for surface tension, in the most basic

sense.⁴⁴ In a thermodynamic sense, surface tension is defined as the Helmholtz energy per unit area at constant temperature, volume, and number of molecules:⁶

$$\gamma = \left[\frac{\partial F}{\partial A}\right]_{T,V,n} \tag{1.2}$$

Molecules at the surface have greater free potential energies, due to the non-zero net force, and contraction of the interface occurs to reduce this potential energy.⁶ Surface tension has units of force per length or free energy per area. Interfacial tension is similar in concept but applies to colloidal systems of two immiscible liquids (emulsions). Molecules at the interface still encounter non-zero net forces, and minimization of the interfacial area and interfacial free energy will occur.⁶ Adsorption of surfactants prevents water molecules at the interface from packing as tightly, and surface (or interfacial) tension decreases as a result of reduction in the free energy.

1.1.5 Foamability

Dynamic surface tension influences the foamability of surfactant solutions. Wet foams occur in the initial stages of formation, when the foam is of high water content and gas dispersions (bubbles) are generally spherical in shape.^{6,45} As these bubbly dispersions are generated, surfactant molecules will begin diffusing from the bulk liquid and adsorb to the freshly formed interface. As liquid content in between bubbles drains out over time, the volume fraction of the gas in the dispersion increases and the bubbles deform into polyhedral shapes.⁶ At this point, foams are referred to as dry, having low water content.⁴⁵ Furthermore, as interfaces deform and change in interfacial area during foam formation, the response of surfactants during these changes influence foam stability.

During the formations of foams, a film between adjacent bubbles will expand and deform as a local thinning or stretching of the interface occurs. Without a mechanism to establish a uniform surface tension, the film will continue to thin and rupture without reaching an equilibrium surface tension. During expansion of surfactant-stabilized interfaces, the surface excess (a measurement of the amount of surfactants at the interface) decreases and an increase in local surface tension occurs.⁴⁴ To counter this increase in local surface tension, a surface tension gradient arises, and the interface contracts as bulk liquid flows within the interface from areas of low surface tension to high surface tension.⁴⁴ This mechanism, known as the Marangoni effect,^{6-7,44-45,48} contributes to a resisting force to further thinning, before equilibrium surface tension is established. Furthermore, the film must be elastic to withstand deformational breakage. This film elasticity, or Gibbs surface elasticity,^{44,48} is characterized as the change in surface tension with surface area,⁴⁴ and can be represented as:

$$E = \frac{d\gamma}{dlnA} \tag{1.3}$$

where *E* is the Gibbs elasticity, γ is the surface tension, and *A* is the surface area. The film elasticity and its ability to establish a uniform surface tension to prevent film rupture is known as the Gibbs-Marangoni effect.^{6-7,44-45,48} There are instances when film rupture occurs despite the Gibbs-Marangoni effect. For example, if the aqueous solution is dilute, there may not be enough surfactant molecules to establish a uniform surface tension that would prevent film thinning and rupture. Also, if the diffusion process is slow, a uniform surface tension may not be established before rupture occurs. Thus, foam formation is dependent on the ability of a surfactant to reduce the surface tension of a solution as well as its diffusion characteristics. Insight into the ability of surfactants to diffuse to a fresh interface can be determined through the measurement of dynamic surface tension. Once surfactant concentration rises beyond a critical concentration, called critical micelle concentration (cmc), self-assembled structures called micelles form within the solution. The equilibrium surface tension remains nearly constant above this concentration. The surface tension values, $\gamma(t)$, above cmc are additionally influenced by micellizationdemicellization kinetics and the approach to equilibrium surface tension occurs faster at higher concentration.

1.1.6 Forces in Thin Liquid Films Which Influence Foam Stability

The presence of surfactants not only influences the ability to form foam but also influences the stability of foams. Forces arise due to surfactants and aggregates, which stabilize and destabilize foams. In a foam system, adjacent gas dispersions are separated from each other by thin liquid films that are interconnected by Plateau borders,⁶ toward which the liquid will drain. After the thin liquid films drain, coalescence between the gas dispersions occurs, until complete separation of the two phases is achieved. Thus, how quickly these thin films drain is a determining factor in the lifetime and stability of foams. Depending on the characteristics of the surfactant head group, surface forces can arise during thinning, which inhibits the drainage rate. The lifetime of foam is also affected by the diffusion of gas from smaller sized bubbles to larger bubbles, leading to bubble coarsening.^{3,46} The effect is called disproportionation and is a result of a greater Laplace pressure in the smaller bubble.³

During the initial stages of foam formation, gravity is the main driving force of drainage. Bulk viscosity of the aqueous solution is a major contributor to how quickly the liquid can drain due to gravity from these initial thicker films.⁷ Thus, the addition of electrolytes and other additives that increase bulk viscosity decreases the rate of drainage during this period.⁷ Furthermore, presence of a viscous liquid crystalline phase at concentrations above the critical micelle concentration can potentially stabilize the foam by inhibiting drainage.⁷ Over time, the interface of bubbles within the foam will develop significant curvature, and a pressure difference arises across the interface. The pressure difference is represented by the Young-Laplace equation:

$$\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2}\right) \tag{1.4}$$

where ΔP is the pressure difference across the interface, γ is the surface tension, R_1 and R_2 are the radii of curvature. At the Plateau borders, the curvature of the gas-liquid interface is greater compared to the plane-parallel region, resulting in a lower pressure region within the Plateau area.⁴⁴ Pressure is higher at the plane-parallel region of the film, and this pressure difference forces liquid to flow towards the Plateau borders.⁴⁴

The lifetime of foam is dependent on the drainage rate of the thin liquid film that exists between adjacent bubbles. For aqueous solutions above the critical micelle concentration, drainage occurs through stratification, the layer by layer thinning of an ordered structure inside the thin liquid film.⁵⁵⁻⁶¹ Above the critical micelle concentration, surfactants self-aggregate to form micelles. Within the confined volume of the thin film, micelles organize into layers, forming an ordered structured due to micelle interaction via long range screened electrostatic repulsion.⁵⁸ The layering is an entropic phenomenon that occurs due to the limitations of the number of surfactants that can occupy an interface;⁵⁷ it is enhanced by the electrostatic forces, which adds a distance equal to Debye length.⁶¹⁻⁶² The micellar chemical potential is uniform across the film but changes sharply across the Plateau border, and this chemical potential gradient is the driving force of stratification.⁵⁶ During drainage, and removal of these layers, spot formation occurs due to the vacancies condensation mechanism.^{56-57,59,61} The higher chemical potential potential of the micelles within the film causes the diffusion of micelles to the meniscus,⁵⁷

As the thickness of the thin liquid film decreases to several tens of nanometers,⁶ the influence of intermolecular and surface forces between the surfactant-rich surfaces of a thin liquid film give rise to an excess pressure known as disjoining pressure, \prod , which can counterbalance the suction by the Laplace pressure gradient that influences the drainage process, and foam stability. These surface forces include attractive steric forces ($\prod < 0$) and repulsive electrostatic forces ($\prod > 0$).⁶ Thermodynamically, the disjoining pressure can be described as the negative derivative of Gibb's free energy with respect to thickness of the film and is represented in the equation:^{54,63}

$$\prod(h) = -\left(\frac{\partial G}{\partial h}\right)_{T,P,A,n} \tag{1.5}$$

A quantitative description of the forces occurring between two surfaces interacting in a thin liquid film was developed by Derjaguin, Landau, Verwey, and Overbeek (DLVO).^{54,63} The DLVO theory accounts for the electrostatic double-layer and van der Waals forces and is represented as:^{54,63}

$$\prod(h) = \prod_e + \prod_{vdw} \tag{1.6}$$

Over time, it has been shown⁶³ that the stability of thin films cannot be explained solely by the DLVO theory; other interactive forces are at play. Some of the other interactions to be accounted for include steric forces and structural forces.

Electrostatic double-layer forces occur due to the charged surfaces of interfaces in close proximity of each other. As the film thins over time, the distance between the interfaces decreases, resulting in the overlap of double-layers and effectively stronger repulsive forces. This in turn stabilizes the film against drainage and increases the time in which foams can exist. When the distance between the two interfaces equals the Debye length, another force is needed to bring the interfaces together.⁵⁴ The existence of electrostatic forces in the presence of non-ionic surfactants leads to the understanding that the air-water interface carries a charge as well. The electrostatic contributions can be represented as:

$$\prod_{e} = 64n^{0}k_{b}T\gamma^{2}exp^{-\kappa h} \qquad (1.7)$$

where n^0 is the number density of the ions, $\gamma = \frac{\exp(\frac{Z}{2}) - 1}{\exp(\frac{Z}{2}) + 1}$, $Z = \frac{e\psi_0}{kT}$, *e* is the elementary charge, and ψ_0 is the surface potential.

The van der Waals forces contribution to disjoining pressure, \prod_{vdw} , exists regardless of a compound's molecular nature. They include dipole, dipole-induced dipole, and induced dipole interactions. The latter, also known as London dispersion forces, exist between all pairs of molecules and are short acting. Dipoles are temporarily induced neutral molecules due to the orientation of the molecules and interactions between electrons and protons. The contribution of van der Waals forces to disjoining pressure is represented as:⁵⁴

$$\prod_{vdw} = -\frac{A}{6\pi h^3} \tag{1.8}$$

where *A* is the Hamaker constant, and accounts for components surrounding the thin film. For foam films surrounded by the same components throughout, the Hamaker constant is positive and a destabilizing attractive force exists.

Steric (or entropic) forces arise due to atoms having a preferred shape and taking up a certain amount of space within a molecule. As molecules approach each other, an associated energy cost exists due to overlapping electron clouds. The physical origins of these forces were outlined by Israelachvili and Wennerstroem,⁶⁴ and are classified as undulations, peristaltic, head-group overlap, and protrusions.^{54,64} Undulations are forces caused by wave-like movements at

the interface.^{54,64} Peristaltic forces are caused by the contraction and relaxation of the two interfaces.^{54,64} Head-group overlap causes steric forces due to the head-group of surfactant molecules.^{54,64} Protrusions of surfactant molecules at the interface result in a steric hindrance.^{54,64}

Structural forces exist when micelles (or other surfactant structures) are present within the thin liquid film.^{54,61} Micelles organize into layers as more surfactants are added to the solution. As the film thins, these layers are pushed out and changes in osmotic pressure occur. These changes cause an oscillatory force due to alternating regions of attraction and repulsion, and the force is represented by the approximate expression:⁶⁵

$$\prod_{os} = -k_b T \rho_s(\infty) \cos\left(\frac{2\pi h}{d}\right) exp^{\frac{-h}{d}} \qquad (1.9)$$

where $\rho_s(\infty)$ is the particle concentration in the subsurface, *h* is the film thickness, and *d* is the diameter of the particle. The expulsion of micellar layers is observed as stratifications within foam films and can occur in a stepwise fashion.

