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Emulsion Characterization Study for Improved Bilgewater Treatment and Management

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EMULSION CHARACTERIZATION STUDY FOR IMPROVED BILGEWATER TREATMENT AND MANAGEMENT

by

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B.S. Chem. E., Industrial University of Santander, 2015

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ABSTRACT

The need for proper management of bilgewater to meet discharge regulations (e.g., 15 ppm oil) has revealed the necessity to expand the current understanding of bilgewater emulsions. This study proposed to evaluate emulsion stability under various environmental conditions and to identify governing parameters for emulsion formation. The stabilizing properties of eight-commercial cleaners and two-neat surfactants were evaluated. *In situ* characterization techniques were used for monitoring emulsion stability. Additionally, a needle-type pH microsensor and fluorescence spectroscopy were used for analyzing mass transfer at the oil-water interface. Water quality of extracted bilgewater showed to highly vary between vessels (e.g., conductivity: 1.74–24 mS/cm, chemical oxygen demand [COD]: 1,279–42,800 mgO_2/L, and total suspended solids [TSS]: 256–4,248 mg/L). Emulsion stability was significantly affected by surfactant type, temperature, and salinity. In particular, increase in salinity and temperature greatly reduced emulsion stability by enhancing emulsion coalescence. From the surfactants/detergents tested, emulsion stability was in the order of Type 1> SDS> B&B> Power green> Solid surge> Calla= PRC> Triton X-100> 6% AFFF= Blast-off from most to least stable. Suspended solids stabilized emulsions under certain environments, particularly at $0.5\times CMC_{log}$. Alkalinity of emulsifiers was found between 3.3–413 mg/L $CaCO_3$ and the presence of unknown additives in the NSBM#4 showed to increase emulsion alkalinity. pH microprofiles demonstrated the diffusion of additives at the interface, which was verified by the increase in bulk-water fluorescence, indicating the diffusion of organic compounds. In addition, the diffused additives enhanced the formation of stable emulsions. Overall, this study presents a systematic investigation of bilgewater emulsion characteristics using multi-faceted experimental approaches from conventional methods to a novel microsensor technique. The effect of environmental parameters on the formation and stability of bilgewater emulsions was evaluated.

This work intended to assist in the selection of more suitable bilgewater treatment techniques and the detection of bilgewater conditions triggering emulsion stability.

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CMC$_{log}$ – Logarithmical critical micelle concentration

COD – Chemical oxygen demand

COTs – Commercial of the shelf

EEM - excitation-emission matrix fluorescence spectroscopy

HCl – Hydrochloric acid

NSBM #4 – Navy Standard Bilge Mix #4

NSWCCD - Naval Surface Warfare Center Carderock Division

OPA – Oil pollution abatement

O/W – Oil-in-water emulsions

OWS – Oil-water separators

PAHs - polycyclic aromatic hydrocarbons

RF – Random forest

SDS – Sodium dodecyl sulfate

SS – Suspended solids

TBN – Total base number

TN – Total nitrogen

TP – Total phosphorus

TSS – Total suspended solids

CHAPTER ONE: INTRODUCTION

The release of oily wastewater into marine environments has been related to serious issues regarding water quality degradation, as well as the potential damage to marine and terrestrial life [1]. Adequate treatment of oily wastewater generated from anthropogenic processes has become of great importance to mitigate and control the degradation of aquatic ecosystems [2]. Although oil pollution can occur from food, textile, and petrochemical industries, among others, oily wastewaters obtained from offshore industries and shipboard bilges (bilgewater) are considered to have the highest oil contribution [3, 4]. Bilgewater effluents, resulting from ocean-going vessels are considered a potential oil pollution source, accounting for around 20% of the million tons of oily wastewater discharged into the sea [1, 2, 5].

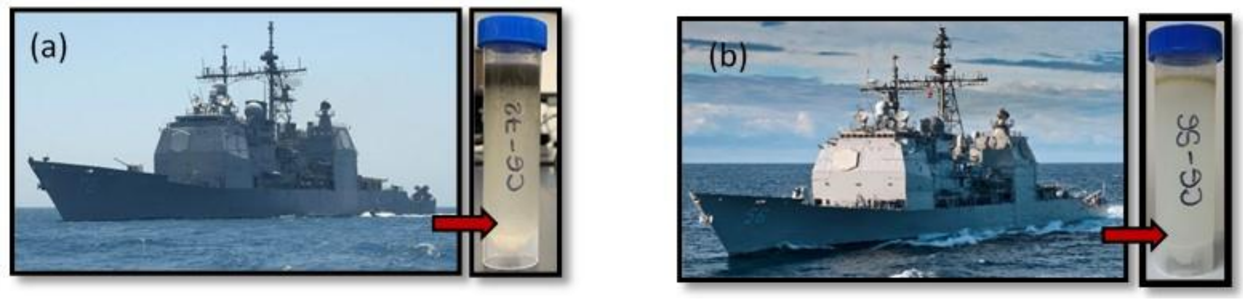


Figure 1. Bilgewater collected from (a) USS CG-72 (1991) and (b) USS CG-56 (1985).

Bilgewater is a regulated wastewater mixture that accumulates at the bottom of vessels and is generated from machinery leakage and freshwater wash-downs from on-board activities (Figure 1) [6]. Bilgewater is mainly composed of seawater, lubricant and hydraulic oils, and other contaminants such as cleaning agents, solvents, and suspended solids (SS) [7]. Bilgewater composition is highly variable and depends on the ship's operations, vessel's age, equipment maintenance, among others [1, 6]. The International Convention for the Prevention of Pollution from Ships (MARPOL 73/78, Annex I) stipulated a maximum oil concentration limit of 15 ppm for bilgewater disposed within 12 nautical miles from the nearest land [1, 8]. Oil and water are immiscible liquids that could be easily separated using gravitational and centrifugal processes. However, the presence of emulsifiers in bilgewater causes the formation of chemically stabilized oil-in-water (O/W) emulsions, challenging bilgewater treatment. Traditional oil-water separators (OWS) have shown to be effective treatment techniques when discrete phases of oil and water are present. Yet, these techniques have shown to be less effective to comply with discharge regulations when there is emulsified oil present in the mixture. Therefore, it is often required the use of additional treatment processes such as electrocoagulation [2, 9], membrane filtration [5], flotation [10], and biological processes [11] to break or separate oil-in-water emulsions. Although commercially available technologies can be implemented for oily wastewater treatment, the high variability in influent bilgewater characteristics can affect their performance. Additionally, treatment techniques are often selected based on a set of treatment performance criteria rather than in accordance to the specific bilgewater characteristics. Lack of information related to the physicochemical properties of chemically stabilized emulsions formed in Armed Forces vessels has grown concerns related to the suitability and efficiency of treatment processes. Therefore, by improving the current understanding of bilgewater emulsion formation and stability, it is expected that more appropriate treatment technologies can be applied and developed.

In many disciplines, it has been demonstrated that the stability of O/W emulsions strongly depends on the physicochemical and thermodynamic properties of the mixtures [12, 13]. However, information related to the formation of bilgewater emulsions and the role of environmental parameters on emulsion formation and stability is still incomplete. Emulsions in bilgewater are mainly stabilized by commercial cleaners percolated from on-board activities. These cleaners are often proprietary blends with unknown compositions, which makes it difficult to predict emulsion stability on a fundamental basis. Environmental factors such as temperature, salinity, and SS have shown to influence emulsion stability by affecting the physicochemical properties of oil, water, and surfactant molecules. Changes in the properties of the mixture can alter positively or negatively the oil/water interface, affecting emulsion stability. For this reason, it is important to understand the role of bilgewater components in the formation and stability of emulsions to avoid conditions that could enhance emulsion stabilization.

The main objective of this study was to characterize the stability of oil-in-water emulsions under various environmental conditions and to identify the governing parameters for oil-in-water emulsion formation and separation in simulated bilgewater mixtures. The knowledge obtained from the research will expand the current knowledge of bilgewater emulsions to improve bilgewater treatment and management. Bilgewater emulsions were prepared using a Navy Standard Bilge Mix (NSBM) #4, 8 commercial of the shelf (COTs) cleaners, and 2 neat surfactants. These surfactants were selected as representative emulsifiers commonly found in bilgewater. The effect of environmental parameters such as salinity (NaCl), SS (Arizona dust), temperature, and pH on emulsion formation and stability was analyzed. These parameters were evaluated within common ranges found in bilgewater. In this work, the analysis of emulsion stability was achieved using simple, rapid, and *in-situ* characterization techniques. Changes in the morphology of emulsions were analyzed using visual observation, image analysis (e.g., grayscale intensity, droplet distribution, and relative oil layer height), and bulk-water analysis (e.g., turbidity, macro-phase separation, and alkalinity). Additionally, the mass transport of solutes at the oil-water interface was investigated using an innovative pH needle-type microsensor and excitation-emission matrix (EEM) fluorescence spectroscopy.

Overall, the goal of this study was to experimentally determine the relationship between bilgewater components and emulsion stability to gain a deeper understanding of factors contributing to emulsion formation in bilgewater systems. For practical implications, this study will provide important information and a data set for developing an emulsion stability guideline to assist scientists, engineers, and shipboard operators in the selection of appropriate type of surfactants and bilgewater treatment techniques as well as in the detection of conditions triggering emulsion stability.

CHAPTER TWO: LITERATURE REVIEW

Bilgewater is a multi-component wastewater mixture that accumulates at the bottom of vessels and is generated from machinery leakage and freshwater wash-downs from on board activities [6, 9]. It is common that oily fluids generated in the vessel's engine room tend to accumulate in the bilge. Without adequate separation, the oil can be pumped out along with the wastewater, not only degrading water quality but also representing a threat to human and marine life [2]. Bilgewater is mainly composed of seawater, lubricant and hydraulic oils, and other contaminants such as cleaning agents, solvents, suspended solids, etc. (Figure 2) [7]. However, its composition can highly vary according to the ship's operations, vessel's age, equipment maintenance, among others [1, 6]. The volume of bilgewater production can vary depending on the vessels magnitude; however, it is estimated a generation of 0.5–50 m^3/d [5].

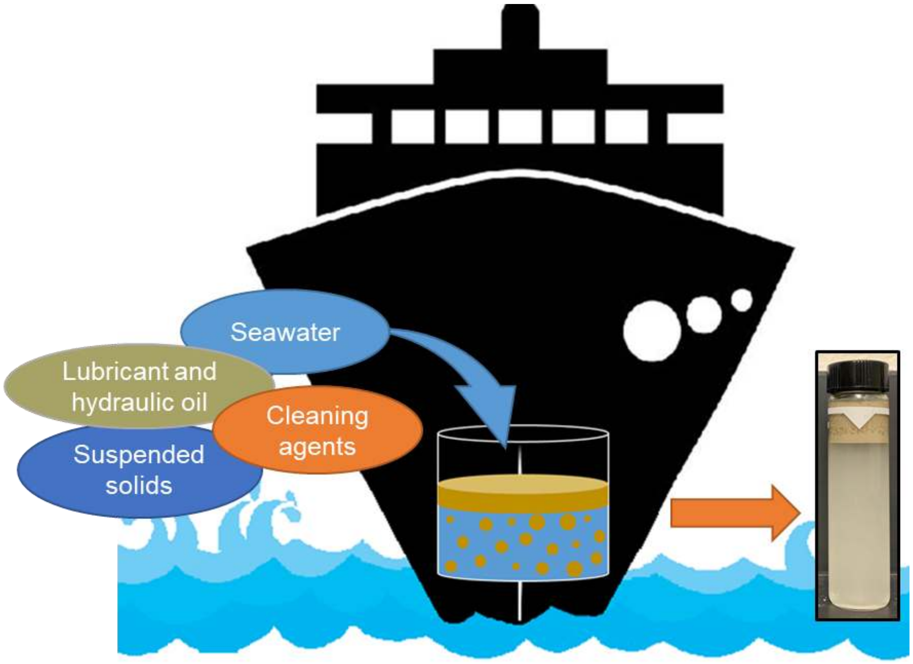


Figure 2. Composition and formation of bilgewater emulsions.

Bilgewater discharge was first regulated in 1973 by the International Convention for the Prevention of Pollution from Ships, which was further modified in 1978 (MARPOL 73/78)[14]. Today, it is stipulated a maximum oil concentration limit of 15 ppm if disposed within 12 nautical miles from the nearest land [1, 8], as regulated by MARPOL Annex I and Armed Forces vessels, DoD Regulation 4715.06-V2 [15]. Despite the fact that oil and water are immiscible liquids, which could be easily separated using gravitational and centrifugal processes, the presence of surfactants (e.g., cleaning agents) in the bilge leads to the formation of chemically stabilized oil-in-water (O/W) emulsions. The presence of emulsions challenges bilgewater treatment using commercial oil-in-water separators (OWS) and often requires the use of secondary treatments. As a result, the development of new treatment systems has been necessary to significantly modify previous methods and meet the new discharge regulations [16].

2.1 Oil-in-water Emulsions Formed in Bilgewater

An emulsion is defined as a thermodynamically unstable mixture of two immiscible liquids where droplets (greater than 0.1 μm) of one phase are dispersed into the other (the continuous phase). In specific, an oil-in-water emulsion (O/W) is considered a system where oil droplets are dispersed within a continuous water phase [17]. For emulsions to form it is required the presence of two immiscible or mutually insoluble phases, sufficient agitation to disperse one phase into another, and an emulsifying agent to prevent emulsion separation. Thus, the kinetic stability of emulsions is the result of small droplet sizes and the presence of surface-active agents surrounding the droplets [17, 18]. In the context of bilgewater, O/W emulsions are formed when the oil phase (e.g., engine and lubricant oils) is exposed to surfactant solutions (e.g., cleaning agents) present in the bilge and sufficient mixing energy occurs [19]. In ocean-going vessels, mechanical dispersion (e.g., homogenization) of bilgewater can occur during pumping and transport between holding tanks or due to shipboard vibrations caused by sea states [12, 20].

2.1.1 Role of Emulsifiers on Emulsion Stability

The presence of surface-active agents (e.g., emulsifiers) enhances the stability of emulsions by significantly reducing the interfacial tension between the dispersed oil droplets and the displacing fluid [18]. Emulsifiers are amphiphilic molecules that contain a polar hydrophilic head and non-polar hydrophobic tail resulting in the presence of both, water-soluble and water-insoluble components. The amphiphilic nature of the molecule allows it to migrate toward the oil-water interface and act as interface stabilizers with the hydrophobic tails remaining inside the oil [21]. Surfactants can stabilize emulsions by either adsorbing at the O/W interface or by forming a protective layer around the droplets [12]. Depending on the charge and chemical structure of the surfactant, the resulting micelles can be cationic, anionic, ampholitic, or nonionic. The critical micelle concentration (CMC) is considered the concentration of surfactant above which the formation of micelles becomes thermodynamically favorable [22]. According to Possoco et al., (2016), at concentrations exceeding CMC the molecules spontaneously self-assembly into micelles, lowering the interfacial tension to a minimum [21].

2.1.1.1 Type of Stabilization Mechanisms

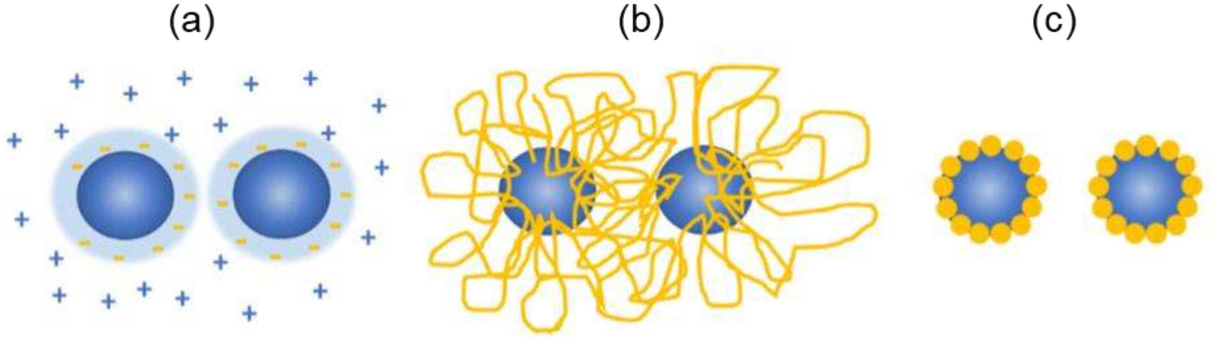


Figure 3. (a) Electrostatic, (b) Steric, and (c) Particle emulsion stabilization mechanisms [12].

In emulsion stabilization, the charge and size of the surfactant headgroup can result in different stabilization mechanisms caused by electrostatic, steric, and particle interactions (Figure 3).

Electrostatic stabilization occurs when charged surfactants absorb to the oil-water interface and form a charged cloud around the droplet [23]. According to Gouy-Chapman and Stern theory [24], the charged cloud forms a double layer, whose thickness depends on the electrolyte concentration and valence. It is typically observed that ionic surfactants (e.g., SDS) stabilize emulsions using electrostatic mechanisms; however, it has also been observed in systems with spontaneous charging of the oil/water interface [25].

Steric stabilization is essentially caused by nonionic or polymeric surfactants that present large bulky headgroups. In this mechanism, the large heads cover the oil-water interface and prevent the interaction between emulsion droplets by overlapping of hydrophilic groups, thus inhibiting the coagulation of the suspension [12]. Steric stabilization is especially useful in systems of high ionic strengths as it has shown to be relatively insensitive to the presence of electrolytes, playing a major role in the stabilization of bilgewater emulsions [26]. Considering this, destabilization mechanisms caused by salting-out or coagulation are likely not observed in systems stabilized by steric mechanisms[27].

Particle stabilization (Pickering emulsions) is evidenced when colloidal particles (e.g., suspended solids) act like surfactant molecules and absorb to the oil-water interface, enhancing emulsion stability [28]. As noted by Pickering [29], 'Pickering emulsions' are formed when the colloidal particles are wetted more by water than oil causing them to reside at the interface. Therefore, the wettability of the particles is an important factor in determining its effectivity to stabilize emulsions, as too hydrophilic or too hydrophobic particles tend to remain suspended in the system, leading to very unstable emulsions [28, 30]. Particle stabilization is expected to be present in bilgewater due to the abundance of suspended solids in actual bilgewater systems [31]

2.1.2 Emulsion Destabilization Mechanisms

Emulsion stability is a kinetic concept related to the change in the emulsion characteristics (e.g., droplet size and size distribution, phase separation) over an experimental timescale [32]. The term typically refers to the ability of an emulsion to resist changes in its properties and remain suspended over time. However, emulsions tend to be thermodynamically unstable systems and can present various ways of instability known as creaming, sedimentation, flocculation, coalescence, and Ostwald ripening (Figure 4) [12].

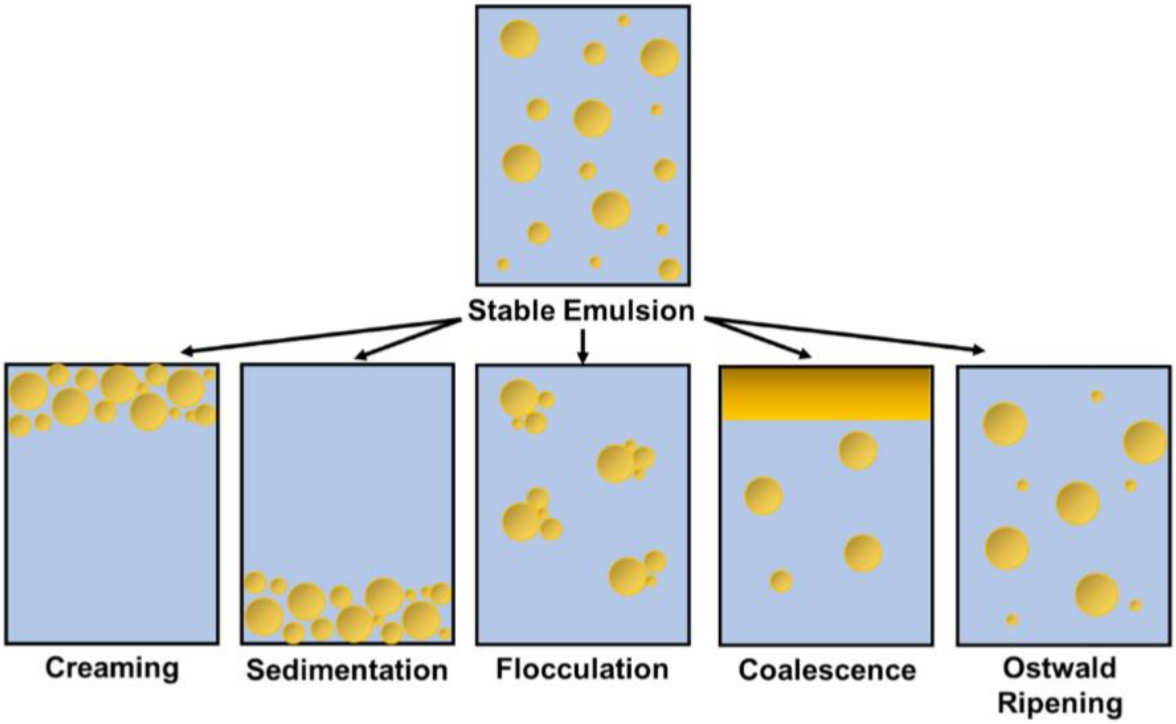


Figure 4. Diagram of creaming, sedimentation, flocculation, coalescence, and Ostwald ripening emulsion destabilization mechanisms [12].

Creaming and sedimentation. In O/W emulsions, creaming and sedimentation occur when the movement of oil droplets under gravity or centrifugal forces exceeds the Brownian motion of droplets. This destabilization mechanism results in the formation of a concentrated layer at the top (creaming) or at the bottom (sedimentation) of the solution [23]. The development of a creaming or sedimentation layer depends on the density of the droplets with respect to the medium. If the density of the droplets is less than the medium, the droplets will move more rapidly to the top; meanwhile, higher density droplets will sink to the bottom [33]. The developed layer is comprised of closely packed emulsions droplets, which may coalesce if there is a disruption of the liquid film between them.

Flocculation. Emulsion destabilization caused by flocculation occurs when there are no sufficient repulsion forces between droplets at distances where the van der Waals forces are weak [33]. This process results in the aggregation of droplets into larger units that will later float or sink within the container. Flocculation of the emulsion system can be induced by adding chemical coagulants or by electrocoagulation which can neutralize the repulsive electrostatic forces between droplets [12].

Coagulation. This refers to the process in which two or more droplets fuse into larger droplets caused by the thinning and disruption of the liquid film between particles and it is irreversible. Coalescence typically proceeds after creaming, sedimentation, or flocculation, when the droplets are closely packed and the van der Waals forces are strong, preventing its separation [12].

Ostwald Ripening. Emulsion destabilization triggered by Ostwald Ripening is caused by the increase in the average droplet size. This occurs as a result of the diffusion of molecules in small droplets through the continuous phase that becomes deposited in larger droplets [34]. This effect arises due to the finite solubility of the oil phase in the aqueous phase. Despite both liquids are considered immiscible, they often have very low solubility, which can contribute to emulsion destabilization.

2.1.3 Environmental Factors Affecting Emulsion Stability

As previously mentioned, emulsions are considered thermodynamically unstable systems that tend to separate over time. Multiple environmental factors such as temperature, ionic strength, suspended solids, pH, and mixing intensity have shown to impact the stability of oil-water emulsions by affecting the characteristics of its components [17]. These parameters can either enhance emulsion stability or can result in rapid emulsion separation at an early stage. In bilgewater emulsion systems, it has been reported temperatures from 4 to 60°C [35], conductivities from 679 to 8,400 μS/cm [2, 36], pH of 6.6 to 9 [37, 38], and solid particle densities ranging between 41to 2,684 mg/L [31]. The high variability of bilgewater properties requires to further understand the role of environmental factors in bilgewater emulsion stability, which has been of particular interest for this project.

Temperature has shown to significantly affect emulsion stability due to its effect on the oil viscosity, surface tension, and surfactant solubility in the oil and water phases [17]. As temperature increases, the thermal energy of the droplets also increases which intensifies the frequency of droplet collision, thus enhancing emulsion separation due to creaming and/or coalescence [12]. Additionally, the increase in temperature reduces the interfacial viscosity which results in a faster film-drainage rate, increasing droplet coalescence [39]. Jones et al (1978) showed that increased temperature instigated the destabilization of the oil/water interfacial film; however, at extremely high temperatures (e.g., 65°c) a kinetic barrier to droplet coalescence can still be present [40]. The formation of kinetic barriers depend on the interfacial viscoelastic properties of the film and make droplet coalescence more difficult [41].

Ionic strength of the aqueous phase has shown to be an important factor in controlling emulsion stability. The increase in ionic strength can reduce the electrostatic repulsion between droplets through electrostatic screening. Additionally, the counter ions present in the salt can attach to oppositely charged groups in the droplet surface, decreasing the zeta potentials and reducing electrostatic repulsion. The decrease in droplet repulsion allows an increase in droplet interaction, thus enhancing emulsions destabilization [42, 43]. In addition, the presence of salts in the system can influence the solubility of surfactants (e.g., salting out) and increase the density of the aqueous phase, lowering the stability at the oil-water interface [44].

