



EMULSION CHARACTERIZATION STUDY FOR IMPROVED BILGEWATER TREATMENT AND MANAGEMENT

WP18-C1-1114

FINAL REPORT

March 2021

Ms. Danielle Paynter

and

Dr. Jared Church

Naval Surface Warfare Center, Carderock Division

REPORT DOCUMENTATION PAGE					Form Approved OMB No. 0704-0188	
The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.						
1. REPORT DATE (DD-MM-YYYY) 31/03/2021		2. REPORT TYPE SERDP Final Report			3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Emulsion Characterization Study for Improved Bilgewater Treatment and Management				5a. CONTRACT NUMBER		
				5b. GRANT NUMBER		
				5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) Ms. Danielle Paynter and Dr. Jared Church Naval Surface Warfare Center, Carderock Division Jeffrey Lundin Naval Research Laboratory Woo Hyoung Lee University of Central Florida				5d. PROJECT NUMBER WP18-1114		
				5e. TASK NUMBER		
				5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Surface Warfare Center, Carderock Division 9500 MacArthur Boulevard Building 60 Room 104 West Bethesda , MD 20817				8. PERFORMING ORGANIZATION REPORT NUMBER WP18-1114		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Strategic Environmental Research and Development Program (SERDP) 4800 Mark Center Drive, Suite 16F16 Alexandria, VA 22350-3605				10. SPONSOR/MONITOR'S ACRONYM(S) SERDP		
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) WP18-1114		
12. DISTRIBUTION/AVAILABILITY STATEMENT DISTRIBUTION STATEMENT A. Approved for public release: distribution unlimited.						
13. SUPPLEMENTARY NOTES						
14. ABSTRACT The primary objective of this project was to advance the current understanding of emulsion science for chemically stable emulsions formed in Armed Forces applications. While commercially available equipment can be implemented for bilgewater emulsion mitigation, there is little knowledge surrounding the physical, chemical and thermodynamic properties of the emulsions created in an Armed Forces vessel environment. Thus, targeted treatment and management of these fluids become conjecture and calls for a deliberate and thorough understanding of fundamental emulsion stability properties. This project focuses on three segments: (1) Scoping Study for Review of Armed Forces Vessels Oil-in-Water Emulsions, (2) Characterization of Prepared and Extracted Bilgewater Emulsions, and (3) Data Analysis, Interpretation and Publication.						
15. SUBJECT TERMS Emulsion Characterization, Improved Bilgewater Treatment and Management						
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON	
a. REPORT	b. ABSTRACT	c. THIS PAGE			Danielle Paynter	
UNCLASS	UNCLASS	UNCLASS	UNCLASS	164	19b. TELEPHONE NUMBER (Include area code) 301-227-5089	

Abstract

Introduction and Objectives

The primary objective of this project was to advance the current understanding of emulsion science for chemically stable emulsions formed in Armed Forces applications. While commercially available equipment can be implemented for bilgewater emulsion mitigation, there is little knowledge surrounding the physical, chemical and thermodynamic properties of the emulsions created in an Armed Forces vessel environment. Thus, targeted treatment and management of these fluids become conjecture and calls for a deliberate and thorough understanding of fundamental emulsion stability properties. This project focuses on three segments: (1) Scoping Study for Review of Armed Forces Vessels Oil-in-Water Emulsions, (2) Characterization of Prepared and Extracted Bilgewater Emulsions, and (3) Data Analysis, Interpretation and Publication.

Technical Approach

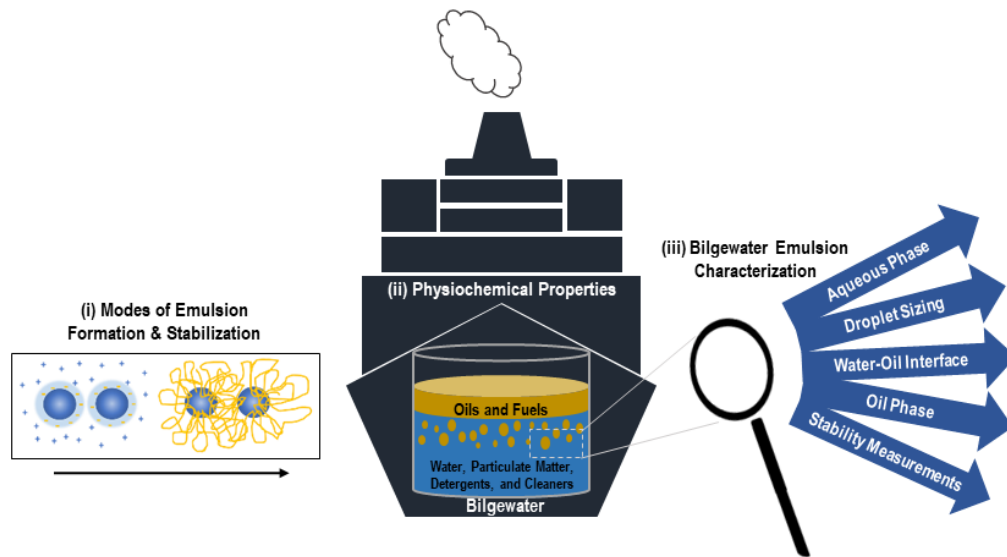
This research focused on the systematic characterization of both prepared emulsions and extracted bilgewater to determine emulsion stability under various conditions. First, a scoping study of armed forces vessels oil-in-water emulsions was conducted to help define the analytical techniques, types of cleaners, and environmental conditions used for experimental testing. Next, emulsion solutions were systematically investigated using identified Navy relevant oils and cleaners. In particular, these studies evaluated the impact that environmental parameters, cleaner properties, and oil properties had on emulsion stability. Actual bilgewater samples from three Navy ships were also characterized for water quality and oil properties. Results from experimental tests were interpreted using machine learning methods and used to develop a preliminary emulsion stability prediction model.

Results

Results from this multi-scaled investigation of bilgewater emulsions has furthered the understanding of the formation and stabilization of bilgewater emulsions. A scoping study of emulsifiers used on Armed Forces Vessels resulted in the data driven identification of 8 commercial cleaners/emulsifiers, which were tested for critical micelle concentration (CMC), interfacial tension (IFT), micelle size, and zeta potential. In addition, over 925 emulsion samples were generated and characterized for emulsion stability based on droplet size distribution, oil separation, and creaming rate. Results indicated that 1) emulsion stability is significantly affected by surfactant type, ionic strength, and temperature, 2) the CMC of commercial cleaners is a good indicator of coalescence stability in simulated bilgewater emulsions, 3) water quality parameters range significantly in actual bilgewater samples, and 4) fuel components play an important role in bilgewater emulsion stability. Based on the results from experimental testing, an emulsion stability model was developed to help disseminate findings to bilge operators. The random forest classifier showed the highest prediction of emulsion stability with an F1 score of 0.8868. Sensitivity analysis showed that salinity and temperature were dominant factors in predicting emulsion stability for the conditions tested.