Recently Yilixiati *et al.*⁶⁶ presented a phenomenological expression to represent the influence of surfactant and salt concentration on the magnitude and decay length of the supramolecular oscillatory structural forces. The modified phenomenological expression is

$$\Pi_{os} = \frac{(c - cmc)N_A}{N_{agg}} f(\varphi)k_b T cos\left(\frac{2\pi h}{d}\right) \exp\left[\left(\left(\frac{d}{\Delta h}\right)^3 - \frac{h}{\Delta h}\right)g(\varphi)\right] \quad (1.10.a)$$

$$f(\varphi) = \frac{(1 + \varphi + \varphi^2 + \varphi^3)}{(1 - \varphi)^3};$$

$$(1.10.b)$$

$$g(\varphi) = \frac{\sqrt{2/3} + a_1\Delta\varphi + a_2(\Delta\varphi)^2}{(b_1/\Delta\varphi) - b_2}$$

where $\rho = (c - cmc)N_A/N_{agg}$ is the number density of the micelles, $f(\varphi)$ is the compressibility factor, $^{65}\Delta h$ is the step size, $g(\varphi)$ is the geometric factor, $^{67}\varphi$ is the effective volume fraction of the micelles defined as $\varphi = \rho \pi d^3/6$, $\Delta \varphi = \pi/3\sqrt{2} - \varphi$, and the parameters (defined by Kralchevsky and Denkov⁶⁵) $a_1 = 0.24$, $a_2 = 0.63$, $b_1 = 0.49$, $b_2 = 0.42$. The supramolecular oscillatory structural force model describes its contributions to the disjoining pressure by providing an estimate for the amplitude, $\rho f(\varphi) kT$, and decay length, $\Delta h/g(\varphi)$. The oscillation wavelength of the disjoining pressure curve is equated to the experimentally measured step size, as the oscillatory nature of the disjoining pressure is captured by the cosine term. The amplitude, decay length, and wavelength together describe the nature of step size and number of stepwise transition for micellar foam films. Using the model and experimental measurements of stratification, it was observed that an increase in surfactant concentration led to an increase in decay length, leading to the observed increase in stepwise transitions. Furthermore, the model, with step size measurements, shows by increasing salt concentration for a fixed surfactant concentration, the amplitude, decay length, and wavelength decreases, leading to a decrease in step size and number of stepwise transitions.

1.2 Motivation

The research described in this thesis characterizes the adsorption kinetics of sodium naphthenates and characterizes stability and drainage of aqueous foam thin films produced from them. With no published data on dynamic surface tension measurements for the surfactant, the information presented provides an eye opener to sodium naphthenate surfactants and their role in the stabilization in comparison to other naturally occurring surface active components found in crude oil. Chapter 2 presents a study on the surface adsorption properties of sodium naphthenates using the pendant drop method and maximum bubble pressure technique. Chapter 3 presents a

study on thin liquid films formed from sodium naphthenate aqueous solutions. Both chapters include theoretical background relevant to the studies, a description of the methods used, and a report of the results obtained from the analysis.

2. ADSORPTION KINETICS OF SODIUM NAPHTHENATE

2.1 Introduction

The ability for sodium naphthenate surfactants to form and stabilize foams is correlated with their adsorption kinetics. The rate at which surfactants transport to an interface, determines whether foam can form in the presence of sodium naphthenates. The transport of surfactants follows the diffusion-controlled or the mixed-kinetic diffusion adsorption kinetics. Characteristics of the surfactant molecule influence the transport, such as, whether the surfactant head group possesses a charge or not. The elastic characteristics of a resulting interface, populated by sodium naphthenates, capture the ability of the surfactant to stabilize foam. While critical micelle concentration has been measured for sodium naphthenate aqueous solutions, ^{15,37,68} there have been no reported attempts to characterize how sodium naphthenates transport to an interface to the best of our knowledge.

2.1.1 <u>Method for Surface Tension Measurements</u>

The transport of surfactants, dynamic adsorption, and Gibbs elasticity of the resulting interface can be characterized through a variety of tensiometry methods used for measuring surface tension of solutions.^{49,69} Dynamic surface tension measurements follow the change in surface tension over time brought about by variation in interfacial concentration that, in turn, depends on the rate of diffusion and adsorption of surfactant molecules. The transport of surfactants from the bulk to a freshly formed interface requires time and a freshly created interface that displays a surface tension value close to the solvent used. As surfactants begin populating the interface, the value of surface tension decreases over time, and an equilibrium surface tension is reached after the interfacial concentration reaches equilibrium with the bulk concentration. Equilibrium surface tension represents the point at which surface tension value

reaches a constant value. Methods for measuring dynamic and equilibrium surface tension can be categorized into five classes:⁶⁹

- 1. Direct measurement using a microbalance
- 2. Measurement of capillary pressure
- 3, Analysis of capillary-gravity forces
- 4. Gravity-distorted drops
- 5. Measurement of a distorted drop

Wilhelmy plate^{49,70} and Du Noüy ring⁷⁰ methods incorporate direct measurement of surface tension using a microbalance. The plate or ring is brought into contact with the interface and is completely wetted by the liquid. The liquid will climb up the probe, resulting in a capillary force that pulls the probe towards the interface.^{69,71-72} The capillary force is measured through a microbalance that is connected to the probe, and surface tension is calculated using an equation that relates it to the measured force:⁴⁹

$$\gamma = \frac{F}{pcos\theta} \tag{2.1}$$

where *F* is the measured force, *p* is the wetted perimeter, and θ is the contact angle between the liquid and probe. The wetted perimeter is dependent on the dimensions of the probe. For a plate,⁶⁹ p = 2w + 2d, whereas for a ring, $p = 4\pi r$.

A method to determine surface tension through capillary-gravity forces is the capillary rise method.⁴⁹ The height of a meniscus within a cylindrical glass tube, with known inner radius, is measured. If the inner radius is much smaller than the height of the meniscus, surface tension can be calculated using:^{49,73}

$$\gamma = \frac{\Delta \rho g h r}{2 cos \theta} \tag{2.2}$$

where $\Delta \rho$ is the difference in density between air and the liquid, *g* is gravity, *h* is the height of the meniscus, *r* is the inner radius of the glass tube, and θ is the contact angle of the meniscus. Drop weight method also falls within the classification, and involves measuring the weight of droplets as they slowly drip from a capillary.⁷⁴ Surface tension is determined using Tate's law:^{49,74}

$$\gamma = \frac{Wg}{2\pi r} \tag{2.3}$$

which approximates the balance between gravitational and surface tension forces acting on the droplet just before it detaches from the capillary. W is the weight of the droplets, g is gravity, and r is the radius of the capillary tip.

The spinning drop technique is a method of obtaining surface tension by measuring the reinforced distortion of a drop. The method involves suspending a gas bubble in a liquid under rotation in a horizontal tube, spinning about its longitudinal axis.^{69,75} As the rotational velocity, ω , is increased, the bubble adopts a cylindrical shape. By measuring the radius of the cylindrical shape, surface tension can be calculated using:^{70,75-76}

$$\gamma = \frac{1}{4}r^3 \Delta \rho \omega^2 \qquad (2.4)$$

where *r* is the radius of the cylindrical bubble, $\Delta \rho$ is the difference between the density of the liquid and density of air, and ω is the rotational velocity.

Determining which method to use for surface tension measurements requires a critical understanding of the typical timescale of the diffusion and adsorption process in comparison with time resolution of each method. Pendant drop and direct measurement of surface tension using a microbalance are sufficient in obtaining equilibrium surface tension measurements⁶⁹ for systems that take hours to days before reaching equilibrium. However, many typical methods prove to be unsuitable for measuring dynamic surface tension, $\gamma(t)$, for small molecular surfactants due to the inability to measure transport processes that occur within milliseconds. It has been reported that the time scale for the methods reviewed above spans from seconds to days.⁶⁹ In contrast, maximum bubble pressure technique (MBPT) allows for the pressure inside a bubble to be precisely and continuously measured during the formation and detachment from a capillary tip.⁶⁹ The exclusive ability to monitor pressure at the very beginning of bubble formation permits dynamic surface tension measurement over a range of growth rates^{51,69} and measurement of dynamic surface tension of surfactant solutions in the short time range down to milliseconds.^{51,77-79} Therefore MBPT is ideally suited for measuring dynamic surface tension of sodium naphthenate aqueous solutions, which adsorb to an interface relatively quickly (we report measurements for timescale < 50 ms).

2.2 <u>Method</u>

2.2.1 <u>Maximum Bubble Pressure Technique</u>

A gas-liquid interface is deformed and gains curvature during bubble growth from a capillary tip in a solution. The pressure difference across the interface due to surface tension can be computed using the Young-Laplace equation.⁴⁹ As the radius of curvature of the gas-liquid interface becomes smaller, the pressure difference across the interface increases. A maximum pressure is achieved when the radius of the bubble and capillary are equal (Figure 2, Label II), before the bubble detaches from the capillary (Figure 2, Label III) and pressure reduces back to the ambient pressure. The total time taken for bubble growth and detachment is called the



Figure 2. Pressure evolution over time as a function of bubble radius. (a) A typical pressure curve during the lifetime of one bubble for 0.1 wt.% Nan at a flowrate of 0.1 mL/min. (b) The cycle of bubble growth is as follows: Bubble growth begins as it emerges from the capillary and curvature radius, \mathbf{R} , is large (I). The bubble grows, and the curvature radius decreases to a minimum value equal to the radius of the capillary, \mathbf{R}_c , at which maximum pressure is measured (II). The bubble continues to grow as the curvature radius increases until the bubble detaches (III), followed by a decrease in pressure.

bubble lifetime, t_a , and is influenced by the flowrate chosen. Surface age represents the period of growth from the start of bubble formation to when the radius of the bubble is equal to the radius of the capillary and maximum pressure is reached.⁷⁸ Dead time follows until the bubble detaches from the capillary, as the pressure decreases from the maximum.^{78,80} When the bubble at the tip of the capillary is spherical in shape, the radii of curvatures in the Young-Laplace equation are equal, and the equation becomes:⁴⁹

$$\Delta P = \frac{2\gamma}{R} \tag{2.5}$$
where ΔP is the difference between the maximum pressure and a correction factor that arises. Taking into account the hydrostatic force, the final Young-Laplace equation for determining surface tension becomes:⁸⁰

$$P = \frac{2\gamma}{R_c} + \rho g H + \text{correction factor} \qquad (2.6)$$

where γ is the dynamic surface tension, *R* is the capillary radius, ρ is the solution density, $g = 9.8 \text{ m/s}^2$, *H* is the depth of the capillary tip in the solution, and the correction factor corrects for the system pressure and sensor calibration. By measuring the maximum bubble pressure during bubble formation, dynamic surface tension values can be determined⁶⁹ using Equation 2.6.