Suspended solids (SS) present in the system are capable of affecting emulsion stability; however, its effectiveness depends on factors such as particle size, inter-particle interactions, and particle wettability [39]. As presented earlier, particle stabilization or Pickering emulsions occurs when the solids diffuse to the oil/water interface and inhibit the coalescence of the droplets. It has been established that the particles used to stabilize emulsions should be smaller than the targeted emulsion droplet size. Indeed, the use of larger particle sizes would require longer adsorption times at the interface, resulting in larger droplets and thus lower emulsion stability [45]. For particles to stabilize emulsions, it must be wetted by both the oil and the water phases and it must be present at the oil/water interface [39].

Water-phase pH can have a strong influence on emulsion stability because the presence of inorganic acids or bases can affect the physicochemical properties of the stabilizing film [39]. Kokal et al (2005) reported that the brine composition of the solution can lower the optimum pH for water separation from pH 10 (DI water) to pH 6-7 [39]. In emulsions stabilized using electrostatic mechanisms (ionic surfactants), the pH can significantly change the zeta potential of the emulsion, particularly near the surfactant's isoelectric point. Changes in zeta potential can result in emulsion destabilization [46]. The change in pH can also affect the solubility and effectiveness of nonionic surfactants.

Mixing Intensity. For emulsification to occur, it is necessary the application of mixing energy in order to break the oil phase into larger droplets that will subsequently be broken down into smaller ones. Overall, the purpose of homogenization is to form a stable emulsion by breaking down the large oil droplets into smaller drops [12, 17]. Chen et al (2005) demonstrated the relationship between stirring intensity and the relative volume of emulsions and it was reported that more stable emulsions were achieved with the increase in stirring speed; however, the use of higher speeds could cause the emulsifier to break away from the oil-water interface [17].

2.2 Bilgewater Treatment Techniques

Bilgewater management is achieved through the use of oil pollution abatement (OPA) systems, which consist of equipment to collect, hold, treat, and analyze oily wastewater on board ships [12]. The use of OPA systems is aimed to manage oily wastewater to meet discharge regulations. Traditionally, ocean-going vessels use oil-water separators (OWS) devices to treat oily wastewater [47]. OWS devices usually comprise the use of gravity or centrifugal separation, which employs the difference in density between oil and water to separate bilgewater. These devices have shown to be effective to separate free and dispersed oil; however, these separators often fail to comply with bilgewater discharge regulations when emulsified oil is present in the bilge. For this reason, it is often required the use of OWS with one or more additional unit operations to reduce oil concentration to environmental regulation standards [47]. Additional unit operations often imply the use of absorption, adsorption, biological treatment, coagulation/flocculation, flotation, and membrane technologies (Figure 5).

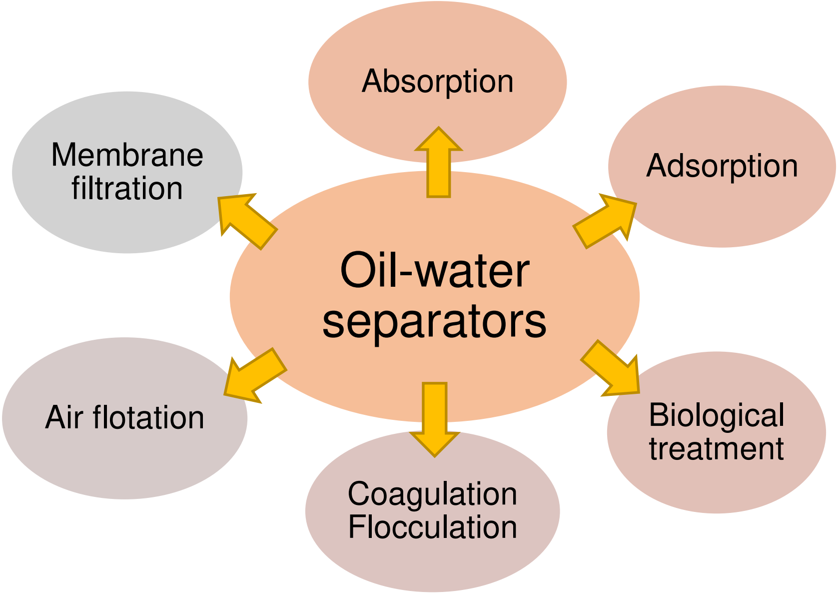


Figure 5. Bilgewater treatment techniques consisting of oil-water separators (OWS) plus additional unit operations often required.

Absorption techniques require the use of granular substrates and absorbents, or modified surfaces with oil affinity (e.g., organoclay [48] and curable polymeric surfactant [49]). *Adsorption* techniques requires the use of adsorption media such as granular activated carbon (GAC) to effectively remove emulsified oil from water [49]. The use of absorption has advantages such as low capital cost; however, the GAC is vulnerable to high SS and oil loadings, lowering the effectivity of the process. Overall, sorption techniques are suitable for small vessels and may require frequent media replacement that can result in high operational costs [47].

Biological treatment of bilgewater often consist of an OWS, the bioreactor, and a final clarifier. In the bioreactor, microorganisms are utilized to aerobically degrade organic waste (e.g., oil) into CO_2, cell components, and other products [4]. Even though this technique is very promising for oil removal, the biological units can easily malfunction due to nutrient shortening, surfactant toxicity, and microorganisms' sensitivity to pH and temperature. Overall, capital costs are high, although operating cost can be relatively low [47, 49].

Coagulation and flocculation of emulsified bilgewater is used to aggregate small colloidal particles into readily settable or floatable aggregates [50]. Coagulation of oily wastewater particles is effective if the type and dose of coagulant is properly applied. Bilgewater physicochemical properties highly vary between vessels depending on operational and environmental conditions; therefore, the coagulant addition needs to be optimized according to changes in the influent quality in order to effectively separate oil from water to the required concentration [51]. Additionally, the use of coagulation/flocculation can result in high operational costs and can generate large quantities of sludge [47].

Air flotation is used to enhance gravity separation by using the differential density between the oil droplets attached to the air bubbles and the water [52]. Since the oil/air bubbles have lower density than water, they will float and can be subsequently removed by skimming. Air flotation often requires the use of flocculating agents to enhance the separation.

Membrane operations usually include the use of ultrafiltration (UF), nanofiltration (NF), or reverse osmosis (RO) depending on the particle size, molecular weight, and ion and organic water components. Normally membranes act as barriers to specific components (e.g., oil), which lowers their susceptibility to influent variations. The use of membrane filtration systems has shown promising results for the separation of oily bilgewater; however, surface accumulation of organic, inorganic, and biological materials can results membrane fouling. Repetitive membrane cleaning to restore the membrane permeability can increase maintenance cost and complexity of the treatment [47].

2.3 Electrochemical Microsensors for the *In Situ* Monitoring of Chemical Compounds

Needle-type electrochemical microsensors (e.g., microelectrodes) are a reliable tool for the measurement of chemical species of interest in a wide range of microenvironments [53, 54]. Indeed, their small tip diameters ranging from 10-100 μm have been applied for the study of biofilms [55, 56], galvanic corrosion [57], and chemical oceanography [53], among others; however, as of today, this remarkable technology has not yet been fully applied for the characterization of emulsions [58]. Using microsensors, it can be constructed a one-dimensional (1D) microprofile of the concentration of a chemical compound according to a samples' distance. Additionally, using Fick's law (Eq. 1), it can be estimated the kinetic parameters for diffusion at an interface of interest.

$$J = -D \times \frac{dC}{dZ} \tag{1}$$

where J is a flux rate (mol/cm^2·s), D is the diffusion coefficient (cm^2/s), and C is the concentration of the chemical specie of interest at a given depth (Z). According to Jared et al (2017) the pH microprofile of a simulated bilgewater emulsion allowed the detection of mass transport of unknown additives across the oil/water interface, which can have major impact on the resulting emulsion stability [58].

2.4 Thesis Statement and Tasks

The overall objective of the present study was to advance in the current understanding of chemically stable shipboard bilgewater emulsions generated in Armed Forces Vessels. The ultimate goal was to gain fundamental information in emulsion formation and stability to assist in the selection of appropriate treatments techniques based on specific bilgewater conditions. This way, bilgewater treatment and management can be improved to comply with environmental discharge regulations. This was accomplished with the following four tasks: 1) Water quality characterization of collected bilgewater samples, 2) Characterization of simulated bilgewater emulsions, 3) Analysis of alkalinity and chemical diffusion at the oil-water interface, and 4) Data analysis and correlation using modeling algorithms.

Task 1. Water Quality Characterization of Collected Bilgewater Samples

Bilgewater composition is highly variable and mainly depends on the ship's operations, vessel's age, and equipment maintenance. Many components in bilgewater play an important role in the formation and stabilization of bilgewater emulsions. Therefore, it is important to determine the water quality characteristic of extracted bilgewater samples in order to identify parameters of relevance and their common ranges of incidence. For this task, the water quality characteristics of three bilgewater samples collected from different cruises in the U.S. navy were determined in accordance with Standard Methods. The samples were tested for various water quality parameters such as turbidity, alkalinity, UV_{254}, TN, TP, COD, TS, TSS, conductivity, and pH. Relevant parameters and their relative value ranges were used as a base for the analysis of the effect of environmental parameters on the stability of simulated bilgewater emulsions.

Task 2. Characterization of Simulated Bilgewater Emulsions

To further understand the formation and stability of bilgewater emulsions, synthetic bilgewater mixtures were developed using chemical components commonly found in shipboards (Figure 6). For emulsion preparation, it used a Navy Standard Bilge Mix (NSBM) #4 as oil phase. The bulk-water phase was simulated by adding contaminants such as commercial cleaners, surfactants, and solid particles at various conditions commonly found in navy ships. The commercial off-the-shelf (COTs) cleaners and neat surfactants tested were selected based on interviews conducted to shipboard personal. To evaluate the effect of environmental parameters on emulsion stability, simulated emulsions were analyzed in the presence of suspended solids (e.g., Arizona dust), salinity (NaCl), and under a range of temperature and pH conditions. These experiments were aimed to better understand the effect of the physicochemical and thermodynamic characteristics of bilgewater on emulsion formation.

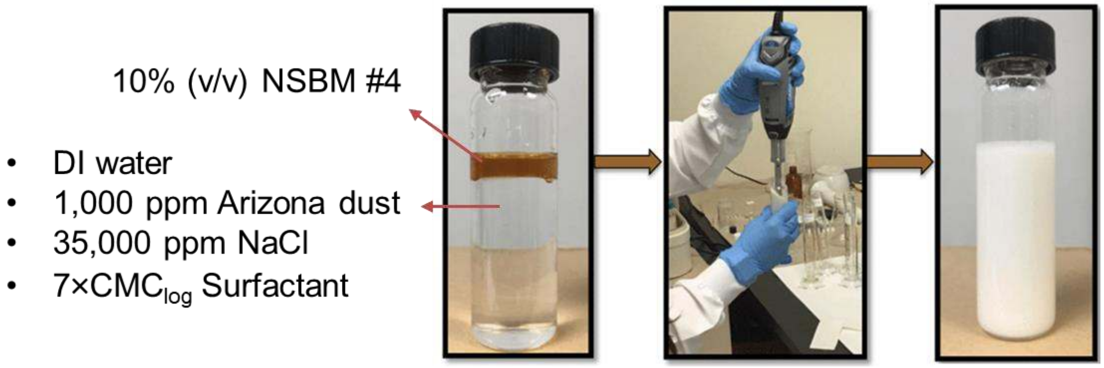


Figure 6. Preparation of synthetic bilgewater mixtures.

Characterization of simulated bilgewater emulsion was accomplished using techniques such as visual observation, droplet distribution, relative oil layer height, turbidity, grayscale intensity, and macro-phase separation. Emulsion stability was analyzed based on the tendency of emulsions to form an oil layer as this was considered a key parameter for bilgewater treatment. It was anticipated that the findings from this task would provide with meaningful information regarding the effect of surfactant type and environmental conditions on the stability of bilgewater emulsions.

Task 3. Analysis of Alkalinity and Chemical Diffusion at the Oil-water Interface

In this task, it was be evaluated the effect of surfactant type and oil additives in the overall alkalinity of the synthetic bilgewater mixtures. Additionally, using an innovative pH microsensor the possible diffusion of solutes at the oil-water interface was studied. pH microprofiles were recorded for bulk-water solutions (surfactant + DI water) in contact with NSBM #4 to investigate changes in the bulk-water pH over time. All microprofiles were measured inside a Faraday cage (Technical Manufacturing Co., Peabody, MA) to shield the electrochemical microsensor from possible electromagnetic interference. For the positioning and movement of the microsensor tip in the samples, it was used a three-dimension (3D) manipulator (UNISENSE A/S, Denmark). To generate the microprofile at the interface, it was used a 20 µm step-size with a waiting period of 1 min between measurements. Data was collected using a multimeter (UNISENSE A/S, Denmark) and it was processed using pH calibration curves before/after each experiment. It was expected that this task would provide with information regarding the buffering capacity of each surfactant, which can affect the pH of the solution and thus emulsion stability. Additionally, the alkalinity measurement of emulsions would corroborate the presence of alkaline additives in NSBM #4, which could affect the pH of the solutions and the efficiency of pH-dependent treatment techniques. Microprofiles of the samples allowed the detection of chemical diffusion at the oil-water interface, which has shown to contribute with emulsion stability [58].

Task 4. Data Analysis and Correlation Using Modeling Algorithms

Data collected from previous tasks was interpreted for better understanding of factors affecting emulsion formation and stability in Navy bilgewater systems. Inter-correlation between measured parameters and changes in emulsion stability was achieved using modeling data analysis. It was investigated the use modeling methods such as of Random Forest (RF) algorithms to predict emulsion stability based on the physicochemical properties of bilgewater. In this task, it was collected data from the Naval Surface Warfare Center Carderock Division and UCF to develop an emulsion stability guide. This guide was expected to assist researchers and shipboard operators in the selection of appropriate bilgewater treatment techniques as well as in the detection of conditions triggering emulsion stability.

CHAPTER THREE: MATERIALS AND METHODS

3.1 Water Quality Analysis of Bilgewater Samples

Bilgewater samples analyzed in this study were collected from three different cruisers in the U.S. Navy, USS Vella Gulf (CG-72), USS Truxtun (DDG-103), and USS San Jacinto (CG-56). Samples received were stored in a dark refrigerator at 4°C to ensure sample preservation prior to analysis. Water quality was investigated shot-term after samples were received and the experiments were run in triplicate to guaranty the accuracy and reliability of the data collected. Additionally, parameters measured were compared to common ranges reported from literature.

Water quality testing of bilgewater samples consisted of ten different tests used to measure the physical and chemical characteristics of each sample. Test procedures evaluating pH, conductivity, turbidity, alkalinity, UV_{254}, Total Nitrogen (TN), Total phosphorus (TP), Chemical Oxygen Demand (COD), total solids (TS), and total suspended solids (TSS) were performed in accordance with Standard Methods [59] as shown in Table 1.

Table 1. Test procedures used for the water quality analysis of bilgewater samples.

Test	Procedure
Turbidity	Nephelometric method
Alkalinity	Titration using 0.1 N HCl
UV_{254}	Absorption at 254 nm wavelength
Total Nitrogen (TN)	Persulfate digestion (HACH 10072)
Total Phosphorus (TP)	Molybdovanadate with acid sulfuric digestion (HACH 10127)
Chemical Oxygen Demand (COD)	USEPA reactor digestion method (HACH 8000)
Solids analysis (TS and TSS)	Samples dried at 104°C and 550°C

3.2 Preparation of Simulated Bilgewater Emulsions

Emulsion samples were prepared using 40 mL glass TOC vials (GLC-01020, Qorpak, PA, USA) carefully cleaned to remove possible contamination that could affect the results consistency. Prior to sample preparation, vials were rinsed multiple times with hot water and soap (Dri-clean, Decon Labs, Prussia, PA) and brushed using a test tube brush to remove solids or oil attached to the glass. Afterward, vials were rinsed with a solution of 1 M HCl, washed 5 times using deionized (DI) water, and left to air dry at room temperature.

For emulsion preparation, Navy Standard Bilge Mix (NSBM) #4 provided by the Naval Surface Warfare Center Carderock Division (NSWCCD) and DI water (pH 6.6) were used as immiscible phases. NSBM #4 constituents are 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). Eight navy cleaners and two neat surfactants were selected as representatives of emulsifiers commonly found in shipboards: Type 1, Solid Surge plus, Calla, B&B 3100, Super Blast-off, PRC Deck Cleaner, 6% AFFF, and Power Green (nonionic detergents), Triton X-100 (nonionic surfactant), and sodium dodecyl sulfate (SDS) (anionic surfactant). Emulsions were prepared by adding together 10% (v/v) NSBM #4, seven times the logarithmical critical micelle concentration $(\mathrm{CMC})_{\log}$ per surfactant (Table 2), and DI water in a TOC vial for a total sample volume of 30 mL. Surfactant dosage was used significantly above $\mathrm{CMC}_{\log}$ (7 times) in order to ensure micelle formation and complete coverage of the oil-droplet surface [60]. To homogenize the sample, a hand-held homogenizer probe (Omni Tissue Master, Model 125, 10 mm generator probe) was inserted halfway into the sample and it was turn on to max power (33,000 rpm) for 2 min. Probe level was carefully checked between samples to ensure identical homogenization conditions and sample replicability. After homogenization, the vials containing the samples were capped and left under undisturbed conditions for 5 days. Emulsions were placed in front of a digital camera (PowerShot A480, Cannon) and images were recorded every 30 min for the first 24 hrs and every 3 hrs for the rest of the 5-day experiment. Images recorded were stored for subsequent analysis of emulsion stability.

Table 2. Logarithmical Critical Micelle Concentrations (CMC_{log}).

Surfactant	Type	CMC_{log} (ppm)
Type 1	nonionic	86.7
Solid Surge plus	nonionic	97.5
Calla	nonionic	328.2
B&B 3100	nonionic	361.1
Super Blast-off	nonionic	934
PRC Deck Cleaner	nonionic	1,871.2
6% AFFF	nonionic	3,399
Power Green	nonionic	3,824
Triton X-100	nonionic	102
SDS	ionic	1,547.4

Experimental design. To evaluate the effect of environmental parameters on simulated bilgewater emulsion stability, four different conditions were analyzed (ionic strength, temperature, SS, and pH). To evaluate salinity and SS effect, Sodium Hydroxide (NaCl) and Arizona Test Dust (Power Technology Inc, Arden Hills, MN) were used. Specific parameters and concentrations were selected as a representation of environmental conditions commonly present on the bilge and in accordance with the water quality evaluation of the collected bilgewater samples [12]. As shown in Table 3, emulsion samples were prepared and analyzed using two salinity concentrations (0 ppm - 35,000 ppm NaCl), three temperatures (4°C, 25°C, and 35°C), two suspended solids (Arizona coarse test dust) concentrations (0 ppm- 1,000 ppm), and three pH conditions (unadjusted, 4, and 10). If emulsions were being tested at a set temperature, the glassware containing DI water and reagents, the NSBM #4 oil, and the equipment were allowed to come to temperature overnight prior to sample preparation. After acclimation, samples were prepared using the emulsion protocol described above. For every temperature, one sample was prepared without additions (neither NaCl nor suspended solids) and it was used as a control for comparison.

Table 3. Environmental parameters evaluated.

Parameters tested	Conditions modified (additions)
Unadjusted (control)	No additions
Salinity	35,000 ppm NaCl (0.6 M)
Temperature	4°C, 25°C, 35°C
SS	1,000 ppm Arizona dust
Salinity + SS	35,000 ppm NaCl, 1,000 ppm Arizona dust
pH	Unadjusted, 4, 10

3.3 Analytical Methods for Emulsion Characterization

3.3.1 Droplet Distribution

For analyzing droplet distribution, a 10-µL emulsion sample was collected from the center of the emulsion 1 hr after homogenization, dispensed onto a microscope slide (Cat. No. 12-544-3, Fisher Scientific, PA, USA) and covered with a glass slide (Cat. No. 12-553-451, AmScope, CA, USA). Using a microscope (M83EZ-C50S, OMAX) integrated with a digital camera (A3550S, OMAX) microscopic images were taken using a 400× magnification for each sample. Images were then processed using an image analysis software (MIPAR, Worthington, OH) to automatically identify and measure emulsion droplets and to generate a droplet distribution profile. In this work, two different images were collected per sample as duplicate to determine droplet size and morphology and an average of the data was presented.

3.3.2 Relative Oil Layer Height

Relative oil layer height was determined using a Java-based image-processing program (ImageJ, NIH). The oil layer height was measured throughout the duration of the experiment to obtain a time-course monitoring of the destabilization characteristics of each emulsion sample. For every measurement, a photo of the sample was uploaded into ImageJ and the height of the oil film at the top of the emulsion was carefully measured. As major changes occurred within the first day after homogenization, photos were analyzed every 2 hrs for the first 12 hrs, then every 24 hrs for the rest of the 5-day experiment.

3.3.3 Grayscale Intensity Profiles

A grayscale profile of an emulsion sample is a non-destructive image analysis technique that displays a two-dimensional (2D) graph of the intensity of pixels along a line in an specific image [61]. The variation in the grayscale intensity allows the detection of changes between two consecutive images, which are often an indicative of destabilization events occurring in the emulsion [62]. For the analysis of emulsion samples, images previously recorded were converted from RGB color into 8-bit grayscale using a Java-based image-processing program (ImageJ, NIH). Posteriorly, a grayscale profile was plotted from top to bottom of the sample and a 2D graph was generated, where the y-axis represented the grayscale intensity and the x-axis represented the height of the sample (Figure 7). In 8-bit grayscale images, the lightest color (white) is represented by 255, meanwhile the darkest (black) is represented by zero; indicating a linear scaling from 0-255 [61]. As observed in Figure 7 (a) and (b), the grayscale intensities were found to be higher in the creaming and emulsion layer of both samples compared to the oil layer formed in Figure 7(a). For characterization purposes, the oil layer (e.g., tendency to coalescence) was represented by considerably low intensity levels with values between 0-50 indicating sole oil separation (limited to the oil layer only). Meanwhile, the emulsion layer was represented by higher values, which varied according to the emulsion destabilization. Thus, higher grayscale intensities along the sample represented higher emulsion stability. Large emulsion destabilization (e.g., low turbidity) could result in emulsion layers with grayscale intensity values below 100.

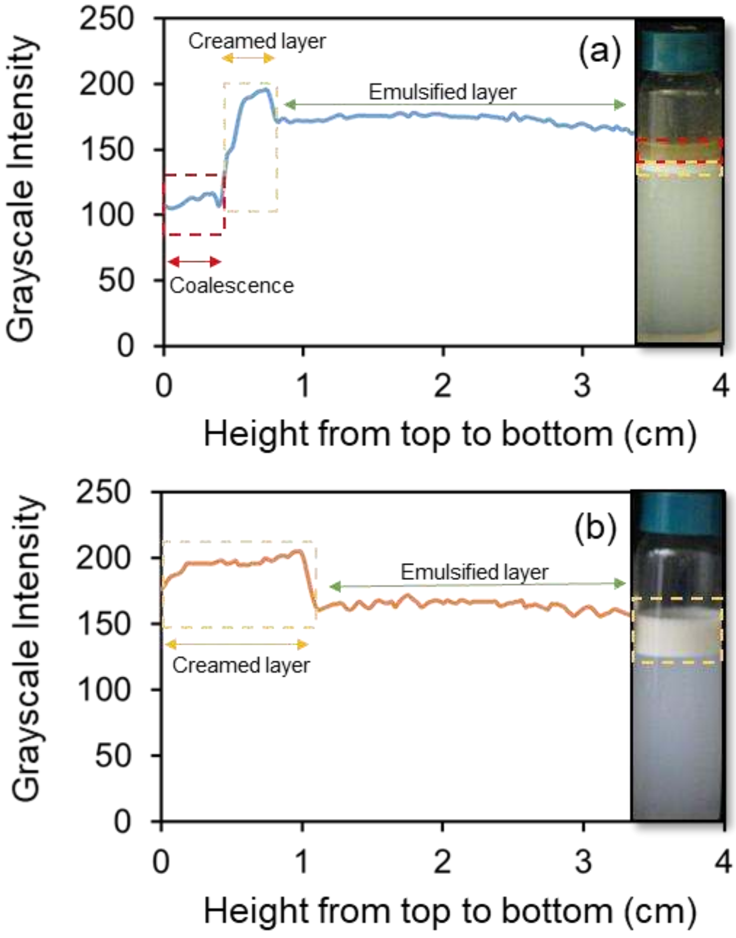


Figure 7. Grayscale profile of emulsion samples destabilized by different mechanisms generated using a grayscale intensity method. (a) Creaming + Coalescence destabilization (b) Creaming destabilization.