Benefits

Current bilgewater treatment methods do not rely on targeted techniques to increase the effectiveness of emulsion removal. Hence, this research focused on discovering the underlying principles of emulsion formation and stability such that informed research decisions can be pursued. The purpose of this work was not to just recommend treatment technologies for bilgewater emulsions; rather, the purpose was to contribute to the current research field and to assist shipboard personnel in identifying why emulsions are creating treatment issues. Knowledge gained from this research has already helped inform bilgewater management decisions within the Armed Forces. Currently, the methods for characterizing bilgewater emulsions, developed under this project is being leveraged by U.S. Navy for recommending bilge cleaners that prevent the generation of stable bilgewater emulsions. The insights from this work also aid in improving other fields where surface active compounds are prevalent. For example, knowledge gained under this project can also be used to help develop new fluorine free firefighting foams based on the fundamental understanding of how compounds transport between fuel and aqueous phases.



Executive Summary

Introduction

Use of oils, fuels, and lubricants are critical to the operation of every ship and watercraft used in the Armed Forces. These include Navy ships, Army transports, Coast Guard cutters, and Air Force recovery vessels. Oily water is generated on vessels during machinery washes, condensation, leak, and spill collection. As a result, oily water is collected in the bilge or oily waste holding tanks of ships and must be treated. Bilgewater discharge was first regulated in the 1970's by the International Convention for the Prevention of Pollution from Ships (1973), which was further modified in 1978 (MARPOL 73/78) (Sharp, 1993). Today, bilgewater discharge from commercial and Armed Forces vessels must have an oil content below 15 ppm, as regulated by MARPOL Annex I for commercial vessels and DoD Regulation 4715.06-V2 (U.S. DoD, 2017) for Armed Forces vessels.

Oil pollution abatement (OPA) systems are employed for the purpose of managing shipboard oily waste to comply with environmental regulations. OPA systems are composed of equipment to collect, hold, treat, and analyze oily waste onboard ships. However, the presence of oil-in-water emulsions makes bilgewater difficult to treat solely by gravity driven separation processes and often requires the use of secondary treatment systems.

Emulsions, or dispersions of one or more immiscible liquid phases in another, are often created in bilgewater when an oil phase is exposed to surfactants and mixing energy (McClements, 2007). Surfactants align at the oil/water interface, which reduces the interfacial energy and allows for energy inputs from pumps and shipboard vibrations to develop an emulsion. Emulsified oil in bilgewater, created by either mechanical dispersion or chemical surfactant stabilization, can be difficult to treat because the emulsion's small droplet size and neutral buoyancy prevent gravimetric separation (McLaughlin et al., 2014). Highly stable oil-in-water emulsions are particularly challenging to meet stringent marine discharge standards and is frequently required to be stored until pierside disposal is available.

U.S. Navy and Army OPA systems typically use parallel-plate oil-water separators (OWSs) to treat bilgewater. These separators are effective at removing bulk oil and emulsions larger than 20 μm ; however, the presence of surfactants in the bilgewater and shipboard vibrations can generate small oil droplets that can pass through a parallel plate OWS. This results in long operational durations, leading to increased maintenance from continued processing and reprocessing of emulsions. In order to remove smaller oil emulsions, ceramic membranes have increasingly been installed as a secondary treatment technology for Navy produced bilgewater. While these systems are effective, high membrane fouling rates require frequent cleaning or replacement. Operational costs from membrane procurement and associated logistics from onboard storage of spares and cleaning reagents are increased.

Currently, treatment methods target bilgewater as a whole and do not specifically focus on breaking emulsions into a separated oil phase for removal. Hence, current knowledge on bilgewater tends to concentrate on empirically determined treatment methods and lacks information on bilgewater emulsion characteristics. While emulsion formation and stability have been widely studied in other adjacent industries for emulsification (e.g., food science, cosmetics, agro-chemicals, paints, and pharmaceuticals), these specific properties have not been thoroughly investigated for demulsification to separate oil-in-water (O/W) emulsion, particularly, in Armed Forces bilgewater. In addition, most emulsion studies have been conducted under carefully selected conditions that help stabilize emulsions based on the dispersed or continuous phases. Given that bilgewater is extremely dynamic, making it difficult to pinpoint the major stabilizing mechanisms, thorough systematic research on bilgewater emulsion stability would enhance our understanding of this topic. A better understanding of the generation and fundamental mechanisms of

emulsion stability, reliable methods of O/W emulsions treatment can assist in resolving existing bilgewater emulsion treatment challenges.

Objectives

The primary objective of this effort was to advance the current understanding of emulsion science for chemically stable emulsions formed in Armed Forces applications. While commercially available equipment can be implemented for bilgewater emulsion mitigation, there is little knowledge surrounding the physical, chemical, and thermodynamic properties of the emulsions created in an Armed Forces vessel environment. Thus, targeted treatment and management of these fluids become conjecture and call for a deliberate and thorough understanding of fundamental emulsion stability properties.

Technical Approach

Emulsion formation and stability in the presence of surfactants is highly dependent on chemical, physical and thermodynamic properties of the solution. By studying these properties, a deeper fundamental understanding of emulsions stabilized by surfactants common on Armed Forces vessels can help guide current research and treatment technology selection. This effort focused on three segments: (1) Scoping Study for Review of Armed Forces Vessels O/W Emulsions, (2) Characterization of Prepared and Extracted Bilgewater Emulsions, and (3) Development of Emulsion Stability Guide. An illustration of the focus segments are shown in Figure 1.