While there are commercial MBPT tensiometers available (Bubble Pressure Tensiometer BP50 from KRÜSS GmbH and Maximum Bubble Pressure Tensiometer BPA1S from SINTERFACE Technologies), an in-house MBPT instrument (Figure 3), built and developed by the research group, was utilized. The instrument incorporates a three-way valve as a bridge between a capillary (r = 0.13 mm), 20 cc syringe (d = 19.49 mm), and pressure transducer (OMEGA). Bubbles were produced within a solution at a constant flow rate using a syringe pump (Harvard Apparatus PHD 2000), and pressure measurements were recorded through a software program (DaqView) throughout the formation of bubbles. Pressure readings were transferred from the software onto an Excel sheet before being uploaded into a MATLAB code developed by Theodore Walker, an undergraduate research assistant. The code was used to convert the pressure readings into dynamic surface tension values.

Fifty milliliter plastic bottles were used to contain the solution to be measured and a closed system was achieved using paraffin film. Before measuring the pressure during bubble formation, a calibration run was performed to determine a correction factor for the pressure



Figure 3. Maximum bubble pressure technique set-up. (a) Schematic of the instrument where a three-way valve connects a syringe, capillary, and pressure sensor. The data acquisition component obtains pressure measurements from the sensor and passes it to the DaqView software on the computer. (b) Schematic showing the capillary submerged in the solution at a depth, *H* (see Figure 2), which is measured manually.

transducer, and to ensure the system was closed. The correction factor accounted for the difference between the assumed atmospheric pressure by the transducer and ambient pressure of the lab. The calibration run was performed by lowering the steel capillary into the bottle, just above the solution, so that the capillary tip was exposed to the open air of the system. The DaqView software was initiated to record the ambient pressure for thirty seconds. The average pressure of the first run was recorded before stopping the software. A second run was immediately initiated to confirm the average pressure determined in the first run. If the average pressure of the second run was within \pm 5.5 Pa of the first run, the value of the first run was used as the correction factor. Upon completion of the calibration run, the capillary tip was submerged

into the solution at a fixed height. An increase in pressure was observed when the DaqView software was allowed to continue running during this step, due to hydrostatic pressure of the system.

A flowrate was manually entered, and the syringe pump was started, introducing air flow into the solution. When air flow is introduced into a solution, aerodynamic and hydrodynamic resistance⁸⁰ must be accounted for if the effects are to be significant. Aerodynamic resistance occurs as air flows through the capillary, and arises due to an excess pressure between the capillary tip and bubble at initial growth.⁸⁰⁻⁸¹ Hydrodynamic effects account for the viscous resistance of liquid against a moving bubble.⁸⁰⁻⁸¹ For the system studied, both effects were neglected due to the use of relatively low flow rates and the use of solutions with relatively low viscosity. The flowrates used in the study ranged from 0.1 - 10 mL/min, going up in increments of 0.1 mL/min between the range of 0.1 - 1.0 mL/min, and in increments of 0.5 mL/min for flowrates above 1.0 mL/min. As air flowed through the capillary, bubbles began forming at the tip. Once bubble formation occurred at a constant rate the software was initiated to observe pressure-time measurements. When the measurements were consistent between each bubble formation (maximum pressure and bubble lifetime values were nearly constant), sixty seconds worth of data was collected. This was repeated a second time, so that at least two runs were taken for each flowrate used. The data collected in the DaqView software were transferred to an Excel file and saved for analysis. Measurements were performed at room temperature $(22 - 25^{\circ}C)$.

2.2.2 <u>Maximum Bubble Pressure Code</u>

To analyze the data, a MATLAB code developed by Theodore Walker, an undergraduate research assistant, used the raw pressure-time data from the Excel sheet to extract surface age and surface tension at the point of maximum pressure during bubble formation. The user input

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known values into the code, including the submerged height and radius of the nozzle, gravity, density of the solution, and the correction factor that was determined during calibration. The code searched within the initial few seconds (a time interval that can be customized by the user) of the pressure-time data to determine the minimum pressure value within the interval. The value input by the user, to customize the initial time interval to be analyzed, represented a fraction of the total time in which data were collected. Thus, if a minute's worth of data were collected, and the value was set to 0.1, the first six seconds of the data would be used to obtain the minimum pressure.

The first few data points following the initial minimum (and every minimum and maximum point thereafter) were skipped because they give rise to error as the steady periodic bubble formation is established after some delay. The number of data points skipped after the initial minimum can be modified by the user. The code proceeds through the data set in increasing time, comparing each data point one at a time. When the code encounters a data point that is greater in pressure compared to the previous data point, it must be determined whether the true maximum is nearby. To resolve this, the code (1) determines the average pressure for all data points between the initial minimum and the current data point, (2) determines the average pressure for all data points within a range (set by the user) between the current data point and future data point, and (3) compares the average pressure between the two intervals. If the average pressure of the initial interval (1) is less than the average pressure of the future interval (2), the data is still trending upwards and a maximum pressure has not been reached. Conversely, if the initial interval is greater than the future interval, the data is trending downwards, and a maximum pressure must exist in the future interval. The code then determines the maximum pressure value on the future interval and stores the pressure-time coordinates as a maximum. Starting at the

maximum, the code then proceeds in a similar but modified fashion as it looks for the next minimum.

This interval between the current and future data point is set by the user through a value that acts as a multiplier that defines how many data points ahead of the current point to go. For example, if twenty points were analyzed between the last maximum and current point, the code would look twenty data points into the future. If the value were set to two, the code would look at the next forty data points following the current data point. The code continues recording the coordinates for determined maximums and minimums throughout a set fraction of the data points, which can be altered. From these collected data points, the surface age and surface tension can be determined using the modified Young-Laplace equation (Equation 2.6) and known values that were input into the code.

2.2.3 Pendant Drop Tensiometry

The pendant drop tensiometry method (measurement of surface tension from the shape of a gravity-distorted drop) was used to measure equilibrium surface tension through an in-house instrument built and developed by the research group (Figure 4). Before taking measurements of the sample, a calibration run was performed by measuring the surface tension of deionized water, which also ensured that the Teflon nozzle (d = 0.162 cm) was clean. Deionized water was withdrawn into the nozzle, which was fixed onto a steel capillary that was attached to a 20 cc syringe. The nozzle was inserted into a closed glass cuvette with a reservoir of water at the bottom to prevent evaporation effects. The cuvette was placed on a stage (Velmex, Inc.), which could be manually adjusted in the xyz-direction to aid in focusing the image. A drop was created manually and was illuminated by a white light source with a diffuser attachment to achieve monochromatic images that were captured using a DSLR camera (Nikon D5200) mounted on a



Figure 4. Pendant drop tensiometer set-up. A pendant drop is produced within a cuvette using a syringe pump, which allows control of drop volume. A light source with diffuser illuminates the drop and images are taken over time using a DSLR camera. Software is used to collect the images for analysis.

tripod. A macro-lens camera attachment was used to magnify the drop during imaging. The stage and tripod were manipulated so that the drop and nozzle tip were visible within the image. Once the drop was in focus, the digiCamControl software was initiated and set up to capture nine images over a period of ninety seconds, the same amount of time to be used for samples. The images were uploaded to a MATLAB code, developed by the research group, to determine the surface tension over the specified time range. If measurements were within the surface tension value of water ($\gamma = 72 \pm 0.5$ mN/m), calibration was complete. Deionized water was removed from the nozzle, and the nozzle was allowed to dry before sample solutions were tested. Sample solutions were loaded into the nozzle and set up as previously explained. An extra step was taken by mounting the syringe onto a syringe pump (New Era Pump Systems, Inc. NE-1000 Programmable Single Syringe Pump), to ensure that pendant drops of relatively consistent volume were created between each trial for sample solutions. The desired volume of the pendant drop was controlled through a fill volume input option in the pump system. The drops created at the nozzle tip took on a pendant shape due to the interplay of surface tension and gravitational effects. Images of the pendant drop were captured over a minute and stored for analysis. Three trials were performed at room temperature $(22 - 25^{\circ}C)$ for each concentration to ensure consistency of measurements and new nozzles were used for each concentration to prevent cross-contamination. Calibration of the instrument was performed each time a new nozzle was used.

Still images of the pendant drop shape were analyzed through an axisymmetric drop shape analysis (ASDA) code developed by the ODES-lab (compiled by Yiran Zhang), similar to the one developed by Hoorfar and Neumann.⁸² The analysis used the Young-Laplace equation due to a pressure difference across the interface of the curved drop. Accounting only for gravitational forces, the pressure difference across the interface of the droplet can be described as:^{49,83}

$$\Delta P = \Delta P_0 + (\Delta \rho)gz \qquad (2.7)$$

where ΔP_0 is the pressure difference at the apex of the drop, *z* represents the vertical coordinate of the drop, and $\Delta \rho$ is the difference in density between the droplet and its surrounding. By relating the Young-Laplace equation to Equation 2.7, an equation can be obtained that describes the shape of a pendant drop:⁴⁹

$$\gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = \Delta P_0 + (\Delta \rho)gz \qquad (2.8)$$

Assuming that the interface is symmetric about the z-axis, R_1 is characterized by the change in arc length and change in the angle of inclination of the interface to the horizontal (Figure 5):⁸²⁻⁸³



Figure 5. Pendant drop with curvature as defined per axisymmetric drop shape analysis. $\frac{1}{R_1}$ is represented by the curves in the vertical direction and $\frac{1}{R_2}$ is represented by the curves in the horizontal direction.

$$\frac{1}{R_1} = \frac{d\Phi}{ds} \tag{2.9}$$

The other radius of curvature, R_2 , is characterized as:

$$\frac{1}{R_2} = \frac{\sin\phi}{x} \tag{2.10}$$

With the assumption that the interface is axisymmetric at the interface, the curvature at the apex of the droplet is constant in all directions.⁸² Thus, the pressure difference at the apex can be assumed spherical and is represented as:

$$\Delta P_0 = 2b\gamma \qquad (2.11)$$

$$b = \frac{1}{R_1} = \frac{1}{R_2} = \frac{1}{R_0}$$
(2.12)

$$\frac{d\Phi}{ds} = 2b + cz - \frac{\sin\Phi}{x} \qquad (2.13)$$

$$c = \frac{(\Delta \rho)g}{\gamma} \tag{2.14}$$

Two geometrical relations are defined to characterize the outline of the drop shape:⁸²

$$\frac{dx}{ds} = \cos\phi \qquad (2.15)$$
$$\frac{dz}{ds} = \sin\phi \qquad (2.16)$$

(2.16)

Equations 2.13, 2.15, and 2.16 represent three first order differential equations that define the shape of a drop and can be solved simultaneously to determine the surface tension of the drop from image analysis.

2.2.4 Pendant Drop Tensiometry: Description of Algorithm and Code Used for Obtaining **Surface Tension Value**

An image or a set of images is uploaded to the MATLAB code developed by the research team, and each image contains the information needed for the analysis, in the form of pixels. By obtaining a monochromatic image of the drop, the pixel values, defined as the intensity, are simplified to 256 gray levels, which represent the image where 0 represents black and 255 represents white.⁸² Through this, an image can be represented numerically by an array of real numbers⁸² from 0 to 255. First, the drop profile of an image is determined through a canny edge detection method built into the software.