3.3.4 Turbidity of the Emulsion Layer

For the determination of the emulsion layer turbidity, each sample was individually transferred into a previously cleaned glass cell (HACH, Product No. 2084900, CO, USA). Prior to transferring the sample, the oil and creaming layers were removed using a pipette to avoid any possible mixing that could affect the final emulsion layer characteristics. Turbidity was measured after 5 days of undisturbed conditions using a turbidimeter (HACH, 2100N, CO, USA) in accordance with Standard Methods [59].

3.3.5 Macro-phase Separation

The destabilization of emulsions is often dominated by oil separation due to coalescence or phase separation due to creaming. For some emulsions tested, it was observed a simultaneous formation of a creaming and oil layer, which made it difficult to have a clear view of the separated oil phase. Therefore, the oil separation was quantified using a separation technique termed macro-phase separation. After the emulsions were under undisturbed conditions for four days, the samples were poured into a 100 mL separatory funnel and left to settle for 24 hrs to allow the samples to separate into its oil, creaming, and oil layer. After 24 hrs (i.e., 5 days of the total experiment duration), the separatory funnel was placed in a holder and the oil layer was collected in a pre-weighted beaker and then weighted to determine oil separation (Figure 8). The oil separation percentage (%, w/w) was then calculated by diving the weight of the collected oil per sample by the weight of the total oil used in the emulsion preparation (3 mL of NSBM#4 oil, 2.54g).

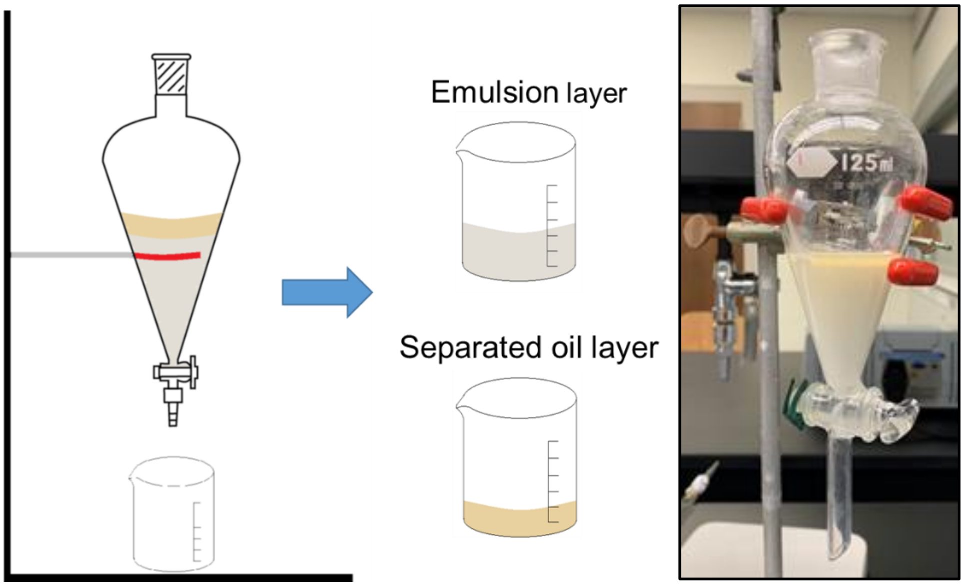


Figure 8. Macro-phase separation.

3.3.6 Alkalinity of Surfactants and Bulk-water Emulsions

The alkalinity of surfactants and emulsion samples was measured using titration methods in accordance with Standard Methods [59]. First, a solution of 0.1 N hydrochloric acid was prepared by adding 8.3 mL of hydrochloric acid (Fisher chemical, Cat. No. A144s-500, NJ, USA) in 1 L of deionized (DI) water. To measure the alkalinity of each surfactant, a sample was individually prepared using 7 times the CMC_{log} of surfactant diluted in DI water (pH 6.6) to a total volume of 60 mL. For emulsion alkalinity measurements, 60 mL samples were prepared following the same emulsion preparation protocol described in Section 3.2, using Solid surge, Triton X-100, PRC, Type 1, and DI water (control) and 10% v/v NSBM #4. If alkalinity was to be measured over time, multiple replicates of the same sample were individually prepared, covered with parafilm tape for preservation, and left under undisturbed conditions.

To measure the alkalinity of surfactants and the initial emulsion alkalinity (day 0), the total sample volume (60 mL) obtained after homogenization was placed in a previously cleaned glass beaker (100 mL). Subsequently, a burette previously filled up with a standardized 0.1 N HCl was assembled, and the pH probe (HACH, Product No. PHC735, UT, USA) was inserted into the solution. To avoid emulsion separation and guaranty homogeneity of the sample, the solution was gently mixed with a magnetic stirrer throughout the duration of the experiment. Once the pH probe reached equilibrium, the HCl was added dropwise in increments of 0.2 mL or less and it was left to stabilize after each addition. The HCl volume used was recorded and the alkalinity was calculated using Eq. 2:

$$\text{Alk (mg/L CaCO}_3\text{)} = \frac{A \times N \times 50{,}000}{\text{mL sample}} \tag{2}$$

where A is the volume of standard acid used (mL) and N is the normality of standard acid. To measure the change in bulk-water emulsion alkalinity over time (alkalinity variation in the emulsion layer only), the creaming/oil layer (of the previously separated sample) was carefully removed using a pipette to avoid the combination of layers during the test, which could result in inaccurate readings. Lastly, the alkalinity measurements were performed using the same titration method stated above.

3.3.7 In-situ Characterization of Emulsions Using pH Microprofiles

To investigate the possible diffusion of oil additives, a needle-type microsensor (100-µm tip size, UNISENSE A/S. Denmark) was used to generate pH microprofiles at the microscale for the analysis of mass transport at the oil/water interface. For the calibration of the microelectrode, three standard buffer solutions were used, pH 4, 7, and 10 (Thermo Scientific, MA). The pH microsensor was calibrated prior and after use in order to consider possible signal obstruction due to the glass tip exposure to oil for long periods. For the determination of pH, the microsensor was connected to an Ag/AgCl reference milli-electrode (MI-401, Microelectrodes Inc., Bedford, NH) and the potential signals between the electrodes were monitored and recorded using a multimeter (UNISENSE A/S, Denmark). pH microprofiles were performed in a Faraday cage to avoid possible electrostatic fields interfering with the readings [12, 63].

To generate profiles at the microscale, the pH microsensor was placed in an automatic 3D manipulator (World Precision Instruments, Sarasota, FL), which allows readings down to 10 µm steps. For microprofiling, the sample was place into the Faraday cage and the reference sensor was inserted halfway into the solution. Initially, using the 3D manipulator, the pH microsensor was placed into the oil and allowed to reach equilibrium for accuracy of the reading (5 min). Afterwards, the glass tip was positioned at the air/oil interface, which was considered the top of the sample (0 µm) (Figure 9). pH measurements were taken every 200 µm, 20 µm, and 200 µm at the oil, interface, and bulk water, respectively, with waiting times of 60 s between measurements. The duration of one 1D pH microprofile measurement was approximately 100 min. The total sample volume was 30 mL, consisting of 27 mL of bulk-water containing the respective surfactant (e.g., solid surge, B&B 3100, Triton X-100, and Type 1) and 3 mL of NSBM #4 (10% v/v). Oil and water solution were put into contact (no homogenization) and left undisturbed for 5 days. The samples were analyzed without homogenization to investigate the spontaneous diffusion at the oil-water interface without external mixing. Microprofiles were taken at 0 hrs (initial oil – water/surfactant contact), 3 hrs, 1 day, and 5 days, from 0 µm perpendicularly until 15,000 µm. Duplicates of each microprofile in the same direction (top to bottom) were taken and the resulting profiles, presented in this work, are the average values obtained from both replicates at pre- and post- calibration.

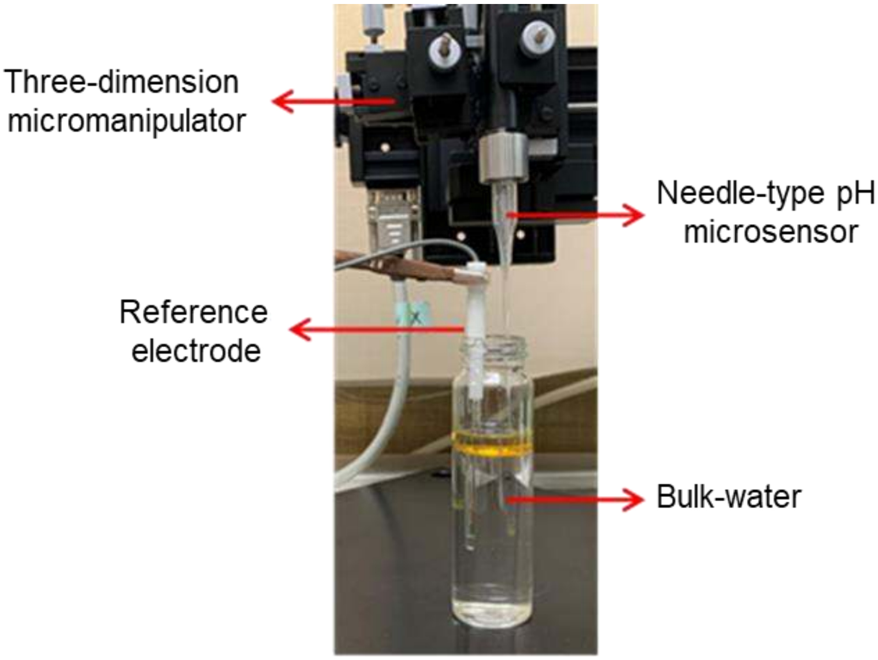


Figure 9. Microprofiling set-up using a needle-type pH microsensor.

CHAPTER FOUR: RESULTS AND DISCUSSION

4.1 Water Quality Characterization of Collected Bilgewater Samples

Table 4 presents the results for water quality characterization of the collected bilgewater samples. As expected, the physicochemical characteristics of bilgewater highly varied between vessels. Bilgewater samples presented a pH fairly neutral from 7.0 to 8.4, except for CG-56 with pH of 5.1. On the other hand, parameters such as conductivity, COD, and TSS displayed large variation within samples. Conductivity ranged from 1.74 to 24.0 mS/cm, COD from 1,279 to 42,800 mg/L, and TSS from 256 to 4,248 mg/L. Church et al (2019) reported similar water characteristics in bilgewater samples collected from various vessel types, emphasizing in the large variability in bilgewater quality [12]. TN and TP were found between 12 to 19 mg/L N and 3.8 to 16.4 mg/L P, respectively, a fairly low value compared to concentrations of 60mg/L N and 120 mg/L P reported in Vyrides et al (2018) [64].

Table 4. Water quality characterization of collected bilgewater samples.

Parameter	CG-56	CG-72	DDG-103
pH	5.1	7.0 - 7.2	7.8 - 8.4
Conductivity (mS/cm)	1.74 ± 0.05	16.3 ± 0.1	24.0 ± 0.4
Turbidity (NTU)	10,402 ± 20	1,104 ± 104	52 ± 2.3
COD (mg/L)	42,800 ± 1,500	1,279 ± 87	12,085 ± 775
TS (mg/L)	3,043 ± 502	13,793 ± 146	20,320 ± 500
TSS (mg/L)	1,848 ± 58	4,248 ± 212	256 ± 16
$UV_{254}(cm^{-1})$	0.38 ± 0.00	0.22 ± 0.02	0.08 ± 0.01
Alkalinity (mg/L $CaCO_3$)	5 ± 0.0	230 ± 4.1	92 ± 2.4
TN (mg/L N)	18 ± 13.7	12 ± 3.6	19 ± 1.7
TP (mg/L PO_4^{3-})	12.6 ± 0.5	3.8 ± 0.1	16.4 ± 0.3

Figure 10 shows that CG-56 and CG-72, laid down in 1985 and 1991, respectively, had a turbid consistency with discrete oil on top of the bulk water, while DDG-103, laid down in 2005, presented a clear water appearance. This indicates that vessels' age is an important parameter influencing water quality characteristics.

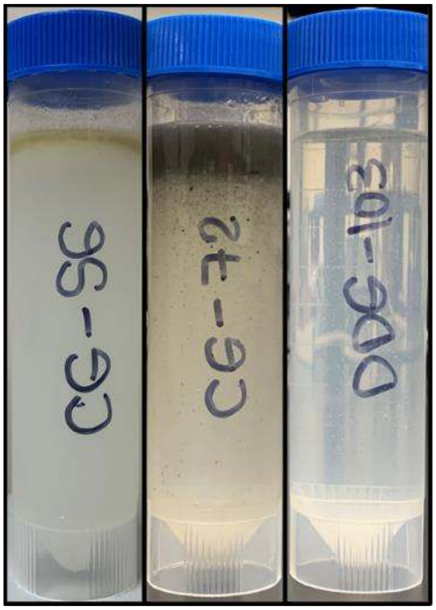
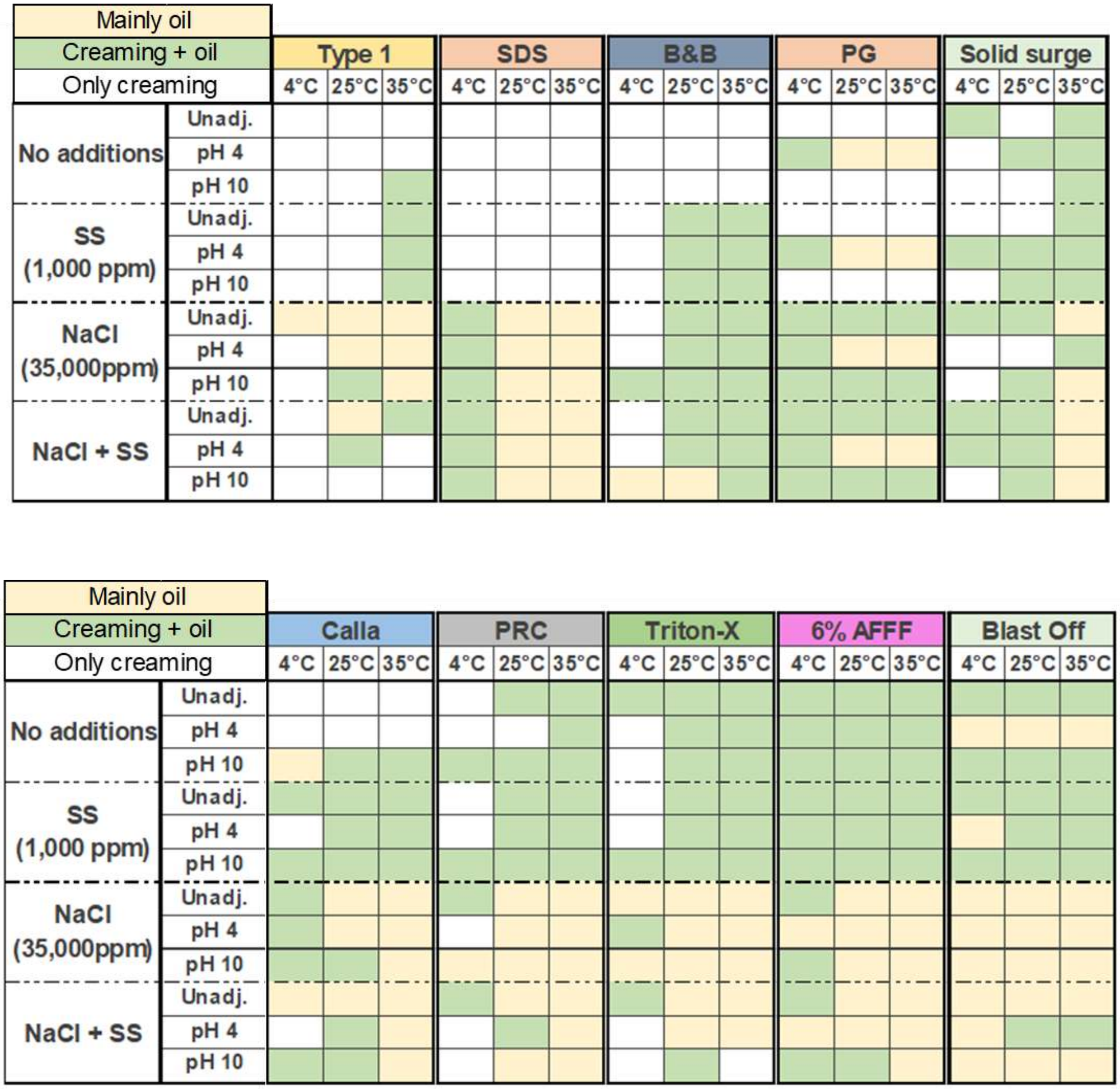


Figure 10. Bilgewater samples collected.

From the water quality characterization of the collected samples, it is possible to perceive the large variability in the physicochemical properties of bilgewater prior to collection and treatment on OPA systems. This water quality variability makes it hard to predict emulsion stability as well as to determine the adequate conditions for effective bilgewater treatment. For example, the low TN and TP concentration in samples tested can indicate low suitability of these waters to be treated using biological processes. Additionally, it is known that certain parameters such as high SS and conductivity can affect oil separation as well as the effectivity of other treatment techniques like absorption and reverse osmosis. Therefore, it is important to gain a deeper understanding of the role of environmental factors on bilgewater emulsion stability to develop more effective treatment technologies.

4.2 Effect of Environmental Factors on Emulsion Stability

In this study, time-course visual observation was proposed as a pre-screening method to evaluate the stability of emulsions by analyzing the behavior of the samples (e.g., macro-phase separation) throughout the duration of the experiment. Emulsions were analyzed at various time intervals up to 5 days after which there was no noticeable changes in appearance. As observed in Appendix A, emulsion stability was highly dependent on surfactant type, temperature, and ionic strength (NaCl addition). Figure 11 presents an overview of the influence of each environmental factor of interest in the destabilization of emulsions. Samples were characterized depending on the morphology of the emulsions after the 5-day experiment. Yellow, denoted as "mainly oil", was used for emulsions with more than 90% oil separation or samples with coalescence as main destabilization mechanism. Green, "creaming + oil", was used for emulsions presenting an oil layer formation as well as a predominant creaming layer. White, "only creaming", was used for samples with less than 10% oil separation. Emulsion separation due to creaming is not definitive and can be easily re-dispersed, while the formation of an oil layer is typically considered permanent. In this study, emulsion stability was analyzed based on the formation of an oil layer, which is more important for bilgewater treatment. Based on the results, Type 1 showed to produce the most stable emulsions with the lowest oil separation while the use of 6%AFFF and Blast-off resulted in the most unstable emulsions. The resulting emulsion stability based on surfactant type from most stable to least stable was Type 1, SDS, B&B, Power green (PG), solid surge, Calla, PRC, Triton X-100, 6% AFFF, and Blast-off. In bilgewater management, the formation of thermodynamically unstable emulsions is desired because it is easier to separate emulsified oil from water. Therefore, it is recommended to avoid the use of commercial cleaners such as Type 1, which led to the formation of stable emulsions in environmental conditions commonly found in bilgewater.



🟨	Mainly oil
🟩	Creaming + oil
⬜	Only creaming

		Type 1			SDS			B&B			PG			Solid surge		
		4°C	25°C	35°C	4°C	25°C	35°C	4°C	25°C	35°C	4°C	25°C	35°C	4°C	25°C	35°C
No additions	Unadj.	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	🟩	⬜	🟩
	pH 4	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	🟩	🟨	🟨	⬜	🟩	🟩
	pH 10	⬜	⬜	🟩	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	⬜	🟩
SS (1,000 ppm)	Unadj.	⬜	⬜	🟩	⬜	⬜	⬜	⬜	🟩	🟩	⬜	⬜	⬜	⬜	⬜	🟩
	pH 4	⬜	⬜	🟩	⬜	⬜	⬜	⬜	🟩	🟩	🟩	🟨	🟨	🟩	🟩	🟩
	pH 10	⬜	⬜	🟩	⬜	⬜	⬜	⬜	🟩	🟩	⬜	⬜	⬜	⬜	🟩	🟩
NaCl (35,000ppm)	Unadj.	🟨	🟨	🟨	🟩	🟨	🟨	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟨
	pH 4	⬜	🟨	🟨	🟩	🟨	🟨	⬜	🟩	🟩	🟩	🟨	🟨	⬜	⬜	🟩
	pH 10	⬜	🟩	🟨	🟩	🟨	🟨	🟩	🟩	🟩	🟩	🟩	🟩	⬜	🟩	🟨
NaCl + SS	Unadj.	⬜	🟨	🟩	🟩	🟨	🟨	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟨
	pH 4	⬜	🟩	⬜	🟩	🟨	🟨	⬜	🟩	🟩	🟩	🟨	🟨	🟩	🟩	🟨
	pH 10	⬜	⬜	⬜	🟩	🟨	🟨	🟨	🟨	🟩	🟩	🟩	🟩	⬜	🟩	🟨

🟨	Mainly oil
🟩	Creaming + oil
⬜	Only creaming

		Calla			PRC			Triton-X			6% AFFF			Blast Off		
		4°C	25°C	35°C	4°C	25°C	35°C	4°C	25°C	35°C	4°C	25°C	35°C	4°C	25°C	35°C
No additions	Unadj.	⬜	⬜	⬜	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
	pH 4	⬜	⬜	⬜	⬜	⬜	🟩	⬜	🟩	🟩	🟩	🟩	🟩	🟨	🟨	🟨
	pH 10	🟨	🟩	🟩	🟩	🟩	🟩	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
SS (1,000 ppm)	Unadj.	🟩	🟩	🟩	⬜	🟩	🟩	⬜	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
	pH 4	⬜	🟩	🟩	⬜	🟩	🟩	⬜	🟩	🟩	🟩	🟩	🟩	🟨	🟩	🟩
	pH 10	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
NaCl (35,000ppm)	Unadj.	🟩	🟨	🟨	🟩	🟨	🟨	🟨	🟨	🟨	🟩	🟨	🟨	🟨	🟨	🟨
	pH 4	🟩	🟨	🟨	⬜	🟨	🟨	🟩	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨
	pH 10	🟩	🟩	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟩	🟨	🟨	🟨	🟨	🟨
NaCl + SS	Unadj.	🟨	🟨	🟨	🟩	🟨	🟨	🟩	🟨	🟨	🟩	🟨	🟨	🟨	🟨	🟨
	pH 4	⬜	🟩	🟨	⬜	🟩	🟨	⬜	🟨	🟨	🟨	🟨	🟨	🟨	🟩	🟩
	pH 10	🟩	🟩	🟨	⬜	🟨	🟨	⬜	🟩	⬜	🟩	🟩	🟨	🟨	🟨	🟨

Figure 11. Summary of emulsion stability under all conditions tested (ordered according to emulsion stability from stable to unstable).

In general, all surfactants tested easily formed an oil layer under high ionic strength conditions. Particularly, samples prepared with SDS (anionic surfactant) were characterized for their low stability in the presence of NaCl. This could be explained by the low resistance of electrostatically stabilized emulsions to saline conditions. In addition, it was observed that emulsion coalescence increased with temperature. For example, emulsions prepared with Type 1 presented an 8%, 42%, and 67% tendency to coalescence at 4°C, 25°C, and 35°C, respectively, under the tested conditions. These percentages were obtained by dividing the number of samples forming an oil layer by the total number of samples (e.g., 1/12 for Type 1 at 4°C), (Figure 11). Power green showed to be more resistant to temperature changes, exhibiting similar emulsion stability for all conditions tested. Overall, the stronger effect of surfactant type, temperature, and salinity on emulsion stability compared to pH and suspended solids was demonstrated using visual observation. It was found that NaCl additions clearly enhanced emulsion coalescence as well as the increase in temperature.

The analysis of relative oil layer height provided an insight of the coalescence rate characteristic of each specific surfactant at every condition of interest. The rate of coalescence is directly related to emulsion stability (Appendix B). It was noticed that major oil separation in samples containing NaCl occurred within the first 24 hrs, reaching a stable macro-phase separation afterwards. These results indicate that saline conditions enhance rapid emulsion coalescence at early stage. In specific, for emulsions prepared with SDS and NaCl, it was observed more than 90% relative oil separation within the first 2 hrs compared to non-salinity samples which showed no evidence of coalescence. For most of the conditions tested, the increase in temperature resulted in higher oil layer heights, indicating higher emulsions instability.

Table 5. Average micelle size of emulsion samples formed at 7×CMC_{log} (No additions, 25°C).