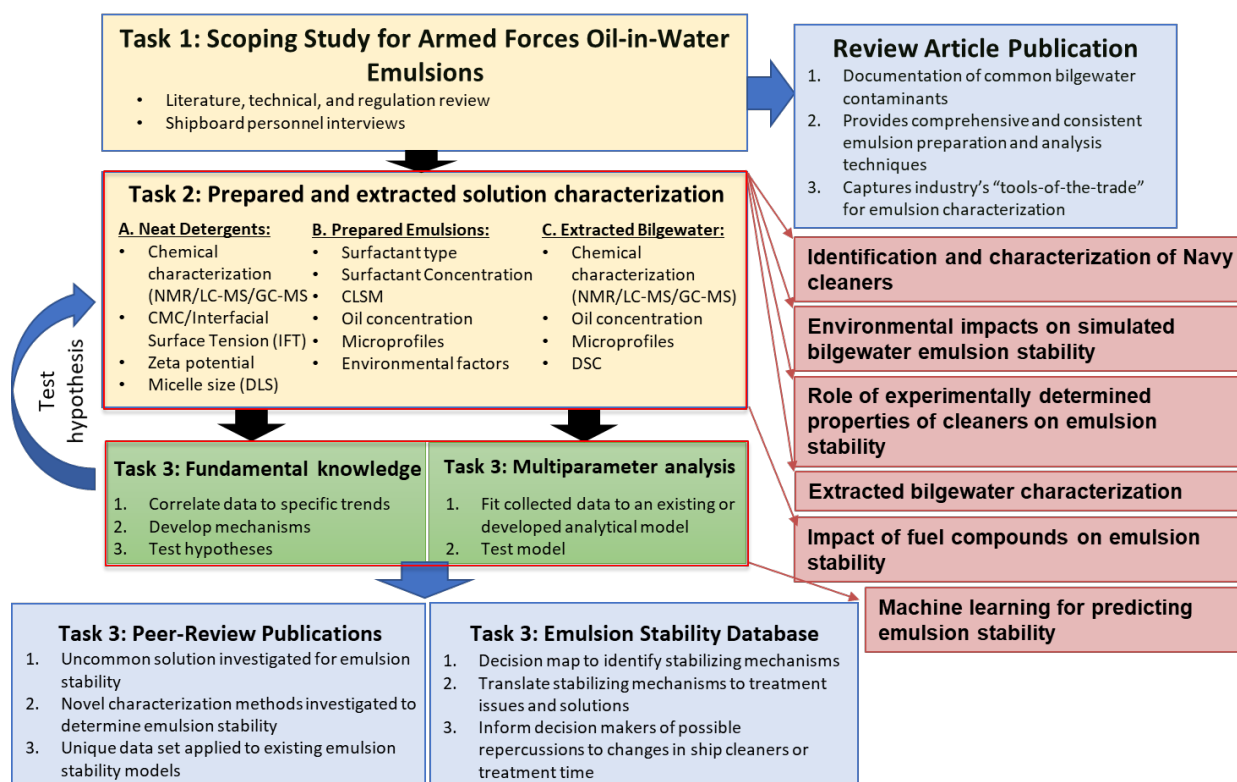


Figure 1. Technical approach to studying emulsions for improved bilgewater management

First, a scoping study of armed forces vessels oil-in-water emulsions was conducted to help define the analytical techniques, types of cleaners, and environmental conditions used for experimental testing. Next, emulsion solutions were systematically investigated using identified Navy relevant oils and cleaners. In

particular, these studies evaluated the impact that environmental parameters, cleaner properties, and oil properties had on emulsion stability. Actual bilgewater samples from three Navy ships were also characterized for water quality and oil properties. Results from experimental tests were interpreted using machine learning methods and used to develop a preliminary emulsion stability prediction model.

Results and Discussion

First, a review of literature was conducted to determine common approaches for studying emulsions (Church et al, 2019). Information on the formation and stability of bilgewater emulsions was discussed as well as pertinent physiochemical properties that are known to influence emulsion stability. Bilgewater emulsion characterization techniques were also discussed in detail, where the importance of kinetic and coalescence emulsion stability on bilgewater processes was outlined. The review also investigated bilgewater characteristics reported in literature, which was found to be highly variable. For example, oil concentrations in bilgewater has been reported as low as 5 ppm and as high as 12,900 ppm. In an effort to better understand the types of surfactants that might be present in bilgewater, a survey of U.S. Navy cleaners was conducted. In total, 10 cleaners were identified as likely to be found in bilgewater based on the total procurement of each cleaner. Overall, the review helped define the analytical techniques, definition of emulsion stability, types of cleaners, and environmental conditions used for experimental testing.

Cleaners identified in the review were then characterized for properties related to emulsion stabilization, including: critical micelle concentration (CMC), interfacial tension (IFT), micelle size and zeta potential (Table 1). It was found that the primary surfactant between the cleaners were similar; mostly composed of alcohol ethoxylates or cocamide diethanolamines. However, the properties of the cleaners varied significantly; likely due to the presence of builders and other compounds in the cleaners. Extracted bilgewater samples, pictured in Figure 2, were highly variable but were within water quality ranges that have been reported in literature. Results from the cleaner and extracted bilgewater analysis validated the use of detergent mix #4 and Navy Standard Bilge Mix (NSBM) #4 for the preparation of simulated bilgewater emulsions. The cleaners used in detergent mix #4 were found among the highest cleaners procured by the Navy. In addition, the tested cleaners were found to only include nonionic surfactants; which is also the primary surfactant type in detergent mix #4. This is noteworthy because the current bilgewater standard used to test commercial oil-water separators, MEPC.107(49) test fluid “C”, uses a anionic surfactant, which provides different emulsion stabilizing mechanisms (e.g. electrostatic vs steric). In addition, bilgewater samples taken from Navy ships in Spring 2019 (Bilgewater #1 and #2) both had gas chromatography mass spectroscopy (GC-MS) chromatographs similar to NSBM #4.



Figure 2. Extracted bilgewater samples

Table 1. Properties of cleaners used on U.S. Navy Ships

Cleaner	Primary surfactants	CMC (ppm)	Surface tension (mN/M)	IFT with NSBM #4 (mN/M)	Micelle size (nm)	Zeta Potential (mV)
AFFF 6% (Chem Guard)	Flourosurfactant (e.g., Capstone 1157)	3,399	15.2 ± 0.2	2.3 ± 0.6	55 ± 2	-24 ± 5
B&B™ 3100 (Vantage)	- Cocamide diethanolamine 1-buoxyethanol (alcohol ethoxylate)	361	25.0 ± 0.5	7.8 ± 0.1	21 ± 1	-28 ± 6
Super Blast Off (Elsco Inter. Inc.)	Cocamide diethanolamine	934	27.7 ± 0.5	3.4 ± 0.1	111 ± 7	-63 ± 3
Calla 855 (Zip-Chem Products)	- Alcohol ethoxylate (c10-c14) - Cocamide diethanolamine - Capriloamphorionate	328	27.3 ± 0.3	5.7 ± 1.1	5 ± 2	-39 ± 8
Power Green (LHB Industries)	Surfactant blend	3,824	26.1 ± 0.7	3.5 ± 0.4	7 ± 5	-13 ± 3
PRC Deck Cleaner (Werth Sanitary Supply Co. Inc.)	Alcohol ethoxylate	1,871	30.5 ± 0.1	7.7 ± 0.3	6 ± 1	-13 ± 2
Ecolab Solid Surge Plus NP (Ecolab # 6117905)	Alcohol ethoxylate (c12-16)	98	27.4 ± 0.3	7.3 ± 0.1	23 ± 5	-15 ± 4
Type 1 Detergent (MILSPEC: MIL-D-16791)	Alkyl aryl polyether alcohol	87	30.2 ± 0.4	2.5 ± 0.3	18 ± 1	-28 ± 6

After establishing relevant properties of cleaners and bilgewater, the effect of environmental factors on emulsion stability was investigated. In particular, the impact of salinity, temperature, suspended solids (SS), and pH on the formation and stability of emulsions was evaluated. The findings suggested 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 > SDS > B&B > Power Green > Solid Surge > Calla = PRC > Triton X-100 > 6% AFFF = Blast-off. For all cleaners tested, except Power Green, it was found that increasing temperature accelerated emulsion separation by enhancing coalescence of the droplets. Ionic strength was shown to have the largest influence on emulsion destabilization, resulting in oil separation at early stage. Overall, the experiments provided significant information regarding the contribution of bilgewater components to the formation and stability of emulsions in Navy bilgewater systems. Results from this work were also used to help train an emulsion stability prediction model.