The canny edge detection is an algorithm that employs five different steps to detect and define the edge of an image. The first step of the edge detector applies a Gaussian filter that smooths the image, removing noise in the process. A convolution kernel is generated following a Gaussian function, with the highest value falling in the center. The value of sigma represents the variance in the values of the kernel from the center, and a higher sigma value provides a more blurred image. The kernel is convolved with the image and returns a value for the pixel lying in the center of the kernel. The new values result in a blurred image, eliminating noise surrounding the edges. Different sized kernels can be used, with smaller kernels having higher detection sensitivity, but taking more time to run. Next, the intensity gradients of the image are determined. The image gradient is defined as the directional change in the intensity (or color) in an image. Four filters are used to detect the horizontal, vertical, and diagonal edges in a blurred image. The filters are matrices of a certain size and return values for the change in the horizontal direction, G_x , and vertical direction, G_y . G_x and G_y can be imagined as two sides of a right-triangle, thus the edge gradient can be calculated as the hypotenuse:

$$G = \sqrt{G_x^2 + G_y^2}$$
 (2.17)

The direction of the gradient can be calculated using:

$$\theta = \arctan\left(\frac{G_y}{G_x}\right) * \frac{180}{\pi}$$
 (2.18)

with θ being rounded to one of four angles representing the vertical, horizontal, and two diagonal directions (0°, 45°, 90°, 135°). For the case when $G_x = 0$, 1 or a smaller number can be substituted in. Once the intensity gradients are estimated, the edges are thinned using a non-maximum suppression technique, which suppresses gradients to zero except for the local

maximal, which is generally characterized as the location with the sharpest change in intensity value. The technique compares the edge strength of a pixel with the edge strength of the surrounding pixel in the positive and negative gradient directions. If the edge strength of the pixel is the largest in comparison to the other pixels, it will be kept. Otherwise, the pixel is suppressed. At this point, edge pixels due to noise should be mostly removed. To remove remaining noise, edge pixels are filtered as weak gradient or high gradient values using high and low threshold values, which are defined to differentiate between the two types of pixels. Edge pixels with gradient values higher than the high threshold are marked as strong edge pixels, whereas edge pixels with gradient values falling between the high and low threshold are marked as weak edge pixels. Edge pixels with gradient values below the low threshold are suppressed. Once the edge pixels are filtered as strong or weak edge pixels, the final step can be applied to suppress the weak edge pixels that are a result of noise and keep those which are a result of the true edge. To differentiate between the causes of the weak edge pixel, a weak edge pixel resulting from the true edge is connected to a strong edge pixel and weak edge pixels not connected are a result of noise. The edge connection is tracked by comparing a weak edge pixel with the pixels connecting to it. If there is one strong edge pixel connected, the weak edge pixel is preserved.

The code developed by the lab allows for the variation of two variables to improve edge detection. The high threshold applied to differentiate between strong and weak edge pixels, can be modified. For images that do not return the full edge of the drop profile, this value can be increased to improve the edge detection. The second variable that can be modified includes a command that eliminates pixels less than the value provided. Increasing the value improves edge detection for incomplete drop profiles. Once the edge detection method is applied, the image is

reduced to an edge profile of the drop and is shifted to the origin of a coordinate system represented in pixels.

The theoretical Laplacian curves that are to be generated will follow units of length. Thus, a calibration between pixels and units of length is necessary to compare the experimental profile to the theoretical profile. This is achieved by measuring the outer diameter of the nozzle used to create the drop and inputting that value into the code. During the procedure of uploading the image to the code, two points (near the top and bottom) on the nozzle are chosen. The distance between the edges of the nozzle at these two points is determined using lines of the same slope at the two points. The average distance in pixels is determined and coincides with the input outer diameter of the nozzle, allowing for the calibration between pixels and unit of length (defaulted to meters in the code).

The determination of surface tension of a droplet from an image is contingent on fitting a theoretical Laplacian curve to the experimental profile of the drop. The initial Laplacian curve is generated by calculating initial values of b and c, and incorporating them into the three first order differential equations (Equations 2.14 to 2.16), which are solved simultaneously. The initial value of c is solved using values initially input into the code. These values include the density of the drop, the density outside the drop (air), gravity, and an initial guess for surface tension. To solve the initial value of b, the radius of curvature at the origin needs to be determined. This is done by shifting the experimental drop profile to the origin and fitting a circle to the drop at the origin. Once an initial Laplacian curve is generated, the difference between it and the experimental drop profile is calculated as the absolute value of closest distance between a Laplacian point and experimental point. Multiple error values are calculated for different points on the drop profile and summed together.

2.3 <u>Materials</u>

Sodium naphthenates used in the study were obtained from TCI America and used as received. Twelve solutions of concentrations, ranging from 0.1 - 50.0 wt.%, were prepared by dissolving a predetermined amount of sodium naphthenate in deionized water and stored within 50 mL plastic bottles. The amount of sodium naphthenate needed to make a desired concentration was determined using the equation

$$wt.\% = \frac{weight of sodium naphthenate (g)}{total weight of solution (g)} \quad (2.19)$$

assuming the density of water was 1.00 g/mL. To prevent formation of foams during preparation, samples were placed on a rotary mixer to be gently mixed for 24 hours and allowed to sit undisturbed for an additional 24 hours. Densities of the solutions were calculated using a reported⁸⁴ sodium naphthenate density value of 1.059 g/mL. The amount of sodium naphthenate and deionized water used for each concentration is reported in Table I, along with the calculated density of each solution. The calculated densities were essential in calculations to determine dynamic and equilibrium surface tension. The naphthenate salts as received were yellow in color. As a result, shades of yellow were observed to be more prominent as more sodium naphthenate was added (e.g., solutions for 45 and 50 wt.% concentrations were dark yellow). It was also apparent that the solutions became more viscous with increasing concentration and were also observed to be almost gel-like in 45 and 50 wt.% concentrations.

2.4 <u>Results and Discussion</u>

2.4.1 Foamability and Stability of Sodium Naphthenate Aqueous Solution

Figure 6 shows that surface age decreases with increasing bubble frequency for a fixed concentration, indicating dynamic surface tension measurements at shorter time are achieved by

TABLE I

AMOUNT OF SODIUM NAPHTHENATE AND DEIONIZED WATER USED FOR
EACH CONCENTRATION OF SODIUM NAPHTHENATE AQUEOUS SOLUTION
AND CALCULATED DENSITIES

Concentration (wt.%)	Sodium Naphthenate (g)	Deionized Water (mL)	Density (g/mL)
0.1	0.0404	40	1.00006
0.3	0.1353	45	1.00017
0.5	0.2262	45	1.00028
0.8	0.3629	45	1.00045
1.0	0.4042	40	1.00056
3.0	1.392	45	1.00167
5.0	2.368	45	1.00279
8.0	3.478	40	1.00448
10.0	5.000	45	1.0056
30.0	12.86	30	1.017
45.0	20.42	25	1.02569
50.0	20.00	20	1.02865



Figure 6. Comparison of pressure measurements between different flowrates. As the flowrate is increased, formation of bubbles becomes quicker as observed by the surface age, t_{age} . Maximum bubble pressure also increases.

increasing flowrate. Furthermore, an increase in maximum pressure is correlated with a higher surface tension, and higher maximum pressure values are obtained at faster flow rates (as shown in Figure 7). The increase in maximum pressure for initial flowrates is not drastic, indicating that the adsorption process is more prominent within the initial range of flowrates. Beyond the critical flow rate (which is concentration dependent), a drastic increase in maximum pressure is observed. As a drastic increase in maximum pressure occurs, bubble formation transitions from periodic to aperiodic. Other studies have reported similar observations, as bubble formation transitions from transitions from a bubbling regime to a jetting regime, indicative by a critical flow rate.^{79-80,85-87} During the jetting regime, complications from dynamic effects arise in periodic bubble growth,



Figure 7. Pressure vs. Flowrate plot. Plotted for 0.1 wt.%, 0.3 wt.%, 0.5 wt.%, 0.8 wt.%, and 1.0 wt.% NaN. The transition from bubble flow regime to the jetting regime is seen by the sharp increase in maximum pressure.

and include "hydrodynamic processes" that take place in the gas and liquid phases, "inertial properties" of the gas and liquid media, and "gas compressibility".^{77, 79, 87} Because of the errors that arise due to aperiodic bubble in this regime, analytical data for values above the critical flow rate are neglected.

According to Rosen^{7,88} a typical dynamic surface tension curve can be divided into four different regions, an (i) induction region; (ii) rapid fall region; (iii) meso-equilibrium region; and (iv) equilibrium region. The first three regions are important for systems where mass transport to the interface occurs quickly.⁸⁸ The induction region represents a range of time during the early stages of bubble formation. Diffusion from the bulk to the subsurface dominates and the interface is bare of surfactants, with little change to surface tension. The rapid-fall region covers the range of time when surfactant population at the interface increases. A rather rapid decrease of surface tension is observed. The meso-equilibrium region represents a delay in achieving equilibrium surface tension and can arise due to an adsorption barrier near or at the interface. The fourth region occurs when surfactant population at the interface equilibrates and equilibrium surface tension is achieved. From the log(t) plot of raw dynamic surface tension measurements (shown in Figure 8b), it is apparent that only the end of the rapid fall region is observed for 0.1 and 0.3 wt.% concentrations. The meso-equilibrium region is observed for all concentrations studied. Dynamic surface tension curves of sodium naphthenate show a decrease in surface tension, $\gamma(t)$, with apparent surface age, t_a . Apparent surface age is the adsorption time measured using the in-house MBPT set-up without taking into consideration an expanding interface. The rate of decrease was more pronounced with increasing concentration, as diffusion to the subsurface occurs within milliseconds. Adsorption from the subsurface to the interface is



Figure 8. Raw dynamic surface tension for sodium naphthenate aqueous solutions. (a) Plotted against apparent surface age, t_a and (b) plotted against log t. The rapid fall and meso-equilibrium region are observed.

observed to take longer than the diffusion process, suggesting that a mixed-kinetic diffusion model should be used for analyzing these datasets.