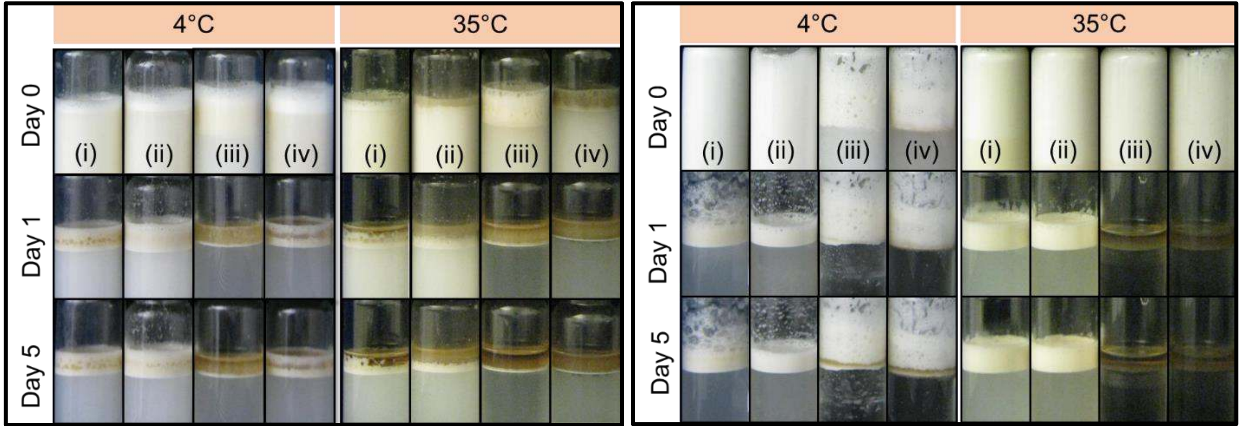
Surfactant	Av. Micelle size (µm)
Type 1	3.21 ± 0.16
SDS	5.66 ± 0.66
B&B 3100	3.29 ± 0.03
Power Green	3.78 ± 0.24
Solid Surge	3.74 ± 0.03
Calla	5.09 ± 0.24
PRC	3.65 ± 0.27
Triton X-100	3.00 ± 0.18
6% AFFF	3.01 ± 0.02
Blast-off	4.10 ± 0.16

Table 5 shows the average droplet size (e.g., diameter) of emulsion samples prepared using each surfactant at seven times the CMC_{log} (25°C). Average droplet sizes measured after 1 hr were found to be ranging between 3.0 to 5.7 µm. 1 hr after homogenization, emulsions prepared with Type 1 and Triton X-100 presented similar micelle sizes. However, the density of droplets in suspension was considerably higher for Type 1 than Triton X-100 (Appendix C). This suggests that Triton X-100 emulsions presented a higher tendency to coalescence during this period, resulting in only smaller droplets in suspension. Higher tendency to coalescence for emulsions prepared with Triton X-100 at 25°C compared to samples with Type 1 was corroborated in the previous stability test (Appendix B). The higher droplet sizes observed for emulsions prepared with Calla and SDS could be related to the coalescence of droplets while the interfacial area is being saturated with surfactant. Emulsifiers often have different dynamic interfacial tensions which are related to the adsorption of the surfactant at the interface [65].

4.2.1 Temperature Effect on Emulsion Stability

The impact of temperature on emulsion stability was evaluated for emulsion samples prepared at 4°C, 25°C, and 35°C (Appendix A). It was found that emulsion stability was clearly affected by temperature variations with more stable emulsions formed at lower temperatures. Overall, it was observed that emulsions subjected to high temperature environments (35°c) presented a higher tendency to coalescence and were more likely to form an oil layer at early stage (Appendix B). On the other hand, phase separation at lower temperature often resulted in a creaming layer formation with oil separation mostly observed for samples containing NaCl. The low sensitivity of emulsions prepared with Power green to temperature variations was related to the composition of the surfactant, in specific to the presence of sodium citrate. In Peng et al (2009), the addition of sodium citrate to milk protein emulsions demonstrated to significantly enhance the heat stability of the samples [66]. Overall, all surfactants tested, except Power green, showed to be susceptible to temperature variations, resulting in enhanced emulsion destabilization with temperature increase.

For example, in emulsions prepared with Triton X-100, SDS, and B&B, it was clearly observed an increase in emulsion coalescence when temperature increased from 4°C to 35°C (Figure 12). Stability of SDS emulsions prepared in low ionic strength conditions showed not to be affected by temperature changes. However, coalescence was clearly enhanced in SDS emulsions formed in saline environments. This finding suggests that samples emulsified with SDS are less sensitive to temperature variations in low salinity environments. Oppositely, for the samples prepared using B&B the oil separation increased from nearly 0% to 75% in samples containing SS (Figure 12(c)). Overall, the increase in temperature led to higher rates of coalescence in agreement with previous studies [17, 39]. It is well known that temperature has an adverse effect in the interfacial tension, oil viscosity, and surfactant absorption that can cause the deterioration of emulsions [12]. Increasing temperature raises the kinetic energy imparted to the droplets, which increases the probability of collision, enhancing emulsion destabilization by oil separation [67].



(a) Triton X-100

(b) SDS

(c) B&B

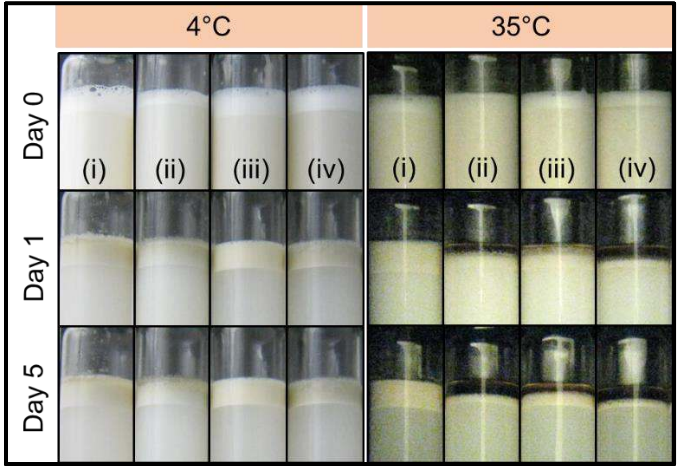


Figure 12. Time-course visual observation of emulsion samples prepared using (i) DI water (ii) 1,000 ppm SS (iii) 35,000 ppm NaCl (iv) 1,000 ppm SS and 35,000 ppm NaCl at 4°C and 35°C. Surfactants used were (a) Triton X-100, (b) SDS, (c) B&B.

4.2.2 Suspended Solids (SS) Effect on Emulsion Stability

The effect of SS on emulsion stability showed to be dependent on the surfactant type and temperature conditions. For some emulsifiers tested, the addition of SS enhanced emulsion destabilization by increasing the tendency to coalescence, particularly at higher temperatures. For instance, in emulsions prepared with B&B at 35°C, oil separation increased from 0 to ~70% when SS were added to the system. At 4°C, the addition of SS to emulsions prepared with Triton X-100 showed to counteract the effect of NaCl on emulsion destabilization. In these samples, it was observed an average reduction from ~84 to 21% in oil separation. Contrariwise, for other emulsifiers the addition of SS showed no major effect on emulsion stability (e.g., Type 1, SDS, and Solid surge). In emulsion systems, solid particles have demonstrated that can function in similar ways to surfactants, affecting the stability of emulsions through the formation of Pickering emulsions. Some properties such as particle wettability, partitioning coefficient, and particle size are unique for each particle type and can affect their ability to stabilize emulsions [68]. In this study, one possible explanation to the low impact of SS could be related to the high concentration of surfactant ($7\times CMC_{log}$), which could overcome the stabilizing properties of the solid particles. Therefore, to have a better understanding on the effect of SS on emulsion stability, it was evaluated the impact of SS on emulsion prepared below the CMC_{log} (0.5 times).

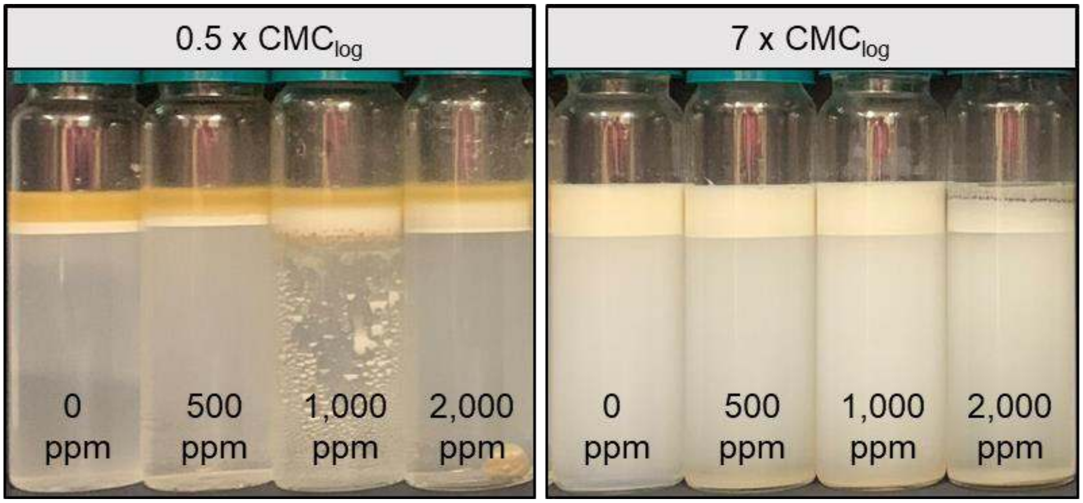


Figure 13. SS effect on emulsions prepared using Type 1 at low concentration ($0.5\times CMC_{log}$) and high concentration ($7\times CMC_{log}$).

In Figure 13, the emulsions prepared with Type 1 exhibited a higher effect of SS on emulsion stability when below the CMC (0.5×CMC_{log}) than above (7×CMC_{log}). Above the CMC, SS additions showed no influence on emulsion stability except at 2,000 ppm, which presented a relatively thin oil layer formation. Below CMC (i.e., 0.5×CMC_{log}), it was observed that the increase in SS concentration reduced the tendency to coalescence from 67 to 39% for 0 and 2,000 ppm, respectively (Figure 14). Additionally, it was observed that the increase in SS concentration resulted in the formation of larger creaming layers, decreasing turbidity in the emulsion layer (Figure 14). The increase in creaming layer formation could be related to the size difference between the solid particle and the oil droplet. In Albert et. al (2019), it is suggested that solid particles should be substantially smaller than the targeted droplet size to stabilize emulsions. This indicates that particles larger than the droplet will take longer to absorb at the interface, resulting in the formation of larger oil droplets. In this study, the Arizona dust size distribution ranged from 0.97 to 176 μm, which is relatively larger in size than Type 1 emulsion droplets (~3.5 μm average droplet diameter (D) which was obtained at 1 hr after homogenization) formed at 0.5×CMC. This could explain the increase in creaming layer formation of Type 1 with the addition of SS.

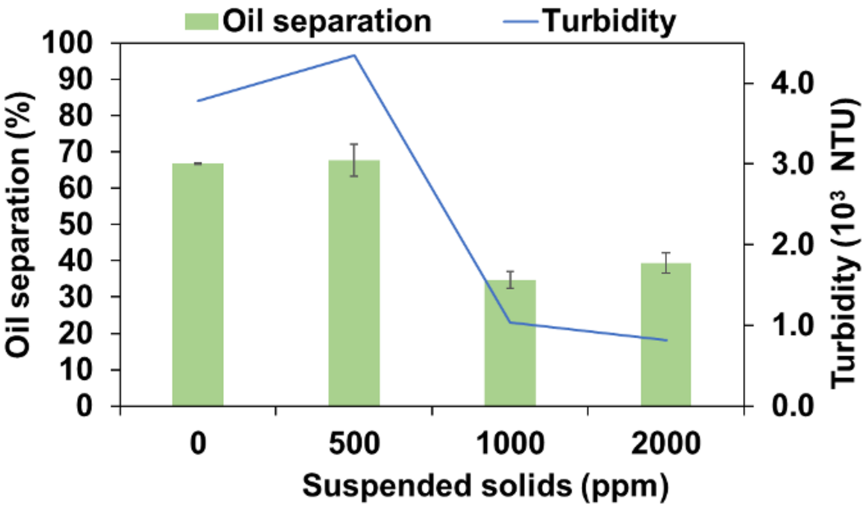


Figure 14. Oil separation and turbidity analysis of Type 1 emulsions prepared at 0.5×CMC.

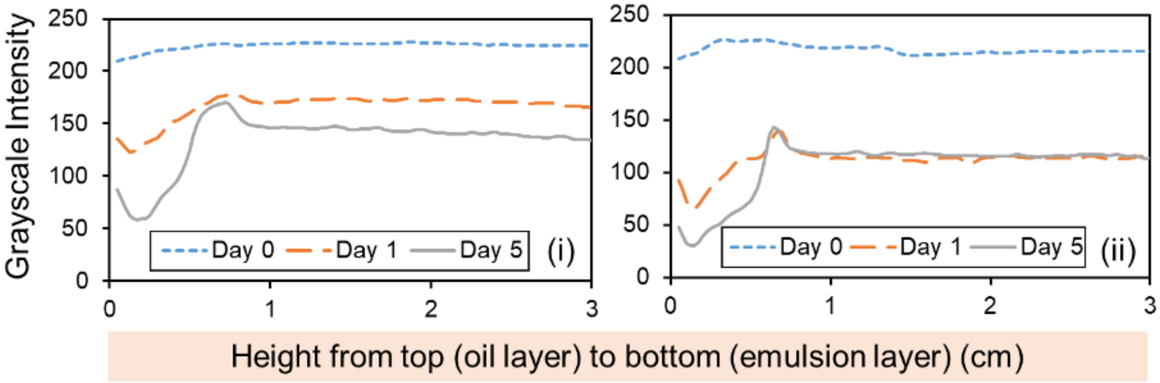
Figure 14 also showed a decrease in the turbidity of the emulsion layer with the increase in SS concentration, which is likely related to the increase in creaming layer formation. This indicates that SS enhance the temporary separation of emulsions (due to creaming); however, it decreases the definitive separation of samples by reducing coalescence.

In Appendix D, it is shown the effect of SS on the stability of emulsion samples prepared with Triton X-100, PRC, Solid surge, Blast off, and SDS at 0.5×$\mathrm{CMC}_{\mathrm{log}}$. Triton X-100 (D~3.1 µm) and PRC (D~4.0 µm), just like Type 1, presented a decreased in oil separation with increasing solids concentration as well as an increase in the formation of a creaming layer. Emulsions prepared with Solid surge (D~5.9 µm) and blast off (D~4.7 µm) showed no variation in the samples' morphology at any of the SS concentrations. Contrariwise, samples emulsified with SDS (D~3.6 µm) presented a lower emulsion stability (e.g., higher coalescence) in the presence of SS. Overall, the effect of SS on emulsion stability can highly vary depending on the surfactant concentration and type, temperature, and the size ratio between the solid particle and the oil droplet. In bilgewater systems, it is commonly observed diluted concentrations of surfactants which may indicate that solid particles could play a major role in stabilizing bilgewater emulsions.

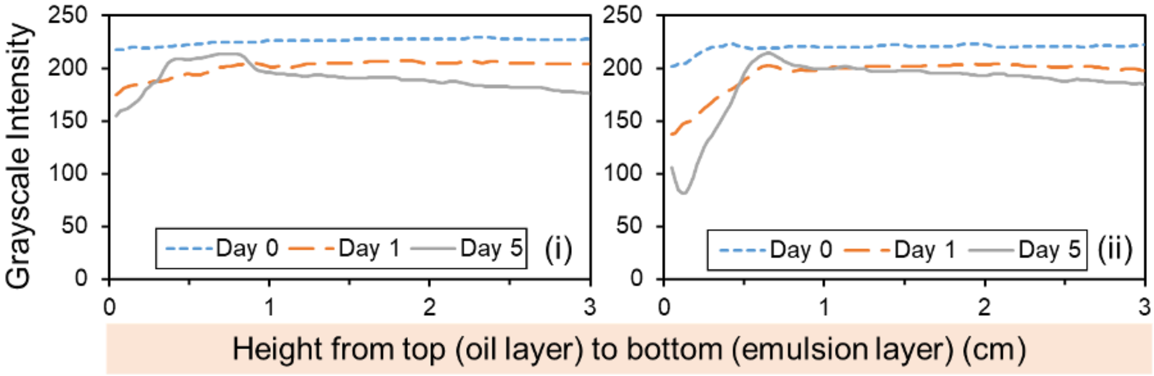
4.2.3 Salinity Effect on Emulsion Stability

For all surfactants tested, the presence of high ionic strength conditions demonstrated to have a significant effect on emulsion stability. Particularly, in electrostatically stabilized emulsions (e.g., SDS) it was observed rapid coalescence at early stage. For example, emulsions prepared with Triton X-100, SDS, and B&B presented a considerably lower grayscale intensity under NaCl additions compared to samples prepared without the salt (Figure 15).

(a) 7×CMC$_{log}$ Triton X-100



(b) 7×CMC$_{log}$ B&B



(c) 7×CMC$_{log}$ SDS

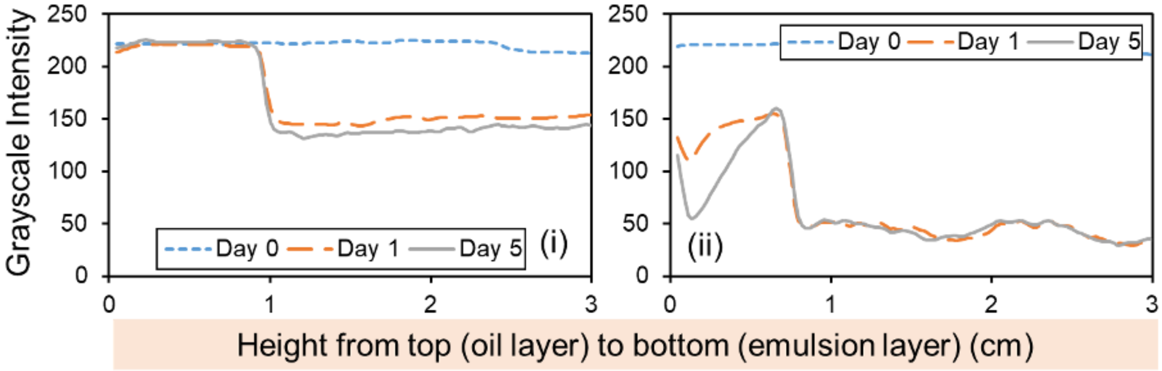


Figure 15. Time course evolution of the grayscale intensity profiles of emulsions prepared at 25°C with (a) Triton X-100, (b) B&B, and (c) SDS using (i) DI water only (ii) 35,000 ppm NaCl. 0 to 3 cm represent the depth of the sample from the surface. Zero to 250 represents the gray level intensity profile (0 – Black, 250 – White).

Low grayscale intensities at the top of the samples is used as indicative of emulsion's coalescence. Grayscale intensity of the emulsion layer is an indirect prediction of the concentration of droplets in suspension (e.g., turbidity).

After 1 day, samples emulsified with Triton X-100 under NaCl addition showed a decrease in the grayscale intensity from 130 to 70 (oil layer) and 170 to 115 (emulsion layer) compared to control samples. Likewise, emulsions with B&B showed a decrease from 175 to 140 (oil layer) and 210 to 200 (emulsion layer) under NaCl addition. SDS emulsions in the presence of salinity showed a rapid decrease in the grayscale intensity, resulting in almost complete separation within the first day after homogenization. These findings suggest that the addition of NaCl strongly enhances emulsion instability by increasing oil separation, thus resulting in lower oil droplets in suspension (e.g., lower turbidity). Likewise, microscopic photos of the samples taken after homogenization showed a decreased in droplet density for samples with high ionic strength, corroborating lower emulsion stability (Appendix E). These results are in agreement with previous works performed by Jared et al (2017) and Moradi et al (2011) which demonstrated the direct relationship between ionic strength and emulsion stability, concluding that salinity enhances emulsion separation [43, 58].

Electrostatically stabilized emulsions (e.g., SDS) showed higher instability in saline environments compared to other emulsifiers due to the high sensitivity of these surfactants to the addition of electrolytes. When the ionic strength of the solution increases, the protective layer surrounding the micelle (e.g., electrostatic shielding) is reduced, allowing the droplets to interact and increase in size (Figure 16). Additionally, ionic surfactants can precipitate (i.e., salt out) at high salt concentrations forming crystalline particles in solutions, lowering the surfactant stabilizing effect at the interface. According to Iyota et al (2009), the salting out of SDS can be related to the effect of the added salts to the solubility of the surfactant [69].

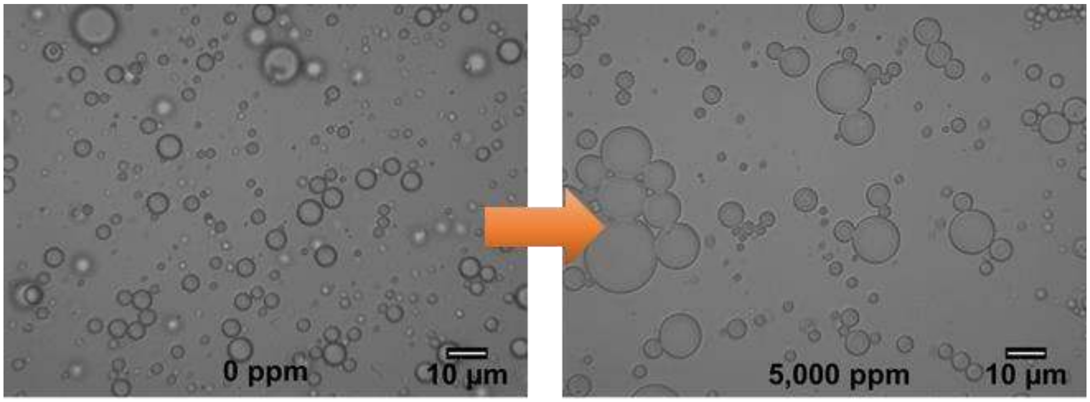


Figure 16. Microscopic photos of emulsions samples prepared with SDS using 0 ppm (control) and 5,000 ppm NaCl. Scale bar is 10 µm.

In Appendix F, it is shown the resulting emulsion stability of control emulsion samples prepared at different aqueous-phase salinity values (no surfactant added). These emulsions exhibited a decrease in stability with the increase in NaCl concentration. In fact, concentrations above 1,000 ppm of NaCl resulted in fast coalescence and enhanced phase separation (Figure F.2). Similar results were observed for emulsion samples prepared with Blast-off, PRC, and Solid surge at 0.5×CMC_{log}, which exhibited higher coalescence and lower emulsion turbidity at concentrations above 5,000 ppm (Appendix G). Overall, high ionic strength environments demonstrated to strongly enhance emulsion destabilization by increasing the tendency to coalescence. It is widely accepted that the increase in ionic strength can lower the zeta potential of the droplets, causing an increase in droplet interactions that results in the formation of larger droplets. In addition, the aqueous-phase salinity can affect the solubility of the emulsifier, which can impact the stability at the interface or cause the drag out of the surfactant (e.g., ionic surfactants). This indicates that at sufficient ionic strengths, fast coalescence resulting in major phase separation will likely occur.

4.2.4 Effect of Initial Bulk-Water pH on Emulsion Stability

Bulk-water pH effect on emulsion stability showed to highly vary depending on the surfactant type, temperature, and the presence of NaCl and/or SS in solution. From the stability tests, it could be observed that each surfactant was impacted differently by the initial bulk-water pH (Appendix A). For example, for Type 1 at 25°C it was observed higher emulsion stability at bulk-water pH 10 (Figure A. 2 #9); however, at 35°C no clear effect was observed. Emulsion prepared with SDS showed no effect of initial pH on emulsion stability as samples with/without salinity showed a similar trend. Power green was the only surfactant showing a clear impact of bulk-water pH on emulsion stability. It was observed a high emulsion instability (e.g., increase in tendency to coalescence) for Power green samples prepared in acidic pH. Emulsion prepared with Calla without NaCl/SS additions showed to be more stable at acidic or unadjusted initial pH; however, in the presence of additives no effect of observed. In this study, the effect of NSBM #4 additives was not considered in the overall pH values of the system. After homogenization, it was observed that the pH of the solution increased to around 6-8, for acidic and unadjusted bulk-water pH. For this reason, to study the actual pH effect on emulsion stability it is important to ensure acidic conditions even after homogenization.

Overall, this study investigated the effect of initial bulk water pH on emulsion stability; however, no clear trend was found as the pH effect varied with different surfactant solutions. NSBM #4 tested in this study showed to have a relatively high buffering capacity due to unknown additives. Therefore, in the typical pH conditions of bilgewater (pH 6.8 to 9), the effect of acidic pH on emulsion stability could be neglected.

4.3 Monitoring of Chemical Diffusion at the Oil-water Interface

4.3.1 Bulk-water Alkalinity Variation

Table 6 shows the initial pH values and alkalinity of emulsifier solutions prepared at 7×CMC_{log}. The results showed that the contribution from these emulsifiers to bilgewater alkalinity can range from 3.3 to 413 mg/L $CaCO_3$.

Table 6. Alkalinity of emulsifiers tested at 7xCMC_{log}.