Experimental properties of emulsion systems that could be used to predict emulsion stability were also investigated (Church et al 2020). The impact of IFT, CMC, and CMC in the presence of oil (CMC_{IFT}) on macro-phase oil separation in model surfactants and commercial cleaners was evaluated. The emulsion samples shifted from predominantly separated oil to stabilized emulsion at surfactant concentrations correlating closely with CMC_{IFT} , as shown in Figure 3. The change in emulsion behavior was due to the packing of surfactant at the oil/water interface.

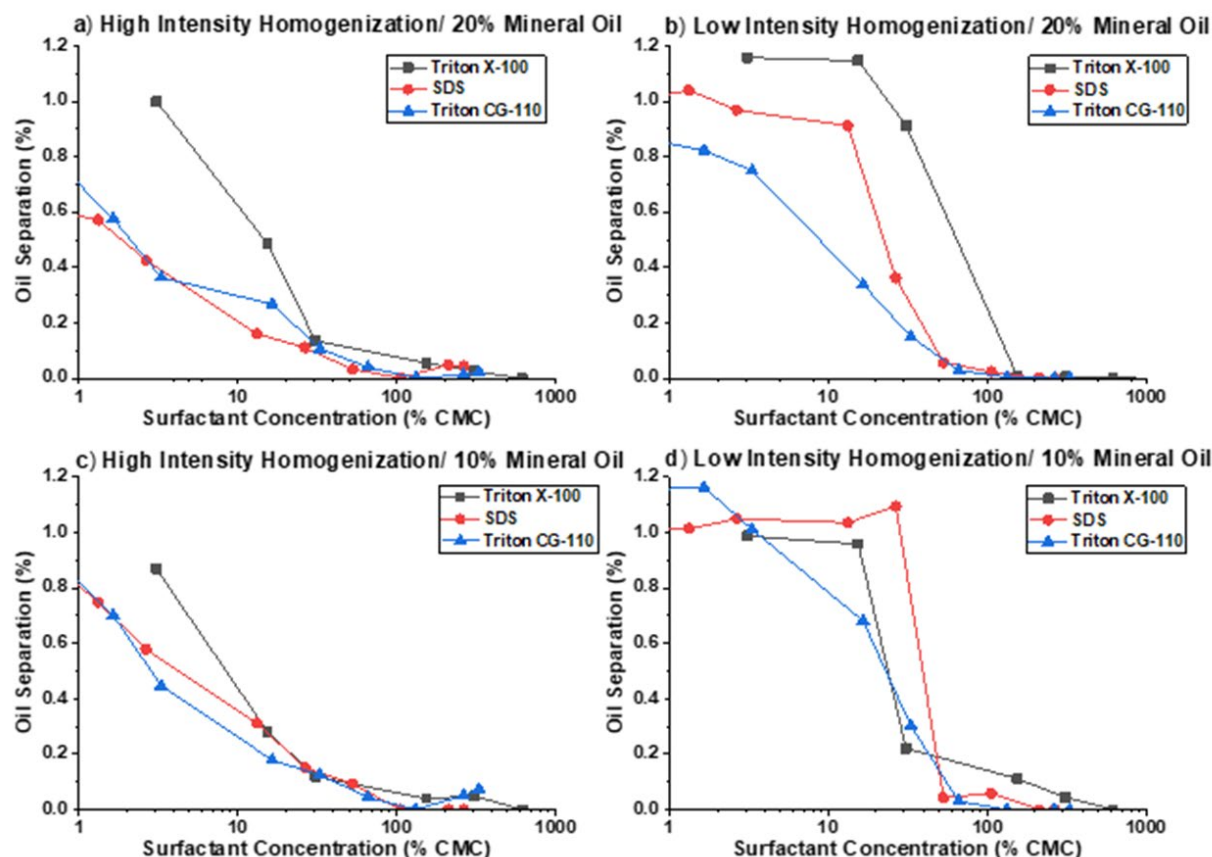


Figure 3. Macrophase oil separation as a function of surfactant concentration in model oil-in-water emulsions after 72 h

As the surfactant concentration approached CMC_{IFT} , the amount of surfactant adsorbed at the interface approached its highest packing density and the mechanical stability of the surfactant layer was expected to be largest, thus improving emulsion stabilization. In addition, it was found that neither IFT nor droplet size was directly related to the breaking of a cream layer into a separate oil layer. Therefore, the stability of the emulsions was best explained by an electrostatic/steric stabilizing mechanism rather than the initial droplet formation. Overall, CMC_{IFT} was demonstrated as a practical method for predicting emulsions stability in complex systems. Cleaners developed for use on ships could be tested for CMC_{IFT} using a representative oil and flagged as having a greater potential contribution to bilgewater emulsion stability if the cleaner's CMC_{IFT} was found to be low.

Based on changes in CMC observed in the presence of NSBM #4, the impact of fuels on bilgewater emulsion stability was also investigated. It was found that components in bilgewater oils and fuel can contribute to the stability of emulsions. The conductivity, pH, and surface tension of water was significantly altered after exposure to bilgewater oils for 24 h (Figure 4). Likewise, UV and GC-MS data suggested the transport of aromatic compounds from the oil to aqueous phase. It was found that aromatic compounds, containing oxygen and nitrogen functional groups leached into the water phase and helped stabilize emulsions. Emulsion stability experiments showed compounds found in DFM were most likely to stabilize emulsions, followed by Lube Oil 2190 and then by Lube Oil 9250. Further research is needed to provide exact identification of the compounds involved in bilgewater emulsion stabilization and determine the full impact of these additives on emulsion stability and bilgewater treatment.