The electrostatic double layer that arises due to the characteristics of sodium naphthenate surfactants, alters the adsorption process to the interface. As charged surfactants populate the interface, an increase in surface charge density and electric potential occurs, repelling surfactant molecules transporting from the bulk solution, and decelerating the adsorption process. Because of this, diffusivity for the sodium naphthenate system could not be treated by the traditional Ward and Tordai equation,⁸⁹ which only accounts for dynamic adsorption by nonionic surfactants. For sodium naphthenates, a diffusion model must account for two adsorbing species, including the naphthenate ions and the sodium counterions. The diffusion model must also account for an expanding fluid interface that occurs during bubble growth when using the maximum bubble pressure technique. Danov *et al.*⁵² formulated an asymptotic expression for dynamic surface tension to account for the two adsorbing species and an expanding interface:

$$\gamma = \gamma_{eq} + \frac{s_{\gamma}}{t_{age}^{\frac{1}{2}}}$$
(2.24)

 $\gamma(t)$ is the surface tension at a particular time point, γ_{eq} is the equilibrium surface tension, s_{γ} is the slope parameter for an immobile interface, and t_{age} is the surface age. Under the assumption that counterions are the same and that the valence of the surfactant ions and counterions are opposite in sign, the concentrations of the different species can be determined through the convective diffusion and Poisson equation. The equations account for the inner region, which accounts for a quasi-static electric double layer with a narrower length scale than the outer region. The electroneutral outer region is accounted for by adsorption equations for the surfactant ion and counterion. By applying these equations to the Gibbs adsorption equation to account for the time dependent surface tension, Danov *et al.* derived:⁵²

$$s_{\gamma} = \frac{kT\Gamma_{1,eq}^{2}\lambda}{\left(\pi D_{eff}\right)^{\frac{1}{2}}\gamma_{\pm}} \left(\frac{1}{c_{1\infty}} + \frac{1}{c_{2\infty}}\right) \quad (2.25)$$
$$\frac{1}{D_{eff}} = \frac{1}{2} \left(\frac{1}{D_{1}} + \frac{1}{D_{2}}\right) \quad (2.26)$$

where k is the Boltzmann constant, T is the absolute temperature, $\Gamma_{1,eq}$ is the equilibrium surfactant adsorption, λ is the dimensionless apparatus constant of the maximum bubble pressure technique instrument that can be determined in calibration experiments,⁷⁸ D_{eff} is the effective diffusivity, which depends on concentration of surfactant and salt, γ_{\pm} is the activity coefficient, $c_{1\infty}$ is the bulk surfactant concentration, and $c_{2\infty}$ is the bulk concentration of counterions.

The raw dynamic surface tension curves, for time range of milliseconds (10 ms) up to 4 seconds, were fit (as shown in Figure 9) to Equation 2.24. Raw dynamic surface tension data for a given concentration provided values for surface tension, meso-equilibrium surface tension



Figure 9. Dynamic surface tension fit using asymptotic expression. Results of sodium naphthenate aqueous solutions represented by symbols and the lines represent the fit obtained from the asymptotic expression from Equation 2.24.

(Figure 10), and surface age. These values were plugged into the asymptotic expression (Equation 2.24) to solve for the slope parameter, unique to the concentration, and an average slope parameter value was calculated. The calculated average slope parameter value was used with the known meso-equilibrium surface tension and experimental surface ages to construct dynamic surface tension curves for the diffusion and adsorption processes. Slope parameters for the range of concentrations studied are reported in Table II. In order to compare the measurements from our MBPT set-up with other tensiometers and account for an expanding interface, the universal surface age is determined:

$$t_u = \frac{t_{age}}{\lambda^2}$$

where t_{age} is the experimental apparent time determined from the MBPT set-up and λ is the dimensionless apparatus constant ($\lambda = 2.47 \pm 0.22$) determined by Uribe-Ortiz.⁹⁰ In comparing



Figure 10. Meso-equilibrium surface tension plotted against concentration. Plotted for range 0.1 wt.% - 50.0 wt.%, cmc is indicated by the concentration at which surface tension no longer changes with increasing concentration. The size of the symbols is equal to the size of error or less.

TABLE II.

AVERAGE SLOPE PARAMETER VALUES CALCULATED FOR THE RANGE OF CONCENTRATIONS USING MESO-EQUILIBRIUM SURFACE TENSION VALUES FROM DYNAMIC SURFACE TENSION RAW DATA

Concentration (wt.%)	Meso-equilibrium Surface Tension (mN/m)	Sγ
0.1	44.74 ± 0.15	2.34
0.3	36.22 ± 0.03	0.65
0.5	34.91 ± 0.05	0.32
0.8	33.24 ± 0.05	0.19
1.0	31.89 ± 0.01	0.21
3.0	32.01 ± 0.07	0.60
5.0	31.76 ± 0.06	0.39
8.0	31.04 ± 0.10	0.13
10.0	31.40 ± 0.09	0.12
30.0	31.86 ± 0.03	0.16
45.0	31.74 ± 0.01	0.27
50.0	31.82 ± 0.11	0.52

Figure 11 to Figure 9, we observe that the dynamic surface tension data is shifted to the left on the graph. This shift is in part due to universal surface age accounting for interfacial expansion, which makes the bubble surface younger.⁷⁸ Calculating universal surface age for dynamic surface tension curves of sodium naphthenate aqueous solutions, allows for comparison between any future dynamic surface tension curves obtained using other tensiometers, as it is independent of the tensiometer used and its specific apparatus function.⁷⁸

The adsorption rate of sodium naphthenate surfactants are compared to surfactants studied by Fainerman, who measured dynamic surface tension curves for several ionic surfactants (including sodium tetradecyl sulfate, sodium dodecyl sulfate, and sodium decyl sulfate) at room temperature using a similar maximum bubble technique.⁹¹ The adsorption rate of sodium naphthenates appears to be quite similar to sodium decyl sulfate, which reached mesoequilibrium within milliseconds.⁹¹ In contrast with adsorption rate of sodium tetradecyl sulfate and sodium dodecyl sulfate rate of adsorption is much slower, reaching meso-equilibrium within



Figure 11. Dynamic surface tension of sodium naphthenates from MBPT with universal surface age. Plots comparing (a) raw data and (b) data fit using the asymptotic expression and accounting for universal surface age. It is observed that the dynamic surface tension data is shifted to the left, as the bubbles have shorter surface age than measured.

minutes and seconds, respectively.⁹¹ In comparing concentrations of the surfactants and mesoequilibrium surface tension, it is determined that sodium naphthenates reach a lower mesoequilibrium at comparable concentrations of the surfactants studied by Fainerman.⁹¹

2.4.2 <u>Equilibrium Surface Tension and Critical Micelle Concentration of Sodium</u> Naphthenate Aqueous Solutions

From the pendant drop analysis, equilibrium surface tensions were obtained for the range of concentrations examined and reported in Table III. An increase in concentration coincides with an increase in surfactant population at the interface. At 1.0 wt.% concentration and above, equilibrium surface tension values are relatively the same, indicating the interface is completely populated by sodium naphthenate surfactants. The concentration, at which equilibrium surface tension becomes relatively constant with increasing concentration, is known as the critical micelle concentration.⁴⁹ Due to complete coverage of the interface, remaining surfactants within the bulk begin to spontaneously self-aggregate into micelles.

TABLE III

AVERAGE EQUILIBRIUM SURFACE TENSION VALUES MEASURED FOR EACH CONCENTRATION USING THE PENDANT DROP INSTRUMENT

Concentration (wt.%)	Equilibrium Surface Tension (mN/m)
0.1	43.66 ± 0.25
0.3	36.22 ± 0.14
0.5	33.28 ± 0.13
0.8	31.18 ± 0.07
1.0	30.27 ± 0.05
3.0	30.57 + 0.05
5.0	30.81 ± 0.04
8.0	30.11 ± 0.11
10.0	30.47 ± 0.04
30.0	30.78 ± 0.15
45.0	30.47 ± 0.05
50.0	29.99 ± 0.10

By plotting the concentration against the coinciding equilibrium surface tension (Figure 12), the critical micelle concentration is determined to occur at a concentration of $c_{cmc} = 1.0$ wt.%. Surface tension was $\gamma = 30.27 \pm 0.05$ at critical micelle concentration, and equilibrium surface tension values above the critical micelle concentration are about the same. The critical micelle concentration obtained in this study is in good agreement with past findings. In three separate studies, ^{15,37,68} the critical micelle concentration was determined to be $c_{cmc} = 1.0$ wt.%. Moran and Czarnecki³⁷ and Mirmontazeri *et al.*⁶⁸ obtained surface tensions of $\gamma = 30.9 \pm 0.8$ mN/m and $\gamma = 30.8$ mN/m, respectively. The surface tension at critical micelle concentration for Gao *et al.*¹⁵ was $\gamma = 31.0$ mN/m. Moran and Czarnecki reported a critical micelle concentration of $c_{cmc} = 0.1$ wt.% (and surface tension of $\gamma = 26.8$ mN/m) from a previous study. Differences in



Figure 12. Equilibrium surface tension results plotted vs. concentration for the range 0.1 wt.% - 50.0 wt.%. The plot compares measurements of equilibrium surface tension between the pendant drop analysis (close symbols) and maximum bubble pressure technique (open symbols).

reported critical micelle concentrations for sodium naphthenates is most likely due to variance between naphthenates from source to source. Sodium dodecyl sulfate, a well-known and often used surfactant in the industry,⁹² possesses a critical micelle concentration^{1,93-94} of ~8.3 *mM*, with surface tension of 36 mN/m at critical micelle concentration¹. Cetrimonium bromide, a surfactant common in the medical industry, possesses a critical micelle concentration⁵⁵ of 0.9 mM, with surface tension of $\gamma = 37$ mN/m at critical micelle concentration. In comparison with sodium naphthenates, it is clear that formation of micelles in sodium dodecyl sulfate and cetrimonium bromide occur at a lower concentration. Despite this, sodium naphthenates tend to have a lower critical micelle surface tension.

The surface excess concentration, Γ , represents the surface concentration of surfactants at the interface relative to surfactant concentration in the bulk^{6,15} and can be estimated using the Gibbs adsorption isotherm equation:^{6-7,44,95}

$$\Gamma = -\frac{1}{RTm(C, C_s)}\frac{d\gamma}{dlnC} \qquad (2.25)$$

where *R* is the gas constant with units (J/mol*K), *T* is the temperature in Kelvins, and $m(C, C_s) = (2C + C_s)/(C + C_s)$. For systems that do not have added electrolytes, $C_s = 0$, and m = 2. Estimations of the surface excess concentration for sodium dodecyl sulfate, using the Gibbs adsorption isotherm, were compared to values reported in literature and direct measurements obtained using techniques such as the radiotracer method and neutron reflectivity, and found to be in good agreement.⁹⁵ The Gibbs isotherm method is suitable for concentrations below critical micelle concentration,⁹⁵ represented by the linear regime of the γ vs. ln*C* graph (Figure 12). In the linear regime, surface tension reduces drastically as concentration increases as surfactants, in the monomeric form, transport to the interface. The surface excess concentration was estimated to be $\Gamma = 1.18 * 10^{-6} \text{ mol/m}^2$ for sodium naphthenate aqueous solutions. The positive surface

excess concentration is indicative that the concentration of surfactant at the interface is higher than the concentration in the bulk, and correlates with the reduction of surface tension.⁶ By taking the reciprocal of the surface excess, the effective molecular cross-section area of the sodium naphthenate surfactant is estimated to be 1.41 nm^2 . For comparison, Gao *et al.*¹⁵ estimated effective molecular cross-section area of 0.97 nm² for sodium naphthenate aqueous solutions. The difference between values estimated could be due to the source of sodium naphthenates used for each study, since the composition of sodium naphthenates varies. Gao *et al.*¹⁵ also estimated the effective molecular cross-section area of 0.51 nm² for sodium naphthenates in a model oil made of n-heptane and toluene (4:1 v/v). In comparison with the value of our study, it is postulated that the smaller cross-section area of sodium naphthenate surfactants enables a higher surface concentration of sodium naphthenates at the emulsion interface.