Surfactant	Volume (µL)	Initial pH	Alkalinity (mg/L as $CaCO_3$)
Solid Surge	410	12.2 ± 0.1	412.5 ± 3.7
Power Green	1,606	9.9 ± 0.0	366.5 ± 6.9
Blast-off	392	10.5 ± 0.1	171.0 ± 6.5
6% AFFF	1,428	6.8 ± 0.0	68.9 ± 1.6
Calla	138	8.6 ± 0.0	27.1 ± 1.7
B&B	152	8.8 ± 0.1	21.0 ± 3.3
SDS	6,500	6.3 ± 0.7	7.4 ± 0.5
PRC	786	6.9 ± 0.1	6.4 ± 0.5
Triton X-100	42.8	6.7 ± 0.0	3.5 ± 0.4
Type 1	36.4	6.4 ± 0.0	3.3 ± 0.6

In specific, it was observed that neat surfactants (SDS and Triton X-100) presented relatively low alkalinities compared to commercial cleaners such as Solid surge and Power green. Commercial cleaners opposite to model surfactants, identified as substances, are proprietary blends with unknown chemical structures obtained from the combination of builders, stabilizers, and secondary surfactants [12]. Therefore, higher unpredictability in the effect of commercial cleaners on the physicochemical properties of bilgewater was expected. For example, Solid surge and PRC are both nonionic cleaner blends containing alcohol ethoxylate as main surfactant, yet the alkalinities of Solid surge and PRC were found to be 412 and 6.4 mg/L $CaCO_3$, respectively. The dissimilarity in alkalinity between these cleaners is due to differences in the mixtures' composition since Solid surge also contains sodium hydroxide and sodium carbonate, while PRC contains isopropyl alcohol. In this regard, it is essential to identify the bulk-water alkalinity contribution of emulsifiers commonly found in the bilge and their impact on the pH of the system. pH variations depending on buffering capacity (e.g., alkalinity) can affect the stability of bilgewater emulsions and interfere with the efficiency of pH-dependent treatment techniques.

In bilgewater systems, the contact of water, oil, and cleaners/surfactants can result in unpredicted variations in the alkalinity of the mixtures which may be considered as an important parameter for bilgewater treatment processes. In this study, the bulk water alkalinity changes of the simulated bilgewater emulsions were measured over time to determine possible buffering contributions from the NSBM #4 and emulsifiers into the bulk water. The time-course monitoring of bulk-water alkalinity in solutions of DI water, Triton X-100, Solid surge, PRC, and Type 1 emulsified with 10% NSBM #4 is presented in Table 7. In the presence of NSBM #4, the alkalinity of DI water increased from < 1 to 94.7 mg/L $CaCO_3$, indicating the presence of alkaline additives in the oil often referred to as the oil total base number (TBN) [70]. The oil TBN is the result of basic additives and detergents that are added to the oil mixture that possess an acid neutralizing effect to prevent oxidation and problems in the engine performance [71]. The TBN of oil samples can highly vary depending on the quality and application of the fuel and it usually ranges from 15-80 mg KOH/g for marine grade lubricants [72]. A larger TBN is often indicative of higher alkaline reserves added to the oil. Interestingly, the alkalinity of the DI water emulsion sample decreased as oil separation increased, resulting in a value of 11 mg/L $CaCO_3$ after 10 days. This indicates that the buffering capacity of the solution is related to the concentration of oil droplets in suspension. For example, water individually homogenized with 0.1%, 1%, and 5% NSBM #4 resulted in alkalinities of 5.5, 38, and 49 mg/L $CaCO_3$, respectively.

Table 7. Time-course monitoring of bulk-water alkalinity in emulsified oil-water emulsions.

Sample	**Day**	**0**	**5**	**10**
DI water + 10% NSBM #4 (**control**)	Alkalinity (mg/L $CaCO_3$)	94.7 ± 11	8.6 ± 1.2	11 ± 3
DI water + 10% NSBM #4 + **Triton X-100** (714 ppm)		245 ± 5	62.5 ± 0	67 ± 5
DI water + 10% NSBM #4 + **Solid surge** (683 ppm)		602 ± 27	435 ± 16	413 ± 38
DI water + 10% NSBM #4 + **PRC** (13,098 ppm)		250 ± 12	47.3 ± 2	51.1 ± 5
DI water + 10% NSBM #4 + **Type 1** (607 ppm)		247 ± 8	63.2 ± 1	78.6 ± 12

In emulsions prepared using NSBM #4 oil and surfactants, the bulk-water alkalinity was found to be considerably higher compared to samples emulsified using oil only (Table 7). The resulting emulsion alkalinity was considered as the addition of the surfactant alkalinity and the oil acid neutralizing effects. For example, Triton X-100, PRC, and Type 1 (low alkalinity surfactants) resulted in significantly lower bulk-water alkalinity compared Solid surge. However, the oil buffering contribution increased for emulsions homogenized with low buffering surfactants. For instance, the alkalinity contribution from oil to Solid surge emulsions was 190 mg/L $CaCO_3$, while the contribution to the other samples was averaged as 242 mg/L $CaCO_3$. From the results, it was determined that the alkalinity contribution from oil is enhanced be the presence of surfactants and can vary depending on the surfactant properties. As expected, alkalinity decreased throughout the duration of the experiment and the residual alkalinity was attributed to the surfactant and oil droplets remaining in suspension. It was observed that major changes in emulsion alkalinity occurred within the first 5 days and remained nearly constant afterwards. This was considered as an indicative point of equilibrium reached between the oil/creaming and the emulsion layer, suggesting no further emulsion separation. For this reason, emulsion stability was evaluated in a 5-day experimental period as major changes occur within the first days of emulsification.

4.3.2 pH Monitoring at the Oil-water Interface Using pH Microsensors

Figure 17 shows the pH gradients measured for DI water samples in contact with NSBM #4 and mineral oil across the oil/water interface. pH was measured 5 min after adding the NSBM #4 or mineral oil. For NSBM #4 as oil phase, there was a clear increase in bulk-water pH from 6.0 to 7.6 after 1 day of contact. On the other hand, the bulk-water in contact with mineral oil only showed a minimal pH increase of 0.3. In the presence of NSBM #4, the increase in bulk water pH is considered to be the result of unknown oil basic additives partially miscible in water that can be diffusing at the oil/water interface. The presence of unknown additives is related to the alkaline reserves (e.g., TBN) added to marine diesel fuels previously mentioned in Section 4.3.1. For this reason, mineral oil, which is a pure oil with no additives added, should have no effect in the bulk water pH over time. These results were in agreement with findings in Jared et al (2017) where emulsions prepared using NSBM #4 as dispersed phase displayed a pH gradient formation across the interface, which was not observed in the sample containing mineral oil [58].

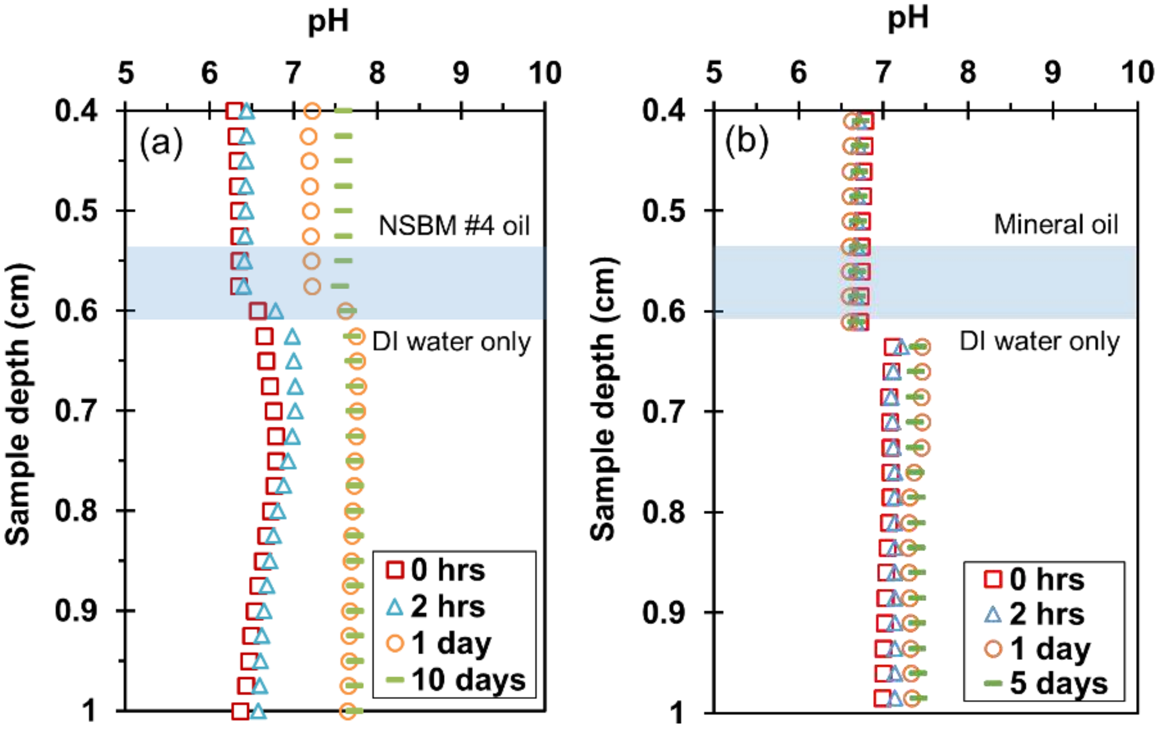


Figure 17. pH changes in samples of (a) NSBM #4 and (b) Mineral oil in contact with DI water. Microprofiles were measured at room temperature (25°C). DI water and oil were not homogenized.

In Figure 18, it can be observed that the diffusion of additives at the oil/water interface can be affected by the physicochemical properties of the surfactant. For low pH surfactants, the bulk-water pH increased from 6.7 and 6.2 to 7.7 for Triton X-100 and Type 1, respectively. Using the Darcy's law, the flux of OH^- at the oil/water interface was calculated as 4.4×10^{-11} and 1.0×10^{-11} $mg\cdot cm^{-2}\cdot s^{-1}$ for Triton X-100 and Type 1, respectively. For high pH surfactants like Solid surge and B&B, the Δ pH were found to be of 0.14 and 0.31, respectively. These findings suggest that bulk water solutions with low buffering capacity may present a higher mass transport of oil additives at the interface (oil to water diffusion). Interestingly, in basic solutions it was observed a greater variation in the oil pH over time compared to neutral solutions. This indicates a possible diffusion of solutes from the bulk-water into the oil, which resulted in the formation of a cloudy oil layer.

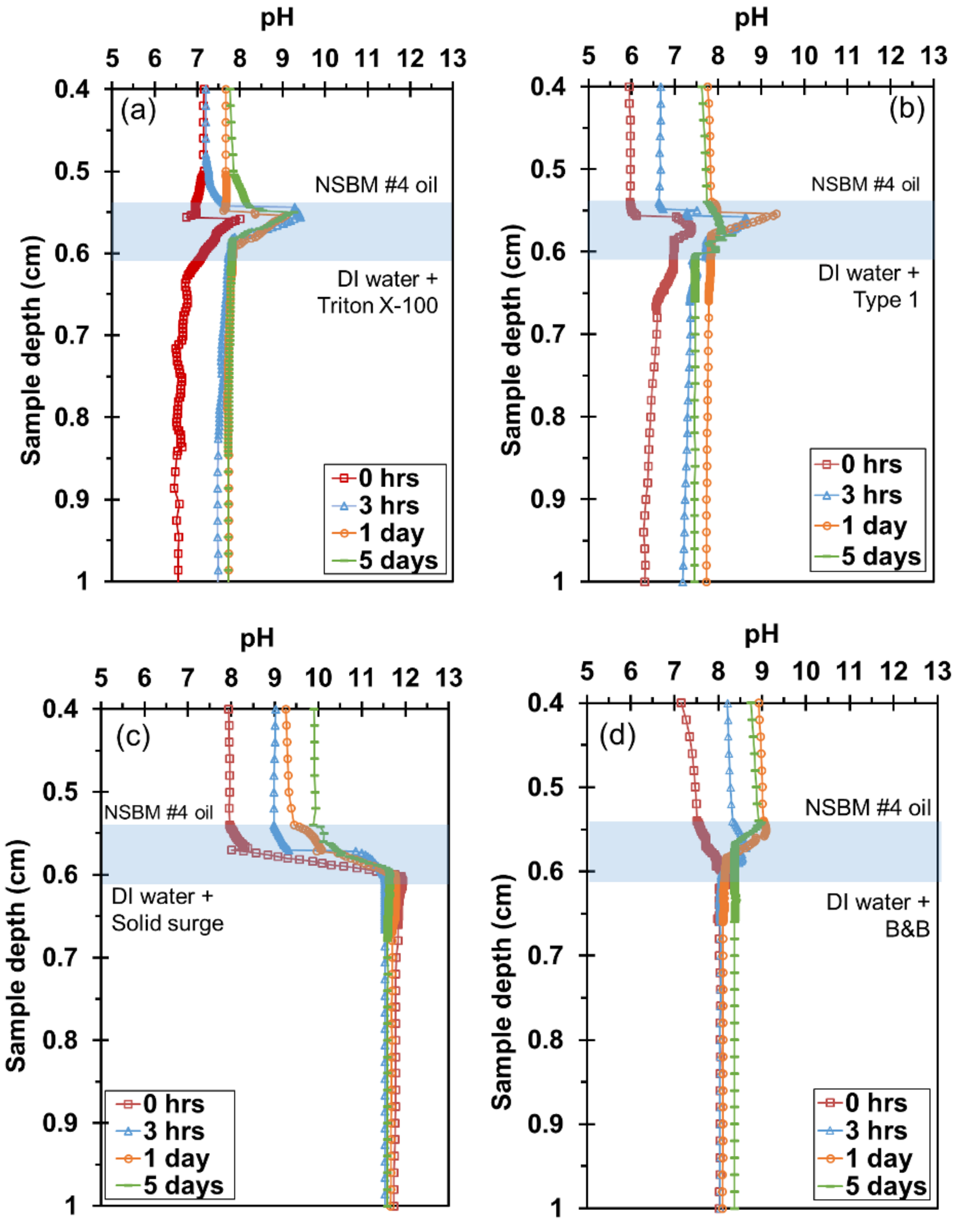


Figure 18. Spatial pH changes in samples of (a) Triton X-100, (b) Type 1, (c) Solid surge, and (d) B&B solutions in contact with NSBM #4. DI water was used to prepare the surfactant solutions. 6 ppm NaCl were added to improve microelectrode response. Microprofiles were measured at room temperature (25°C). DI water and oil were not homogenized.

The measured pH microprofiles showed that oil additives and surfactant properties (e.g., alkalinity) can influence the mass transfer of solutes at the oil/water interface, which can affect the bulk water pH. The variation in the pH of the system can consequently affect emulsion stability and the effectivity of pH-dependent bilgewater treatment techniques (e.g., electrocoagulation). In Dimitrova et al (1988) and Sternling et al (1959), it was mentioned that the mass transfer of surface-active solutes across the interface between two unequilibrated liquids can result in the instability of the interface, thus affecting emulsion stability (Marangoni instability) [73, 74]. Studies evaluating the effect of mass transport on emulsion stability have shown that it depends on the nature and concentration of the solute, the mass transfer direction, and the diffusion time [73]. Although microsensors allowed the study and monitoring of mass transport at the oil/water interface, further experimentation is required to better understand the effect of mass transfer direction in the stability of simulated bilgewater emulsions.

4.3.3 Excitation-emission Matrix (EEM) Analysis

Excitation-emission matrix (EEM) fluorescence spectroscopy is widely used to estimate the presence of organic compounds such as NOM and polycyclic aromatic hydrocarbons (PAHs) in water [75]. In this work, EEM analysis was used to detect the presence of aromatic hydrocarbons in NSBM #4 and DI water based on their location in the EM-EX map. NSBM #4 exhibited a relatively high fluorescence intensity at emissions wavelengths between ~310 and ~380 nm (Figure 19(a)). Major aromatic compounds found within those wavelengths are n- chrysene (~370 nm), dimethylnapthalene (~340 nm), naphthalene (~335 nm), anthracene (380-400 nm), pentylbenzene (~300 nm), and benzopyrene [76] (Appendix H). These results suggest that the organic composition of NSBM #4 oil is mainly related to the presence of naphthalene and dimethylnapthalene. However, further investigation is required to determine other organic constituents of interest.

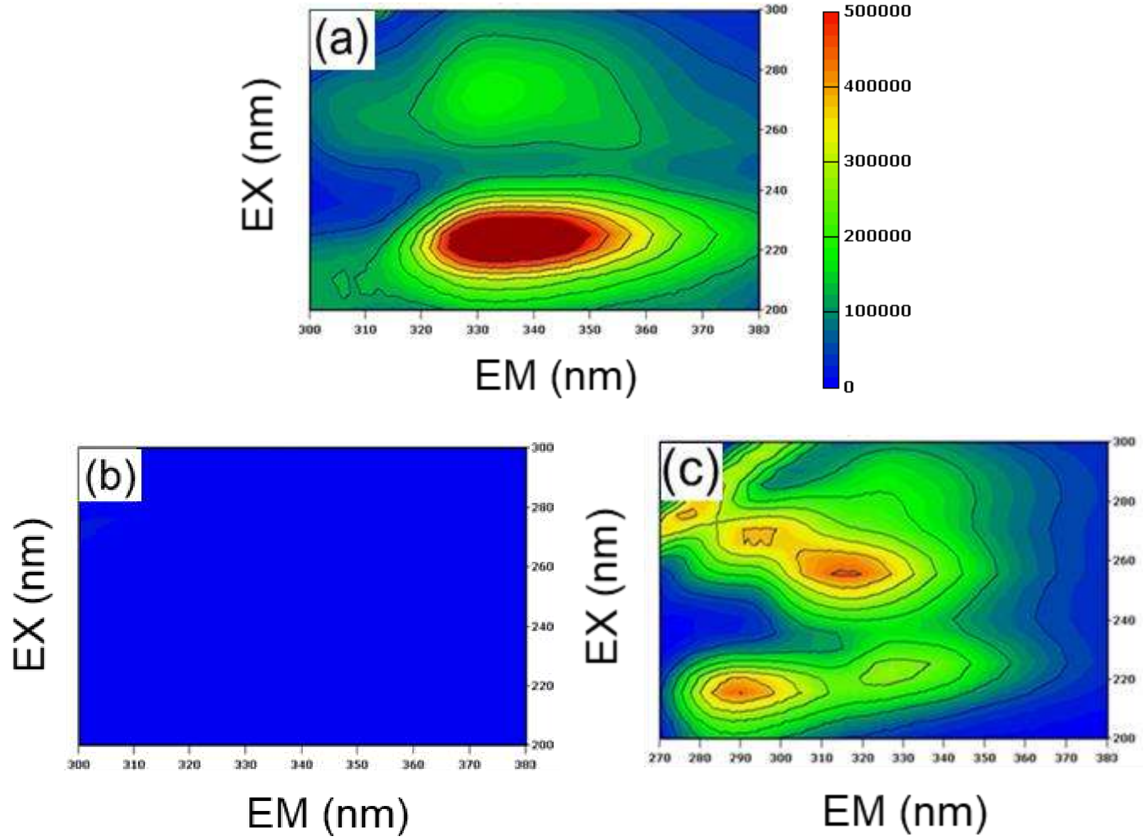


Figure 19. EEM analysis for (a) NSBM #4 (5×10^{-5}% v/v), (b) Clean DI water (as a control), and (c) DI water exposed for 24 hrs to NSBM #4. DI water and oil were not homogenized.

The diffusion of oil additives at the oil-water interface was analyzed by measuring the organic composition of water after exposed to oil contact for 24 hrs. After the contact time of 24 hours, the oil layer was removed from the top of the bulk-water and an EEM analysis was performed with the bulk-water only. Figure 19(b) and (c) indicated an increase in the fluorescence intensity for water in contact with NSBM #4 compare to pure DI water (as a control), which indicated the diffusion of hydrophilic organic additives from the oil into the water. Organic constituents diffused into the water could be associated to the alkaline reserves added to the oil (e.g., basic additives and detergents).

To evaluate emulsion formation and stability, DI water in contact with NSBM #4 for 24 hrs, after the oil layer was removed, was homogenized for 2 min at 33,000 rpm with 10% v/v mineral oil. One emulsion was prepared using pure DI water (no contact with NSBM #4) and mineral oil as a control. Results demonstrated that additives diffused from NSBM #4 into the bulk-water caused the formation of a more stable emulsion compared to the control sample (Appendix I). Emulsion turbidity was increased from 40 to 1,830 NTU for the emulsion sample prepared with the bulk-water in contact with NSBM #4 compared to the control emulsion sample (DI water + mineral oil). The EEM analysis supported the diffusion of oil additives into the bulk-water. Additionally, these additives demonstrated to have an impact in the stability of emulsions, indicating that the use of NSBM #4 will like enhance emulsion formation compared to pure oils (e.g., mineral oil). Therefore, in bilgewater systems it is important to understand and address the influence of oil constituents in the formation of stable emulsions.

CHAPTER FIVE: CONCLUSION AND PRACTICAL APPLICATION

Current environmental regulations have stipulated a maximum oil concentration of 15 ppm for proper bilgewater discharge. The high variability in bilgewater composition and the formation of chemically stabilized emulsions hinder the efficiency of conventional oil-water separators, often requiring the use of additional treatments to comply with discharge regulations. Yet, the lack of information regarding bilgewater emulsion formation and stability often makes it difficult to choose appropriate treatment techniques based on the specific characteristics of the bilgewater system. In this study, the effect of common bilgewater components on emulsion stability was extensively investigated under various environmental conditions. In particular, the effect of salinity, temperature, suspended solids (SS), and pH on the formation and stability of emulsions was evaluated using relevant model and commercial surfactants. Additionally, the mass transport of solutes at the oil-water interface and its effect on emulsion stability was demonstrated.

The findings suggest that emulsion stability is significantly affected by surfactant type, ionic strength, and temperature. The resulting emulsion stability based on surfactant type from most stable to least stable was Type 1 (39%) > SDS (50%) > B&B (56%) > Power green (67%) > solid surge (69%) > Calla (78%) = PRC (78%) > Triton X-100 (81%) > 6% AFFF (100%) = Blast-off (100%). In this work, emulsions prepared with Type 1 presented a 39% tendency to form an oil layer while all samples prepared with 6% AFFF and Blast off resulted in 100% coalescence. For all surfactants tested, except Power green, it was found that increasing temperature accelerated emulsion separation by enhancing the tendency to coalescence of the droplets. Ionic strength showed to have the highest effect on emulsion destabilization, resulting in oil separation at early stage. 87% of emulsions prepared in saline conditions exhibited an oil layer formation. Addition of suspended solids showed to help stabilizing emulsions under certain environments, specifically at low concentrations of surfactant. pH effect was found to highly vary depending on the surfactant type and NaCl/SS additions, yet no clear pattern could be determined. Buffering capacity of emulsifiers tested was found ranging between 3.3 to 413 mg/L $CaCO_3$. Additionally, the presence of alkaline additives in the NSBM #4 oil contributing to the alkalinity of the mixture was demonstrated. Increase in oil concentration from 0.1% to 5% showed to increase alkalinity from 5.5 to 49 mg/L $CaCO_3$, respectively. Results indicated the transfer of alkaline additives at the oil-water interface, which was proven to contribute with the formation of stable emulsions.

In conclusion, this study provided with significant information regarding the contribution of bilgewater components to the formation and stability of emulsions in Navy bilgewater systems. This work was aimed to help researchers and shipboard operators in the detection of conditions triggering emulsion stability and in the selection of appropriate bilgewater treatment techniques.

5.1 Practical Application

The practical application of this work relies on the development of an emulsion stability guide to predict emulsion stability for specific bilgewater conditions. An emulsion stability guide would be a useful tool for selecting appropriate treatment techniques according to the unique characteristics of each bilgewater system. In this way, the selection of oil-water separation techniques would be based on the physicochemical properties of the emulsions present rather than only on standard operational criteria. For the formulation of the guide, it is required the use of data analysis techniques to inspect, transform, and model the data collected to generate effective relationships between parameters [77]. Random forest is a decision learning method that uses a combination of features to grow a decision tree [78]. This technique often assembles multiple trees that help classifying an attribute based on the majority of votes [79].