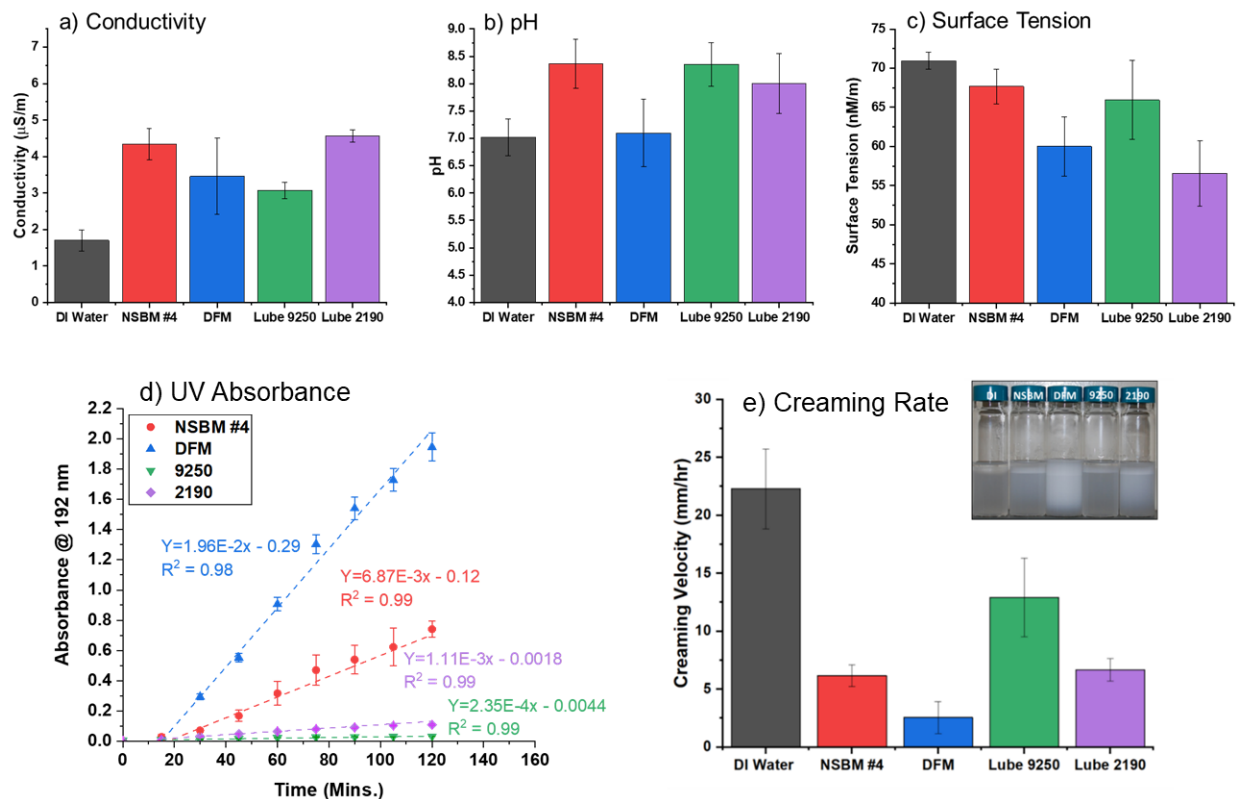


Figure 4. Changes in a) conductivity, b) pH, c) surface tension, and UV Absorbance of DI water exposed to various bilgewater oils. e) Creaming velocity (mm/hr) of mineral oil emulsions prepared with water exposed to bilgewater for 24 hrs. (Inset: Photograph of emulsions after 1 hr)

Finally, various regression and classification machine learning (ML) models were evaluated for predicting emulsion stability using experimentally obtained data from previous studies. Image processed oil values (OV) showed better prediction compared to visually determined oil separation (OS). In regression ML models, the gradient boosting regressor achieved the most accurate prediction for OV (Mean average error = 0.093), while in classification models, the random forest classifier showed the highest prediction of emulsion stability with an F1 score of 0.8868 for OV. Sensitivity analysis showed that salinity and temperature were dominant factors in predicting emulsion stability for the conditions tested. The developed ML models were used for creating a website prototype for bilgewater emulsion stability prediction. Overall, ML-based bilgewater emulsion stability models may benefit future emulsion treatment process selection.

Implications for Future Research and Benefits

Knowledge gained from this research has already helped inform bilgewater management decisions within the Armed Forces. Currently, the U.S. Navy is developing recommendations for bilge cleaners that prevent the generation of stable bilgewater emulsions or negatively impact bilge treatment processes. Insights from this study, on how to best evaluate bilgewater emulsion stability, was transitioned to a Naval Sea Systems Command (NAVSEA) funded investigation of commercial bilge cleaners (NSWCCD-63-TR-2020/38) (Church and Park, 2021) and will be used to develop a commercial item description for future use of bilgewater cleaners aboard Navy ships. Likewise, the improved understanding of bilgewater composition and the role of environmental factors on emulsion stability has validated the selection of the most challenging and representative test conditions for evaluations of OPA equipment.

Future work, looking at fundamental mechanisms of bilgewater emulsion stability, should focus on how emulsions are impacted by different treatment technologies. While important insights into how cleaner and fuel properties can influence bilgewater emulsion stability was realized under stationary bilgewater environments, no work was done looking at how conventional bilgewater treatment can break emulsions. For example, it is currently unknown how emulsions interact with the surface of ceramic membranes that are currently employed by many Navy ships for bilgewater treatment. This information is critical for both the selection and operation of bilgewater treatment technologies.

The insights from this work have potential to not only contribute to mitigating emulsions in bilgewater, but also aid in improving other fields where surface active compounds are prevalent. The transport of compounds between fuel and aqueous phases also have large implications in other areas of research. As fluorine free firefighting foams are being developed to replace per- and polyfluoroalkyl substances (PFAS) laden foams, the impact of cosolvents and interfacial turbulence caused by fuel compounds will likely play a large role in the effectiveness of foams. Expertise gained from this project is being used to support an additional SERDP project looking at the transport of surfactants at liquid-liquid interfaces in the presence of fuels (WP19-1407). Similarly, understanding the transport of benzene, toluene, ethylbenzene, and xylene (BTEX) compounds into the environment is important for oil spill remediation. The Bureau of Safety and Environmental Enforcement (BSEE) is currently involved in several areas of research where knowledge in emulsion science and treatment can be utilized. Research findings developed under WP18-1114 has transitioned to support a FY21-FY23 BSEE investigation to better understand the role of emulsions in *in situ* incineration for oil spill response. The techniques reported here will be used to characterize crude oil emulsions and provide insights into their impact on *in situ* incineration. Similarly, NSWCCD is currently pursuing proposal development in collaboration with Carderock's computation fluid dynamics (CFD) branch. The proposal will address another BSEE need for CFD modeling of water-in-oil emulsion behavior to simulate oil capture with novel boom designs. The fundamental understanding of emulsions gained in this project supports this modeling work.

