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THE EFFECTS OF CRITICAL MICELLE CONCENTRATION AND  
ENVIRONMENTAL FACTORS ON OIL SEPARATION IN SIMULATED  
BILGEWATER EMULSIONS

by

KELSEY LEE RODRIGUEZ DORAN, EIT

B.S. Environmental Engineering, University of Central Florida, 2019

A thesis submitted in partial fulfillment of the requirements  
for the degree of Master of Science  
in the Department of Civil, Environmental, and Construction Engineering  
in the College of Engineering and Computer Science  
at the University of Central Florida  
Orlando, Florida

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2021

Major Professor: Woo Hyoung Lee

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## **ABSTRACT**

Improved bilgewater treatment is necessary because of technological challenges often faced when meeting existing ocean discharge criteria regulations. Since bilgewater is a waste mixture including hydraulic oils, cleaning agents, and seawater, the success of its management is largely attributed to understanding oil-in-water emulsion characterizations. However, the study of bilgewater emulsions is complex due to the multivariate nature of real-shipboard samples. The objective of this study is to develop the relationship between parameters commonly found in bilgewater and emulsion stability. This work is a continuation of a 3-year research project supported by the Strategic Environmental Research and Development Program (SERDP). Previous research (Year 1–2) identified the governing parameters (salinity, suspended solids, pH, and temperature) for oil-in-water emulsion formation and separation using different model surfactants and commercial cleaners. An emulsion stability model with random forest regression and classification algorithms was developed using data from the previous study. This study focused on expanding the database of emulsion stability levels typically encountered in bilgewater. Four surfactants and cleaners were downselected among a list of commonly used products found in bilgewater on Armed Forces vessels. The effects of determining a surfactant's critical micelle concentration in the presence of a representative bilge oil mix, as well as the contribution of surfactant concentration and homogenization intensity on emulsion stability was investigated. Additionally, the effect of a range of environmental parameters (salinity and suspended solids) was evaluated. The work herein added to the range of available emulsion stability model input characterizations. Via nondestructive analytical methods and statistical evaluation, it was found that surfactant concentration, homogenization intensity, and salinity had a significant impact on emulsion stability. However, the newly added data representing more

realistic conditions did not contribute to the emulsion stability prediction model, while adding extended interval ranges for each factor did improve the accuracy of predictions.

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I would like to give thanks to those that played a significant role in the execution of this research including my collaborators from the NSWCCD, Danielle Paynter and Dr. Jeffrey Lundin. I especially would like to acknowledge collaborators, Daniela Diaz and Dr. Jared Church, for their guidance on expanding the scope of this work, Dr. Jongik Chung for helping with the statistical analysis, and Dr. Cheol Young Park for his help on the machine learning model development and simulation.

Most importantly, I would like to give thanks to my friends and family. Their interest in my work and my passion towards environmental engineering has provided me the day-to-day recognition and encouragement that has made this all possible. Ultimately, I would like to

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## LIST OF ACRONYMS

ANOVA	Analysis of variance
AIC	Akaike information criterion
CMC	Critical micelle concentration
EC	Electrocoagulation
EPA	U.S. Environmental Protection Agency
IFT	Interfacial tension
HCl	Hydrochloric acid
MARPOL	The International Convention for the Prevention of Pollution from Ships
ML	Machine learning
NaCl	Sodium chloride
NSBM #4	Navy Standard Bilge Mix #4
NSWCCD	Naval Surface Warfare Center Carderock Division
OCM	Oil Content Monitor
OS	Oil Separation
O/W	Oil-in-water emulsions
OWS	Oil-water separators
RF	Random forest
SDS	Sodium dodecyl sulfate
SERDP	Strategic Environmental Research and Development Program
SS	Suspended solids
UCF	University of Central Florida

## CHAPTER ONE: INTRODUCTION

Bilgewater is the water that collects onboard from various ship operations, freshwater wash-downs from on-board activities, and seawater [1, 2]. Due to the sources that contribute to bilgewater, contaminants primarily include hydraulic oils, lubricants, cleaning agents, debris, particulate matter, and saline water. Bilgewater must meet regulations before discharging into the marine environment to avoid causing harm to the ecosystem [3]. Improved oily bilgewater treatment is required though, because of technological challenges faced when meeting existing regulations for environmental protection [4]. However, due to the multivariate nature of real-shipboard samples, the study of bilge oil-in-water emulsions can be complex. The primary objective of this study is to develop the relationship between parameters commonly found in bilgewater samples and emulsion stability to improve the understanding of bilgewater emulsions.

This work is the continuation and completion of a 3-year research project supported by the Strategic Environmental Research and Development Program (SERDP). Prior results identified the governing parameters (e.g., salinity, suspended solids, pH and temperature) for oil-in-water emulsion formation and separation using different model surfactants and commercial cleaners. By identifying the aforementioned parameters through investigation of prepared bilgewater samples, an ML-based emulsion stability model was developed to aid treatment management. The purpose of this study is to expand the existing database to verify and classify the degree of emulsion stability levels typically encountered onboard to assist bilgewater treatment techniques.

## Thesis Organization

The thesis is organized into five chapters. Chapter 1 discusses introductory information with an overview of the contents to be presented. Chapter 2 holds a literature review of relevant information which supports the purpose of the experimental methods utilized and an understanding of the research results to be discussed further on. Chapter 3 describes the materials and methods used to investigate simulated bilgewater samples for improved treatment and management. This chapter focuses on the experimental procedures used to further the existing database on emulsion stability. Thus, techniques comparable to the previous work were utilized, in addition to methods designed to expand the characterizations of bilgewater emulsion stability.

Chapter 4 of the thesis focuses on the results of the research conducted in Chapter 3. The results can be categorized by two main components: 1) insights on the oil phase of the two immiscible phases in bilgewater emulsions, and 2) analysis of various real environment conditions observed. The first section of this research focused on the effect of using a representative bilge oil in emulsion samples by determining the critical micelle concentration (CMC), which is the surfactant concentration above which micelles start to form and parameters measured become independent of concentration [5]. CMC and interfacial tension (IFT) are two critically recognized parameters for understanding surfactants and droplet stability. Previous work determined that emulsion stability, which the authors described stable emulsions as those with no observable oil separation after 72 h, was most closely related to  $CMC_{IFT}$ , the CMC calculated using IFT measurements [6]. Church et al. (2001) investigated the  $CMC_{ST}$  (CMC calculated using surface tension),  $CMC_{IFT}$  in the presence of a model oil (mineral oil), equilibrium surface tension above CMC ( $\gamma_{cmc(air)}$ ), and equilibrium IFT above  $CMC_{IFT}$  ( $\gamma_{cmc(oil)}$ ). However, the  $CMC_{IFT}$  in the presence of a model oil (mineral oil) may not represent bilgewater

emulsions, thus it was critical to determine and use the  $CMC_{IFT}$  in the presence of a representative bilge mix for the emulsion stability evaluation and associated models development. Since the CMC of a cleaner can change in the presence of oil ( $CMC_{IFT}$ ), the effects of using a representative bilge mix compared to a model oil was studied as a basis for understanding real bilgewater emulsions.

The multivariate nature of shipboard emulsions was further studied by analyzing varying conditions of real environmental samples. Although prior research also identified pH and temperature as governing parameters, suspended solids and salinity were most significant to the developing emulsion stability ML model. Thus, these parameters were selected for study but with a greater interval range. Additionally, the effects of environmental parameters (e.g. suspended solids and salinity) were used to observe the emulsion conditions, surfactant concentration and homogenization intensity. By lowering the interfacial tension, the stress needed to break up a drop is reduced. Surfactants aid this process by reducing interfacial tension and preventing the coalescence of newly formed drops [7]. This suggests that emulsion stability is strongly dependent on surfactant concentrations. Thus, the effect of a high concentration ( $7 \times CMC$ ), which ensures micelle formation and complete coverage of the oil-droplet surface, was investigated. Since a high concentration of surfactant ( $7 \times CMC$ ) could potentially overcome the stabilizing properties of the other parameters (e.g., suspended solids (SS)), the impact of preparing emulsions below the CMC ( $0.5 \times CMC$ ) was additionally studied to ensure that the effect of concentration was accurately observed.

Emulsion formation is non-spontaneous, and energy is required to break up a drop. Thus, to prepare an emulsion, components including oil, water, surfactant, and energy required to expand the interface, are needed [7]. Previous experiments used to gather data for the emulsion stability

model were conducted using high homogenization intensities only (i.e., 33,000 rpm), which may not accurately represent energy levels experienced on ships. Thus, a low homogenization intensity (i.e., 15 rpm) was included in this study.

Through these specific objectives, the work herein is intended to add to the range of available model input characterizations which are understood to affect emulsion stability. The results of the varying conditions on simulated bilgewater samples were analyzed further by ANOVA tests to verify the degree of their effect. Chapter 5 concludes the implications and suggestions gathered from Chapter 4. It also provides a greater outlook to the application of this research for developing a guideline based on the conditions triggering emulsion stability to assist bilgewater treatment techniques. Following the body of the thesis, are the appendices and references which are intended to provide supplemental information.

## **CHAPTER TWO: LITERATURE REVIEW**

### **2.1 Environmental Concern and Regulations**

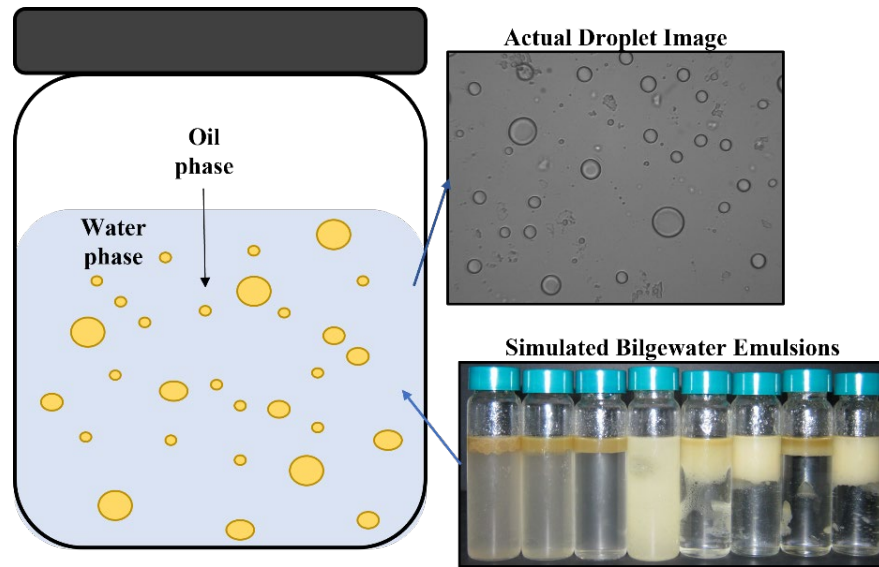
Bilgewater is an environmental concern when it is discharged into the surrounding environment primarily due to the oil fraction sourced from ship processes that use fuel, hydraulic oils, and lubricants. Discharge of the oily wastewater was first regulated by the International Convention for the Prevention of Pollution from Ships (MARPOL) due to the potential damage to marine life, terrestrial life, human health, and the environment [8]. Currently, MARPOL Annex I and DoD Regulation 4715.06-V2 regulate commercial and Armed Forces vessels such that the discharge must maintain an oil content below 15 ppm [9]. Annex I of the MARPOL requires control of oil pollution from vessels and applies to all ships operating in the marine environment, and covers all petroleum products, including crude oil, fuel oil, oily waste, and oily mixtures located in the bilge [10]. Although regulations are in place, the chronic release of oil to the environment by discharges related to ship operations is a significant part of the total inputs worldwide and nears values regarding accidental oil spills at about 270,000 tons of oil per year [11].

The wastewater that accumulates in the bottom of the ship also contains fractions of volatile organic compounds, metals, detergents, degreasers and other chemicals derived from activities on board [12]. In addition to the multivariate characteristics of bilgewater, the mixture of oil and surfactants makes treatment of the two naturally immiscible phases particularly difficult. The mixture of oil and surfactants has also been known to increase the toxicity of the discharge, even more than each of the individual components would intrinsically. O/W emulsions can increase toxicity by causing either a synergistic effect of the toxicity of each component, or result in an

increased dissolution of oil, making exposure to the oily wastewater more bioavailable for organisms [4]. The ecological effects of released bilgewater make meeting or achieving levels below discharge regulations post-treatment critical.

## **2.2 Formation of Bilgewater Emulsions**

An emulsion is a solution of two naturally immiscible fluids in which one phase is fragmented and dispersed into the other [13]. Emulsions are thermodynamically unstable, meaning that their structure does change with time, as well as depend on how they're prepared [14]. In the context of bilgewater emulsions, the two immiscible phases are an organic liquid (e.g., oil) and water (Figure 1). For the oil phase to disperse in water, an emulsifier is required. Typically, that involves mechanical dispersion and a surfactant. Mechanical dispersion, or homogenization, enhances homogeneity by dispersing oil throughout the water by applied energy. Surfactants are surface-active agents which are amphiphilic molecules consisting of lyophobic and lyophilic components [15]. In a vessel, emulsion formation is enhanced due to factors such as ship movement, pumping and transport between holding tanks, and the use of surfactants (e.g. cleaners) during onboard activities.



**Figure 1. Bilgewater emulsion image and schematic with actual droplet image taken by a microscope (M83EZ-C50S, OMAX) integrated with a digital camera (A3550S, OMAX) at 400x magnification.**

### **2.2.1 Interfacial Tension (IFT)**

At the interface between the oil and water phase, IFT can be described as the force between the molecules, a measure of how much energy is required to make a unit area of interface between the two immiscible liquids [16, 17]. Thus, IFT can be useful in predicting the surface energy cost in forming an emulsion and its stability. A lower IFT is expected to decrease phase separation and enhance the stability of an emulsion. In regard to bilgewater, surfactants are emulsifiers expected to reduce the IFT between the different oils and water. Any surface-active substance may be considered an emulsifying agent if it forms a thin interfacial film between the oil and water phases, and minimizes contact, coalescence, and aggregation of the oil phase [18].

The thermodynamic instability of emulsions leads to phase separation. Consequently, the ability of oil to coalesce and separate from the water phase is a fundamental principle to many bilgewater treatment techniques. Unfortunately, the presence of surfactants minimizes oil coalescence and increases the difficulty of oil removal during bilgewater treatment [19]. In

general, a positive correlation between surfactant concentration and emulsion stability can be observed [20].

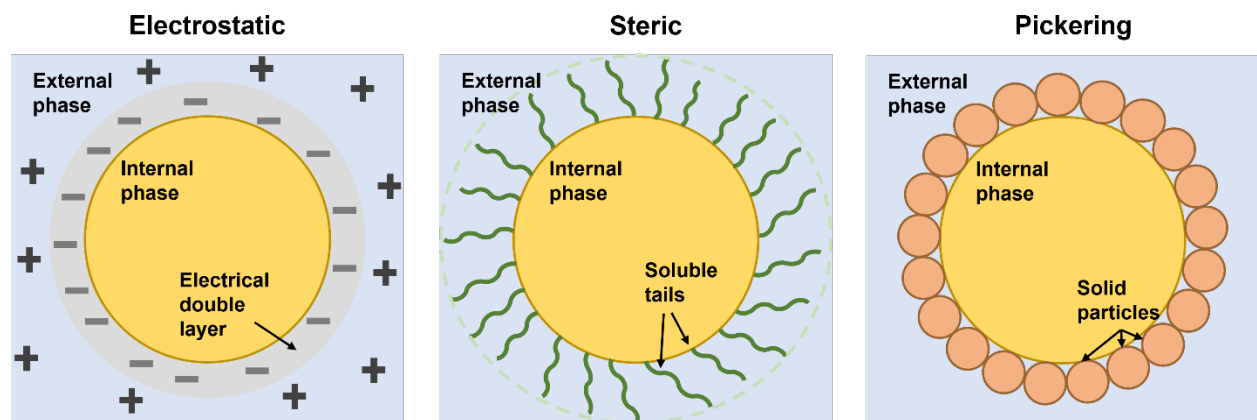
In addition to IFT, the critical micelle concentration (CMC) of a surfactant can be useful in predicting emulsion stability in bilgewater. The CMC is the concentration range of surfactant in which micelle formation occurs [5, 21]. Although adding surfactant typically decreases the IFT between the two immiscible liquids, the IFT is expected to become independent of surfactant concentration above the CMC; thus reaching a minimum due to the thermodynamic favorability of micelle formation [6, 19, 21]. This can significantly affect emulsion stability characterizations. Although there are different methods for determining the CMC, using IFT can be beneficial because it is measured in the presence of the oil phase, unlike surface tension measurements, for example, that are made at the air-water interface [6]. By utilizing IFT measurements to determine the CMC, the effect of various surfactants on emulsion stability in the presence of an actual bilge oil mix can be determined.