2.5 <u>Conclusion</u>

Maximum bubble pressure technique and pendant drop method were used to characterize dynamic surface tension, equilibrium surface tension, and critical micelle concentration of sodium naphthenate aqueous solutions. From dynamic surface tension curves, it is observed that the diffusion process occurs rapidly compared to the adsorption process. It is postulated that an adsorption barrier (electrostatic double layer) exists, and a mixed-kinetic diffusion model was used to analyze the datasets. The asymptotic expression used to treat dynamic surface tension datasets accounts for an expanding interface and adsorption of two species that arises due to the ionic properties of sodium naphthenate surfactants. The universal surface age is calculated to account for an expanding interface and allows the comparison of our data with future data obtained using other tensiometers. Images from the in-house pendant drop instrument were

analyzed using the axisymmetric drop shape analysis (ASDA) to determine equilibrium surface tension for the concentration range studied. From the γ vs. *lnC* plot, critical micelle concentration was determined, $c_{cmc} = 1.0$ wt.%, and coupled with its equilibrium surface tension, $\gamma = 30.27 \pm$ 0.05 mN/m, compared favorably to previous studies by different authors. The Gibbs adsorption isotherm was used to determine the surface concentration of surfactants, $\Gamma = 1.18 * 10^{-6} \text{ mol/m}^2$ for the system. The effective molecular cross-section area of the sodium naphthenate surfactant was estimated to be 1.41 nm² by taking the reciprocal of the surface excess. The foamability of sodium naphthenate aqueous solutions is dependent on the ability of the surfactants to diffuse from the bulk and adsorb at the interface. The diffusion process for sodium naphthenate surfactants occurs within milliseconds of bubble formation. Sodium naphthenate surfactants must overcome an electrostatic double layer, which arises due to the anionic property of the surfactant, to adsorb at the interface. Despite the adsorption barrier, sodium naphthenate surfactants adsorb and stabilize the interface within seconds, to prevent rupturing during bubble growth. The magnitude of stabilization is in part due to the size of sodium naphthenate surfactant molecules. The ability for a large concentration of sodium naphthenate surfactants to adsorb at the interface, due to their size, contributes to the foamability and stabilization through the reduction of surface tension for the aqueous solution.

3. DRAINAGE KINETICS OF SODIUM NAPHTHENATE

3.1 Introduction

The lifetime and stability of foams relies on drainage kinetics of thin liquid films that exist between adjacent bubbles as coalescence occurs over time. As thickness of thin films approach molecular length scales, intermolecular and surface forces contribute an excess thickness-dependent pressure, called disjoining pressure, $\prod(h)$, which can counter the capillary pressure that promotes drainage.^{54,96} The magnitude and influence of disjoining pressure depends on the physicochemical properties of surfactants, its concentration in the bulk and interface as well as the presence of self-assembled structures in the bulk.^{54,61,63,96} Intermolecular and surface forces that arise, contribute to the disjoining pressure that can either accelerate or retard drainage. These forces, the attractive van der Waals and repulsive electrostatic forces, are captured within the DLVO theory.^{7,54,63} Additional non-DLVO forces that contribute to disjoining pressure include steric^{54,64} and structural forces.^{54,61,66} Taylor *et al.*⁹⁷ studied the drainage of sodium naphthenate aqueous thin films in the concentration range of 5-50 wt.% solutions. They observed typical drainage through stratification behavior, manifesting as stepwise thinning, of thin films for concentrations above critical micelle concentration and up to 45 wt.%. At 50 wt.% they observed colored thin films, they described as a "stained glass" film. Taylor et al.⁹⁷ postulated that for concentrations below 20 wt.%, spherical micellar structures existed in the bulk and were responsible for the drainage characteristics of the thin film. For concentrations in the range of 20-45 wt.%, it was postulated that film stratification occurred due to the presence of a lamellar liquid crystal-like organization of surfactant molecules in bilayer structures.⁹⁸⁻⁹⁹ The thickness of the films during drainage were characterized for concentrations up to 45 wt.%.

This study seeks to do the same for 5 and 10 wt.% as well as determining the thickness of the colored domains observed in 50 wt.% concentrations.

3.2 <u>Method</u>

3.2.1 <u>Techniques to Characterize Thin Liquid Film Hydrodynamics</u>

The thinning dynamics of sodium naphthenate aqueous foams are characterized using sequences of images capturing the film drainage process, obtained from the thin film balance and bubble pressed to a surface technique. Consecutive images are taken using a wireless remote during the initial stages of film drainage when the colored film transitions to a grayscale film, until the film reaches a final thickness or ruptures. To analyze images obtained from the techniques, the interferometry digital imaging optical microscopy (IDIOM) method, developed by the research group,^{1,100} is used and provides thickness measurements during drainage. The IDIOM method implores the use of a white light source, introduced into the system to illuminate the film. A beam splitter is used to split the incident light into two separate paths, simultaneously reflecting light from the light source and film. Light hitting the top and bottom of the film is both transmitted and reflected to a digital camera (Nikon D5200) connected to a microscope lens (Navitar Zoom 6000) with a 10x objective. The light waves hitting the film recombine to produce an interference that can either be constructive (resulting in increased amplitude).

The IDIOM method relies on the high-quality sensors in the digital camera (Nikon D5200) to capture, pixelwise, a spatially resolved map of reflected light intensity, I(x, y, t), for each wavelength and image.¹⁰⁰ The light waves reflected into the digital camera are converted into RGB intensity values assigned to each pixel in the image.¹⁰⁰ The images are split into three intensity values, where $\lambda = 650 \ nm$ for red, $\lambda = 546 \ nm$ for green, and $\lambda = 470 \ nm$ for blue,

$$h = \left(\frac{\lambda}{2\pi}\right) \left(\sqrt{\frac{\Delta}{1 + \frac{4R(1-\Delta)}{(1-R)^2}}}\right) \quad (3.1)$$

where λ is the wavelength of light, $\Delta = (I - I_{min})/(I_{max} - I_{min})$, and $R = (n - 1)^2/(n + 1)^2$ is the Fresnel coefficient for conditions of normal incidence and no consideration of polarity. I_{max} and I_{min} are the maximum and minimum light intensities and are dependent on the wavelength of light. The Fresnel coefficient is calculated using the refractive index, n, of the bulk solution. For 5 and 10 wt.% concentration, the refractive index of water is used, n = 1.33, under the assumption that low concentrations of surfactants are within the aqueous solution. For 50 wt.% concentration, the refractive index, n = 1.42, measured by Taylor *et al.*⁹⁷ is used. Equation 3.1 is valid for films with thickness h < 100 nm, under the assumption that adsorption is neglected, a near-normal incidence, and consideration for only zeroth order of interference.¹⁰⁰

A MATLAB code developed by Zhang and Sharma¹ is used to extract RGB intensities from a sequence of RAW images to calculate thickness during film drainage. The importance of obtaining RAW images is due to a desire to analyze uncompressed and unprocessed highresolution image data, with the closest possible light intensity and color to the true value. The user directs the code towards a folder that contains the sequence of images to be analyzed. A small area within the image is selected on the first image of the sequence, and the code allows the adjustment of the area size to be analyzed, in units of pixels. The code then analyzes each image within the folder and analyzes the RGB light intensity at the chosen area, storing the values for calculation. I_{max} is accounted for as the highest intensity value measured within the set of images, and I_{min} is always measured from the last image within the sequence. When capturing the sequence of images during drainage, it is critical to capture an almost bright white film, which occurs after a transition from the colored film, to obtain a maximum intensity. Once the draining process is completed, a minimum light intensity is obtained by shifting the container so that the darkest background of the system is captured by the digital camera.

3.2.2 <u>The Thin Film Balance Technique</u>

The setup for the thin film balance is shown in Figure 13. A free-standing foam film is formed within a Sheludko-like cell¹⁰¹ (Figure 13b), and images are captured throughout the drainage process and analyzed by the MATLAB code described above, to determine the



Figure 13. Schematic of the thin film balance, with the Sheludko-like cell. (a) Digital imaging and high-resolution optics are used to produce RAW images of the stratification and drainage process within the thin film. (b) Schematic of the Sheludko-like cell. The thin film is obtained by withdrawing solution from the side. Plateau region is shown near the walls of the cell. thickness variation of the films. A Sheludko-like cell is made by cutting a piece of flexible tubing, resulting in a cell that is 5 mm in height with an inner diameter of 1.3 mm (Figure 13b). A microliter syringe, with sodium naphthenate aqueous solution, is inserted into the side of the Sheludko-like cell, without protruding the inner wall. The cell is placed inside a closed container with a reservoir of sample solution at the bottom, to reduce evaporation effects. The sample is injected into the cell until a biconcave drop is formed. The cell is observed through the DSLR camera, as sample is slowly withdrawn from the drop until a plane-parallel film of a desired diameter ($d_f = 0.3$ mm) forms at the center, and the film is left to freely drain. Under the assumption of small contact angles between the film and Plateau border (a boundary in-between the domain and thicker region), and perfect wetting of the capillary walls, the estimated capillary pressure within the thin film can be calculated using:⁶²

$$P_c = \frac{4\gamma d_c}{d_c^2 - d_f^2} \tag{3.2}$$

where γ is the surface tension of the solution, d_c ($d_c = 1.3$ mm) is the inner diameter of the cell, and d_f is the diameter of the film. The estimated typical capillary pressure for the foam films investigation sizes is $P_c \approx 102$ Pa.

3.2.3 <u>The Bubble Pressed to a Surface Technique</u>

An alternative setup is explored to observe drainage of curve thin liquid films, named the bubble pressed to a surface technique (Figure 14). The setup is inspired by the method developed by Nikolov and Wasan¹⁰² and adopted recently by Bhamla and colleagues.¹⁰³⁻¹⁰⁵ The capillary pressure in the system is proportional to the Laplace pressure for a gas bubble within a solution:¹⁰²



Figure 14. Schematic of the bubble pressed to a surface technique. An air bubble is produced within the solution. A micromanipulator was used to bring the bubble towards the surface, so the top was protruding. Drainage of the thin film at the surface then occurred.

$$P_c = \frac{4\gamma}{r_f} \tag{3.2}$$

The estimated capillary pressure for the bubble pressed to a surface technique is calculated to be $P_c \approx 835$ Pa, using the measured radius of the thin film ($r_f \approx 0.15$ mm). The sample solution is used to fill a glass cuvette three-quarters of the way full. A microliter syringe filled with air is connected to a hook-shaped nozzle, which is submerged within the solution, with the nozzle tip facing upwards. Air is injected to form a bubble at the nozzle tip, and the static bubble is kept submerged within the solution for a time determined from dynamic surface tension measurements, so that surfactants can diffuse from the bulk solution and populate to the air-liquid interface. A micromanipulator (Narshige International, Inc.) is used to move the bubble towards the surface until a curved thin liquid film is created. The desired diameter ($d_f \approx 0.3$

mm) of the film is achieved through moving the bubble up or down, using the micromanipulator. As drainage of the curved film occurs, sequences of images are captured as described above.