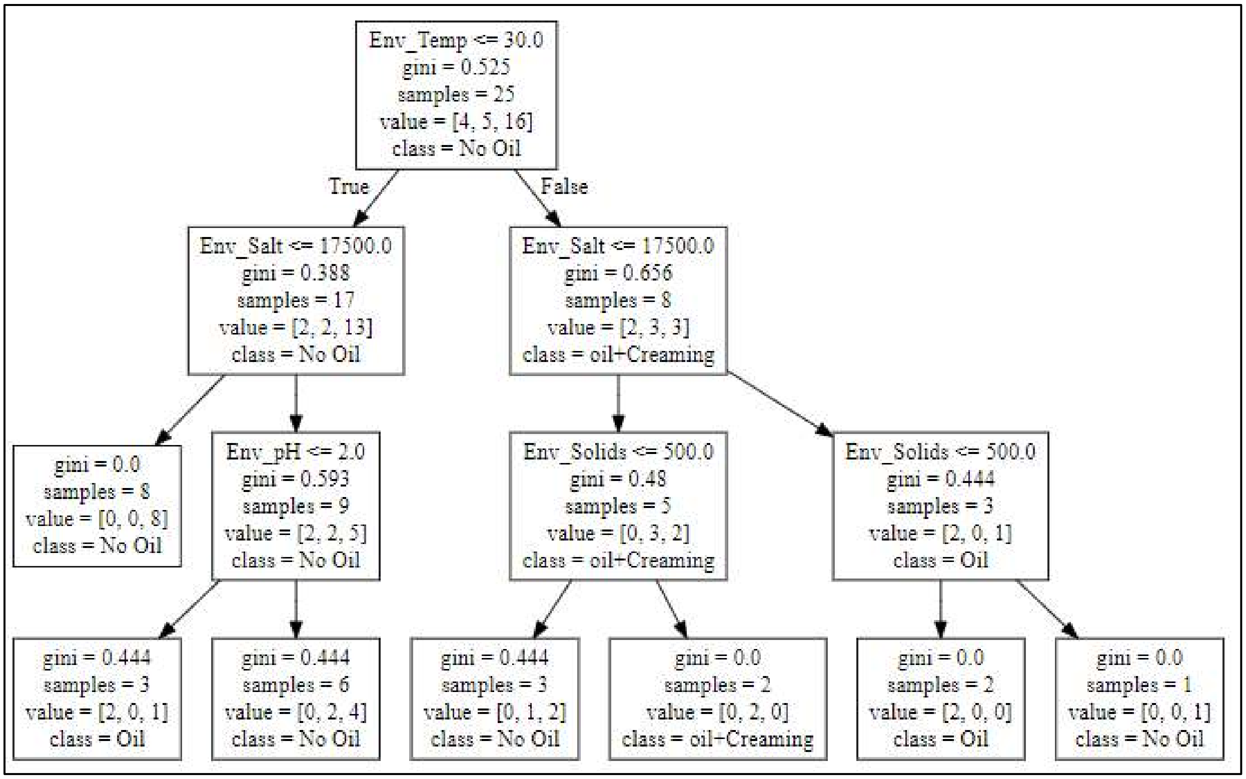


Figure 20. Example of random forest for emulsions prepared with Type 1 (Provided by NSWCCD).

In Figure 20, it is shown a random forest tree used for the prediction of emulsion stability in samples prepared with Type 1. For the model, 70% of the data is used for training and the remaining 30% is used for testing. Classification was based in the macro-phase separation of the emulsions, which is directly correlated to emulsion stability. In this study, emulsion stability data collected from UCF and the NSWCCD was used as experimental data for the development of the model. Preliminary models developed based on data collected from the effect of environmental parameters and CMC on emulsion stability have shown an accuracy of 77% and 91%, respectively (Figure 21). It can be expected that by using the complete data set, an accurate guide for predicting emulsion stability based on characteristics of the bilgewater system can be developed (Figure 22).

It is believed that having a better knowledge about the stability of bilgewater emulsions present in the influent wastewater will help improving bilgewater treatment and management.

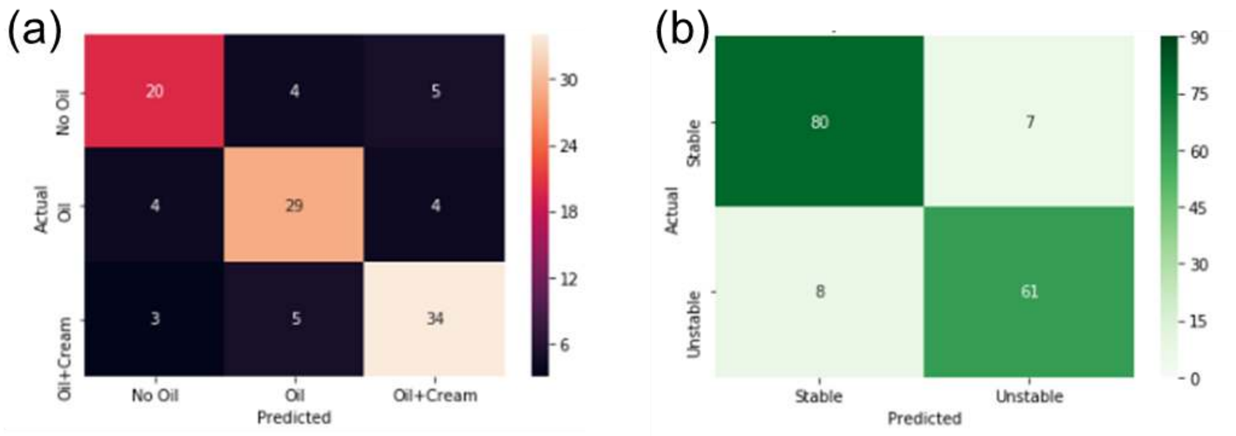


Figure 21. Random forest model based on (a) Environmental conditions (77%) and (b) CMC (91%). (Provided by NSWCCD).

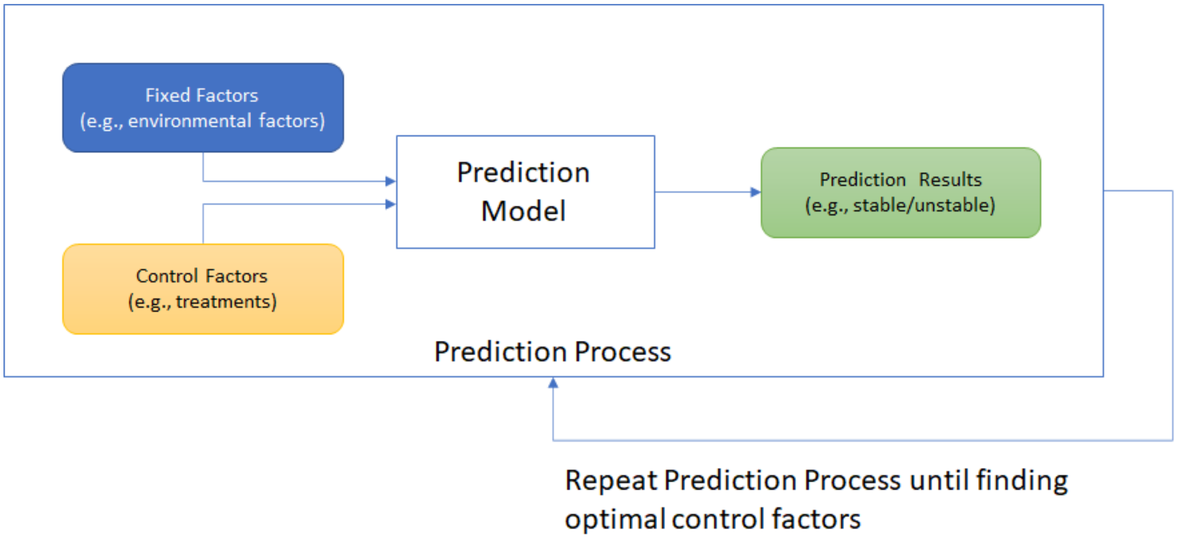


Figure 22. A prediction model example.

APPENDIX A

5^{TH} – DAY VISUAL OBSERVATION OF EMULSION SAMPLES PREPARED AT VARIOUS ENVIRONMENTAL CONDITIONS

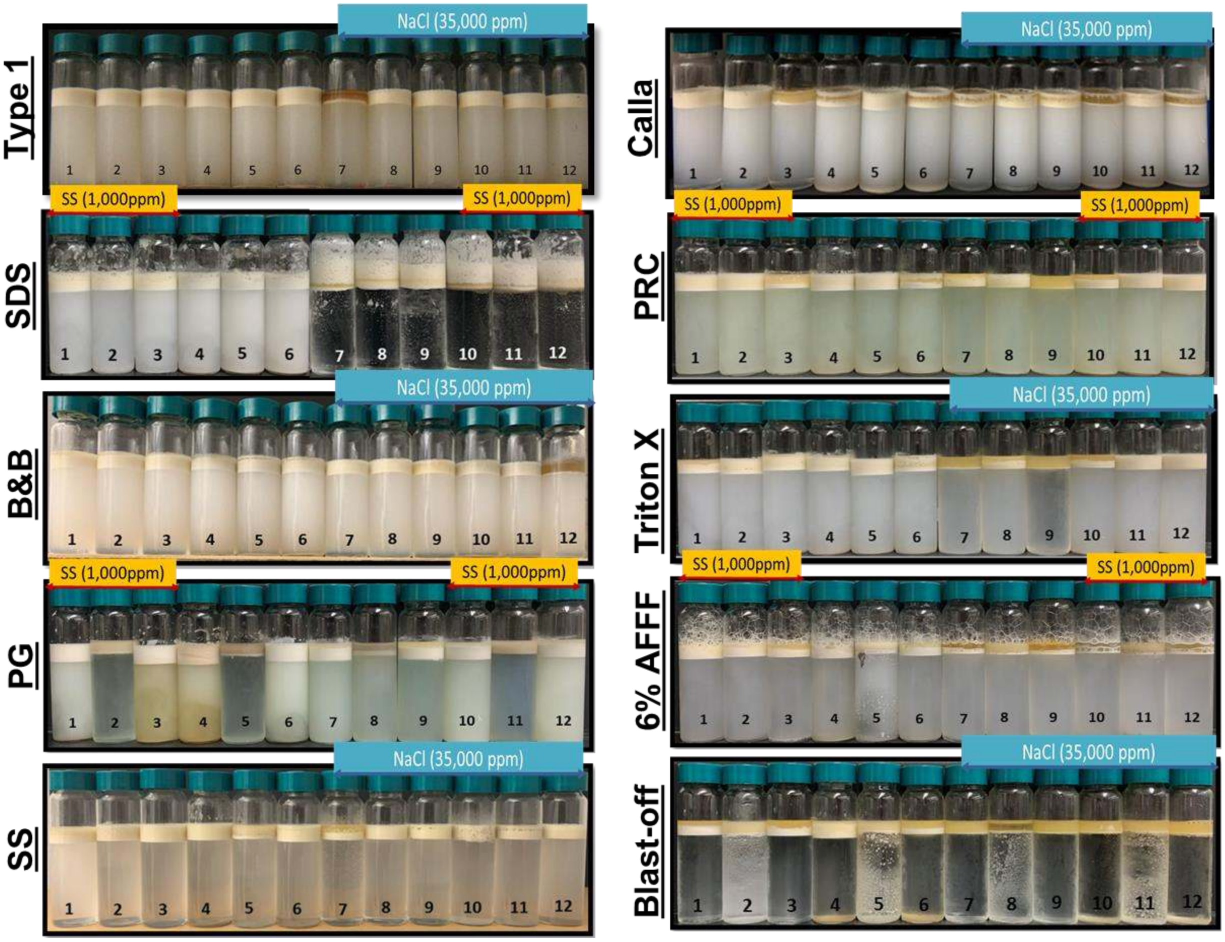


Figure A. 1. 5th-day visual observation of emulsions prepared at 4°C.

Sample	Description		
	pH	Suspended solids (SS)	Salinity
1	Unadjusted	-	-
2	4	-	-
3	10	-	-
4	Unadjusted	1,000 ppm	-
5	4	1,000 ppm	-
6	10	1,000 ppm	-
7	Unadjusted	-	35,000 ppm
8	4	-	35,000 ppm
9	10	-	35,000 ppm
10	Unadjusted	1,000 ppm	35,000 ppm
11	4	1,000 ppm	35,000 ppm
12	10	1,000 ppm	35,000 ppm

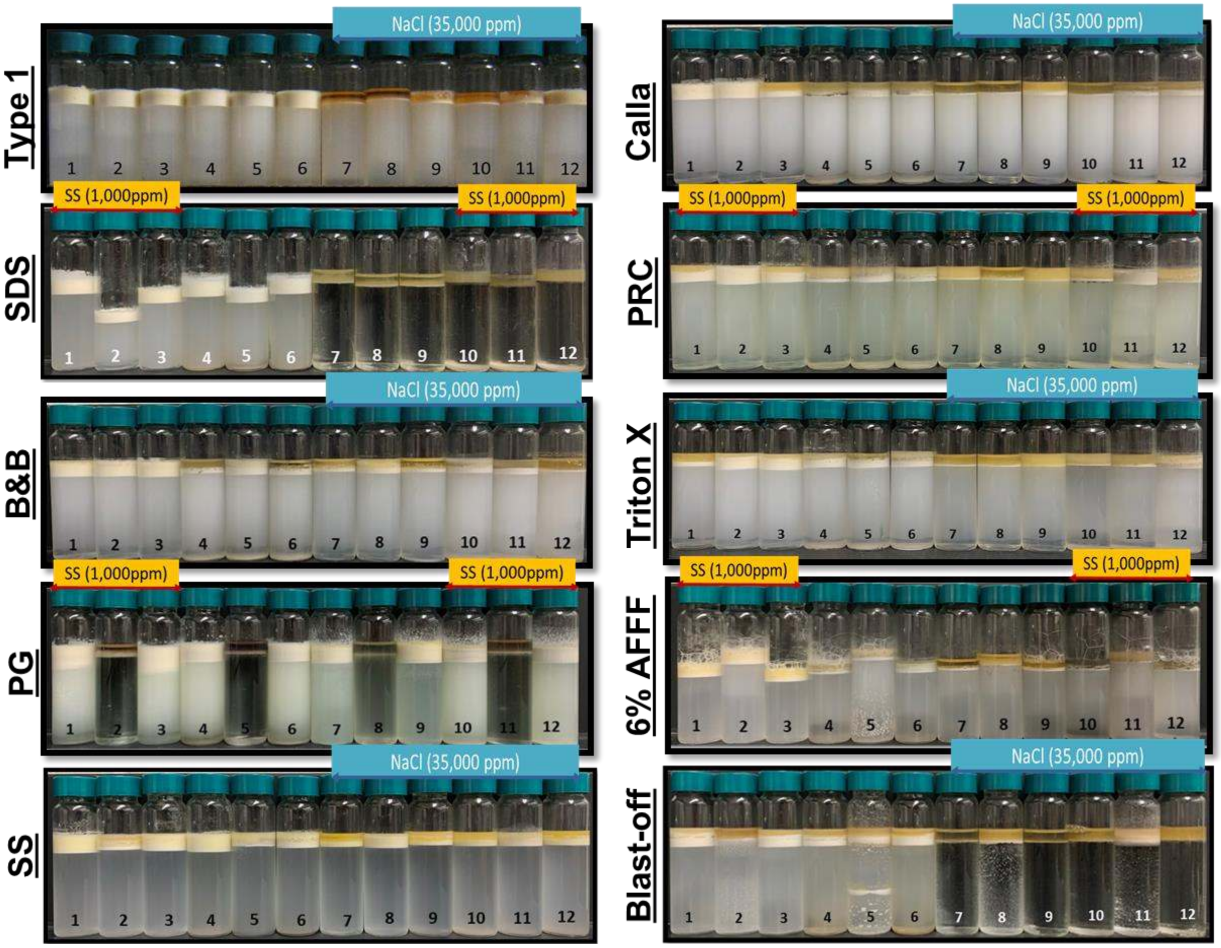


Figure A. 2. 5th-day visual observation of emulsions prepared at 25°C.

Sample	**Description**		
	pH	**Suspended solids (SS)**	**Salinity**
1	Unadjusted	-	-
2	4	-	-
3	10	-	-
4	Unadjusted	1,000 ppm	-
5	4	1,000 ppm	-
6	10	1,000 ppm	-
7	Unadjusted	-	35,000 ppm
8	4	-	35,000 ppm
9	10	-	35,000 ppm
10	Unadjusted	1,000 ppm	35,000 ppm
11	4	1,000 ppm	35,000 ppm
12	10	1,000 ppm	35,000 ppm

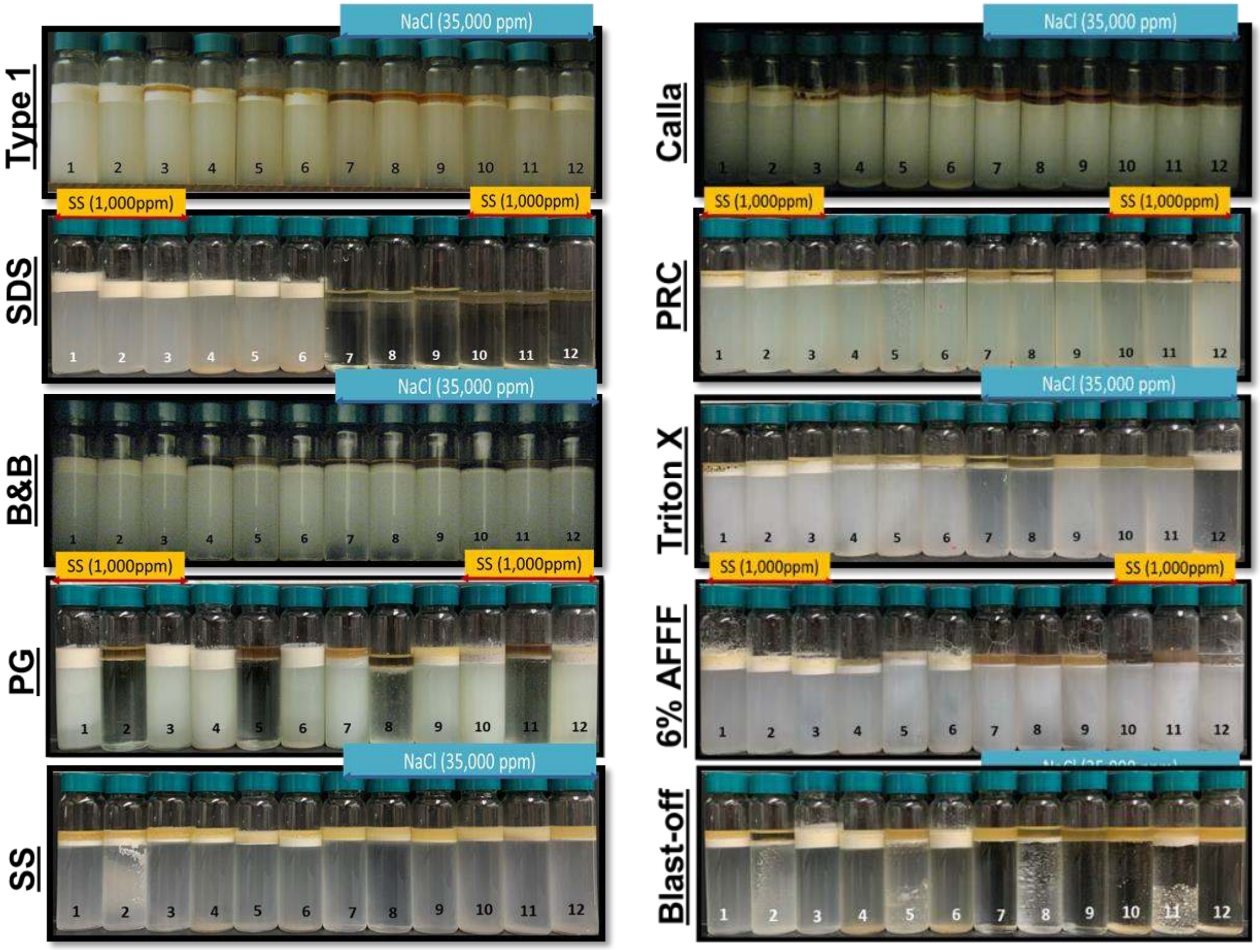


Figure A. 3. 5th-day visual observation of emulsions prepared at 35°C.

Sample	Description		
	pH	Suspended solids (SS)	Salinity
1	Unadjusted	-	-
2	4	-	-
3	10	-	-
4	Unadjusted	1,000 ppm	-
5	4	1,000 ppm	-
6	10	1,000 ppm	-
7	Unadjusted	-	35,000 ppm
8	4	-	35,000 ppm
9	10	-	35,000 ppm
10	Unadjusted	1,000 ppm	35,000 ppm
11	4	1,000 ppm	35,000 ppm
12	10	1,000 ppm	35,000 ppm

APPENDIX B

VARIATION OVER TIME OF THE OIL LAYER HEIGHT OF EMULSIONS PREPARED UNDER VARIUS CONDITIONS

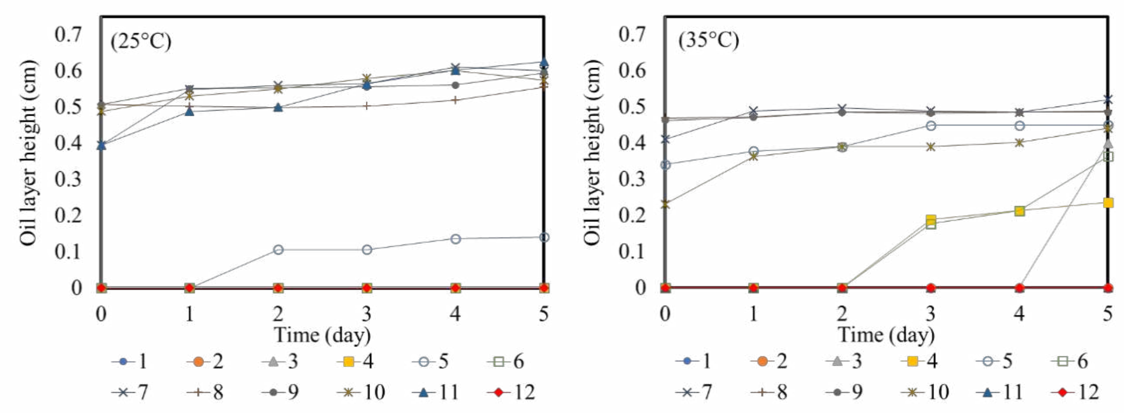


Figure B. 1. Variation over time of the oil layer height of emulsion samples prepared with Type 1.

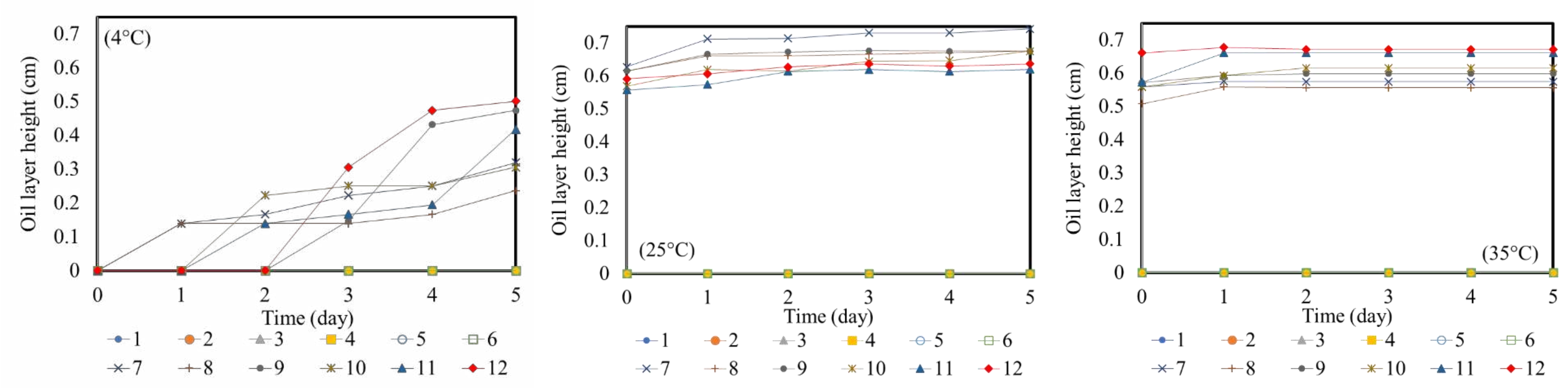


Figure B. 2. Variation over time of the oil layer height of emulsion samples prepared with SDS.

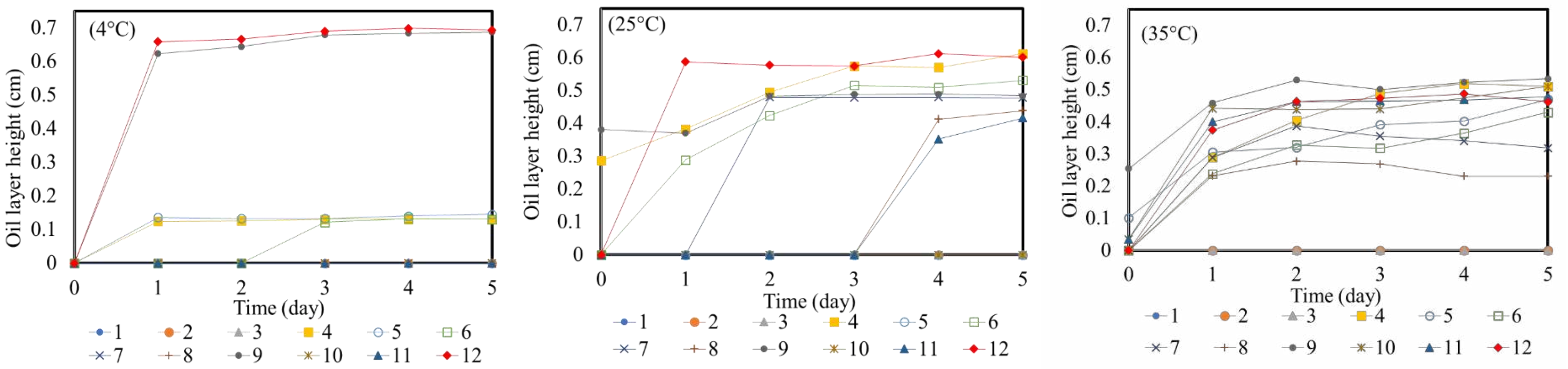


Figure B. 3. Variation over time of the oil layer height of emulsion samples prepared with B&B.