### **2.2.2 Emulsion Stabilization Mechanisms**

A successful emulsion formulation will ensure its stability against droplet coalescence and phase separation. Well-accepted emulsion stabilization mechanisms include electrostatic, steric, and Pickering interactions. Electrostatic stabilization occurs when ionic surfactants are present. When the surfactant surrounds the emulsion droplet, an electrical double layer is produced (Figure 2), and electrostatic repulsion will occur if two or more droplets approach each other [22]. Via electrostatic forces, aggregation of oil droplets and phase separation are prevented [23]. Critical conditions for a sufficient double layer and for electrostatic stabilization to occur include a high zeta potential and surface charge, and a low electrolyte concentration [24].

Steric stabilization occurs with the presence of nonionic surfactants or polymers [25]. The surfactants situated at the oil-water interface produce an adsorbed layer around the oil droplet which can be solvated by the water phase (Figure 2). When two droplets interact, the adsorbed layers overlap and become compressed. The effect of the compression of the layers results in a repulsion between the two droplets, preventing oil coalescence [26].

Pickering emulsions are stabilized by the presence of particles at oil-water interface in place of surfactants. When nanometer to micrometer-sized particles diffuse to the interfacial region, they form rigid structures around the oil droplets (Figure 2) [27]. These particles remain in a stable mechanical equilibrium and prevent other droplets from coalescence. The high resistance to coalescence is a key benefit of Pickering emulsions. A critical parameter in the formulation of Pickering emulsions is the three-phase contact angle. The three-phase contact angle describes the interaction between the particle and the oil and water phases. For a successful emulsion, the particles must be at an angle in which they are wetted more by the external phase (i.e. water for O/W emulsions) [28].



**Figure 2. Schematic of electrostatic, steric, and Pickering emulsion stabilization mechanisms differentiated by the layers surrounding the dispersed droplets. Repulsion occurs due to the interaction of two or more droplets.**

### 2.2.3 Emulsion Destabilization Mechanisms

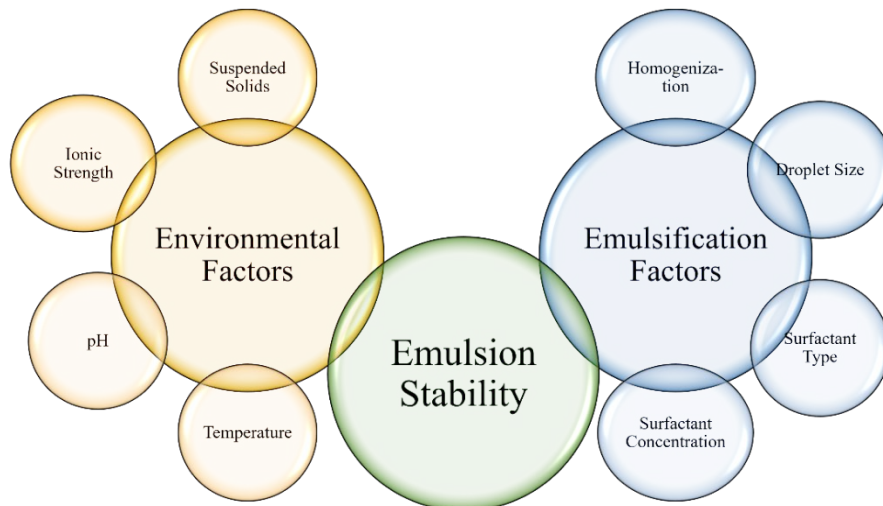
An oil-in-water emulsion signifies that oil is dispersed in the form of droplets in the water phase. However, emulsions are thermodynamically unstable systems consisting of at least two immiscible fluids. Thus, emulsions tend to break down over time and the components separate into their respective phases. For emulsion destabilization to occur, the interfacial film must be destroyed and the droplets made to coalesce [29]. The physiochemical mechanisms known to result in a separation of phases include creaming, flocculation, coalescence, and Ostwald ripening [30].

In bilgewater emulsions, creaming results in the formation of a layer of aggregated oil droplets at the surface. This occurs because the movement of oil droplets due to a density difference exceeds the Brownian motion of droplets [31]. Flocculation is the destabilization mechanism which refers to the general aggregation of dispersed oil droplets throughout the water phase [32]. If the interfacial film between the water and oil droplets is sufficiently weak, coalescence can occur [29]. This process typically follows creaming or flocculation and refers to the adherence of two or more oil droplets. Factors that affect droplet coalescence include the relative magnitude of forces between droplets, resistance of interface to disruption, duration of contact between droplets, and shearing and tearing of interfaces [33].

Although oil and water are considered immiscible, it is possible to find small oil droplets of greater solubility completely diffused into the water phase [25]. Ostwald ripening occurs when those dissolved oil droplets are eventually deposited onto larger drops. This occurs in order to reduce the total interfacial area and reach a thermodynamically more stable state [34].

## 2.3 Factors Affecting Emulsion Stability

There are many factors to consider when characterizing emulsion stability (Figure 3). Environmental factors significant to bilgewater emulsions include the presence of suspended solids (SS), ionic strength (e.g., salinity), pH, and temperature. Other pertinent factors include surfactant type and concentration, droplet size, and homogenization intensity. In particular, the interaction of these factors is what makes studying emulsion stability complicated. Thus, to improve bilgewater treatment, it is relevant to consider how these factors may be affected under real environment conditions and their synergistic effects.



**Figure 3. Various factors affecting emulsion stability.**

### 2.3.1 Applied Emulsification Energy

During emulsification, the interfacial area between the two phases increases. However, the liquids tend to minimize this surface area over time which leads to phase separation [18]. Applying mixing energy to a solution of oil and water can contribute greatly to the formation and stability of emulsions. This agitates the solution causing the shearing and dispersion of oil droplets throughout the water phase. Mechanical energy is often necessary for the emulsification process to proceed and to minimize phase separation.

One of the main causes of emulsion destabilization is the increase in the droplet size. Thus, emulsion stability can be enhanced by reducing the droplet size [35]. Increasing mixing energy and mixing time has been shown to decrease the oil droplet size distribution and create more stable emulsions [18]. Additionally, the applied emulsification energy is not only related to creating smaller droplets, but may also affect the aggregation of droplets [30].

### **2.3.2 Environmental Conditions**

Bilgewater is exposed to many environmental conditions. Notable parameters that are expected to affect emulsion stability are temperature, pH, SS, and ionic strength [21, 25]. Temperature affects the physical properties of oil, water, and interfacial films, as well as the surfactant solubilities [29]. In particular, temperature affects the viscosity of emulsions. An increase in temperature causes the viscosity of the emulsion to decrease, primarily due to the oil fraction, as it is well known, that as the temperature of oil increases, its viscosity decreases. The temperature increase of an emulsion can lead to oil coalescence as the thermal energy increases, causing enhanced droplet collisions [29]. Additionally, a reduction in interfacial viscosity can lead to enhanced oil coalescence as it increases the oil-film drainage rate. pH can also affect the physical properties of the oil-water interface. A change in pH can destabilize emulsions that are stabilized using electrostatic mechanisms by affecting the ionization of the interfacial films, or destabilize emulsions that are stabilized by steric mechanisms by influencing the solubility of nonionic emulsifiers [25, 36, 37].

Suspended solids can be used as a mechanism to stabilize emulsions. Stabilization occurs when the solid particles attach at the oil-water interface to form a barrier or adsorb onto a film already stabilized by a material such as a surfactant, and prevent the oil droplets from coalescence [38, 39]. Additionally, if the solids have a charge, stabilization may be affected in

this regard. Emulsion stabilization characteristics are affected by suspended solid size, interparticle interaction, and wettability by both oil and water phases [29].

Although some studies show the increase of emulsion stability due to salinity, bilgewater O/W emulsions are expected to become less stable as salinity concentrations increase near seawater conditions (0.1-0.6 M) [25, 40, 41]. In this regard, it has been suggested that increased salinity causes a “salting out” effect, a phenomenon that describes the reduced solubility of a compound due to an increase in concentration of salt [42]. It is important to note that in an O/W emulsion, a surfactant has more affinity for the water phase. However, at a level of minimum emulsion stability, a surfactant has an equal affinity for both the oil and water phase. Thus, if an increase in salt causes a reduction in surfactant solubility, there are less surfactant interactions with water, signifying that emulsion stability is closer to its minimum [42, 43]. Additionally, salinity increases ionic strength which may decrease the electrostatic shielding between oil droplets, thus causing coalescence [25].

## **2.4 Bilgewater Treatment Practices**

Bilgewater is a mixture of various oil components and other pollutants from a myriad of sources onboard a vessel. If bilgewater cannot be retained onboard and discharged when the vessel makes land, the wastewater requires treatment before discharge into the marine environment. The most widely used treatment practice for bilgewater are oil-water separators (OWS) based on gravity or centrifugal force. By utilizing the difference in density of the two immiscible phases, OWS effectively separate oil and water into two distinct layers. However, there are a few key drawbacks that make these type of OWS inadequate for meeting oil discharge regulations. Since surfactants are typically a part of bilgewater emulsions, separation of the two layers becomes difficult as the buoyancy differences are too small between emulsified oil

droplets and water [44]. Similarly, OWS function less effectively due to the motion of the ship which can increase agitation and emulsification of the oil-water layers during treatment.

Although centrifugal OWS are more effective at treating emulsions, they are not entirely successful at removing oil, have high capital costs, and require regular maintenance due to the large horsepower motors used [45]. Thus, traditional gravity and centrifugal OWS are typically considered unreliable for sole treatment of bilgewater to environmental regulation standards, often requiring subsequent treatment [46]. Additional treatment systems, referred to as polishing techniques, include absorption, adsorption, biological treatment, coagulation and flocculation, flotation, and membrane technologies. An understanding of conditions triggering emulsion stability, as well as the fundamentals of current treatment practices can aid in improving bilgewater management.

#### **2.4.1 Polishing Treatment Units**

For both absorption and adsorption processes, bilgewater is pumped through the sorption media in a reactor such that the oil is removed. Absorbents are typically made of granular substrates or modified surfaces that have a high affinity for emulsified droplets [47]. Granular activated carbon (GAC) is the most popular adsorption media for the removal of dissolved oil and hydrophobic organic chemicals from bilgewater [48]. Absorption and adsorption are suitable units for smaller vessels (<400 gross tonnage (GT)), require low maintenance, and have low initial capital costs, as well as operational costs [45]. A common setback from sorption techniques is the need to replace media frequently for effective treatment.

Biological treatment typically implies the use of microorganisms comparable to chemical de-emulsifiers such that they break down emulsions yet are generally more compatible with the

environment as they aerobically degrade organics into cell components and other products rather than use additional chemicals [49, 50]. Although biological treatment systems offer a myriad of benefits, loading spikes, high capital costs, and the need for skillful operators can cause difficulty in implementation [10].

Coagulation and flocculation utilize a coagulant to destabilize the solution, allowing large flocs of oil droplets to form. However, this comes with many disadvantages such as high operational costs, chemical requirements, and generation of sludge [51]. In addition, due to the multivariate nature of bilgewater, selecting effective coagulants becomes quite complex [45]. Electrocoagulation (EC) technology maximizes the high conductivity of bilgewater due to its chloride concentration by using electrochemistry and coagulation to destabilize the O/W emulsion, allowing the oil droplets to coagulate and flocculate. Key advantages of EC technology for bilgewater treatment are that it is robust, does not require additional chemicals, and has compact space requirements [2]. However, its energy costs and lifespan are still significant challenges [52].

The difference in density between key components is used as an advantageous characteristic in flotation technology. During flotation, air or gas bubbles attached to oil are less dense than water, allowing the particles to agglomerate, rise to the top of the water, and form a scum layer which can then be removed by skimming [10, 45]. In bilgewater treatment, membrane technology typically includes reverse osmosis, nanofiltration, or ultrafiltration, all of which selectively remove oil from water [53]. Membrane technology is effective and selective yet suffers from fouling due to the surface accumulation of oil and other wastewater constituents [54].

The U.S. Environmental Protection Agency (EPA) states that there is evidence in which bilge separators have difficulty meeting the 15 ppm oil discharge standard even though they were presumed as type-certified to meet the current MARPOL regulations [10]. Minimizing emulsion formation would aid bilge separators in achieving appropriate levels of oil removal. Ideally, predicting emulsion stability levels would thus improve bilgewater management. Accordingly, it is important to study the conditions that affect emulsions through well-designed experiments.

## CHAPTER THREE: MATERIALS AND METHODS

### 3.1 Experimental Design

The purpose of this research is to better understand the effect of the physicochemical and thermodynamic characteristics of emulsions formed in bilgewater of Armed Forces vessels. By gaining a deeper understanding of emulsion formation, the data gathered is designed to aid bilgewater management and treatment selection. Further, this research is intended to increase the likelihood of meeting discharge regulations and improve environmental conditions. The following tasks outline the experimental design behind the scope of this work.

#### *Task 1. CMC determination in the presence of oil*

Interfacial tension is an indicator of emulsion stability and can be used to determine a relative CMC value. It is understood that the CMC value can change in the presence of an oil phase when a surfactant is solubilized by the external phase. Thus, the  $CMC_{IFT}$  of four representative surfactants and commercial cleaners was determined using a naval standard bilge mix (NSBM #4). This task was expected to yield more realistic characterization of bilgewater emulsion stability. To determine the  $CMC_{IFT}$ , the IFT at a series of surfactant concentrations was measured. Then, the  $CMC_{IFT}$  was established once an equilibrium IFT was achieved.

#### *Task 2. Simulated Bilgewater Characterizations*

Task 2 consists of evaluating the effect of a range of environmental parameters on emulsion stability. Two commonly found constituents expected to affect the physiochemical and thermodynamic characteristics of bilgewater on emulsion formation are suspended solids (SS) and salinity. Further, these parameters were utilized to identify the effect of additional parameters, homogenization intensity and surfactant concentration. Homogenization intensity

was expected to represent the various movement levels encountered on ship, and surfactant concentration was expected to represent the inconsistent levels of emulsifiers found in bilgewater. Thus, simulated bilgewater samples were prepared in this task by using a representative bilge oil and shipboard emulsifiers at varying concentrations based on their respective CMC, and emulsified at two different homogenization intensities (15 and 33,000 rpm). To evaluate the effect of commonly encountered environmental conditions, the samples were investigated in the presence of suspended solids between 0-2,000 ppm (Arizona Test Dust) and salinity (NaCl) in the range of 0-35,000 ppm.

### *Task 3. Data Interpretation and Modeling*

The data collected from the bilgewater characterizations was then utilized for analysis and modeling. An analysis of variance (ANOVA) with multiple factors was used for hypothesis testing to examine statistical relationships for *Oil Separation (OS)* and *Turbidity* under the different experimental conditions. In this study, *OS* and *turbidity* were the primary factors used to quantify and compare emulsion stability. In addition, the data was utilized in the machine-learning (ML) algorithms model previously developed by the Naval Surface Warfare Center Carderock Division (NSWCCD) and UCF to predict emulsion stability [55]. The model was developed using random forest (RF) algorithms. In this work, there was an emphasis on determining whether this research would improve the ML model predictions since the experiments were designed to investigate factors affecting emulsions under realistic bilgewater conditions.

### 3.2 Emulsion Preparation

The emulsion samples were prepared in 40 mL glass TOC vials (GLC-01020, Qorpak, PA, USA). Prior to preparation, the vials had been cleaned carefully to avoid contamination. The first step of the cleaning procedure was to rinse each vial with Dri-clean (Decon Labs, Prussia, PA) soap and hot water. A test tube brush was used to remove any particles or oil attached to the vial walls. Then, the vials were rinsed with a 1 M HCl solution, washed 5 times using deionized (DI) water, and left to air dry at room temperature. The vials were examined for residual oil or particles prior to each use. This was an essential step to prepare for later image analyses (Chapter 3.5).