References

- Church J, Lundin JG, Diaz D, Mercado D, Willner MR, Lee WH, et al. Identification and characterization of bilgewater emulsions. *Science of The Total Environment* 2019.
- Church J, Willner MR, Renfro BR, Chen Y, Diaz D, Lee WH, et al. Impact of Interfacial Tension and Critical Micelle Concentration on Bilgewater Oil Separation. *Journal of Water Process Engineering* 2020: 101684.
- Church J, Park J, Bilge Cleaners Test Report (DRAFT). NSWCCD-63-TR-2020/38. Nov. 2020
- McClements DJ. Critical review of techniques and methodologies for characterization of emulsion stability. *Crit Rev Food Sci Nutr* 2007; 47: 611-49.
- McLaughlin C, Falatko D, Danesi R, Albert R. Characterizing shipboard bilgewater effluent before and after treatment. *Environmental Science and Pollution Research* 2014; 21: 5637-5652.
- Sharp T. MARPOL: how to do it: manual on the practical implications of ratifying and implementing MARPOL 73/78. International Maritime Organization 1993.
- U.S. DoD Manual 4715.06-V2. Regulations on Vessels owned or Operated by the Department of Defense: Oil Pollution Prevention, 2017

Table of Contents

List of Figures	xv
List of Tables	xvii
List of Acronyms	xviii
Chapter 1: Background and Objectives	1
1.1 Background	1
1.2 Objectives	2
1.3 Organization	3
Chapter 2: Scoping Study for Armed Forces Oil-in-Water Emulsions	5
2.1 Introduction	5
2.2 Formation and stabilizing mechanisms of bilgewater emulsions	5
2.2.1 Role of emulsifiers	5
2.2.2 Electrostatic stabilization	6
2.2.3 Steric stabilization	6
2.2.4 Particle stabilization (Pickering emulsions)	7
2.2.5 Emulsion destabilization	7
2.3 Physicochemical properties impacting oil-in-water emulsion stability	8
2.3.1 Temperature	8
2.3.2 pH	9
2.3.3 Solid particles	9
2.3.4 Surfactant type and concentration	9
2.3.5 Ionic strength	10
2.3.6 Mixing intensity	10
2.4 Bilgewater oil-in-water emulsion characterization techniques	11
2.4.1 General bilgewater quality parameters	11
2.4.2 Droplet characterization	14
2.4.3 Interface characterization	18
2.4.4 Oil characterization	19
2.4.5 Bilgewater emulsion stability testing methods	20
2.5 Characteristics of bilgewater emulsions	25
2.5.1 General bilgewater characteristics	25
2.5.2 Identification of bilgewater surfactants	27

2.5.3	Standard synthetic bilgewater for OPA system testing	28
2.6	Conclusions	30
Chapter 3:	U.S. Navy Cleaner and Extracted Bilgewater Characterization	32
3.1	Introduction	32
3.2	Materials and Methods	32
3.2.1	Characterization of Surfactant Properties	32
3.2.2	Characterization of Extracted Bilgewater Samples	33
3.3	Results	34
3.3.1	Cleaner properties	34
3.3.2	Water Quality Characterization of Collected Bilgewater Samples	36
3.3.3	Oil analysis.....	38
3.4	Conclusions	40
Chapter 4:	Impacts of Environmental Conditions on Simulated Emulsion Stability	41
4.1	Introduction	41
4.2	Materials and methods	41
4.2.1	Emulsion preparation	41
4.2.2	Experimental design.....	42
4.2.3	Bulk-water analysis.....	43
4.2.4	Image-based analysis	43
4.3	Results and discussion.....	44
4.3.1	Emulsion Stability.....	44
4.3.2	Effect of Environmental Factors on Emulsion Stability	48
4.4	Conclusions	53
Chapter 5:	Impact of Interfacial Tension and Critical Micelle Concentration on Bilgewater Oil Separation	54
5.1	Introduction	54
5.2	Materials and Methods	55
5.2.1	Materials	55
5.2.2	Characterization of Surfactant Properties	56
5.2.3	Preparation of Emulsions	57
5.2.4	Characterization of Bulk Emulsion Stability	57
5.2.5	Determination of Droplet Size Distribution.....	58
5.3	Results	58

5.3.1	Experimentally Determined Properties of Surfactants and Cleaners.....	58
5.3.2	Emulsion Stability: Macro-phase Oil Separation	62
5.3.3	Droplet Size Distribution	66
5.3.4	Commercially Stabilized Emulsions.....	67
5.3.5	CMC _{IFT} as a Practical Method for Qualifying Shipboard Cleaners.....	68
5.4	Conclusions	69
Chapter 6:	Stabilization of Bilgewater Emulsion by Shipboard Oils	70
6.1	Introduction	70
6.2	Materials and Methods	71
6.2.1	Model Bilgewater Fuels and Oils	71
6.2.2	Extracting water miscible components from bilgewater oil and fuels.....	71
6.2.3	Water Quality Analysis	71
6.2.4	Emulsion Preparation.....	72
6.2.5	Emulsion Stability.....	72
6.2.6	Identification of Surface Active Compounds.....	72
6.2.7	Transport of fuel additives and compounds from the oil to the aqueous phase.....	73
6.3	Results and Discussion.....	73
6.3.1	Bilgewater fuels and additives	73
6.3.2	Water Quality Analysis	75
6.3.3	Identification of water miscible compounds.....	76
6.3.4	Transport of fuel components	81
6.3.5	Emulsion Stability.....	82
6.3.6	Impact of fuel components on emulsion stability and bilgewater treatment	83
6.4	Conclusions	85
Chapter 7:	Implementing image processing and machine learning for predicting bilgewater emulsion stability	86
7.1	Introduction	86
7.2	Materials and methods	87
7.2.1	Determination of emulsion stability.....	87
7.2.2	Determination of OS(%) of prepared bilgewater emulsion samples	88
7.2.3	Determination of OV(%) using image processing.....	88
7.2.4	Development of ML-based emulsion stability models	90
7.2.5	Data preprocessing and feature selection.....	90

7.2.6	ML for emulsion stability models	92
7.2.7	Sensitivity analysis for predictor variables for OS, OV, and turbidity	93
7.3	Results and discussion.....	94
7.3.1	Determination and comparison between OS and OV	94
7.3.2	Oil coalescence prediction model using OS and OV: regression and classification.....	96
7.3.3	Turbidity prediction model: regression and classification.....	98
7.3.4	The effect of predictor variables on the prediction of OS, OV, and turbidity.....	98
7.3.5	One predictor variable removal test for OS, OV, and turbidity	99
7.3.6	Practical implications and improvement of emulsions stability prediction models 103	
7.4	Conclusion.....	104
Chapter 8:	Conclusions and Implications for Future Research	105
8.1	Conclusions	105
8.2	Transition and Future Research.....	107
References		109
APPENDIX A.	List of Publications and Presentations.....	121
APPENDIX B:	Supporting Data for Chapter 4	123
APPENDIX C:	Supporting Data for Chapter 5	126
APPENDIX D:	Supporting Data for Chapter 6	132
APPENDIX E:	Supporting Data for Chapter 7.....	133