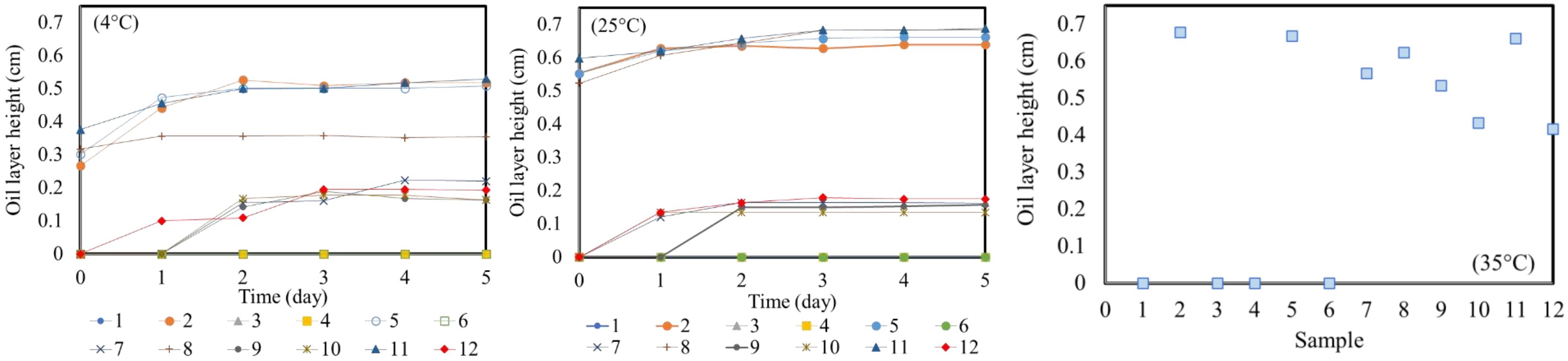


Figure B. 4. Variation over time of the oil layer height of emulsion samples prepared with Power green.

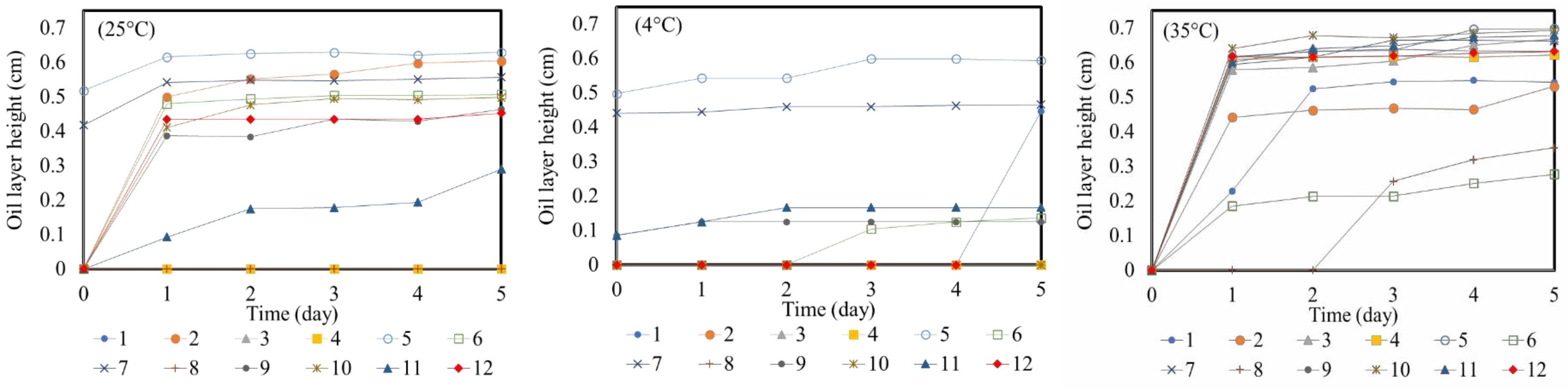


Figure B. 5. Variation over time of the oil layer height of emulsion samples prepared with Solid surge.

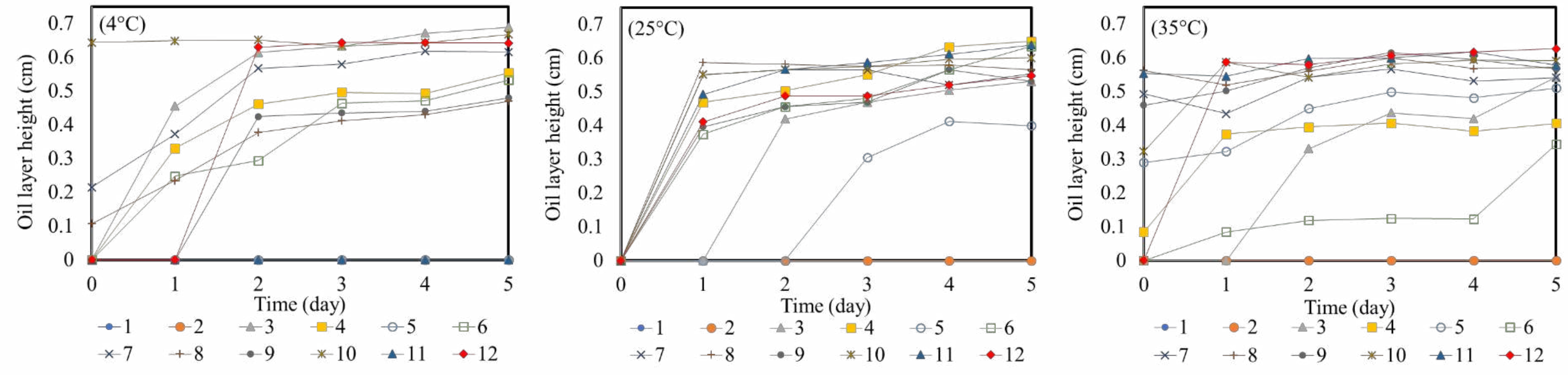


Figure B. 6. Variation over time of the oil layer height of emulsion samples prepared with Calla.

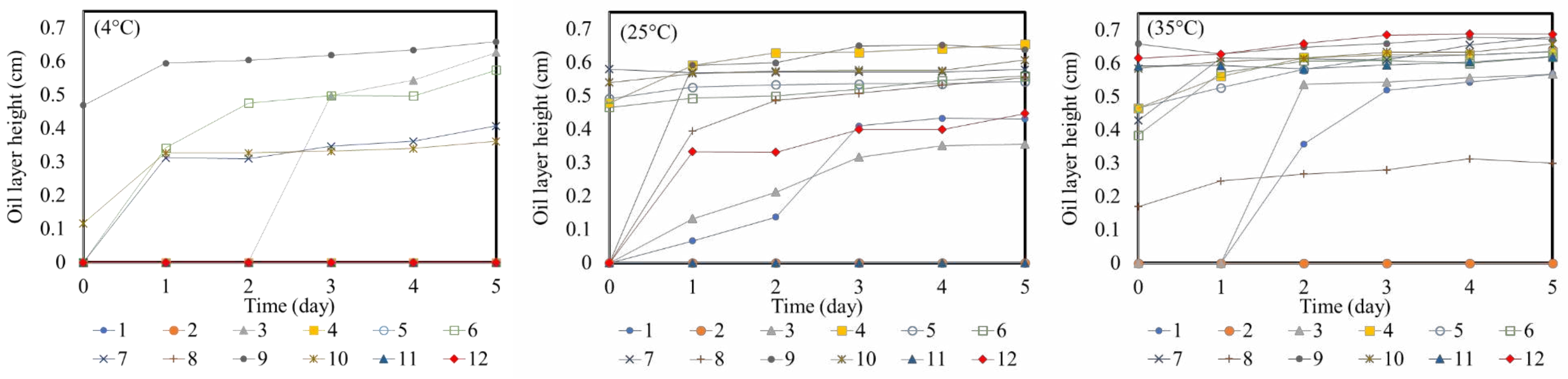


Figure B. 7. Variation over time of the oil layer height of emulsion samples prepared with PRC.

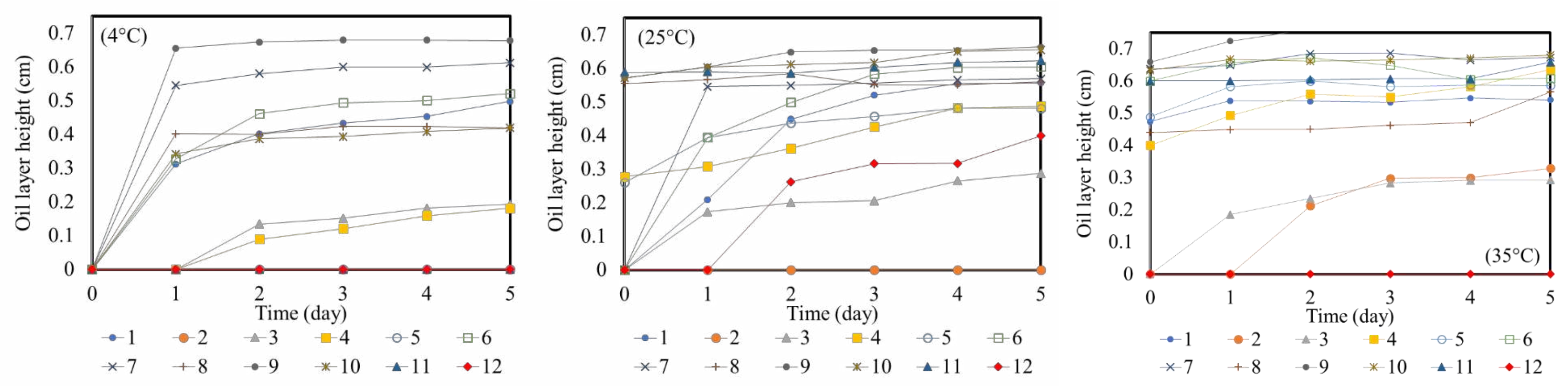


Figure B. 8. Variation over time of the oil layer height of emulsion samples prepared with Triton X-100.

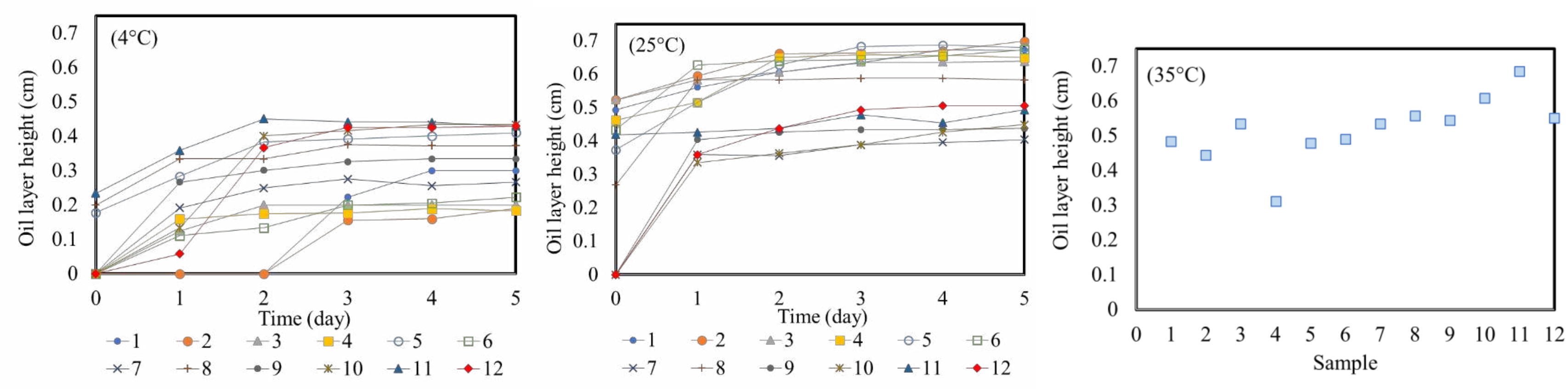


Figure B. 9. Variation over time of the oil layer height of emulsion samples prepared with 6% AFFF.

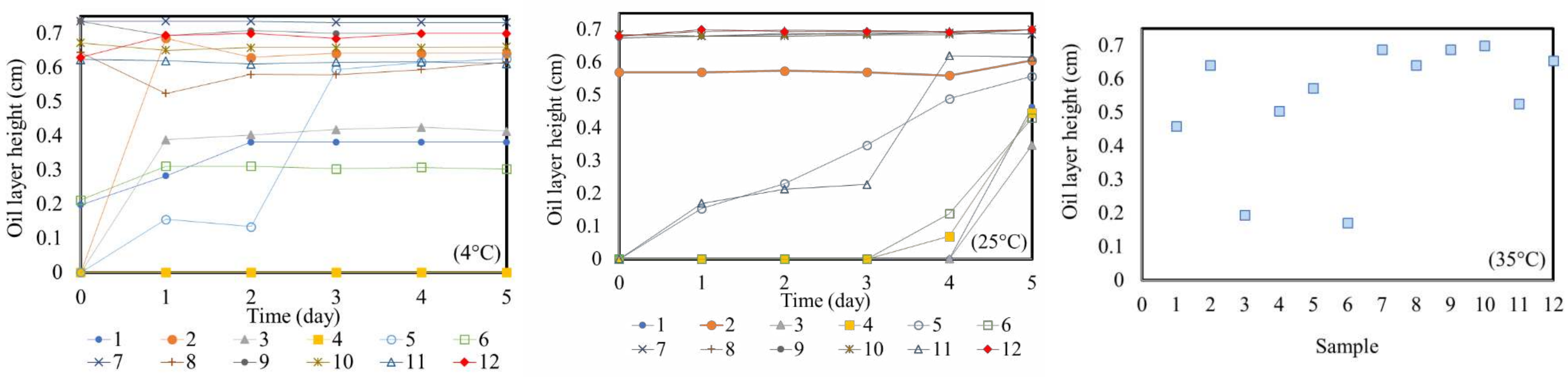
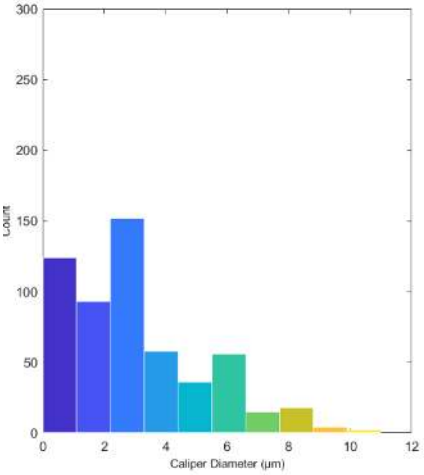


Figure B. 10. Variation over time of the oil layer height of emulsion samples prepared with Blast-off.

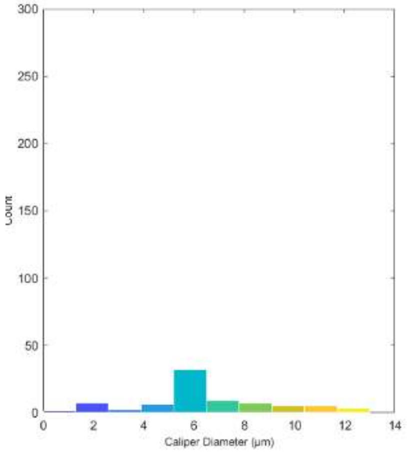
APPRENDIX C

DROPLET DISTRIBUTION FOR EMULSIONS PREPARED AT 7×$\mathrm{CMC}_{\mathrm{LOG}}$ (25 °C)

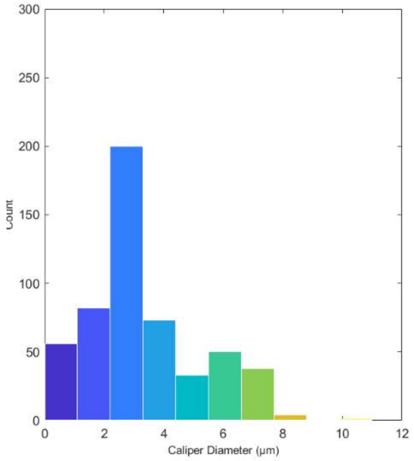
(a) Type 1



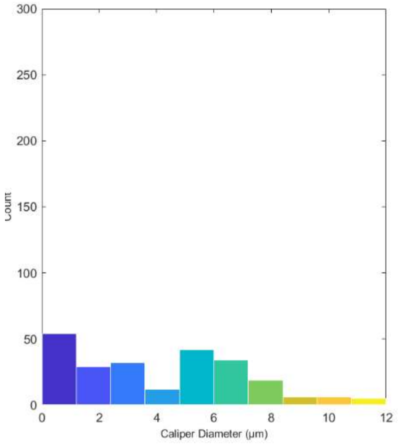
(b) SDS



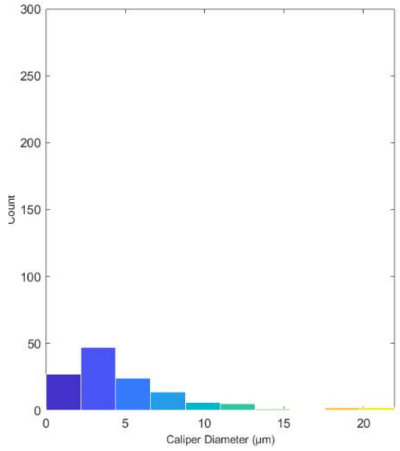
(c) B&B



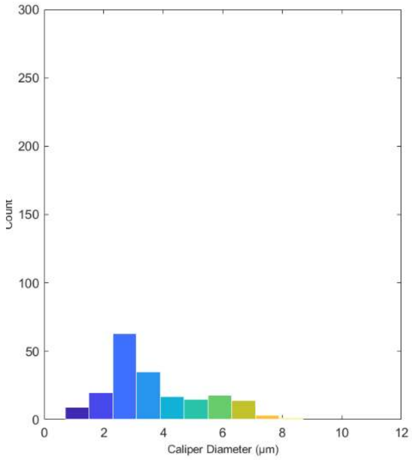
(d) Power green



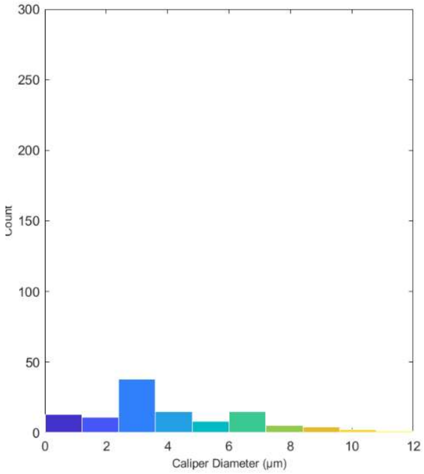
(e) Calla



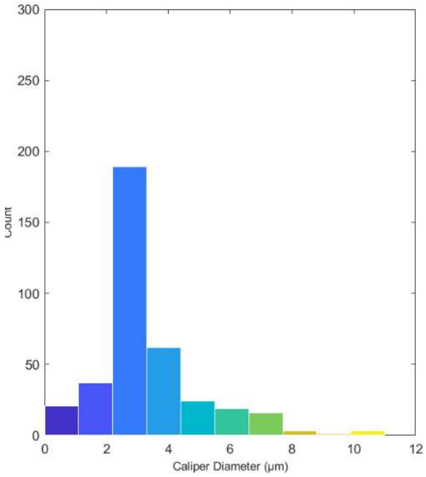
(f) Solid surge



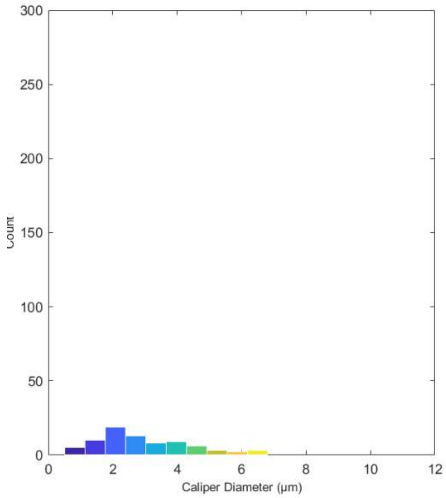
(g) PRC



(h) Triton X-100



(i) 6% AFFF



(j) Blast-off

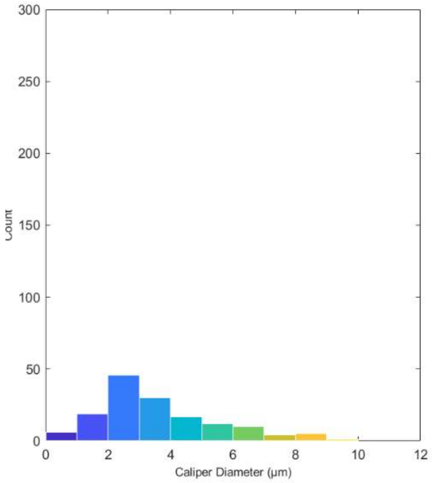


Figure C. 1. Droplet distribution after 1 h of emulsion samples prepared at 25°C using 7×CMC$_{log}$.

APPENDIX D

EFFECT OF SUSPENDED SOLIDS ON EMULSION STBILITY AT 0.5×CMC_{log}

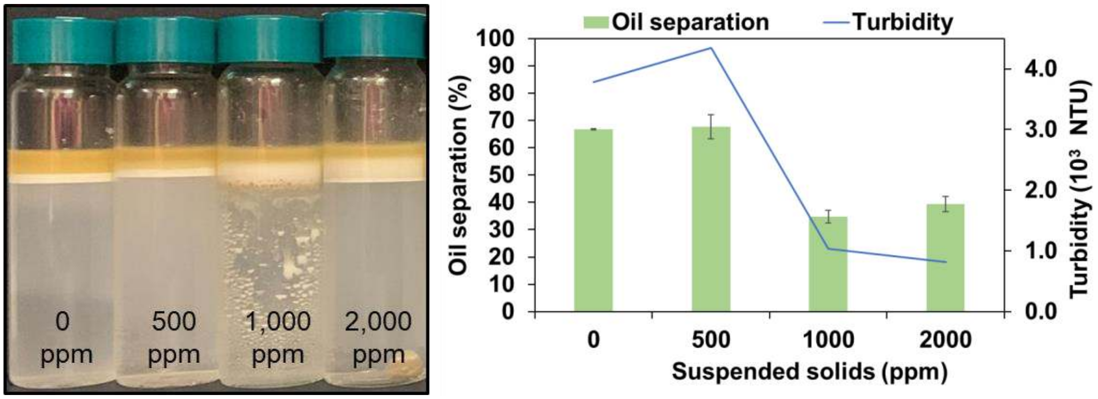


Figure D. 1. Effect of suspended solids in the stabiliy of Type 1 emulsions (0.5×$\mathrm{CMC}_{\log}$).

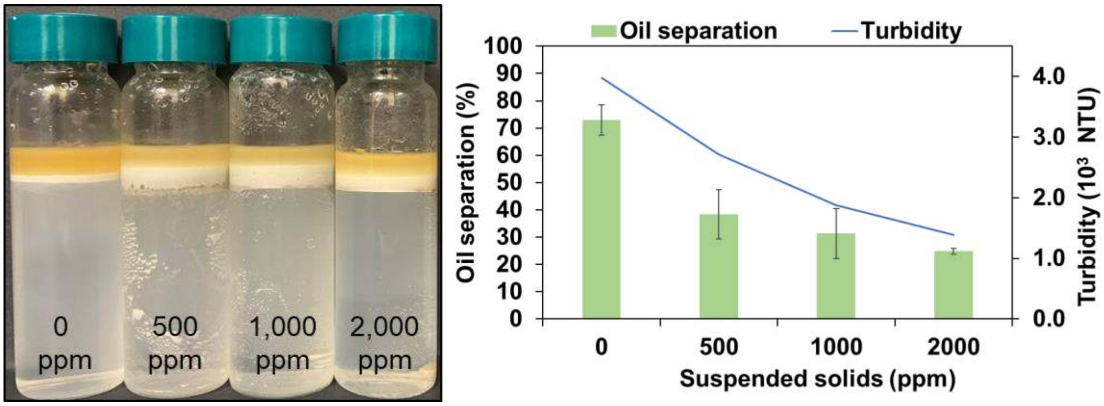


Figure D. 2. Effect of suspended solids in the stabiliy of Triton X-100 emulsions (0.5×$\mathrm{CMC}_{\log}$).