The emulsion samples were made using a representative bilge oil and DI water (pH 6.6, unadjusted) as the immiscible phases. The representative bilge oil, Navy Standard Bilge Mix #4 (NSBM #4), was provided by the Naval Surface Warfare Center Carderock Division (NSWCCD). NSBM #4 components include 50% v/v diesel fuel marine (MIL-DTL-16884), 25% v/v 2190 TEP steam lube oil (MIL-PRF-17331), and 25% v/v 9250 diesel lube oil (MIL-PRF-9000) [56].

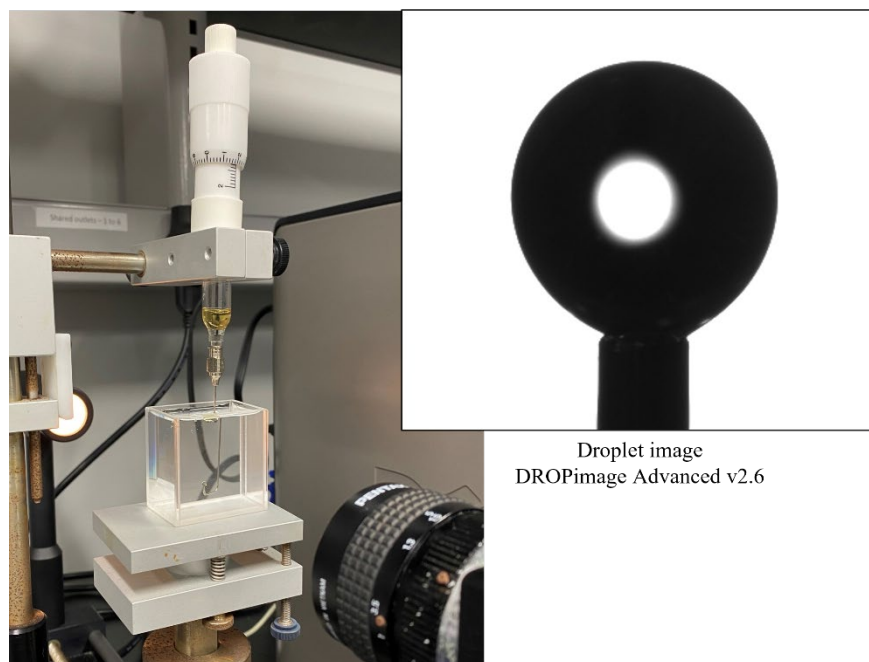
In addition to a representative bilge oil, representative shipboard emulsifiers were utilized to prepare the emulsion samples. From a list of recognized shipboard model surfactants and commercial cleaners, the emulsifiers previously determined as most and least stable were utilized to conduct the experiments [6, 41]. The down-selected model surfactants and commercial cleaners were Triton X-100 and SDS, and Super Blast-off and Type 1, respectively. Triton X-100 (CAS #9002-93-1) and sodium dodecyl sulfate (SDS; CAS #151-21-3) were purchased from Sigma-Aldrich as representative surfactants. Super Blast-off 114 (Elsco International Inc.) and

Type 1 Detergent (MILSPEC: MIL-D-16791 ) were selected among commercial cleaners identified from the U.S. Navy procurement system [25]. All materials were used as received.

### **3.3 Determination of Critical Micelle Concentration by Interfacial Tension**

#### **3.3.1 Interfacial Tension (IFT) Measurements**

Interfacial tension measurements were conducted using a goniometer (Model 100-00, Rame-hart Instruments Co. Succasunna, NJ) by performing the pendant drop method (Figure 4). The sample solutions were prepared by dispensing the appropriate amount of surfactant in DI water and mixed with a magnetic stirrer to ensure complete homogeneity. For each measurement, a 40 mL sample of surfactant was placed in a quartz cell. The concentration of surfactant in each sample ranged between 0 ppm – 12,000 ppm. An oil droplet was carefully formed on an inverted needle by dispensing 5  $\mu$ L of NSBM#4 in solution. The interfacial tension (IFT) was immediately quantified using the software DROPimage Advanced v2.6. Samples were left undisturbed while measurements were taken until surfactant adsorption at the interface reached equilibrium. A plateau in the IFT values observed signified that equilibrium had been reached. The equilibrium IFT in mN/m was used for calculations. Duplicates of each measurement were performed. The IFT results presented in this work are the average values obtained from both replicates.



**Figure 4. IFT measurements using the pendant drop method.**

### **3.4 Simulated Bilgewater Sample Preparation**

Emulsions were prepared using a representative bilge mix and DI water containing emulsifiers commonly found in shipboards, as well as a model suspended solid or salinity to represent environmental parameters. The emulsifiers included Triton X-100, SDS, Super Blast-off, and Type 1 detergent at concentrations below CMC and above (Table 1). For consistency in comparison with prior results, CMC values previously measured by surface tension of an air-water interface were utilized as they are evaluated independent of the representative oil mix [41]. Below CMC ( $0.5 \times \text{CMC}$ ) conditions were used to ensure that stabilizing properties of the different parameters were still observable with the presence of surfactants, while above CMC ( $7\text{CMC}$ ) conditions were used to ensure micelle formation and complete coverage of the oil-droplet surface.

**Table 1. Surfactant Information**

SURFACTANT	TYPE	0.5×CMC (ppm)	CMC (ppm)	7×CMC (ppm)
Type 1	nonionic	43.35	86.7	606.9
SDS	ionic	773.7	1,547.4	10,831.8
Triton X-100	nonionic	51	102	714
Super Blast-Off	nonionic	437	934	6,538

10% (v/v) of NSBM #4 was used as the oil phase to prepare the samples. The second phase of the emulsion samples which contained DI water and surfactant, also comprised of suspended solids or salinity at concentrations ranging between 0 ppm – 2,000 ppm and 0 ppm – 35,000 ppm, respectively, to model the environmental parameters. Arizona coarse test dust (Power Technology Inc, Arden Hills, MN) was used as a model suspended solid (ISO 12103-1 A4 coarse test dust) and sodium chloride (NaCl) (Fisher Scientific, Cat #18-606-411, Waltham, MA) was used for saline conditions.

In this study, two different homogenization intensities were used to emulsify the two phases. Low homogenization was performed by using a tube rotator (MX-RL-E Analog Rotisserie) at 15 rpm for 30 minutes. High homogenization was performed at 33,000 rpm for 2 minutes by inserting a hand-held homogenizer probe (Omni Tissue Master, model 125, 10 mm generator probe) halfway into the sample. Table 2 shows an overview of the different parameters utilized to prepare the emulsions for stability testing.

**Table 2. Emulsion Stability Experimental Parameters**

PARAMETERS	RANGES
Surfactant Concentration (ppm)	0.5×CMC, CMC, 7×CMC
Salinity – NaCl (ppm)	0, 500, 5000, 15000, 35000
Suspended Solids – Arizona Test Dust (ppm)	0, 500, 1000, 2000
Homogenization Intensity	Low: 15 rpm, 30 min.      High: 33,000 rpm, 2 min.

### **3.5 Emulsion Stability Testing**

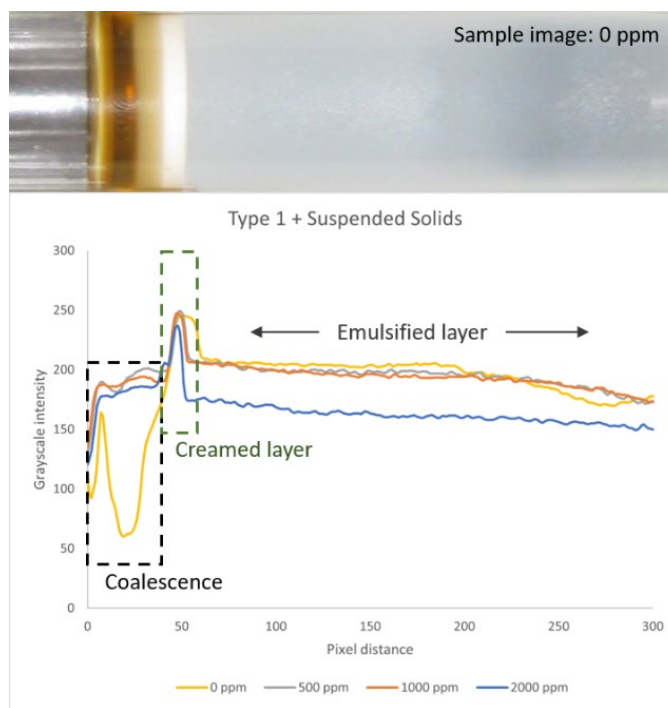
#### **3.5.1 Image-Based Analysis: Oil Separation**

After preparation of the emulsions, photos were taken every 24 hrs. for the 5-day experiment using a digital camera (PowerShot A480, Cannon). The recorded images were used for subsequent analysis as a time-course monitoring technique of emulsion stability for each of the prepared samples. Using a Java-based image-processing program (ImageJ, NIH), the height of the oil film at the top of each emulsion was carefully measured to quantify the oil layer height (cm). Oil separation (OS, %) was calculated by dividing the height of the separated oil layer by the height of the total oil used. Oil separation, which observes the phase separation as a function of time, is significant because it is one of the most common methods available for measuring emulsion stability [29].

#### **3.5.2 Image-Based Analysis: Grayscale Profile**

Grayscale profiles were utilized as a non-destructive image analysis technique in addition to oil separation to give more insight on the destabilization characteristics observed. A grayscale profile displays a two-dimensional (2D) graph of the pixel intensity along a line placed in an emulsion sample image where the axes represent grayscale intensity and pixel distance. The variation in the grayscale intensity over time is intended to show the visual changes in emulsion layers that cannot be determined by the height of oil layer alone. This can be used to describe the destabilization events occurring in each sample. Using the same image processing program as the oil separation procedure (ImageJ, NIH), grayscale intensity profiles were developed for each of the emulsion samples (Figure 5). The original images were converted from RGB color into an 8-bit, linear grayscale in which the lightest color (white) is represented by 255 and the darkest

(black) is represented by zero. To generate the 2D grayscale profile, a plot is developed where the y-axis represents the grayscale intensity, and the x-axis represents the height of the sample from the top of the solution to the bottom.



**Figure 5. A representative grayscale profile of the bilgewater emulsion sample using a grayscale intensity method. The profile shows emulsion destabilization by creaming and coalescence.**

As observed by Figure 5, values closer to 0 represented oil layers and the tendency of oil coalescence. Measuring grayscale intensity differed from oil layer height as the degree of oil separation could be observed by the intensity of pixels, signifying the concentration of oil in the layer. As values increased, greater emulsion formation was observed. Considerably high values nearing 255, signified creaming layer formation.

### 3.5.3 Turbidity

It is valuable to measure the turbidity of the bulk-layer of an emulsion because many oil content monitors (OCMs) use turbidity as a means of measuring the oil content in the effluent

[10]. It also gives insight on the extent of interference other bilge contaminants, such as suspended solids, have on the oil content measurements as a result of increased turbidity. The turbidity of the bulk-layer of the emulsion sample was measured at the end of the 5-day experiments. After each sample was prepared, it was left undisturbed for the duration of the experiment. After 5 days, the oil and creaming layers were carefully removed using a pipette. Leaving just the bulk-layer of the emulsion, the sample was transferred to a clean glass cell (HACH, Product No. 2084900, CO, USA). The turbidity was then measured using a turbidimeter (HACH, 2100N, CO, USA). Duplicates of the turbidity measurement were taken in NTU and then averaged for a final data point.

#### **3.5.4 Statistical Analyzation**

Using R software, an analysis of variance (ANOVA) with multiple factors was used for hypothesis testing to examine statistical relationships for *OS* and *Turbidity* under different experimental conditions. The null hypothesis ( $H_0$ ) in ANOVA is that there is no difference in means, while the alternative hypothesis ( $H_1$ ) is that the means are not all equal for all considered groups. As a first step, fundamental assumptions were checked in ANOVA; (i) the residuals are normally distributed (normality) and (ii) constant variances across groups (homoscedasticity).

Akaike information criterion (AIC) was then used to select the best model which fits our data. The AIC is a commonly used model selection method that estimates the quality of each model given a collection of models for the data. Based on the number of estimated parameters and the maximum likelihood estimate for the model, the best model yields the smallest value of AIC. A one-way, two-way, and three-way ANOVA with or without interaction models were considered as candidates.

## CHAPTER FOUR: RESULTS AND DISCUSSION

### 4.1 CMC Determination in the Presence of NSBM#4

Four surfactants commonly used on Armed Forces vessels were selected for this study. These surfactants include Type 1, Triton X-100, Super Blast-off, and SDS. The CMC for each of these surfactants was determined in the presence of a representative bilge oil, NSBM#4, which was provided by the NSWCCD. To determine each  $CMC_{IFT}$ , the IFT of a series of surfactant solutions were measured and plotted against the surfactant concentration on a semi-log plot. The results are presented in Figure 6. Each value represents the average of the two analyses at each concentration with error bars signifying the standard deviation. The data was then fit with two linear regressions which shows the effect of surfactant concentration. The first fitted line for each set of data points shows the IFT dependent on surfactant concentration, while the second shows the IFT independent of surfactant concentration. The  $CMC_{IFT}$  was determined as the point of intersection of two different linear lines. Table 3 shows the resulting  $CMC_{IFT}$  values and the equilibrium IFT at which micelle formation occurs.

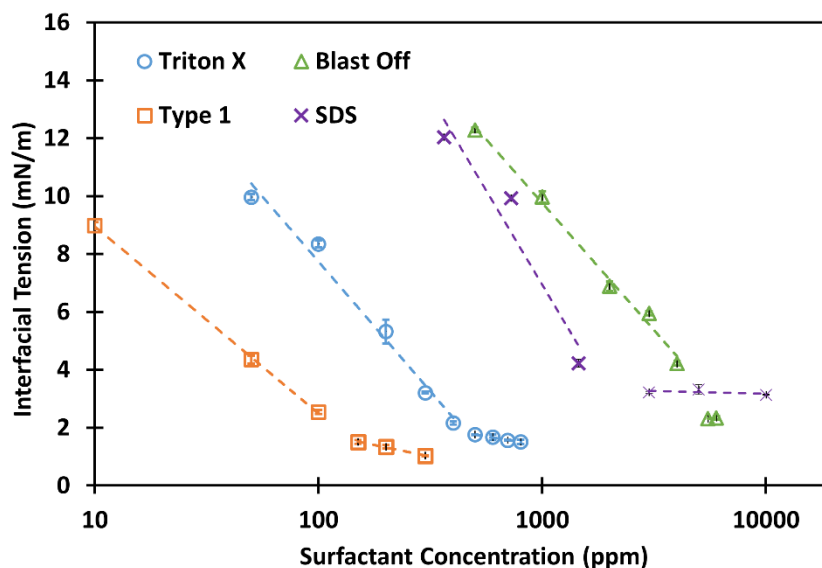


Figure 6. Interfacial tension at different concentrations of surfactant used for CMC determination in the presence of NSBM#4.

**Table 3. CMC determined in the presence of NSBM#4 and equilibrium IFT**

<b>Surfactant</b>	<b>CMC<sub>IFT</sub> – NSBM#4 (ppm)</b>	<b><math>\gamma_{CMC - NSBM\#4}</math> (mN/m)</b>
Type 1	138	1.6
SDS	1,898	3.3
Triton X-100	458	1.8
Super Blast-off	6,893	2.4

Type 1 has the lowest equilibrium IFT at 1.6 mN/m, followed by Triton X-100, Blast-off, and SDS. Equilibrium signifies that the number of surfactant molecules adsorbing to the oil-water interface is equal to the number desorbing such that the net concentration of molecules on the interface is constant [19]. With Type 1 having the lowest IFT, it is expected that the use of this surfactant produces the most stable emulsions, as emulsion droplet size is expected to decrease with decreasing IFT [57]. SDS had a much larger equilibrium IFT than the other surfactants at 3.3 mN/m. Although SDS had the highest equilibrium IFT, Blast-off resulted in the highest CMC<sub>IFT</sub> at 6,893 ppm. This signifies that Blast-off needs approximately 3.6-fold higher concentration of surfactant than SDS to achieve its equilibrium IFT, which demonstrates the importance of both surfactant type and concentration in an emulsion. Type 1, however, resulted in the lowest CMC<sub>IFT</sub> at 138 ppm in accordance with measuring the lowest equilibrium IFT.