List of Figures

Figure 1-1 Typical oil pollution abatement systems on Navy ships	2
Figure 1-2 Technical approach to studying emulsions for improved bilgewater management	3
Figure 2-1 Diagram of electrostatic, steric, and particle emulsion stabilization mechanisms.....	6
Figure 2-2 Diagram of creaming, sedimentation, flocculation, coalescence, and Ostwald ripening emulsion destabilization mechanisms.....	8
Figure 2-3 Example microscopic image of synthetic bilgewater emulsion.....	15
Figure 2-4 An example of CLSM images of emulsion size distribution according to the height of a prepared bilgewater sample. The sample was prepared with 100 ppm Triton X-100 solution and 10% NSBM #4 at 23 °C.....	17
Figure 2-5 Photograph of W/O pendant drops for no surfactant, 100 ppm SDS and 100 ppm Triton X-100 at 10 ⁻⁴ M NaCl.....	19
Figure 2-6 Examples of different types of emulsion stability in simulated bilgewater emulsions.....	21
Figure 3-1 Photograph of bilgewater samples collected.....	38
Figure 3-2 GC chromatographs of a) diesel fuel marine, b) bilgewater #1, c) NSBM #4, and Bilgewater #2 in acetonitrile. These samples were analyzed on an Agilent 7890B3 GC connect to a 5977C MS.	39
Figure 4-1 Summary of emulsion stability under all conditions Orange boxes indicate majority of oil was separated after 5 days, green boxes indicate partial oil separation, and white boxes indicate no oil separation after 5 days.....	45
Figure 4-2 Time course evolution of the grayscale intensity profiles of emulsions prepared at 25°C with 7×CMC of (a) Triton X-100, (b) B&B, and (c) SDS using (1) DI water + surfactant (2) 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, 255 – White).	47
Figure 4-3 Impacts of suspended solids and salinity on emulsion stability based on coalescence	49
Figure 4-4 Visual observation and droplet size and density of emulsion samples prepared with different NaCl concentrations. Samples were prepared as control emulsions using DI water and NSBM #4 only. The microscopic images were taken 30 min after homogenization. (25°C).....	50
Figure 4-5 Impact of temperature on emulsion stability based on coalescence	51
Figure 4-6 Impact of pH on emulsion stability based on coalescence.....	53
Figure 5-1 Interfacial tension measurements with mineral oil as a function of a) model surfactant and b) commercial cleaner concentration	62
Figure 5-2 Macro-phase oil separation as a function of surfactant concentration in model O/W emulsions after 72 h for emulsions prepared with high (a,c) and low (b,d) intensity homogenization and 20% (a,b) and 10% (c,d) mineral oil	64
Figure 5-3 Macro-phase oil separation as a function of interfacial tension in model O/W emulsions after 72 h for emulsions prepared with high (a,c) and low (b,d) intensity homogenization and 20% (a,b) and 10% (c,d) mineral oil	65
Figure 5-4 Comparison of droplet size distribution of model O/W emulsions above CMC with various surfactant and oil combinations and increasing surfactant concentrations under a) high and b) low homogenization.....	66

Figure 5-5 Macro-phase oil separation of commercial cleaner O/W emulsions after 72 h for emulsions prepared with a) high and b) low intensity homogenization with 20% mineral oil	68
Figure 6-1 Changes in a) conductivity, b) pH and c) surface tension of aqueous solutions exposed to various bilgewater oils after 24 h.....	75
Figure 6-2 Chromatographs of water extracts from a) NSBM #4, b) DFM, c) Lube Oil 9250, and d) Lube Oil 2190 with retention time of peaks of interest.....	77
Figure 6-3 Infrared transmission of extracts from water exposed to a) NSBM #4 and b) DFM revealing prominent functional groups	80
Figure 6-4 a) UV absorbance of water exposed to surrogate bilge oil samples and b) change in absorbance at 192 nm of water exposed to oil samples over time.....	81
Figure 6-5 Mineral oil emulsion stability expressed as a) change in cream height over time and b) initial creaming velocity (mm/h) (Inset: Photograph of emulsions after 1 h).....	82
Figure 7-1 A novel approach for bilgewater emulsion stability analysis using image processing and machine learning	87
Figure 7-2 Two variables for determining emulsion stability: coalescence stability (OS or OV) and kinetic stability (turbidity).....	88
Figure 7-3 (a) Illustrative example of OV(%) determination and (b) oil and creaming layers with different OV(%). Non-target layers (i.e., bulk or emulsion layers) were not included in the image processing and black color was used as a background color.	89
Figure 7-4 OV(%) determined using image processing and associated classification with the order of emulsion stability from stable (left) to unstable (right).	95
Figure 7-5 Summary of one predictor variable removal test for OS, OV, and turbidity (RF: Random forest regressor, DT: Decision tree regressor) (SFC: Surfactant concentration, CMC: Critical micelle concentration (CMC), EST: Equilibrium surface tension (ST) above CMC (air), EIT: Equilibrium interfacial tension (IFT) above CMC with NSBM #4, MCS: Micelle size, ZTP: Zeta potential, ALK: Alkalinity, SIP: Surfactant's pH at 7CMC, PH: Initial pH, SSC: Suspended solids (SS) concentration, SLT: Salinity, TPR: Temperature).....	102

List of Tables

Table 2-1 Bilgewater oil-in-water emulsion characterization techniques.....	12
Table 2-2 Physical experimental methods for emulsion characterization	24
Table 2-3 General Characteristics of Bilgewater	26
Table 2-4 Most Procured Cleaners and Detergents by Volume	28
Table 2-5 Composition of current standard challenge mixes for testing OPA system treatment performance in the U.S. Navy.....	29
Table 2-6 Standard Bilgewater Influent Composition for Performance Testing.....	30
Table 3-1 Test procedures used for the water quality analysis of bilgewater samples	34
Table 3-2 Properties of cleaners used on U.S. Navy Ships.....	36
Table 3-3 Water quality characterization of collected bilgewater samples.....	37
Table 4-1 Tested Cleaner Critical Micelle Concentrations (CMC).....	42
Table 4-2 Environmental parameters evaluated.....	43
Table 5-1 CMC and IFT of model and commercial cleaners found in bilgewater	59
Table 5-2 Adsorption properties of model surfactants at a mineral oil-water and oil-air interface	61
Table 6-1 Composition of Synthetic Bilgewater and Possible Additives	74
Table 6-2 Identified Compounds in Aqueous Solutions Exposed to NSBM #4 Components.....	79
Table 7-1 Physicochemical properties of surfactants used for model development.....	91
Table 7-2 Selected factors for ML	92
Table 7-3 Regression and classification results for OS, OV, and turbidity.....	97
Table 7-4 Sensitivity analysis (F-test) for 12 predictor variables for OS, OV, and turbidity	99
Table 7-5 Results of one predictor variable removal test for OS, OV, and turbidity.....	101