3.3 <u>Results and Discussion</u>

Drainage of thin liquid films made from sodium naphthenate aqueous solutions are observed for 5, 10, 45 and 50 wt.% concentrations. Stratification for thin liquid films made from 5 and 10 wt.% sodium naphthenate aqueous solutions, using the thin film balance, proceed as shown in Figure 15. 10 wt.% sodium naphthenate aqueous solutions, using the bubble pressed to the surface technique are shown in Figure 16. Initially for thickness h > 100 nm, colored interference patterns are observed between light reflected from the two air-liquid interfaces of the foam film. The colored film drains quickly until it reaches a critical thickness of $h \approx 100$ nm, at which point the colored interference patterns transition to shades of white. The critical



Figure 15. Montage of typical sodium naphthenate thin liquid film drainage process using the thin film balance. For (a) 5 wt.% NaN and (b) 10 wt.% NaN, stratification is observed in darker and thinner domains appearing over time.



Figure 16. Montage of sodium naphthenate thin liquid film drainage process for 10 wt.% NaN. Montages compare drainage process measured using the a) thin film balance and b) bubble pressed to a surface technique.

thickness is the film thickness at which gray domains spontaneously appear.^{97,106} Below thickness of h < 100 nm, intensity of reflected light is dependent on thickness, and different shades of gray are observed until the thinnest film is achieved. During drainage, regions with different shades of gray are observed, indicating regions of different thicknesses co-existing. Furthermore, the different regions are uniform in color, indicating uniform thickness within those regions. Thinner (darker) domains spontaneously form, expand, and grow within the preceding film thickness, and proceed, with progressively darker domains appearing and growing until a final thickness is achieved. At the final thickness, the film is nearly black colored in characteristic and remains stable for a few seconds or ruptures almost immediately. At times, thinner domains are observed to form within an already expanding domain.

During stratification, brighter and circular domains (or mesas) are observed at localized areas near the contact line of a growing domain (Figure 17); they have been observed in previous



Figure 17. Thicker regions at the boundary of domains. For (a) 5 wt.% NaN thin film and (b) 10 wt.% NaN thin film, areas of thicker regions on the border of growing domains were observed.

studies.¹⁰⁷⁻¹⁰⁸ The mesas spontaneously form under constant pressure at the contact line and are a temporary process with a lifetime spanning the expansion of the thinner domain. Mesas of different sizes travel along the contact line, and it is observed that smaller mesas coalesce with larger ones. Mesas are often observed to form on the contact line of domains that form near the Plateau border (Figure 17). The appearance of these mesas seems to be a response to the increasing rate of drainage under constant capillary pressure. Zhang and Sharma¹⁰⁸ postulated that the supramolecular oscillatory structural force contribution to disjoining pressure is a major contribution to an instability that leads to mesa formation. Thickness perturbations associated with supramolecular oscillatory contributions to disjoining pressure cause rapid thickness jumps that lead to the appearance of mesas or domains.¹⁰⁸ Three distinct regimes during thickness growth were defined, beginning with a slow onset of domain growth diffusively, a sudden burst

at mesa height, and mesas slow growth in width and thickness.¹⁰⁸ These mesa formations are manifestations of the phase transition resulting from a thickness-dependent free energy.¹⁰⁸

Variation in light intensities arises during the thinning of foam films and supplements the calculation of thickness variation during drainage. Thickness measurements are determined for 5 and 10 wt.% concentrations for sodium naphthenate aqueous foam films, using the thin film balance (Figure 18), and also determined for 10 wt.% concentration using the bubble pressed to a surface technique (Figure 19). Thickness variation plots show that drainage occurs in a stepwise fashion, evident by the discrete steps observed in Figure 18. Measurements from the red, green, and blue wavelengths are reported and show good agreement between each other. For the Sheludko-like cell used in the thin film balance, plane-parallel thin films are produced. Using the thin film balance, one step transition is observed for thin liquid films created from 5 wt.% sodium naphthenate aqueous solutions. The final film thickness is determined to be $h_0 = 24.5 \pm$



Figure 18. Thickness measurements using the thin film balance calculated using the interferometry digital imaging optical microscopy (IDIOM) method. Measurements for (a) 5 wt.% NaN and (b) 10 wt.% NaN. Red, green, and blue channels are in good agreement between each other.


Figure 19. Thickness measurement of 10 wt.% NaN. Measurements obtained from the (a) thin liquid balance and (b) bubble pressed to a surface technique. Contrasts are observed in the final thickness between the two techniques.

1.4 nm, and the step size observed is $\Delta h = 22.4 \pm 0.3$ nm. Two step transitions with step size, $\Delta h = 14.0 \pm 0.5$ nm, are observed for 10 wt.% concentration, and the final thickness is $h_0 = 15.2 \pm 0.3$ nm. In contrast to the films created using the thin film balance, curved films are created using the bubble pressed to a surface technique. For 5 wt.% concentration, stable films could not be formed, as film drained and ruptured within seconds, sometimes immediately rupturing, due to the capillary pressure overpowering the disjoining pressure. For 10 wt.% concentration, one step transition is observed before final thickness is reached (Figure 19). The thickness of the step size is $\Delta h = 12.7 \pm 0.1$ nm and the final step size is $h_0 = 10.2 \pm 0.5$ nm. It is observed from the thickness measurements of 5 and 10 wt.% concentration, and the number of steps increases with concentration. Film thickness measurements made using both techniques are in relatively good agreement with measurements made by by Taylor *et al.*⁹⁷ In the previous study, films with diameter $d_f = 0.25$ mm were created in a Sheludko-like cell with inner diameter of $d_c = 2.8$ mm,

and the resulting capillary pressure was much less ($P_c \approx 43$ Pa). For 5 and 10 wt.% concentration, Taylor *et al.* reported final thickness to be $h_0 = 19.2$ nm and $h_0 = 13.2$ nm, respectively. One to two step transitions were observed for 5 wt.% concentrations, whereas three step transitions were observed for 10 wt.% concentration. The step size measure in the study for 10 wt.% concentration was $\Delta h = 6.8$ nm. It is postulated that discrepencies between final film thickness and step size measurements for the two studies are due to differences in composition of sodium naphthenate used.

It is clear from the measurement of thin films made from 10 wt.% concentration that there are disctinctions between the thin liquid film and bubble pressed to a surface technique, due to the plane-parallel and curved films that are created in their respective methods. For films created using the bubble pressed to a surface technique, one step transition is observed, in contrast to two step transitions observed in the thin film balance. The step sizes were relatively close, with $\Delta h = 12.7 \pm 0.1$ nm for curved films and $\Delta h = 14.0 \pm 0.5$ nm for plane-parallel films. There is a significant difference between the final thickness between the two techniques. For the bubble pressed to a surface technique, films reached a final thickness of $h_0 = 10.2 \pm 0.5$ nm, as opposed to a final thickness of $h_0 = 15.2 \pm 0.3$ nm for the thin film balance. Furthermore, the rate of drainage differs, and it is observed that curved films stratified at a quicker rate compared to the plane-parallal film, based on the time it took for each film to reach a final thickness. The difference in rate of drainage is in part due to the capillary pressure difference between the two set-ups, as it has been shown that an increased capillary pressure correlates with an increase in driving force of film thinning.⁶² The capillary pressure estimated for the thin film balance was significantly smaller, $P_c \approx 102$ Pa, compared to the bubble pressed to a surface technique, $P_c \approx$ 835, despite the size of the films created in both techniques being the same ($d_f \approx 0.3$ mm). The

difference in capillary pressure between the two set-ups is due to the higher curvature of the film in the bubble pressed to a surface technique. For a curved film, pressure changes across the interface establish a gas flow (due to gas diffsuion through the film) that destablilizes the micellar structures and increases the vacancies within the film.^{61,102,109} Furthermore, film thickness stability is goverend by a micellar layering phenomena, and the curvature of the thin film destabilizes the layering inside the film.^{61,102,109} It is postulated that the differences in final film thickness and number of step transitions is in part due to the destabilization of the micellar structures and layering, and it is suggested that the layer destabilization effects from supramolecular oscillatory structural forces influence the disjoining pressure that counterbalances the capillary pressure that drives drainage.

In contrast to grayscale images for concentrations much less than 45 wt.% samples, sharply marked regions with distinct colors can be observed for thin films created from much higher concentrations. Initially, pink and green colored interference patterns are observed upon formation of a film, using the thin film balance. Different colored regions (as shown in Figure 20) that dominate the film as drainage progresses, suggests film thickness of h > 100 nm. Distinct boundaries are apparent between each region, and it is observed that some domains grow in area as other domains decrease in size. In time (~ 30 minutes), the rate of domain expansion slowed down, and an almost constant domain area is observed. The appearance and expansion of the colored domains occur over long periods of time, and stable films are observed to exist for up to an hour without rupturing. Evaporation effects eventually dominate and retard the stratification of these films, as gray domains and a final thickness are never observed, despite their being reported previously.⁹⁷ The gray domains observed in Figure 21 are most likely a result of air bubbles trapped within the film. It is possible these gray bead-like inclusions are



Figure 20. Montage of sodium naphthenate thin liquid film drainage process for (a) 45 wt.% and (b) 50 wt.%. Colored domains dominate, and some regions grow in area. Stratification for h < 100 nm, as seen in lower concentrations, was not observed.



Figure 21. 50 wt.% concentration thin film, with gray nodes seen at junctions of colored domains. The gray domains indicate regions of h < 100 nm and are either air bubbles or areas containing the isotropic phase. The arrows indicate areas analyzed for thickness measurements of colored domains.

regions containing the isotropic phase, as these regions (known as nodes) have been observed before in studies.¹¹⁰⁻¹¹¹

The liquid crystal phase and isotropic phase have been shown to coexist^{38,98-99} at concentrations $c \ge 45$ wt.%. It is postulated that the colored characteristics and stratification of films created from 45 and 50 wt.% concentration is due to structures formed from lyotropic liquid crystals.⁹⁷ Liquid crystals, first discovered by Austrian botanist F. Reinitzer, are an intermediate phase between amorphous liquids and crystalline solids.¹¹² Liquid crystals possess both liquid and crystalline properties in that they possess liquid-like order in at least one dimension, possess mechanical properties such as high fluidity, and exhibit anisotropy in their optical and structural properties.¹¹²⁻¹¹³ Because of the amphiphilic nature and concentration dependent phase behavior of sodium naphthenates, these aqueous solutions are characterized as lyotropic liquid crystals.¹¹²⁻¹¹³ Surfactant molecules in this phase tend to be in a hexagonal phase, organized as rows of disc-like micelles, although organization into bilayers has been suggested.¹¹⁴ Taylor *et al.*⁹⁷ suggested that sodium naphthenate surfactant molecules organized into bilayers for concentrations above 20 wt.%. The average step size of the last three step transitions for 30 and 45 wt.% concentrations was determined to be $\Delta h \sim 4.5$ nm, which equated to double the estimated length of a single sodium naphthenate molecule (based on the molecular weight range), which was on the order of 2 nm.⁹⁷