The equilibrium IFT values measured in this study were in the same range, yet slightly lower than those using mineral oil as a model bilge mix [6]. Likewise, a difference in CMC<sub>IFT</sub> values were reported. The CMC<sub>IFT</sub> values achieved using NSBM#4 were slightly greater [6]. This was true for all surfactants except for SDS, the only ionic surfactant tested in this study. The comparison of values measured in this study using NSBM#4 and in a different study using mineral oil can be found in Table 4. The slight difference in values, particularly regarding SDS, could be a result of the oil additives found in NSBM#4. A study completed by Jared et al.

suggests that the additives in oil can react in the emulsion causing a significant change in CMC as determined by in interfacial tension [58].

**Table 4. Comparison of CMC<sub>IFT</sub> and equilibrium IFT values achieved in this study using NSBM#4 and in a different study using mineral oil [6]**

Surfactant	CMC <sub>IFT</sub> – NSBM (ppm)	CMC <sub>IFT</sub> – Mineral Oil (ppm) [6]	$\gamma_{CMC}$ – NSBM (mN/m)	$\gamma_{CMC}$ – Mineral Oil (mN/m) [6]
Type 1	138	105	1.6	2.1 ± 0.1
SDS	1,898	5,130	3.3	9.8 ± 0.5
Triton X-100	458	324	1.8	3.0 ± 0.1
Super Blast-off	6,893	5,381	2.4	3.4 ± 0.1

The lack of knowledge on surfactants due to proprietary information, as well as the multivariate nature of bilgewater components, makes understanding emulsion stability difficult. The results from this study demonstrate the significance of using interfacial tension to determine a relative CMC value for real bilgewater application. This method allows for greater emulsion stability prediction by use of a representative oil and surfactants. Lower IFT and CMC<sub>IFT</sub> values are indicative of emulsion stability and could be reported as such during emulsion stability testing on ships. In general, it is recommended that nonionic surfactants with higher IFT and CMC<sub>IFT</sub> are utilized to reduce emulsion stability. Ionic surfactants should be further investigated for emulsion stability.

#### 4.2 Effect of Real Bilgewater Conditions on Emulsion Stability

Time-course observations of simulated bilgewater samples were utilized in this study to determine the effect of real environment conditions on emulsion stability. The simulated bilgewater samples were prepared of 10% (v/v) NSBM#4 and DI water with solubilized surfactant. In this study, four surfactants were down selected among a list of commonly used surfactants on Armed Forces vessels. The selected surfactants include Type 1, Triton X-100, Super Blast-off, and SDS. Simulated samples were prepared at 0.5×CMC and 7×CMC to study

the effect of surfactant concentration on emulsion stability. In addition, the simulated samples were prepared in the presence of suspended solids and salinity at varying concentrations to represent actual bilgewater characterizations [25]. The suspended solids concentration range included 0, 500, 1000, and 2000 ppm. The samples prepared under saline conditions included 0, 500, 5000, 15000, and 35000 ppm NaCl. Lastly, emulsion preparation included two different homogenization intensities and times: 33,000 rpm for 2 minutes, and 15 rpm for 30 minutes. These characterizations were included to represent the different emulsion formulations that occur onboard due to ship movement and various activities. These experiments resulted in 128 different samples.

The samples were observed over a time period of 5 days, after which no significant visual changes occurred. Appendix A shows the images recorded over this time period at days 0, 1, and 5 for all samples. Primary observations show that the most significant changes occurred between day 0 and 1, although changes did continue to occur over the rest of the 5-day period. Day 0 images show emulsions right after preparation. They are distinct in that they show the greatest level of emulsion formation for each formulation. Figure 7 shows the 5-day images of all the samples in which the final observations of phase separation were observed. Day 5 images were distinct in that they showed the greatest occurrence of phase separation. These images were also the images utilized for the image-based analyses (i.e. grayscale profiles and oil layer height).

To classify emulsion stability, the phase separation of a sample was observed. A distinct oil layer was the greatest indicator of emulsion instability. As opposed to creaming, an oil layer is considered permanent. Creaming is not considered definitive, such that the oil droplets can re-disperse easily to form an emulsion. Thus, samples with the greatest oil separation, as signified by the greatest oil layer height and most pure oil layer, were considered to have the least stable

emulsion formulation. Based on these definitions and visual observations from Figure 7, Type 1 emulsions generally produced the most stable emulsions, whereas Blast-off produced the least stable emulsions. SDS and Triton X-100 tended to form emulsions of similar stability levels based on visual observation alone.

Oil layer height quantified oil separation, while the grayscale intensity profiles were useful in determining the degree of oil purity. This was important for developing the results based on visual observations because samples generally formed an oil layer easily. In addition, due to the small sample volumes, the oil layer heights did not vary on a large scale. Thus, the grayscale profiles were useful in distinguishing samples with similar oil layer heights. The grayscale profiles of day 5 images of all the samples can be found in Appendix B.

Similar to the oil layer, grayscale profiles gave insight on the creaming and bulk emulsion layers formed. As observed in Figure 7, Type 1 samples generally had more creaming and emulsion formation in the bulk layer than compared to Blast-off samples. This data was quantified by the grayscale profiles in Appendix B, in which creaming typically resulted in a spike in intensity that neared the high end of the intensity range.

Although oil separation was the primary factor in determining emulsion stability, turbidity was used for evaluating the bulk emulsion layer. It also gave insight on the extent of interference of other bilge contaminants, such as suspended solids. Turbidity measurements were taken at the end of the 5-day period to assure a relatively stable macro-phase separation had occurred. Thus, the results indicate the typical oil and solids concentration expected to be observed based on the emulsion formulations created at real environment conditions.

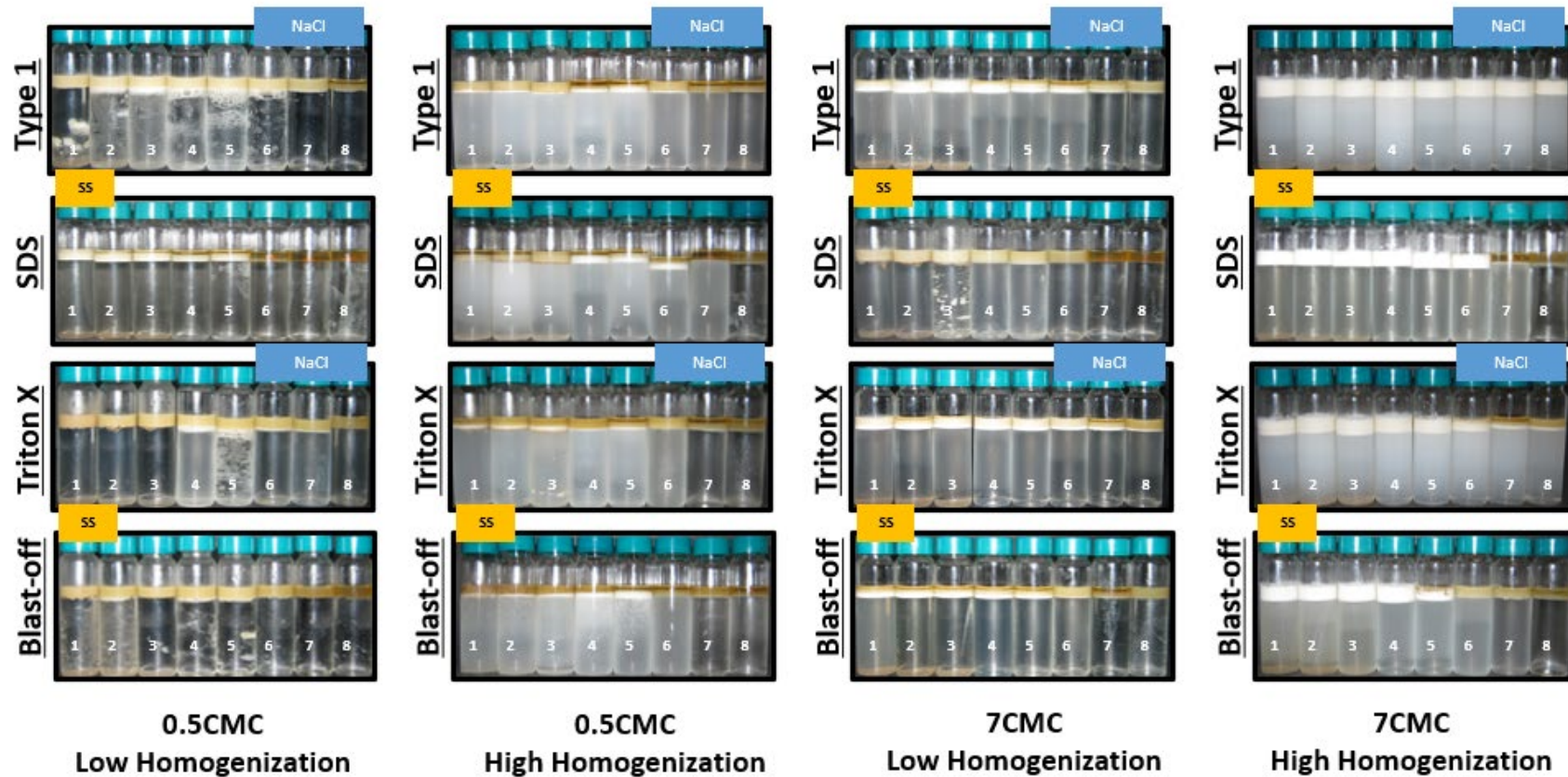


Figure 7. 5-day emulsion sample images. The figure legend, which corresponds sample ID to sample conditions, is on the next page. Sample conditions include two homogenization intensities (Low: 15 rpm for 30 min., High: 33,000 rpm for 2 min.), two surfactant concentrations (0.5×CMC, 7×CMC), SS concentrations (0, 500, 1000, 2000 ppm), and salinity (0, 500, 5000, 15000, 35000 ppm). pH and temperature (~25 °C) are unadjusted.

**Figure 7 Legend**

Sample ID	Conditions	
	Suspended Solids (ppm)	Salinity (ppm)
1	2,000	-
2	1,000	-
3	500	-
4	-	-
5	-	500
6	-	5,000
7	-	15,000
8	-	35,000

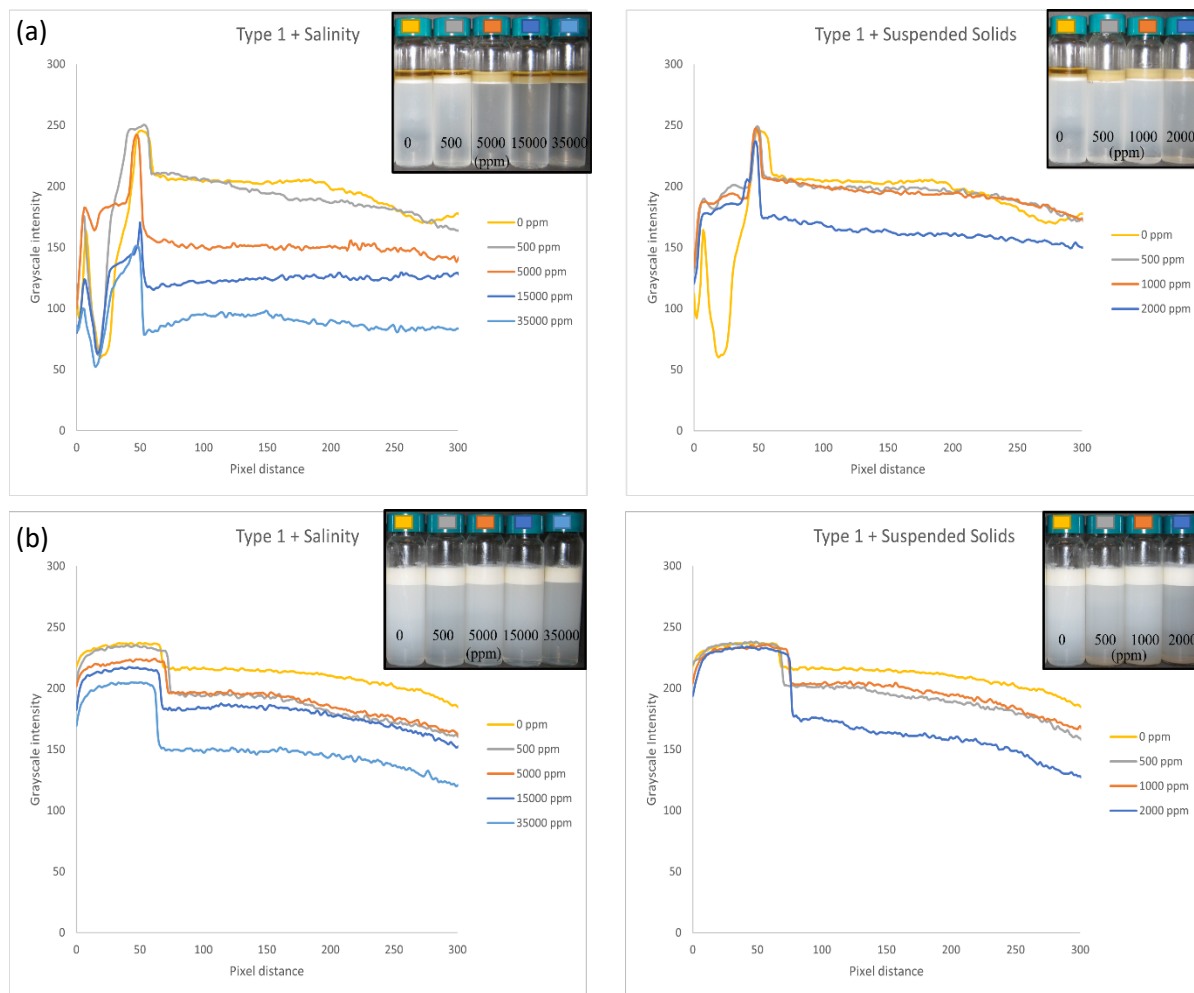
#### **4.2.1 Surfactant Concentration**

The impact of surfactant concentration on emulsion stability was evaluated at 0.5 and 7 times their respective CMC values. The surfactant concentration clearly affected emulsion stability. Samples formulated at  $7\times\text{CMC}$  showed significantly greater creaming formation, whereas samples prepared with  $0.5\times\text{CMC}$  of surfactant had more distinct oil layer separation. This effect was enhanced by samples prepared at high homogenization.  $0.5\times\text{CMC}$  samples also showed a greater tendency to oil coalescence at an earlier stage (e.g. by day 1).

For example, Figure 8, shows the grayscale profiles of samples prepared at high homogenization using Type 1 at  $0.5\times$  and  $7\times\text{CMC}$ . The profiles record the grayscale intensity from the top of the oil layer to the bottom of the vial. For samples prepared using  $0.5\times\text{CMC}$  of Type 1 (Figure 8 (a)), the grayscale intensity starts at values as low as 50, indicating the presence of an oil layer. An upwards spike in grayscale intensity indicates a creaming layer. However, the width of the spike is much smaller compared to the width of the oil layer, signifying that the creaming layer thickness is thin. The plateau in grayscale values indicates the bulk layer of the emulsion in which no significant phase separation occurs. In comparison to Figure 8 (b) which shows samples prepared at  $7\text{CMC}$ , the grayscale intensity starts at much higher values than at

0.5×CMC. The grayscale profile shows a wide plateau at relatively high grayscale values, indicating the presence of a creaming layer with no oil coalescence. The graph then shows an immediate decrease in grayscale intensity which represents the bulk emulsion layer. However, the grayscale continues to decrease slightly until it reaches the bottom of the vial. This indicates that a very gradual phase separation had occurred throughout the bulk layer of the samples.

For high and low homogenization samples, the increase in surfactant concentration generally showed greater emulsion formation in the bulk layer. However, for surfactants SDS and Blast-off, the increase in concentration was less effective than for the other surfactants, as indicated by a smaller change in oil layer separation. This was in accordance with the IFT and  $CMC_{IFT}$  data. Overall, all surfactants tested showed to be susceptible to concentration variations, resulting in enhanced emulsion destabilization with concentration decrease. In particular, at surfactant concentrations much greater than CMC, enhanced creaming layer formation occurred with less oil coalescence.