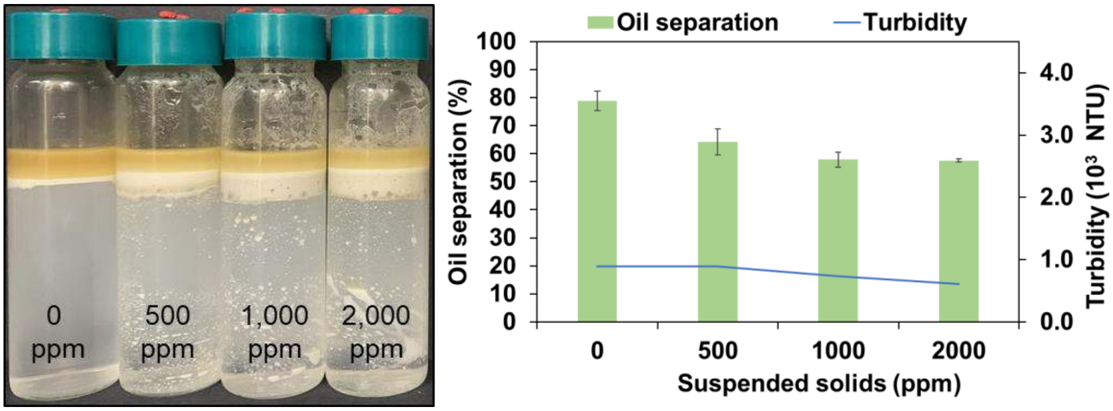


Figure D. 3. Effect of suspended solids in the stabiliy of PRC emulsions (0.5×$\mathrm{CMC}_{\log}$).

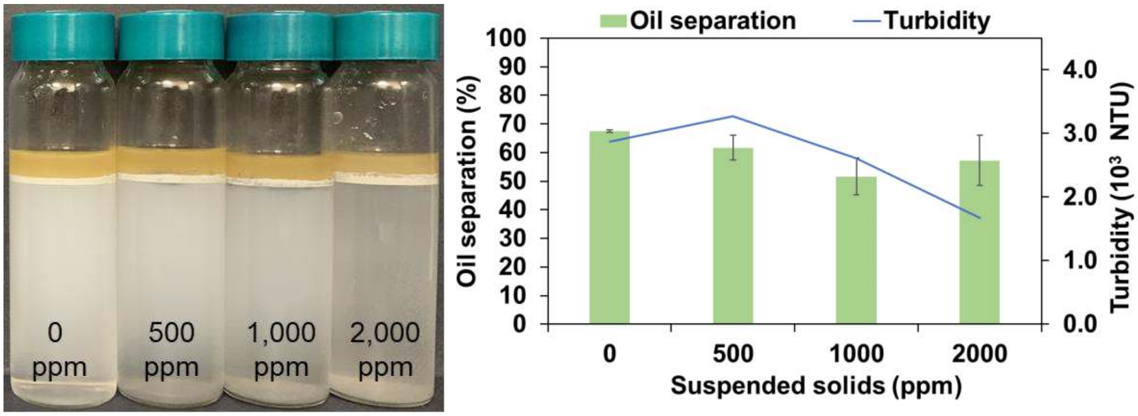


Figure D. 4. Effect of suspended solids in the stabiliy of Solid surge emulsions (0.5×CMC$_{log}$).

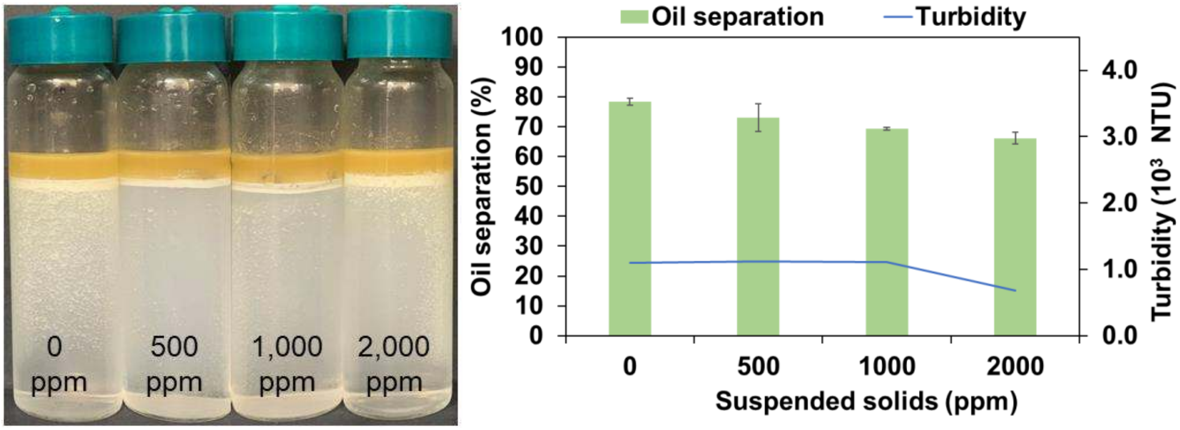


Figure D. 5. Effect of suspended solids in the stabiliy of Blast-off emulsions (0.5×CMC$_{log}$).

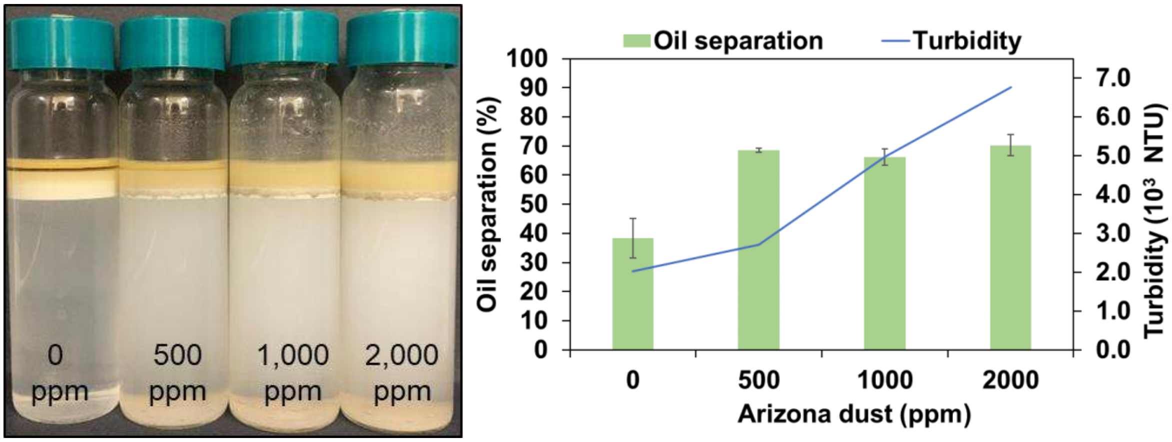


Figure D. 6. Effect of suspended solids in the stabiliy of SDS emulsions (0.5×CMC$_{log}$).

APPENDIX E

DOPLET DISTRIBUTION OF EMULSIONS PREPARED USING DI WATER ONLY AND 35,000 PPM NaCl

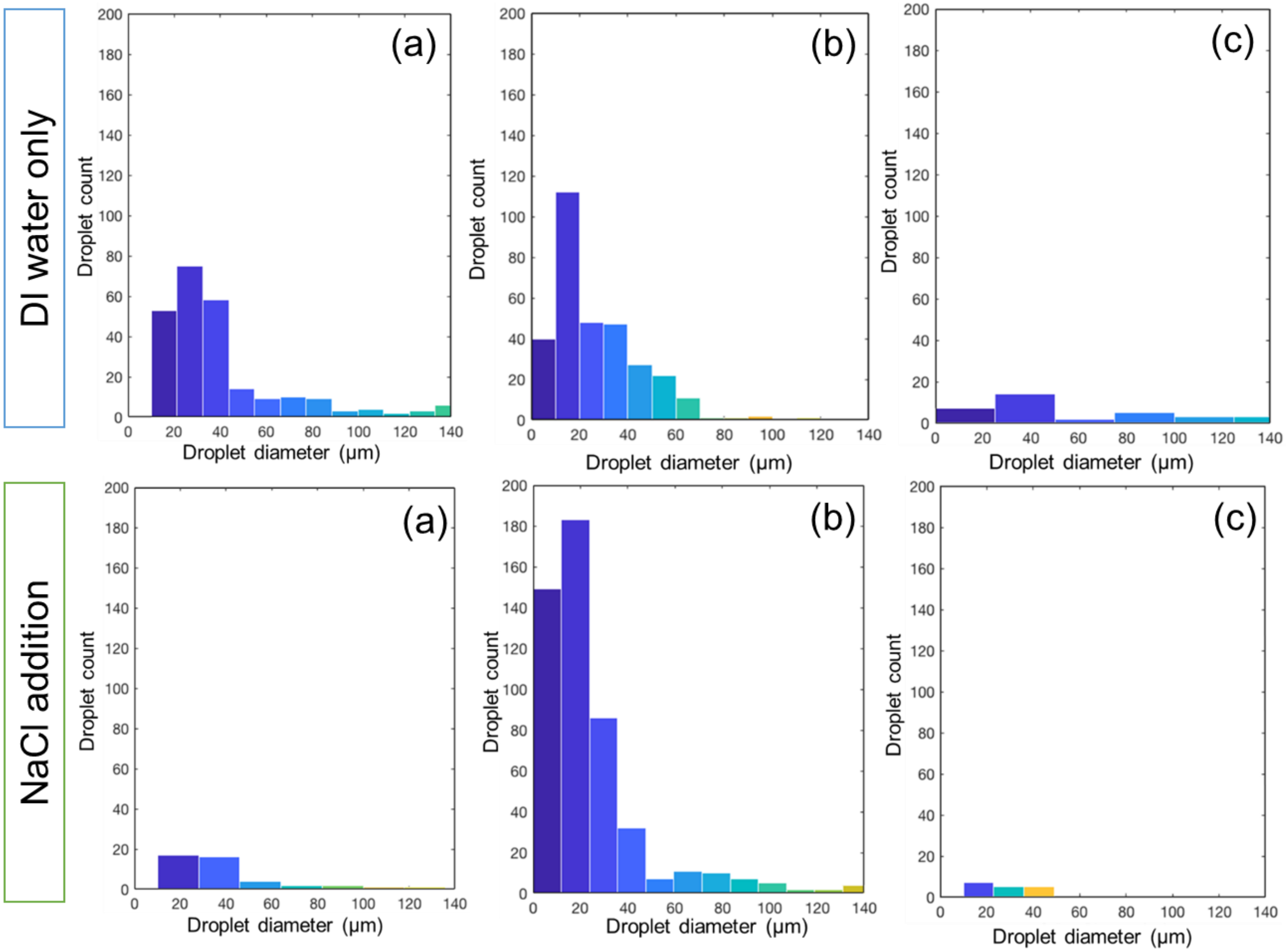


Figure E. 1. Droplet distribution after 1 h of emulsion samples prepared with (a) Triton X-100 (b) B&B 3100 (c) SDS using DI water only and 35,000 ppm of NaCl addition (25°C

APPENDIX F

ANALYSIS OF CONTROL EMULSION SAMPLES PREPARED USING A RANGE OF NaCl CONCENTRATIONS (0-35,000 PPM)

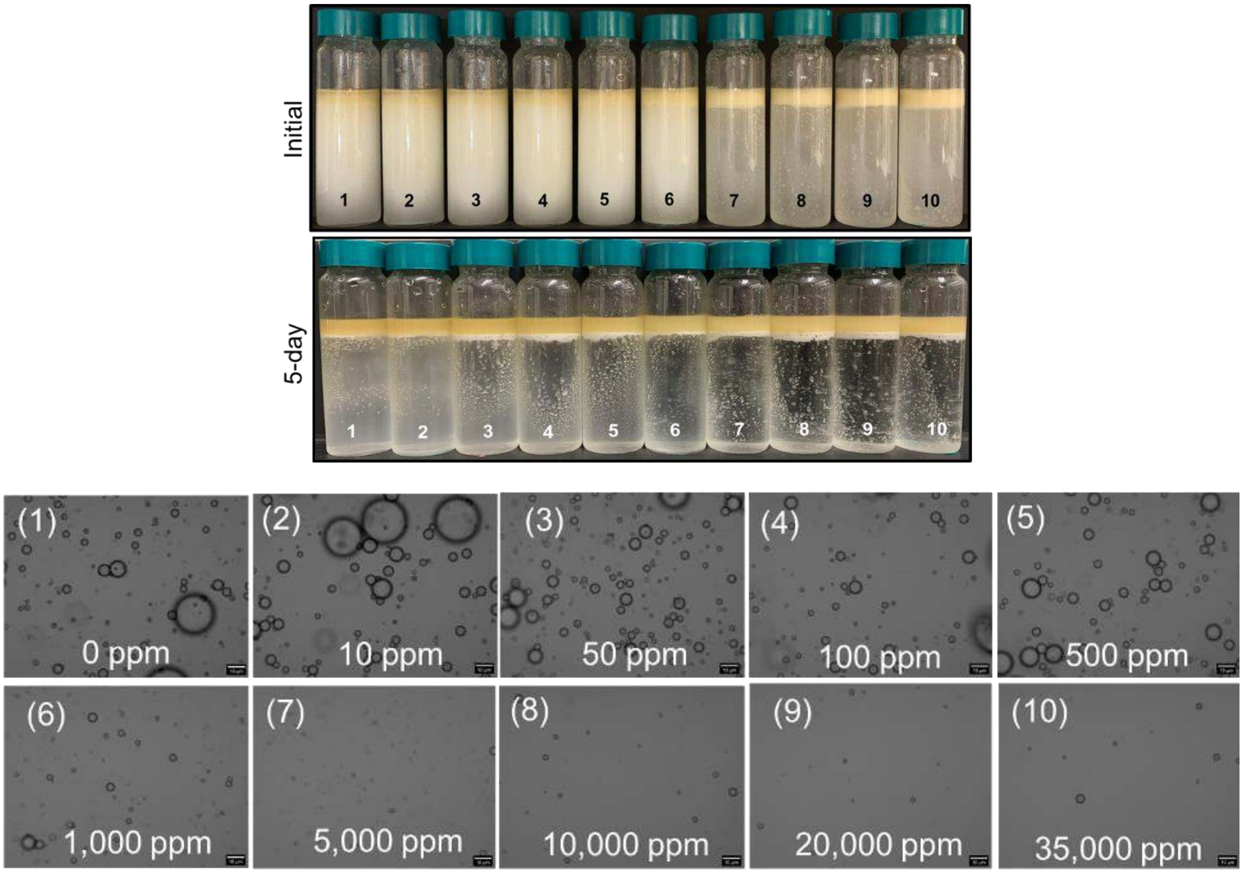


Figure F. 1. Visual observation and microscopic photos of emulsion samples prepared using a range of 0-35,000 ppm NaCl. Samples were prepared as control emulsions (no surfactant). Scale bar is 10µm.

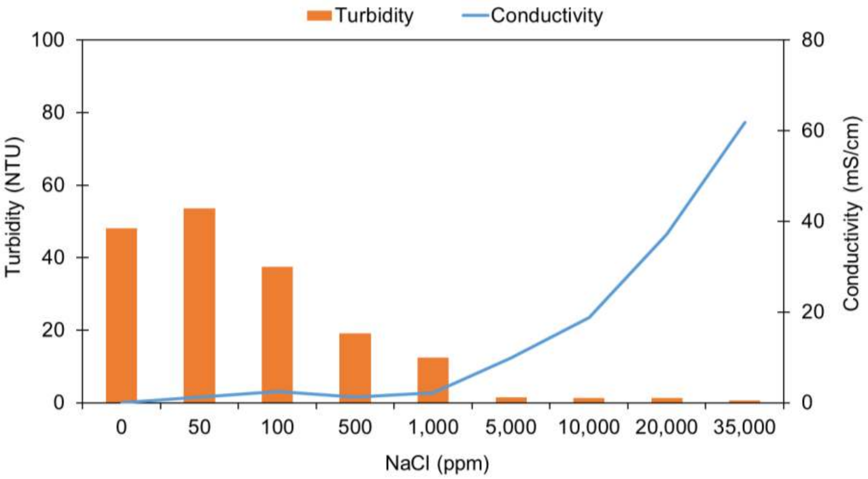


Figure F. 2. Turbidity measurements for control emulsion samples prepared using a range of NaCl concentrations (5th day).

APPENDIX G

EFFECT OF SALINITY ON EMULSION STBILITY AT 0.5×CMC$_{log}$

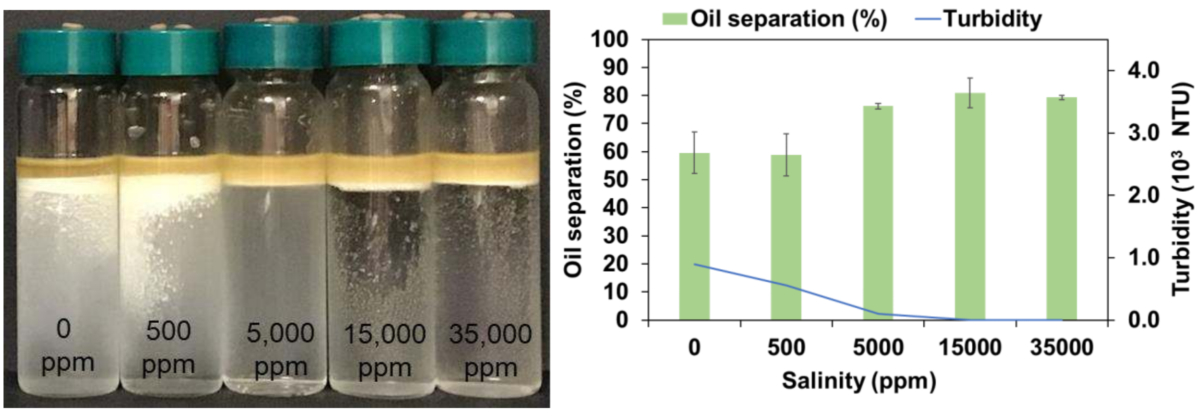


Figure G. 1. Effect of salinity in the stabiliy of Blast-off emulsions (0.5×CMC$_{\log}$).

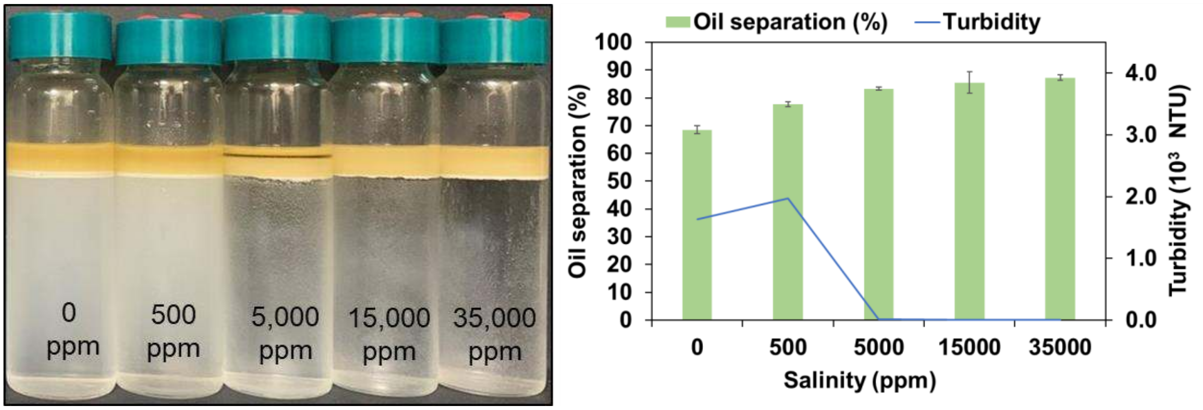


Figure G. 2. Effect of salinity in the stabiliy of PRC emulsions (0.5×CMC$_{\log}$).

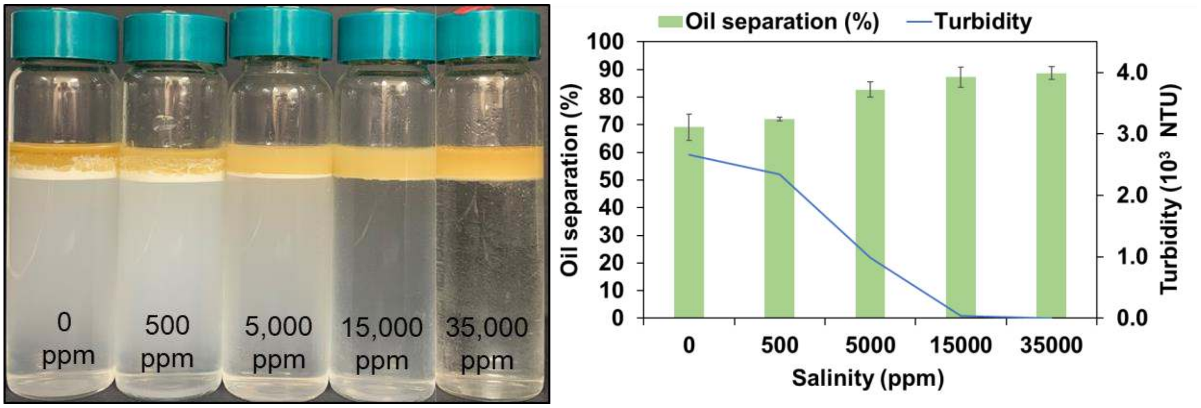


Figure G. 3. Effect of salinity in the stabiliy of Solid surge emulsions (0.5×CMC$_{\log}$).

APPENDIX H

FLUORESCENCE CONTOUR MAPS OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)

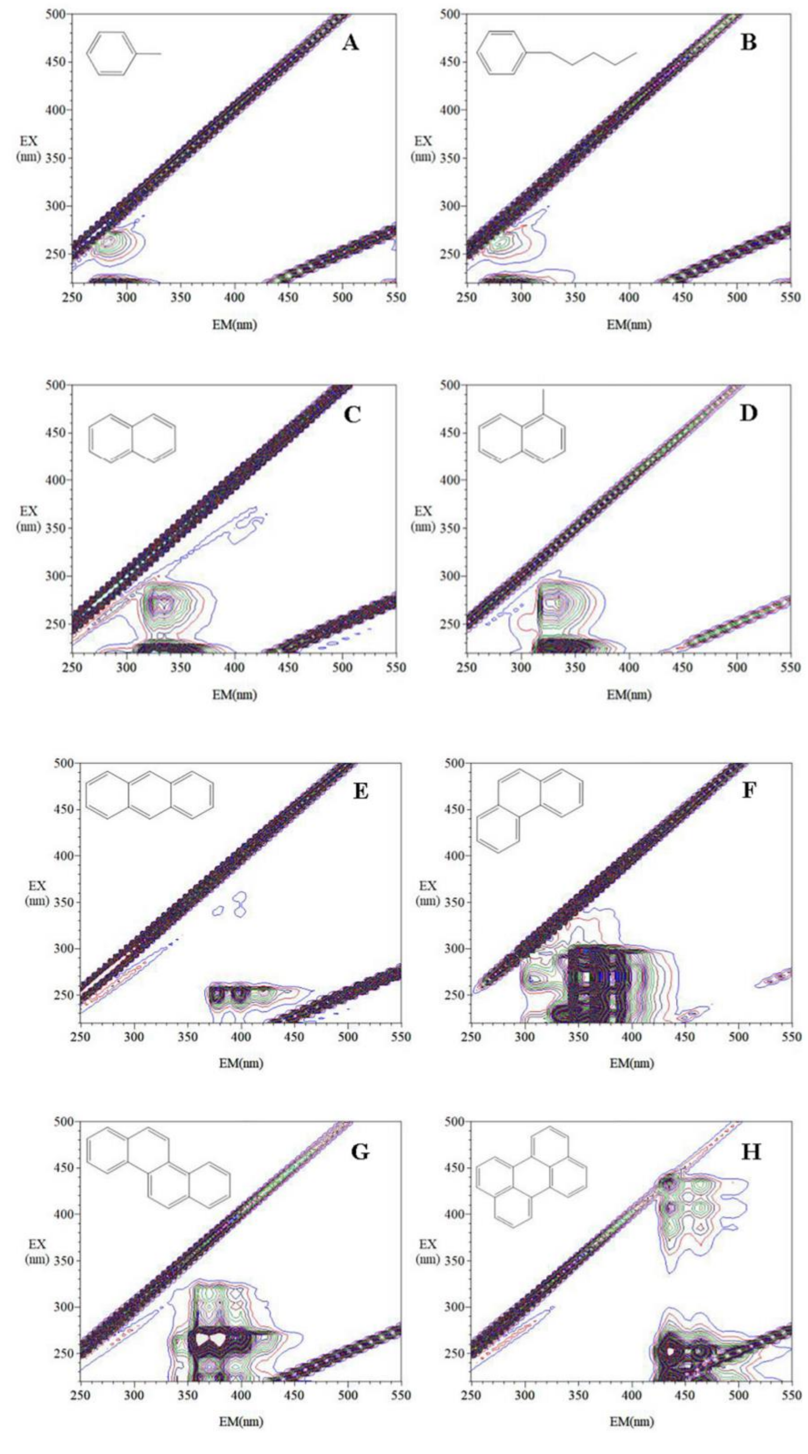


Figure H. 1. Fluorescence contour maps of (A) toluene, (B) n-pentylbenzene, (C) naphtalene, (D) 1-methylnaphthalene, (E) anthracene, (F) phenanthrene, (G) chrysene, and (H) perylene.

(Source: Xie et al (2019) [76])

APPENDIX I

EMULSION FORMATION USING PURE DI WATER AND DI WATER EXPOSED TO NSBM #4

Figure I. 1. Emulsion formation using pure DI water and DI water exposed for 24 hrs to NSBM #4. Bulk-water was emulsified with 10% v/v mineral oil.

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