Due to the thickness (h > 100 nm) for the thin films produced from 45 and 50 wt.% concentrations and an order of interference above zero, Equation 3.2 is not valid. Thickness measurements for these thin films were attempted by using the equation suggested by de Gennes:¹¹³

$$R = \frac{I_r}{I_0} = \frac{f \sin^2\left(\frac{2\pi D}{\lambda}\right)}{1 + f \sin^2\left(\frac{2\pi D}{\lambda}\right)} \quad (3.3)$$

where $f = \frac{(n^2-1)^2}{4n^2}$. The ratio, $R = \frac{I_r}{I_0}$, is calculated by measuring the intensity of the reflected light (I_r) from the thin film and intensity of the incident light (I_0) . The optical thickness, D = nH, is determined by solving Equation 3.3 for three wavelengths (red, green, blue). Upon solving for the optical thickness, the thickness at a certain point on the film, H, is determined using the known refractive index determined experimentally (n = 1.42) by Taylor *et al.*⁹⁷ The intensity of the incident light, I_0 , is measured by placing a reflective mirror at an equal distance to where the thin film is to be created. The RGB intensity values from images of the reflected incident light and a chosen point on the colored thin films are determined using the MATLAB code developed by Zhang and Sharma.¹ The intensity values and refractive index are manually input into a code developed by the research group to simultaneously solve three equations:

$$R = \frac{I_r}{I_0} = \frac{f \sin^2\left(\frac{2\pi D}{\lambda_{Red}}\right)}{1 + f \sin^2\left(\frac{2\pi D}{\lambda_{Red}}\right)} \quad (3.3.1)$$
$$R = \frac{I_r}{I_0} = \frac{f \sin^2\left(\frac{2\pi D}{\lambda_{Green}}\right)}{1 + f \sin^2\left(\frac{2\pi D}{\lambda_{Green}}\right)} \quad (3.3.2)$$
$$R = \frac{I_r}{I_0} = \frac{f \sin^2\left(\frac{2\pi D}{\lambda_{Blue}}\right)}{1 + f \sin^2\left(\frac{2\pi D}{\lambda_{Blue}}\right)} \quad (3.3.3)$$

for the optical thickness. The user puts in an initial guess for thickness, H, for the chosen area in the thin film, and an array of values can be determined for thickness measurements, dependent on the initial guess provided to the code. The sum of errors coinciding with a guess serves as a measurement of discrepancy between the estimated value and "true" thickness value. Using this method to determine the thickness for a region on the thin film, the thickness of a pink region (Figure 21) within the film is estimated to be H = 1012.1 nm, while a green region (Figure 21) is estimated to be H = 269.57 nm. Comparison of the estimated thickness of the green region with a Michel-Levy chart shows reasonable agreement, although the chart is used to estimate the birefringence of an anisotropic material. Thickness measurements of colored films produced from 50 wt.% sodium naphthenate thin films has not been performed before, and it is difficult to determine the validity of these measurements based on the Michel-Levy chart. Methods used in practice to measure thickness for liquid crystals involves the measurement of reflectivity at multiple wavelengths while peeling layer by layer of a film.¹¹⁰ It is possible that a reference metallic mirror is needed to provide a better I_0 value, or that three wavelengths are not sufficient to provide a proper thickness measurement of a colored region.

3.4 <u>Conclusion</u>

Drainage of sodium naphthenate aqueous thin films was studied using the thin film balance and bubble pressed to a surface technique for 5 and 10 wt.% concentrations. The IDIOM method, developed by the research group, was used to measure thickness during drainage by analyzing sets of images taken during the drainage process. Stratification was observed for films at these concentrations, as thinning of the films occurred in a stepwise fashion. Using the thin film balance, one step transition was observed for thin films created from 5 wt.% concentration. The step size was determined to be $\Delta h = 20.1 \pm 0.7$ and the final thickness of the film before rupture was $h_0 = 21.8 \pm 0.7$ nm. For 10 wt.% concentration, two step transitions were observed. The step size, $\Delta h = 13.9 \pm 0.6$ nm, and final thickness, $h_0 = 15.2 \pm 0.3$ nm, were observed to be smaller compared to values determined for 5 wt.% concentration. Using the bubble pressed to a surface technique, stable films were only observed for 10 wt.% concentration. The thickness of each stepsize is $\Delta h = 12.7 \pm 0.3$ nm and the final step size is $h_0 = 10.4 \pm 0.4$ nm. The final film thickness values for the 5 and 10 wt.% concentrations, measured using the thin film balance, were in close agreement with previous studies.⁹⁷ For films of equal diameter and concentration, drainage was observed to occur at a quicker rate using the bubble pressed to a surface technique. This is in part due to the difference in capillary pressure, which was calculated to be $P_c \approx 480$ for the bubble pressed to a surface technique, and $P_c \approx 99$ Pa for the thin film balance. The contrast in capillary pressure is due to the higher curvature of the film created in the bubble pressed to a surface technique. Furthermore, curvature of the thin film resulted in an increase in vacancies within the film and destabilizes the layering of micellar structures within the film. For thin

aqueous foam films created from 45 and 50 wt.% concentrations, colored domains were visible during the drainage of the film and thickness measurements for the colored domains within the film were attempted. The appearance and expansion of different colored domains suggest layers of thickness h > 100 nm co-existing within the film. A lamellar liquid crystal and isotropic phase co-exist at these concentrations, and it is postulated that sodium naphthenate molecules selforganize into bi-layers rather than spherical micelles. The films were observed to remain stable for up to thirty minutes without rupturing. It is possible evaporation effects dominated these thicker films in time, but it was clear that films made from these higher concentrations were much more stable compared to lower concentrations, which rupture within a minute.

4. CONCLUSION

4.1 <u>Summary</u>

Undesired foams arise in the petroleum industry due to commercial surfactants used in enhanced oil recovery and indigenous surface active (also known as surfactant) species found within crude oils. During the processing of crude oil, the undesired foams can damage processing equipment, cause flow assurance problems, and even cause complete shut-down of plants. Furthermore, challenges arise separating foam from processed oil, reducing the amount of desired petroleum recovered. Naphthenic acids are an indigenous species found in crude oil and are found to react with salt ions during crude oil extraction, forming sodium naphthenates. Sodium naphthenates act as anionic head-tail surfactants and are known to stabilize foams and emulsions that arise during extraction and processing of crude oil. Focus from light crude oil to heavy crude oil extraction has occurred due to depletion of light crude oil reserves. Because heavy crude oils tend to have higher fractions of naphthenic acids, it is beneficial to study the influence of sodium naphthenates on foamability and foam stability.

Due to the relatively fast interfacial adsorption of sodium naphthenates (timescale < 50 ms), an in-house maximum bubble pressure tensiometer was adopted over other tensiometry methods such as Wilhelmy plate and Du Noüy ring. Dynamic surface tension curves have not been reported before and were generated using data obtained from the in-house maximum bubble pressure tensiometer. Raw dynamic surface tension curves were treated using an asymptotic expression derived by Danov *et al.*⁵² to account for two adsorbing species (co-ion and counterion) as well as an expanding interface. The universal surface age for the dynamic surface tension curves was determined using the apparatus constant ($\lambda = 2.47 \pm 0.22$). It was observed that diffusion of sodium naphthenates to the subsurface occurred within milliseconds, and the

rate of diffusion increased with increasing concentration. In contrast to the diffusion process, adsorption to the interface took longer, suggesting that sodium naphthenate surfactants follow a mixed-kinetic diffusion model and existence of an adsorption barrier. Due to the anionic characteristic of sodium naphthenate surfactants, an electrostatic double layer arises, which decelerates the adsorption process.

Equilibrium surface tension and critical micelle concentration was measured using an inhouse pendant drop tensiometer. Equilibrium surface tension was observed to decrease with increasing concentration up to a critical micelle concentration. Critical micelle concentration, which indicates when sodium naphthenate surfactants begin to self-assemble into micelles, occurred at $c_{cmc} = 1.0$ wt.%, with an equilibrium surface tension of $\gamma = 30.27 \pm 0.05$ mN/m, and compared favorably to measurements from previous studies. Using the Gibbs adsorption isotherm, the surface excess concentration was determined to be, $\Gamma = 1.18 * 10^{-6}$ mol/m², indicating a higher concentration of surfactants at the interface in comparison to the bulk and a reduction in surface tension. The effective molecular cross-section area of sodium naphthenate surfactants was estimated to be 1.41 nm², which accounts for the area of the interface in which one surfactant molecule occupies.

With an understanding of the critical micelle concentration, sodium naphthenate aqueous solutions with concentrations of 5, 10, 45 and 50 wt.% were studied to see if standard thin films were observed, using an in-house thin film balance technique. Furthermore, an alternate bubble pressed to the surface technique was used to study 10 wt.% sodium naphthenate aqueous solutions to see if there were any differences between the drainage of plane-parallel films and curved films. From the thin film balance, one to two step transitions were observed for 5 and 10 wt.% sodium naphthenate aqueous solutions. Using the bubble pressed to the surface technique,

fewer step transitions and a faster drainage rate were observed, in comparison to thin film behavior observed from using the thin film balance technique. This difference between the two techniques is suggested to be due to layer destabilization effects from supramolecular oscillatory structural forces in curved films, which influence disjoining pressure and counterbalances the capillary pressure that drives drainage. For 45 and 50 wt.% sodium naphthenate aqueous solutions, distinct colored domains were observed to appear and expand during drainage, indicating thin films with thickness h > 100 nm. Films from these concentrations were observed to remain stable for up to thirty minutes without rupture. At 45 and 50 wt.% concentrations, a lamellar liquid crystal and isotropic phase are observed to co-exist, and it is possible that sodium naphthenate molecules self-organize into bi-layers rather than self-assemble to spherical micelles.

4.2 <u>Recommendation for Future Work</u>

The following are recommended for future tasks that can be accomplished.

1. It is recommended that dynamic surface tension and equilibrium surface tension measurements are determined using the maximum bubble pressure technique and pendant drop technique.

2. Viscosity needs to be determined for higher concentration solutions and corrected for dynamic surface tension and equilibrium surface tension measurements.

3. Determine drainage kinetics of sodium naphthenate aqueous solutions.

4. Determine a routine to measure thickness of sodium naphthenate thin films that exhibit distinct colored domains (e.g., 45 and 50 wt.% concentrations).

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APPENDIX

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sylvie.camenen@ifpen.fr

VITA

NAME:	William H. Yang
EDUCATION:	B.S., Statistics, Loyola University Chicago, Chicago, Illinois, 2009
	M.S., Chemical Engineering, University of Illinois at Chicago, Chicago, Illinois, 2019
PROFESSIONAL EXPERIENCE:	Scientist - Formulation, Fresenius Kabi USA, Chicago, Illinois, May 2016-Present
	Teaching Assistant, Chemical Reaction Engineering, University of Illinois at Chicago, Chicago, Illinois, January 2016-May 2016
	Teaching Assistant, Chemistry, University of Illinois at Chicago, Chicago, Illinois, January 2015-May 2016
	Research Assistant, Chemistry Department, Roosevelt University, Chicago, Illinois, August 2012-December 2012