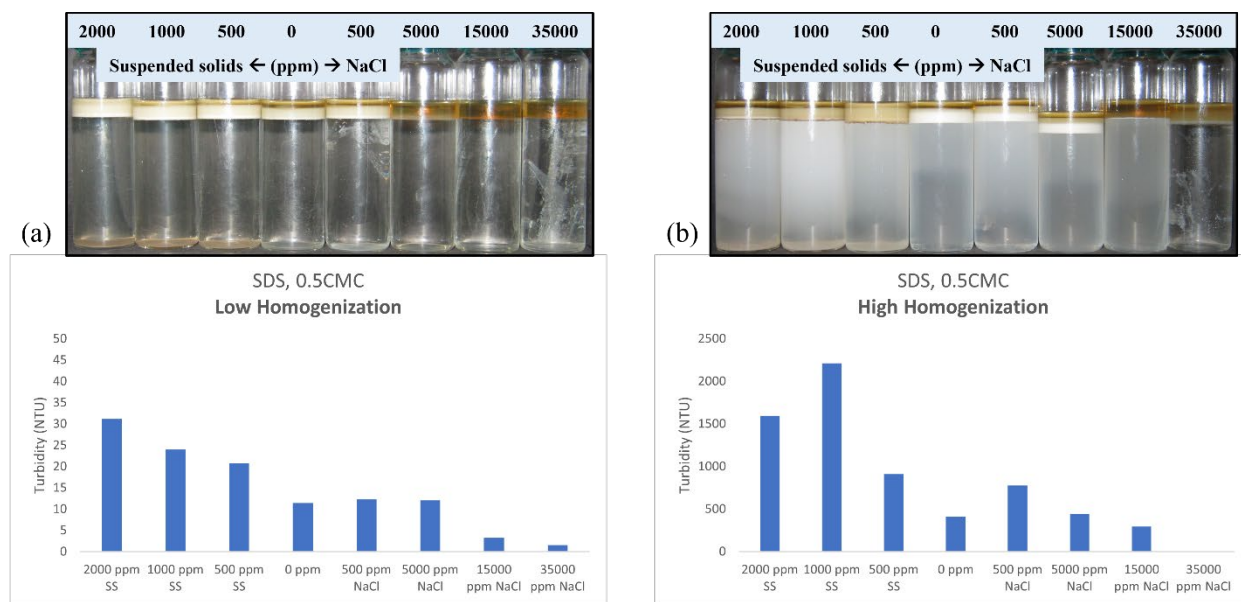


**Figure 8. Grayscale intensity profiles of samples prepared at high homogenization using Type 1 at (a)  $0.5\times\text{CMC}$  and (b)  $7\times\text{CMC}$ .**

#### 4.2.2 Homogenization Intensity

In this study, emulsion formulations of two homogenization intensities were compared. Applying a low homogenization intensity to emulsify the samples indicated the use of a tube rotator at 15 rpm for 30 minutes. High homogenization signified 33,000 rpm for 2 min using a hand-held electric homogenizer. Results indicated that the homogenization intensity was a significant factor affecting visual observations for both oil layer separation and bulk layer emulsion formation. However, the greatest change induced by homogenization intensity was observed within the bulk layer of the samples.

At both  $0.5\times$  and  $7\times$ CMC, a significant increase in bulk layer emulsions due to an increase in homogenization intensity was observed for all surfactants. Figure 9 shows the comparison of samples prepared using  $0.5\times$ CMC SDS at low versus high homogenization intensities. To emphasize the difference in bulk layer emulsion stability, the bulk layer turbidity values of day 5 samples were used for comparison. Under low homogenization conditions, the turbidity values ranged from 1.5 to 31.2 NTU, which was significantly lower than the turbidity values obtained from samples at high homogenization. At high homogenization, the turbidity of the bulk layer of the emulsion samples ranged from 3.6 to 2,210 NTU. Enhanced emulsion stability due to an increase in homogenization intensity was observed for all surfactants by an increase in turbidity.



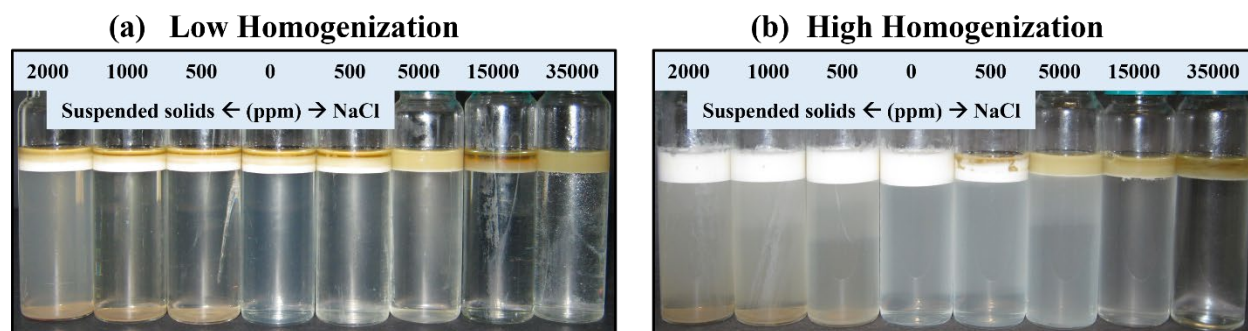
**Figure 9. Turbidity comparison of samples prepared using  $0.5\times$ CMC SDS at (a) low homogenization and (b) high homogenization intensities.**

Although the turbidity range differed substantially between the homogenization intensities, the values became more and more similar with an increase in NaCl concentrations. This suggested that at low concentrations of salinity, the effect of homogenization played a more

significant role in emulsion stabilization. This was observed for all types and concentrations of surfactants.

In addition to greater bulk layer emulsion stability, greater creaming was observed due to an increase in homogenization intensity, particularly for samples formulated at  $7\times\text{CMC}$  (Figure 10). This effect was not as prominent at  $0.5\times\text{CMC}$ . Figure 10 shows the simulated bilgewater samples prepared using  $7\times\text{CMC}$  of Blast-off at low and high homogenization intensities. Similar to Figure 9, greater emulsion stability was observed in the bulk layer for high homogenization samples. However, in addition to bulk layer changes, greater emulsion stability was also observed by less oil coalescence and greater creaming formation. This suggests the significance of homogenization intensity and surfactant concentration in tandem.

Overall, the surfactants demonstrated enhanced emulsion stabilization with an increase in homogenization intensity. This was in agreeance with literature [18]. Increasing the homogenization intensity signifies an increase in energy applied to emulsifying the two phases. This causes shearing and dispersion of oil droplets throughout the water phase which enhances emulsion stabilization.

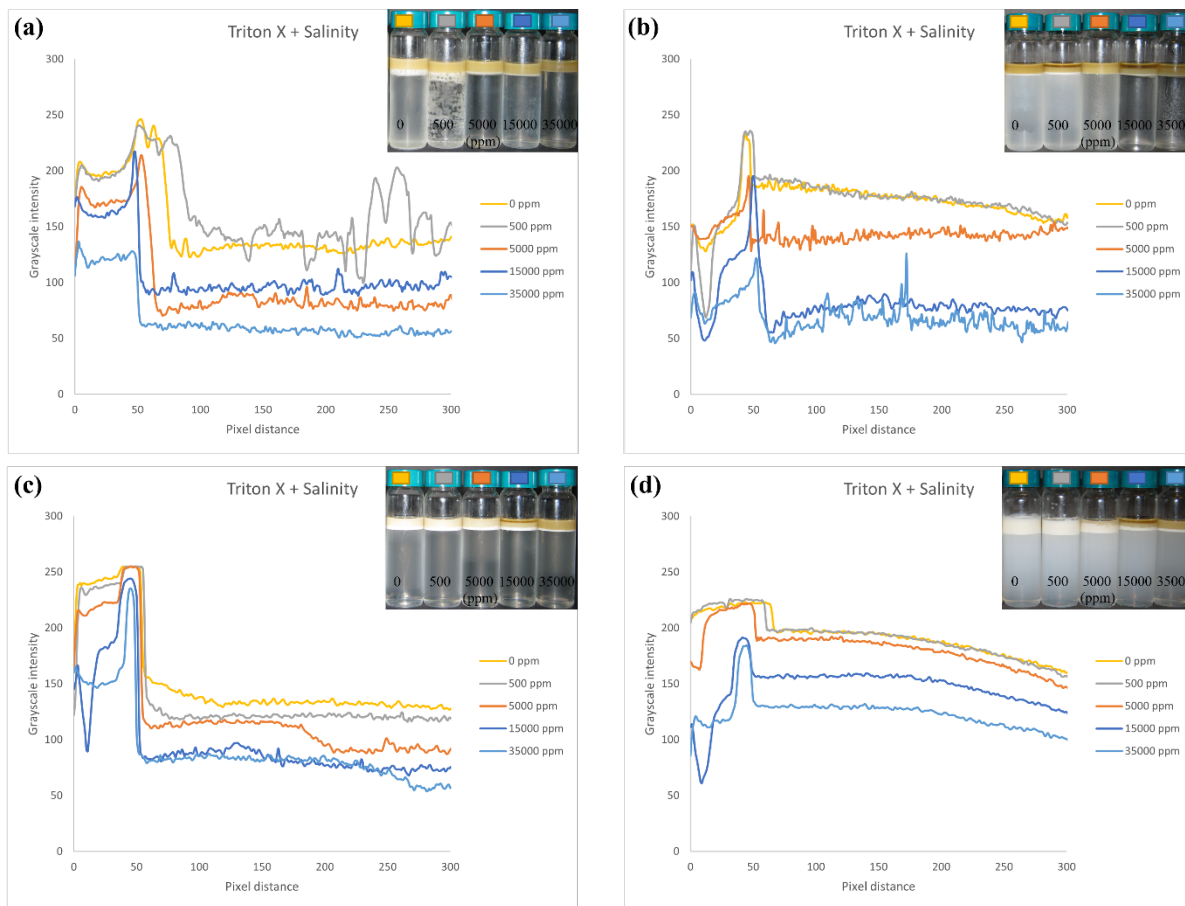


**Figure 10. Homogenization effect on samples prepared using 7CMC Blast-off at (a) low homogenization and (b) high homogenization intensities.**

### 4.2.3 Environmental Factors

The bilgewater samples were prepared under saline conditions and in the presence of suspended solids. The dataset included a range of concentrations to simulate the inconsistent bilgewater emulsion formulations present onboard. Salinity showed to have a clear effect on emulsion stability, however suspended solids did not. The addition of NaCl showed a positive correlation with emulsion destabilization and oil coalescence for all surfactants tested. The effect of salinity is in accordance with previous results reported in literature [56].

The inclusion of salinity in samples led to greater oil coalescence. Figure 11 shows the grayscale profiles of Triton X-100 samples prepared with a range of NaCl concentrations under four different sets of conditions: (a)  $0.5 \times \text{CMC}$  + low homogenization, (b)  $0.5 \times \text{CMC}$  + high homogenization, (c)  $7 \times \text{CMC}$  + low homogenization (d)  $7 \times \text{CMC}$  + high homogenization. Samples prepared at  $0.5 \times \text{CMC}$  produced significant oil layers. However, a decrease in grayscale intensity of the oil layer as the concentration of salinity increases shows the degree of oil coalescence. Similarly, a decrease in grayscale intensity of the bulk layer can be observed. The overall decrease in grayscale intensity values represents the emulsion destabilization that occurred as a result of saline conditions. The samples prepared at  $7 \times \text{CMC}$  (Figure 11 (c) and (d)) showed significant creaming, unlike  $0.5 \times \text{CMC}$  conditions. However, at high concentrations of salinity (15,000 and 35,000 ppm), a significant drop in grayscale intensity occurred which signified oil coalescence. The results show that even at high concentrations of surfactant and high homogenization intensities, saline conditions enhance emulsion destabilization, as observed by significant oil layer separation. This effect was observed for all surfactants and conditions except for Type 1 samples prepared at  $7 \times \text{CMC}$  + high homogenization, in which only creaming was observed. This further demonstrates Type 1 as the most stable surfactant.



**Figure 11. The effect of salinity on grayscale profiles. Samples prepared using Triton X-100 at (a)  $0.5 \times \text{CMC}$  + low homogenization, (b)  $0.5 \times \text{CMC}$  + high homogenization, (c)  $7 \times \text{CMC}$  + low homogenization (d)  $7 \times \text{CMC}$  + high homogenization.**

On the contrary, the presence of suspended solids did not indicate a significant effect on emulsion stabilization through visual observation. The grayscale profiles of samples containing suspended solids (Appendix B) were inconsistent, showing no particular effect on oil coalescence or creaming layer formation as a result of increasing solids concentrations. Images showed that suspended solids had settled to the bottom of the vial by day 5 (Figure 10). Similarly, an increase in suspended solids did not always correlate to an increase in turbidity. Thus, it was assumed that the effect of suspended solids was negligible, primarily due to settling.

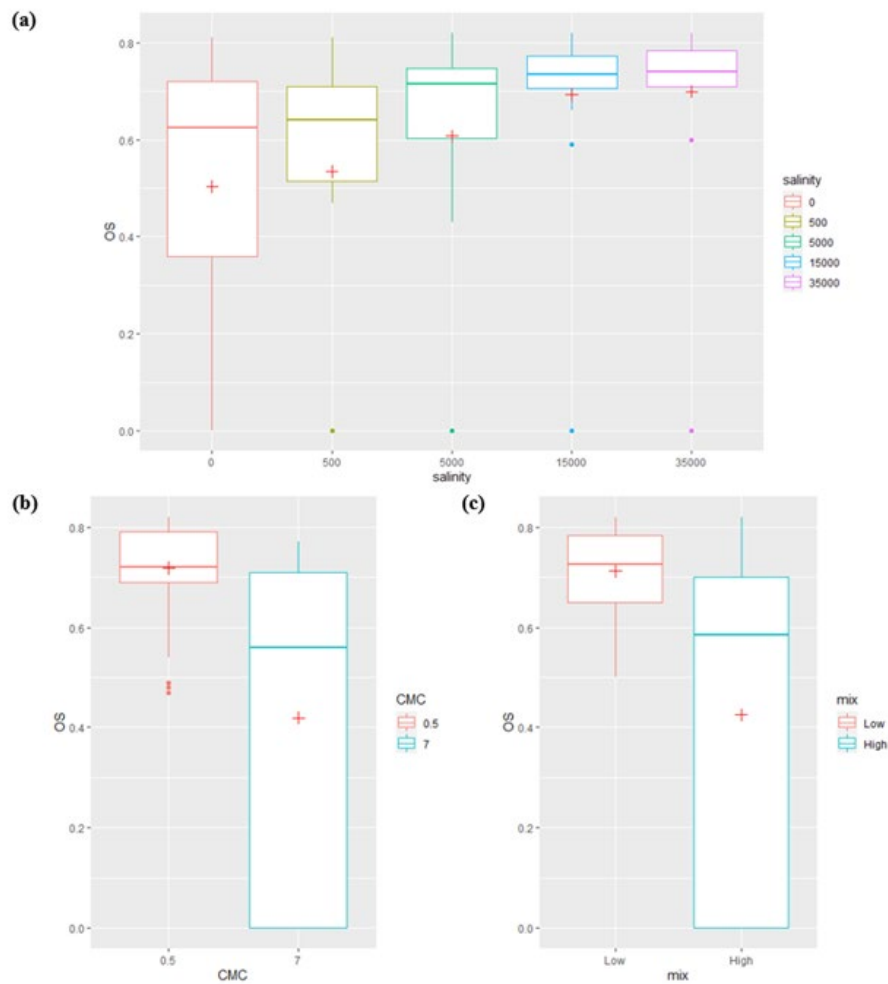
### 4.3 Analysis of Variance

To further quantify the experimental data, an ANOVA was conducted using the dataset consisting of 128 samples with balanced design to investigate the effect on *OS* and *Turbidity* from the different types and levels of explanatory variables (*Cleaner*, *SS*, *Salinity*, *CMC*, and *Mix*; *Mix* signifies homogenization intensity). First, one-way ANOVA was fit to find the effect on *OS* for each explanatory variable. The *p*-values of *Salinity*, *CMC*, and *Mix* were less than 0.05, implying that there is strong evidence that the means of *OS* for different levels for each variable were not the same. In the same regard, the type of cleaner was identified as not having a significant effect on *OS*. Using these results, more complicated ANOVA models were also considered.

Then, two-way ANOVA models were fitted, with different combinations of three variables which were significant in the one-way ANOVA (*Salinity*, *CMC*, and *Mix*). For every combination of the two variables, we found that the effects of the variables were statistically significant ( $p < 0.05$ ). Similarly, the effects of the three variables and their interaction terms were significant ( $p < 0.05$ ) under more complicated models, such as the three-way additive ANOVA and with interaction models.

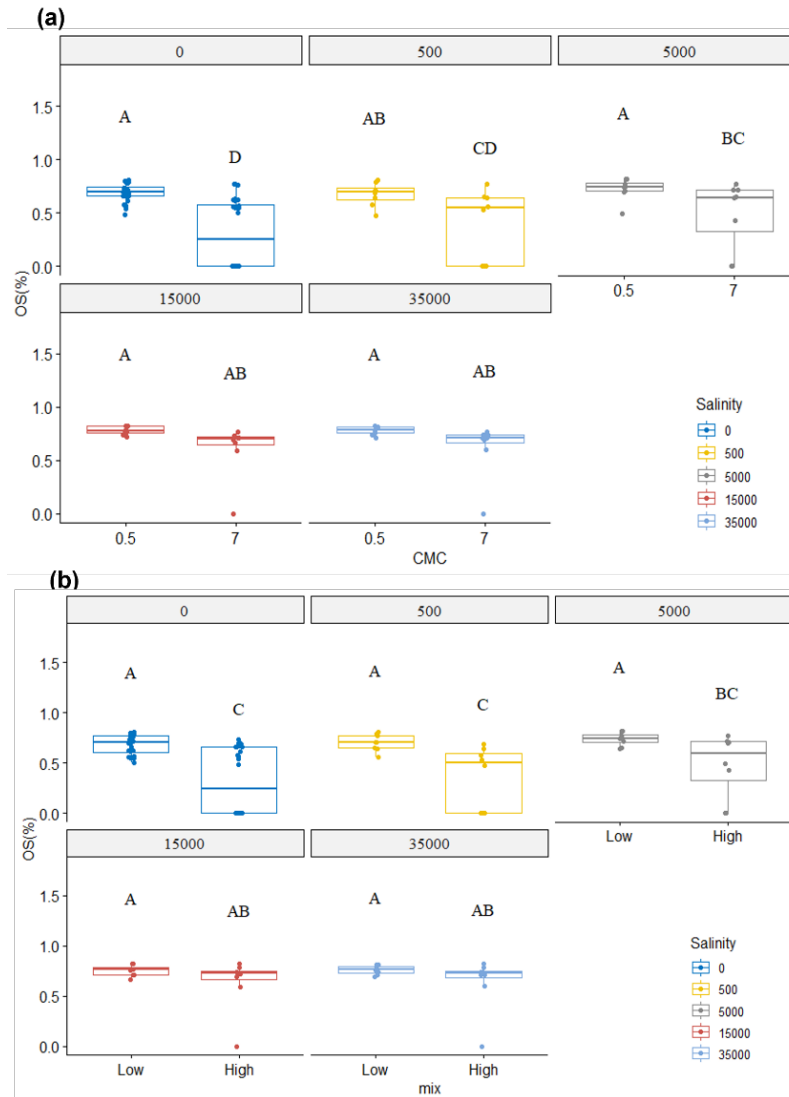
All the ANOVA models that were fitted as candidates were considered and the best-fit model using AIC was selected. The three-way ANOVA with interaction model was selected as the best model with the lowest AIC value (-141.08). The assumptions of ANOVA were also checked for the selected model using the residual plot (for homoscedasticity) and Q-Q plot (for normality). Although there were some outliers, they were not sufficiently extreme to be considered as a violation of the assumptions. Therefore, we kept those observations in the analyses to maintain the balanced experimental design.

In the model, all the main effects of *Salinity*, *CMC*, and *Mix* and two-way interaction terms of all the combinations of the three variables were statistically significant ( $p < 0.05$ ). The three-way interaction term was marginally significant ( $p = 0.0429$ ). This interaction term was excluded from the analysis for clear interpretation. Figure 12 illustrates box plots of *OS* with the three main effects. It was observed that the means of *OS* were high when the level of *Salinity* was high, *CMC* was low, and in low *Mix*.



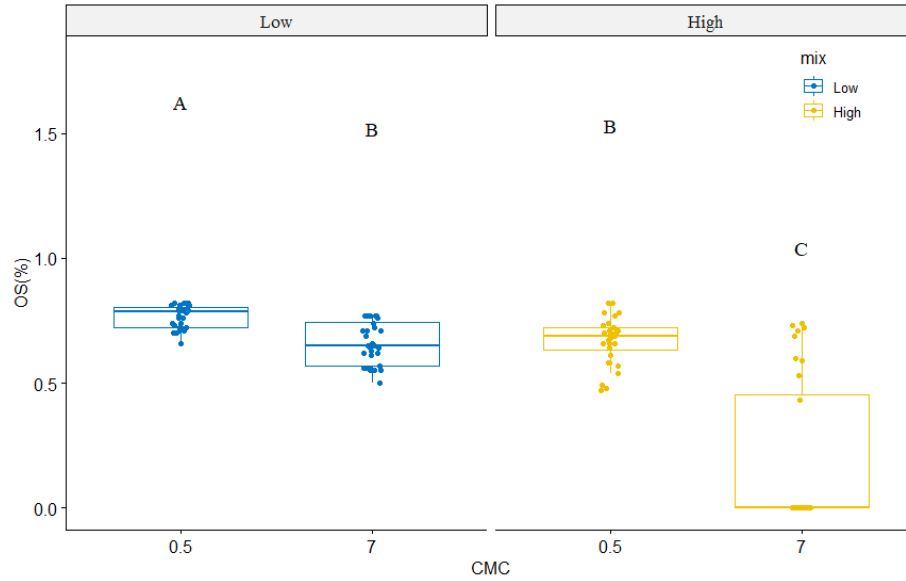
**Figure 12. Box plots of *OS* with (a) Salinity, (b) CMC (0.5× and 7×), and (c) Mix (Low and High) variables.**

In addition, box plots of *OS* were illustrated for the two-way interaction terms, grouped by the combination of the *Salinity* with *CMC* and *Salinity* with *Mix* in Figure 13. Tukey's HSD test was also used as a multiple comparison procedure to find the means that are significantly different from each other. The lettered group was used to distinguish different combinations of the variables. The groups which share the same letter were not significantly different from each other in terms of the mean of the response variable. In general,  $0.5 \times CMC$  showed significantly higher means of *OS* than  $7 \times CMC$  and low *Mix* showed higher means of *OS* than high homogenization in most of the *Salinity* levels (Figure 13). However, the results were most prominent among lower levels of *Salinity*. This suggests that at levels of *Salinity*, such as those near sea water conditions (35,000 ppm), the effects of the other variables (*CMC*, *Mix*) are less critical.



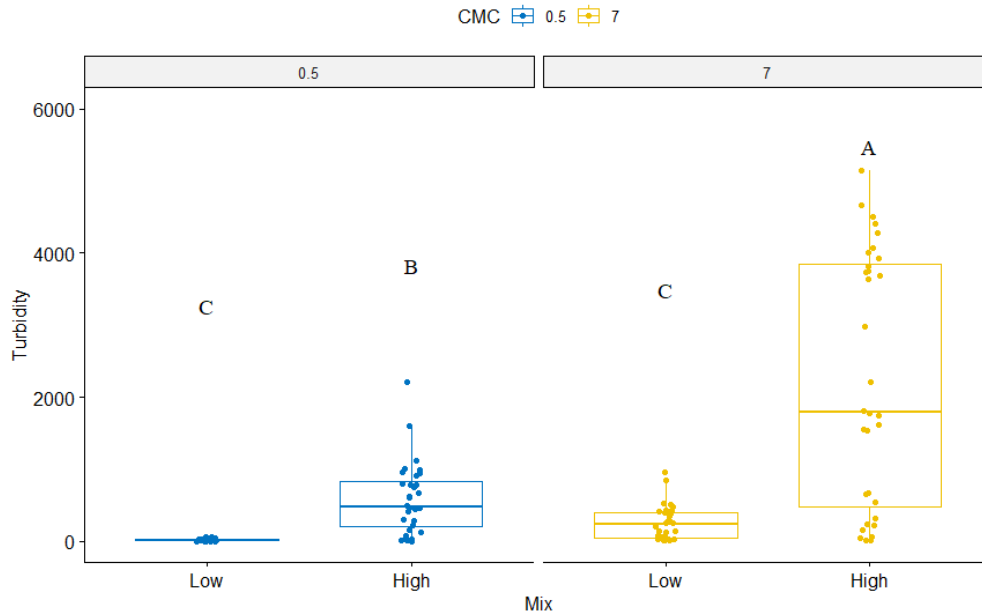
**Figure 13. Box plots of *OS* grouped by level of Salinity, (a) CMC (0.5 $\times$  and 7 $\times$ ), and (b) Mix (Low and High) variables. Letters above the individual box plots correspond to the groups assigned by Tukey's HSD tests.**

Figure 14 displays another set of box plots of *OS* grouped by *CMC* and *Mix* variables. This figure emphasizes the impact of cleaner concentration and homogenization intensity in tandem. High homogenization and high concentration resulted in the greatest emulsion formation, where low homogenization and a low concentration of cleaner resulted in the greatest phase separation.



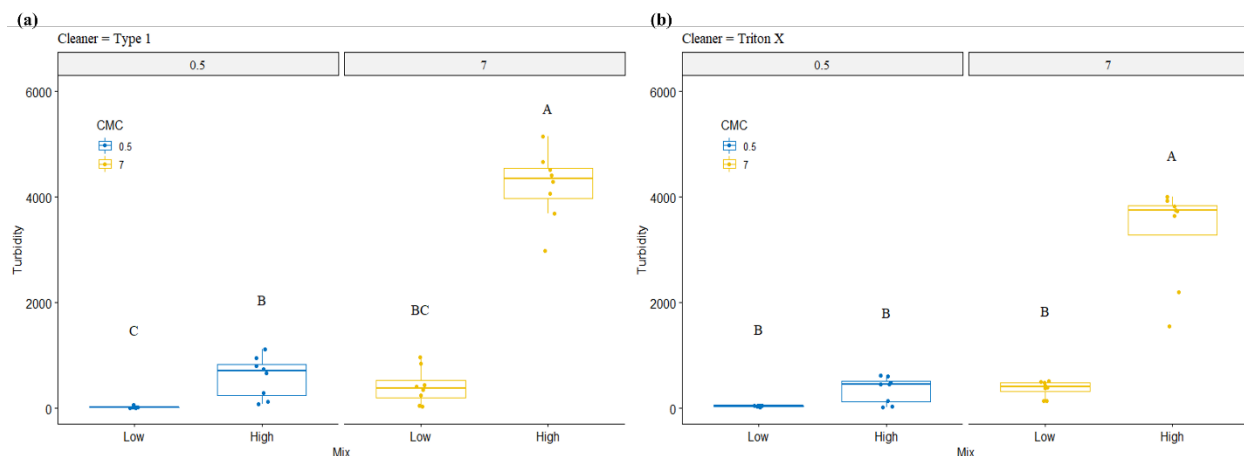
**Figure 14. Box plots of *OS* grouped by CMC (0.5× and 7×), and Mix (Low and High) variables. Letters above the individual box plots correspond to the groups assigned by Tukey's HSD tests.**

Although *OS* is the main indicator of emulsion stability throughout this study, *Turbidity* was utilized to analyze emulsion formation within the bulk layer of the samples. With the same procedure as the response variable of *OS*, several ANOVA models were fitted, and the best-fit model was selected using AIC to investigate the effect of the explanatory variables on *Turbidity*. Similar to the model with *OS*, the three-way ANOVA with interaction model was chosen with the lowest AIC value of 1947.60. In the model, all the main effects and interaction terms were statistically significant ( $p < 0.05$ ), which indicates that the means of *Turbidity* were not equal for each main effect and the combinations of the three variables. Most importantly, Figure 15 demonstrates the effect of *CMC* and *Mix* on *Turbidity*. The mean of *Turbidity* significantly differs for *Mix* for both *CMC* levels. High *Turbidity* was observed for high *Mix* for both levels of *CMC*, emphasizing the effect homogenization intensity has on emulsion formation in the bulk layer.



**Figure 15. Box plots of *Turbidity* grouped by CMC (0.5× and 7×), and Mix (Low and High) variables. Letters above the individual box plots correspond to the groups assigned by Tukey's HSD tests.**

Additionally, the three-way interaction term was statistically significant ( $p < 0.05$ ) in the model for *Turbidity*. Significant three-way interaction term implies that the interaction among the two variables differ across the levels of the third variable. For example, it was found that the two-way interactions of *CMC* and *Mix* differ across different levels of *Cleaner*, which illustrates significant three-way interaction in our model. By Tukey's HSD tests, Figure 16 demonstrates this utilizing different *Cleaners*, (a) Type 1 and (b) Triton X-100. The mean of *Turbidity* significantly differs for *Mix* for both *CMC* levels, when *Cleaner* is Type 1. This differs from Triton X-100 in which the mean of *Turbidity* significantly differs for *Mix* only when *CMC* is 7 times greater. Based on these interactions, the type of cleaner could potentially be an influential parameter to consider during bilgewater management when regarding the bulk layer of the wastewater.



**Figure 16. Box plots of *Turbidity* grouped by Mix (Low and High), and CMC (0.5 $\times$  and 7 $\times$ ) variables for different Cleaners (a) Type 1 and (b) Triton X-100. Letters above the individual box plots correspond to the groups assigned by Tukey's HSD tests.**

#### 4.4 Emulsion Stability Prediction Modeling

An emulsion stability prediction model was previously developed by the Naval Surface Warfare Center Carderock Division and UCF which utilizes the machine learning (ML) technique, random forest (RF), for both regression and classification algorithms. RF is a technique that can operate quickly over large datasets, by producing multiple decision trees [59, 60]. The developed stability model includes the parameters investigated in this study. Thus, the results of this study were implemented to understand the effects of using realistic bilgewater conditions on the model. The selected ML factors are outlined in Table 5. Factors corresponding to this study include  $CMC_{IFT-NSBM}$ , equilibrium IFT, SS concentration, salinity, surfactant concentration, and mixing intensity. The data in Table 6 shows the factor category for the physicochemical properties of the cleaners and surfactants. Highlighted columns show the new data that was gathered during this study, while the other columns show previous data. The new data is distinct in that it shows the  $CMC_{IFT}$  and equilibrium IFT measured in the presence of a representative bilge oil mix rather than a model oil (i.e. mineral oil).

**Table 5. Selected factors for ML**

Factor category	Factors
Cleaners/surfactants information (7)	Critical micelle concentration ( $CMC_{ITF-NSBM}$ ) (ppm)
	Equilibrium surface tension (ST) above CMC (air) (mN/M)
	Equilibrium interfacial tension (IFT) above CMC with NSBM #4 (mN/M)
	Micelle size (nm)
	Zeta potential (mV)
	Alkalinity ( $mg\ CaCO_3\ L^{-1}$ )
	Surfactant's pH
Environmental factors (6)	pH (4, 10, and unadjusted)
	Suspended solids (SS) concentration (0, 1,000, 2,000 and 5,000 ppm)
	Salinity (0, 500, 5,000, 15,000 and 35,000 ppm)
	Surfactant concentration ( $0.5 \times CMC$ and $7 \times CMC$ )
	Temperature (4, 25, and $35^\circ C$ )
	Mixing intensity (high and low)

**Table 6. Physicochemical properties of cleaners and surfactants used for emulsion stability evaluation in this study**

<b>Cleaner/surfactant</b>	<b>Primary surfactants</b>	<b>CMC<sub>IFT</sub> – Mineral Oil (ppm)</b>	<b>CMC<sub>IFT</sub>-NSBM (ppm)</b>	<b>Equilibrium IFT<sub>CMC</sub>-Mineral Oil<sup>c)</sup> (mN/M)</b>	<b>Equilibrium IFT<sub>CMC</sub>-NSBM (mM/M)</b>	<b>Micelle size (nm)<sup>d)</sup></b>	<b>Zeta potential (mV)<sup>e)</sup></b>	<b>Alkalinity (mg CaCO<sub>3</sub>/L)<sup>f)</sup></b>	<b>pH<sup>f)</sup></b>
<b>Type 1 Detergent</b> (MILSPEC: MIL-D-16791)	Alkyl aryl polyether alcohol	105	138	2.1	1.6	18 ± 1	-28 ± 6	3.3	6.4
<b>Super Blast Off</b> (Elsco Inter. Inc.)	Cocamide diethanolamine	5,381	6,893	3.4	2.4	111 ± 7	-63 ± 3	171	10.5
<b>SDS</b>		5,130	1,898	9.8	3.3	1.3	-40	7.4	6.3
<b>Triton X-100</b>		324	458	3.0	1.8	9.1	-16	3.5	6.7

<sup>a)</sup> CMC: critical micelle concentration; <sup>b)</sup> ST: surface tension; <sup>c)</sup> IFT: interfacial tension; <sup>d)</sup> determined using dynamic light scattering (DLS). The cleaner/surfactant solutions were prepared at various concentrations (serial dilutions) and no oil present; <sup>e)</sup> determined at a concentration which is close to CMC; <sup>f)</sup> determined at a 7×CMC

Three different datasets including the data gathered during this study were tested. Results of the ML study are presented in Table 7 in which the RF classifier was used for classification and the RF regressor was used for the regression algorithm for *OS* and *turbidity* prediction. For “Regression”, a lower number close to 0, describing the mean absolute error (MAE), is the better prediction, while “Classification” uses an evaluation metric in which a higher number close to 1, indicates a better prediction.

All datasets include data for the four downselected surfactants/cleaners in this study (Type 1, Triton X-100, SDS, and Super Blast-off). Dataset (1) has a total of 144 data with 36 data for each surfactant and holds the previous values achieved for each of the factors. This dataset does not contain any new information gathered from this study. Dataset (2) also has a total of 144 data (36 data/each surfactant). This dataset has replaced the factors  $CMC_{IFT}$  and Equilibrium IFT with the newly measured data. Lastly, dataset (3) holds a total of 272 data (68 data/each surfactant). Similar to dataset (2), the factors  $CMC_{IFT}$  and Equilibrium IFT were replaced with the newly measured data. However, dataset (3) includes additional intervals for the environmental factors (e.g., salinity interval with 0, 5000, 15000, and 35000). The other datasets only include two intervals for suspended solids (0 and 1,000 ppm) and salinity (0 and 35,000 ppm).

Only datasets (1) and (2) can be compared because they have the same total data at 144. Dataset (2) achieved a slightly lower MAE for both *OS* and *turbidity* compared to dataset (1), however, it did not achieve an improved classification prediction. This data demonstrates that the two newly added factors ( $CMC_{IFT}$  and Equilibrium IFT) which represent more realistic data did not improve the model prediction. This could signify simply that the more realistic data did not have a significant effect on the model. The lack of improvement could also be a result of a similar range of experimental values achieved or inaccuracy within the model.

However, more data with more intervals of each factor (Dataset (3)) could improve the prediction model. For classification, the RF classifiers achieved a slightly better prediction of *OS* with an F1-score of 0.7636. Turbidity also showed a good emulsion prediction with the RF regressor (MAE of 0.0578) and RF classifier (F1-score of 0.9062).

**Table 7. RF regressor and classifier results for *OS* and *turbidity***

ML prediction	Dataset (1) Test results (MAE or F1)		Dataset (2) Test results (MAE or F1)		Dataset (3) Test results (MAE or F1)	
	<i>OS</i>	<i>Turbidity</i>	<i>OS</i>	<i>Turbidity</i>	<i>OS</i>	<i>Turbidity</i>
Regression	0.1799	0.0858	0.1789	0.0745	0.153	0.0578
Classification	0.7828	0.8091	0.7552	0.7864	0.7636	0.9062

## CHAPTER FIVE: CONCLUSIONS AND PRACTICAL IMPLICATION

A challenge exists to meet bilgewater discharge regulations set by MARPOL Annex I and DoD Regulation 4715.06-V2 to regulate commercial and Armed Forces vessels. These regulations are set in place to maintain the oil content discharged and prevent potential damage to the surrounding environment. However, difficulty in meeting these regulations arises due to the technical challenges faced when treating oil-in-water emulsions. Many treatment systems rely on the immiscibility characteristic of oil and water. Thus, the stability of an emulsion is a prominent factor in the effectiveness of treatment and management. In addition to the innate difficulty of treating emulsions, bilgewater consists of many components and can vary in composition significantly. The multivariate nature of bilgewater adds yet another layer of complexity to this area of research.

The objective of this research was to investigate the effects of real bilgewater conditions on emulsion stability. In particular, the effects of determining a surfactant's CMC in the presence of a representative bilge oil mix (NSBM #4) was studied. Additional variables tested for include surfactant concentration, homogenization intensity, and environmental conditions (salinity and suspended solids) at intervals that represent real bilgewater emulsions. Through nondestructive analytical methods and statistical evaluation, it was found that surfactant concentration, homogenization intensity, and salinity had the most significant impact on emulsion stability.

The results of this study emphasized the variance in results obtained using more realistic conditions. The IFT and  $CMC_{IFT}$  values achieved in this study using a representative bilge oil varied slightly than those reported in literature using mineral oil as a model oil [6]. This was true for all surfactants except for SDS, the only ionic surfactant tested in this study. The slight

difference in values, particularly regarding SDS, could be a result of the oil additives found in NSBM#4 [58]. In addition, the interfacial tension data gathered was in accordance with the image-based analyses. The results demonstrated that lower IFT and  $CMC_{IFT}$  values were indicative of emulsion stability, and that emulsion stability was impacted by surfactant concentration. Overall, IFT data from this study and findings within literature support the need to further investigate the role of components added to bilgewater oils which enhance emulsion stability [58].

To further quantify the experimental data, an ANOVA was conducted using the dataset consisting of 128 samples with balanced design to investigate the effect on *OS* and *Turbidity* from the different types and levels of explanatory variables (*Cleaner*, *SS*, *Salinity*, *CMC*, and *Mix*; *Mix* signifies homogenization intensity). In particular, in the model investigating *OS*, all the main effects of *Salinity*, *CMC*, and *Mix* and two-way interaction terms of all the combinations of the three variables were statistically significant ( $p < 0.05$ ). It was observed that the means of *OS* were high when the level of *Salinity* was high, *CMC* was low, and in low *Mix*.

In addition to expanding the current field of emulsions, the intent of this work is to aid bilgewater treatment and management. This information could be utilized to guide against emulsion formulations that enhance stability to increase the effectiveness of current treatment systems. For example, it is suggested that excess use of surfactants and movement from handling be prevented. Further, the practical application of this data was tested in an emulsion stability prediction model using RF classification and regression algorithms. Results showed that the addition of the more realistic data did not actually improve predictions. However, it was demonstrated that the addition of a larger dataset<sup>51</sup> with more intervals was useful. Based on the work presented herein, it is suggested that future studies focus on adding experimental data

within the already selected variables and running multiple replicates to assure model accuracy on contribution to emulsion stability.

## CHAPTER SIX: EXPERIMENTAL RECOMMENDATIONS

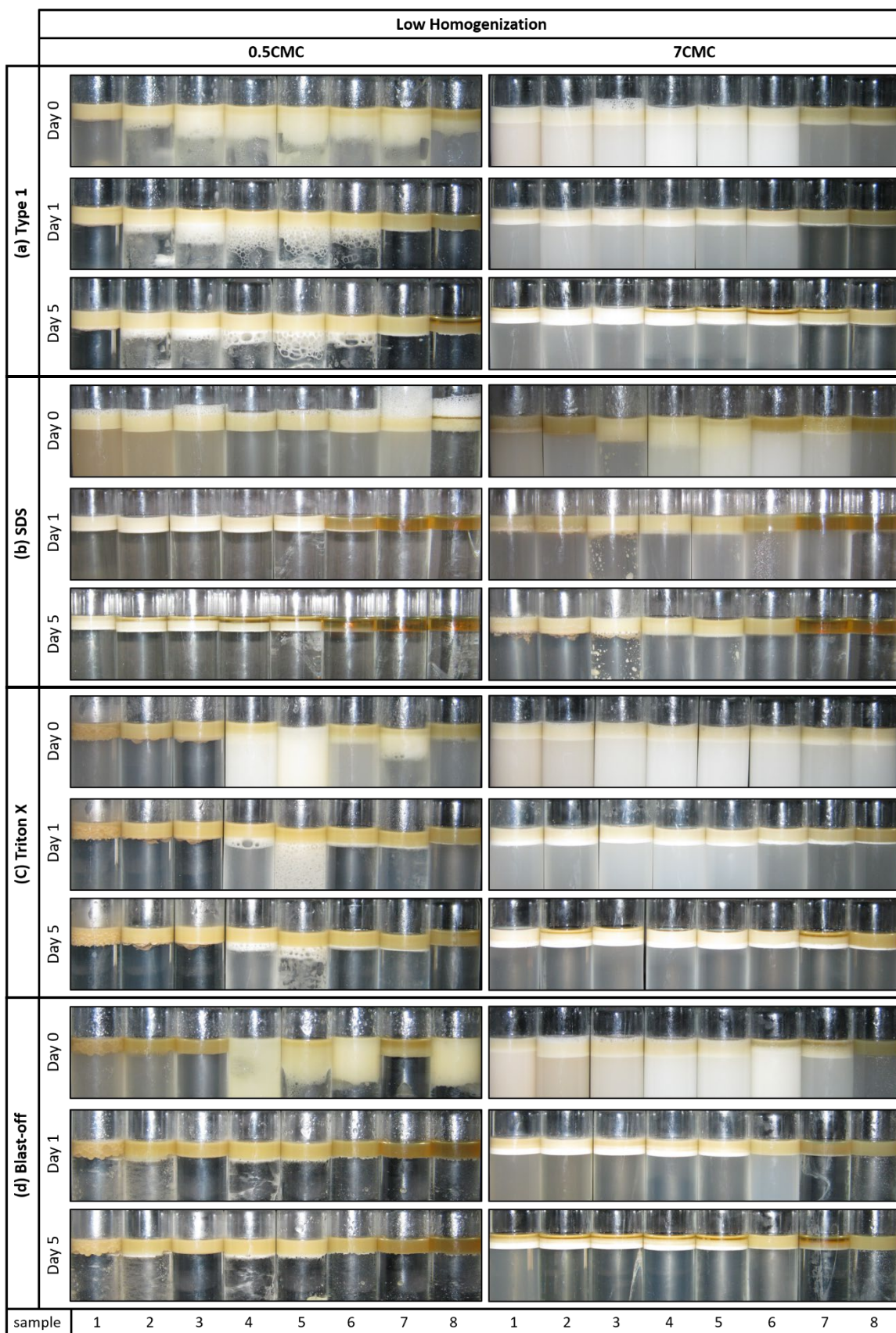
First starting with the IFT measurements, it was found that the oil droplet reacted with the external phase when there was a surfactant present. In general, the reactions caused the droplet size to decrease over time. The continuous decrease in size was cause for concern because it would not allow the droplet to stabilize in order for a final IFT measurement to be made. This effect became increasingly apparent as the concentration of surfactant increased, as well as with surfactants determined as more stable. As a result, a lot more trials had to be run for each of the IFT measurements at higher concentrations, and the readings were significantly less stable. It became particularly difficult to maintain an oil droplet as the concentration of surfactant reached its CMC, which often resulted in a less exact and wider range of potential CMC values. It was believed that oil additives in NSBM#4 were reacting with the surfactants because when replicates were tested using a different oil (mineral oil), the same affects were not observed. Thus, it is recommended that a model oil be used as a controlled variable for testing other parameters, especially when intended for model development. However, for understanding the effects of a representative bilge mix such as NSBM#4, it is recommended that further investigation of oil additives be conducted.

Although image analyses are ideal for onboard experiments due to a lack of space and resources, they come with some drawbacks. Most notably, image analyses are subject to significant human error. To address these concerns, it is recommended that clear, detailed, and repeatable experimental guidelines are developed to minimize discrepancy between analyses for each individual's work. This will also minimize discrepancy of analyzations from person to person. Additionally, it is recommended that experiments be repeated to assure accuracy and precision. This applied to the image analyses as well as the turbidity measurements as it was

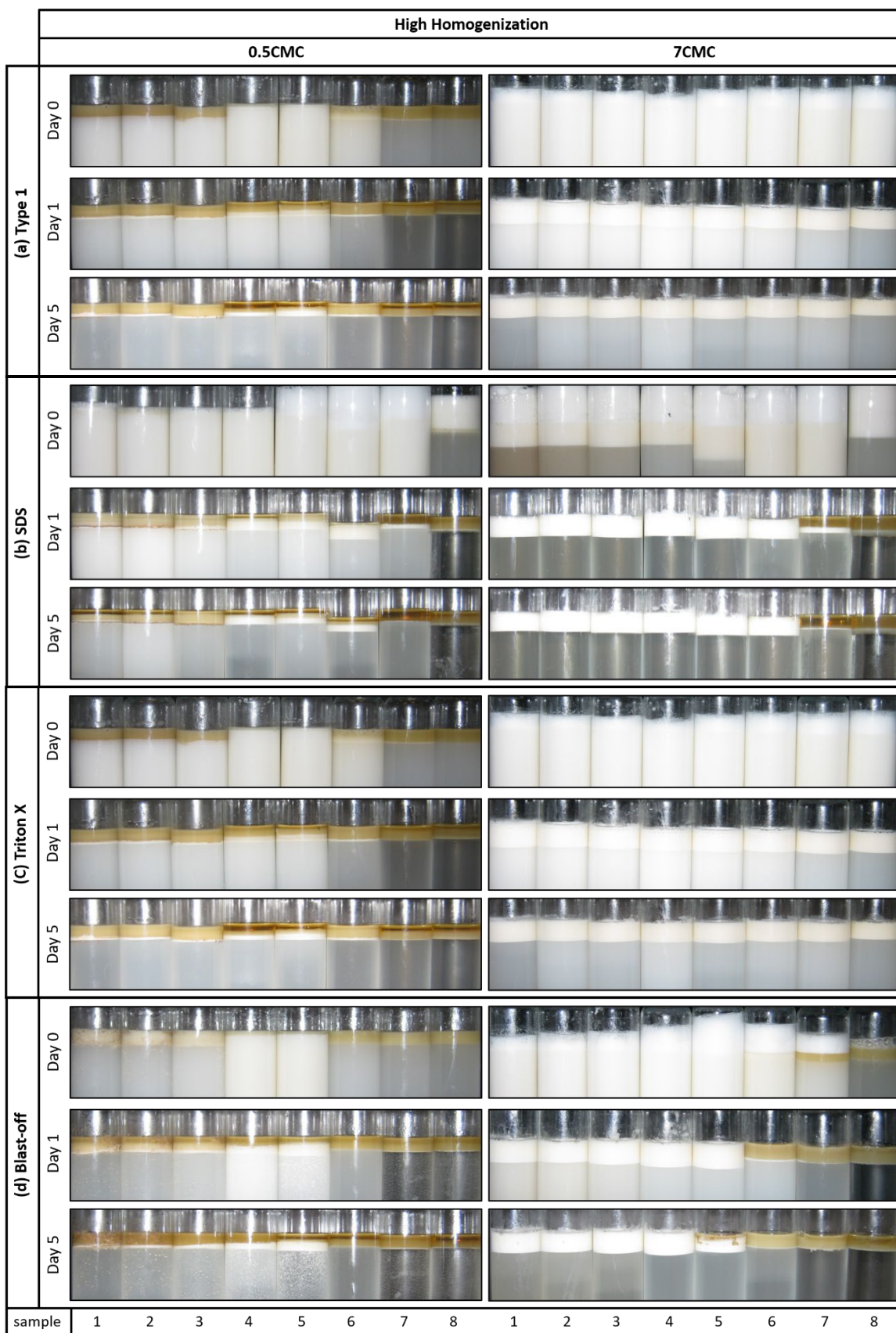
found that there was significant potential for error. Since this work was a continuation of previous research, it was pertinent that the experiments were performed the same and that the data was comparable. To address this, preliminary experiments were conducted for each task. The preliminary experiments were replicates of previous work which assured consistent and repeatable values were being achieved.

Based on the culmination of research completed under the entirety of the project duration, the most notable recommendations include replicates of the data and increased intervals for each of the conditions tested. As recently mentioned, replicates were crucial for bridging the gap between the previous work and the work herein. However, due to the myriad of parameters and large sample size tested, replicates were not completed for each individual sample. Thus, it was discovered that replicates were a necessary part of this work and improving overall accuracy. It is also recommended to increase the interval range for each of the conditions tested to improve model prediction accuracy, as concluded from the results of Chapter 4.4.

# **APPENDIX A: TIME-COURSE OBSERVATION OF EMULSION SAMPLES**



**Figure A 1. Time-course visual observations of samples prepared at low homogenization.**

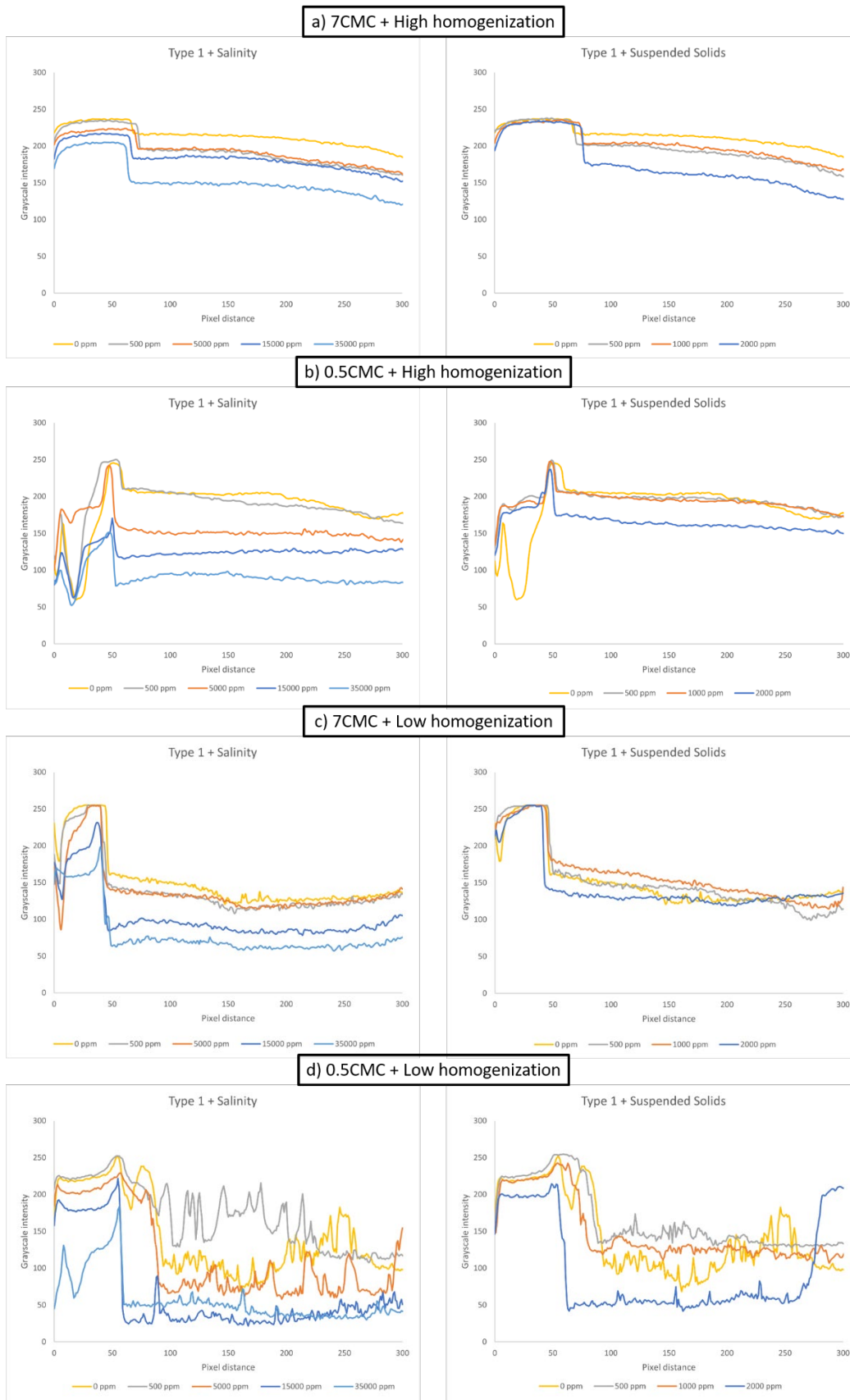


**Figure A 2. Time-course visual observations of samples prepared at high homogenization.**

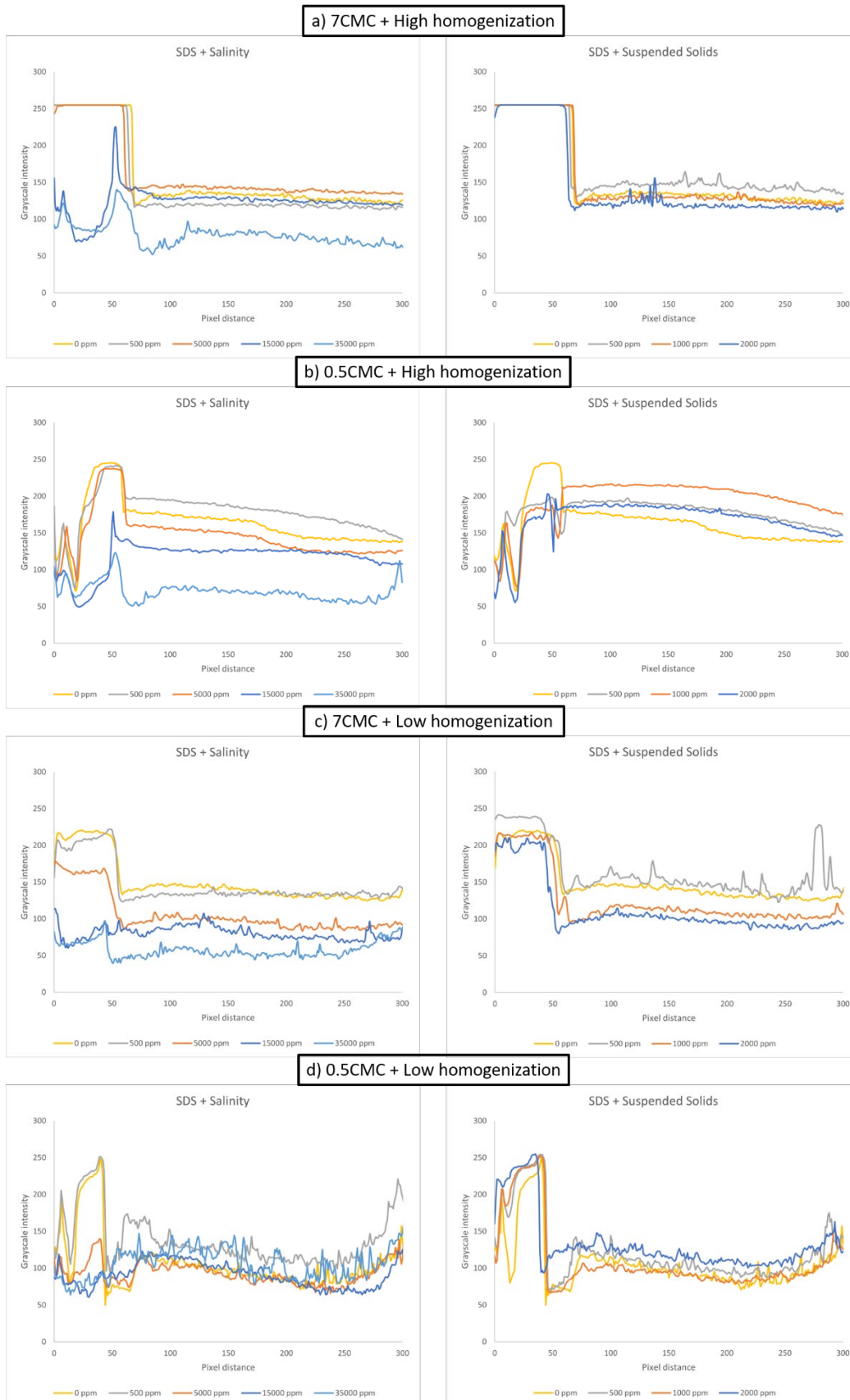
**Figure A Legend**

<b>Sample</b>	<b>Conditions</b>	
	<b>Suspended Solids (ppm)</b>	<b>Salinity (ppm)</b>
1	2,000	-
2	1,000	-
3	500	-
4	-	-
5	-	500
6	-	5,000
7	-	15,000
8	-	35,000

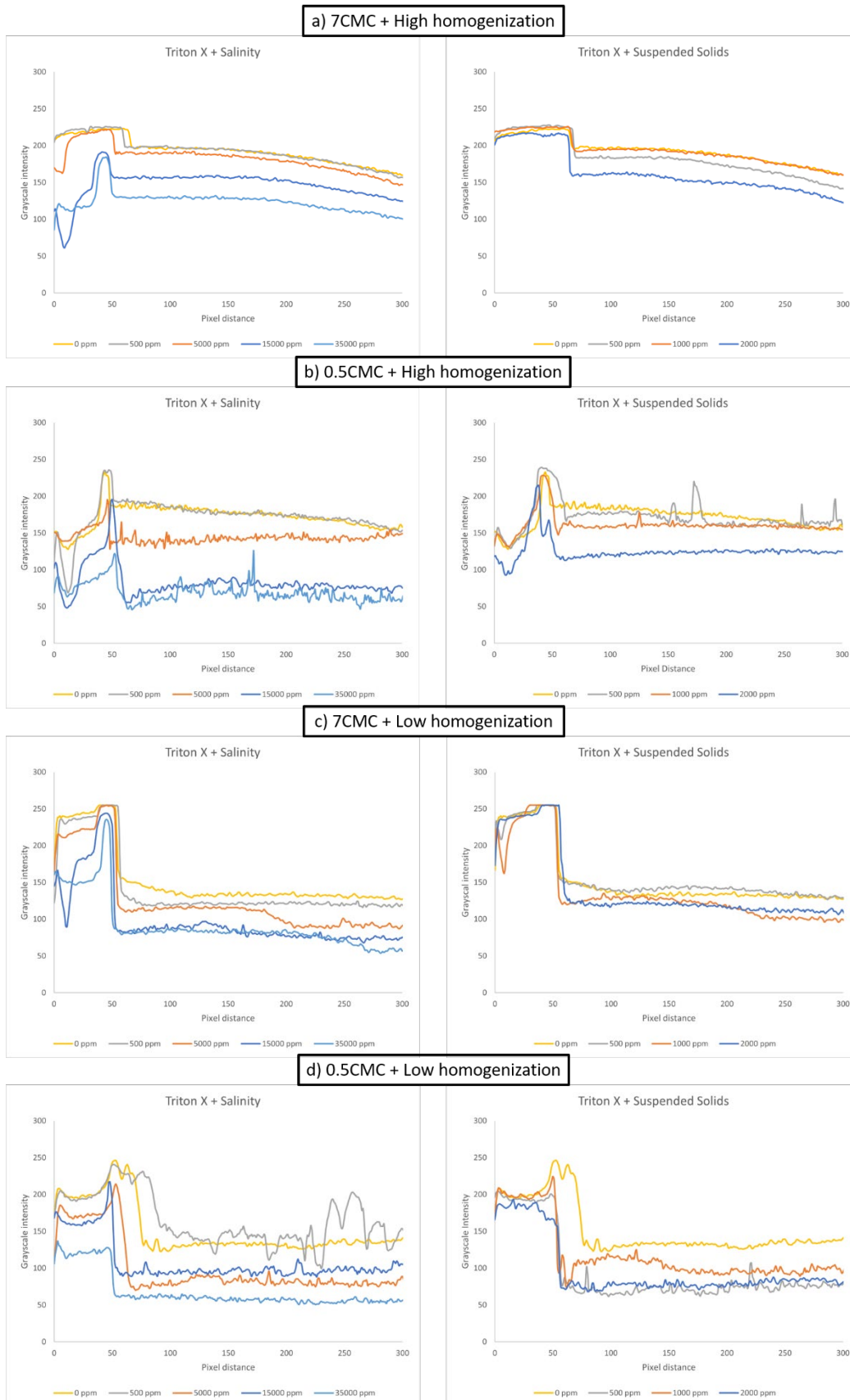
## **APPENDIX B: GRAYSCALE PROFILES OF EMULSION SAMPLES**



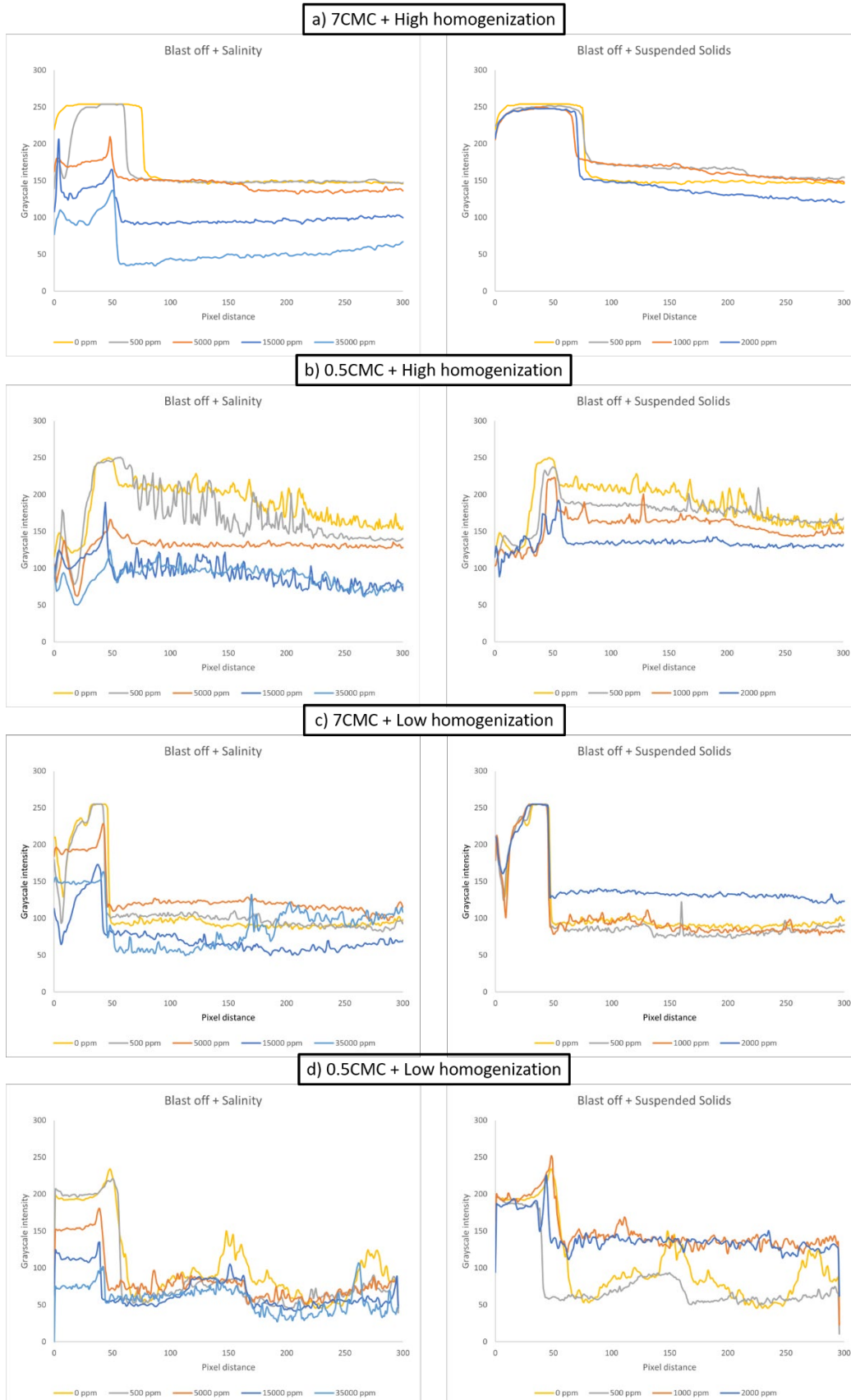
**Figure B 1. Grayscale intensity profiles prepared with Type 1.**



**Figure B 2. Grayscale intensity profiles prepared with SDS.**



**Figure B 3. Grayscale intensity profiles prepared with Triton X-100.**



**Figure B 4. Grayscale intensity profiles prepared with Blast off.**

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