List of Acronyms

AFFF	Aqueous Film Forming Foam
ANN	Artificial Neural Network
BSEE	Bureau of Safety and Environmental Enforcement
BTEX	Benzene, Toluene, Ethylbenzene and Xylenes
CFD	Computational fluid dynamics
CI	Creaming Index
CLSM	Confocal Laser Scanning Microscopy
CMC	Critical Micelle Concentration
CMC _{IFT}	Critical Micelle Concentration based on interfacial tension measurements
COD	Chemical Oxygen Demand
COTS	Commercial Off The Shelf
D50	Droplet Diameter At 50% Cumulative Distribution
DCM	Dichloromethane
DEGME	Diethylene Glycol Monomethyl Ether
DFM	Diesel Fuel Marine
DI	Deionized
DLS	Dynamic Light Scattering
DoD	Department Of Defense
DOSY NMR	Diffusion Ordered Nuclear Magnetic Resonance
DSC	Differential Scanning Calorimetry
DT	Decision Tree
EGME	Ethylene Glycol Monomethyl Ether
EI	Electron Ionization
EPA	Environmental Protection Agency
ETBE	Ethyl-Tert Butyl Ether
FTIR	Fourier Transform Infrared Spectroscopy
GB	Gradient Boosting
GC-FID	Gas Chromatography – Flame Ion Detection
GC-MS	Gas Chromatography – Mass Spectroscopy
HEM	Hexane Extractable Material
HLB	Hydrophilic Lipophilic Balance
HLD	Hydrophilic Lipophilic Difference
HOI	Hydrocarbon oil index
IFT	Interfacial Tension
IR	Infrared
ISEA	In Service Engineering Agent
MAE	Mean Absolute Error
MGO	Marine Gas Oil
ML	Machine Learning
MTBE	Methyl Tert-Butyl Ether
NA	Numerical Aperture

NAVSEA	Naval Sea Systems Command
NMR	Nuclear Magnetic Resonance
NRL	Naval Research Laboratory
NSBM #4	Navy Standard Bilge Mix
NSWCCD	Naval Surface Warfare Center, Carderock Division
NTU	Nephelometric Turbidity Units
O/W	Oil-in-water
OPA	Oil Pollution Abatement
ORP	Oxidation-Reduction Potential
OS	Oil Separation
OV	Oil Value
OVS	Oil/Water Separator
PALS	Phase Analysis Light Scattering
PFAS	Per- and polyfluoroalkyl substances
PFG NMR	Pulse field gradient Nuclear Magnetic Resonance
ppm	Parts Per Million
RF	Random Forest
sCOD	Soluble Chemical Oxygen Demand
SDBS	Sodium Dodecylbenzenesulfonate
SDS	Safety Data Sheet
SDS	Sodium Dodecyl Sulfate
SEM	Scanning Electron Microscope
SERDP	Strategic Environmental Research And Development Program
SMOTE	Synthetic Minority Over-Sampling
SS	Suspended Solids
ST	Surface Tension
SVM	Support Vector Machine
TDS	Total Dissolved Solids
TN	Total Nitrogen
TOC	Total Organic Compound
TP	Total Phosphorus
TSS	Total Suspended Solids
UCF	University of Central Florida
UNDS	Uniform National Discharge Standard
UV-Vis	Ultraviolet Visible
W/O	Water-in-oil
ZDDP	Zinc Dialkyldithiophosphate

Chapter 1: Background and Objectives

1.1 Background

Use of oils, fuels, and lubricants are critical to the operation of every ship and watercraft used in the Armed Forces. These include Navy ships, Army transports, Coast Guard cutters, and Air Force recovery vessels. Oily water is generated on vessels during machinery washes and condensation, leak, and spill collection. As a result, oily water is collected in the bilge or oily waste holding tanks of ships and must be treated. Bilgewater discharge was first regulated in the 1970's by the International Convention for the Prevention of Pollution from Ships (1973), which was further modified in 1978 (MARPOL 73/78) (Sharp, 1993). Today, bilgewater discharge from commercial and Armed Forces vessels must have an oil content below 15 ppm, as regulated by MARPOL Annex I for commercial vessels and DoD Regulation 4715.06-V2 (U.S. DoD, 2017) for Armed Forces vessels.

Oil pollution abatement (OPA) systems are employed for the purpose of managing shipboard oily waste to comply with environmental regulations. OPA systems are composed of equipment to collect, hold, treat, and analyze oily waste on board ships. However, the presence of oil-in-water emulsions makes bilgewater difficult to treat solely by gravity driven separation processes and often requires the use of secondary treatment systems.

Emulsions, or dispersions of one or more immiscible liquid phases in another, are often created in bilgewater when an oil phase is exposed to surfactants and mixing energy (McClements, 2007). Surfactants align at the oil/water interface, which reduces the interfacial energy and allows for energy inputs from pumps and shipboard vibrations to develop an emulsion. Emulsified oil in bilgewater, created by either mechanical dispersion or chemical surfactant stabilization, can be difficult to treat because the emulsion's small droplet size and neutral buoyancy prevent gravimetric separation (McLaughlin et al., 2014). Highly stable oil-in-water emulsions are particularly challenging to meet stringent marine discharge standards and is frequently required to be stored until pierside disposal is available.

U.S. Navy and Army OPA systems typically use parallel-plate oil-water separators (OWSs) to treat bilgewater. These separators are effective at removing bulk oil and emulsions larger than 20 μm ; however, the presence of surfactants in the bilgewater and shipboard vibrations can generate small oil droplets that can pass through a parallel plate OWS. This results in long operational durations, leading to increased maintenance from continued processing and reprocessing of emulsions. In order to remove smaller oil emulsions, ceramic membranes have increasingly been installed as a secondary treatment technology for Navy produced bilgewater (Figure 1-1). While these systems are effective, high membrane fouling rates require frequent cleaning or replacement. Operational costs from membrane procurement and associated logistics from onboard storage of spares and cleaning reagents are increased.

Other examples of bilgewater treatment methods include electrocoagulation (Asselin et al., 2008; Rincón and La Motta, 2014), centrifugation, addition of chemical agents (Ahmad et al., 2006) and other forms of physical/chemical separation (Grzechulska et al., 2000; Talbert et al., 2004).

In addition, more advanced (Moslehyani et al., 2016; Waller et al., 2019) and ecofriendly remediation alternatives (Stamper and Montgomery, 2008; Uma and Gandhimathi, 2019; Vyrides et al., 2018a) have recently been reported but are not commercially available for shipboard use. However, all these treatment methods have associated operation and maintenance costs.

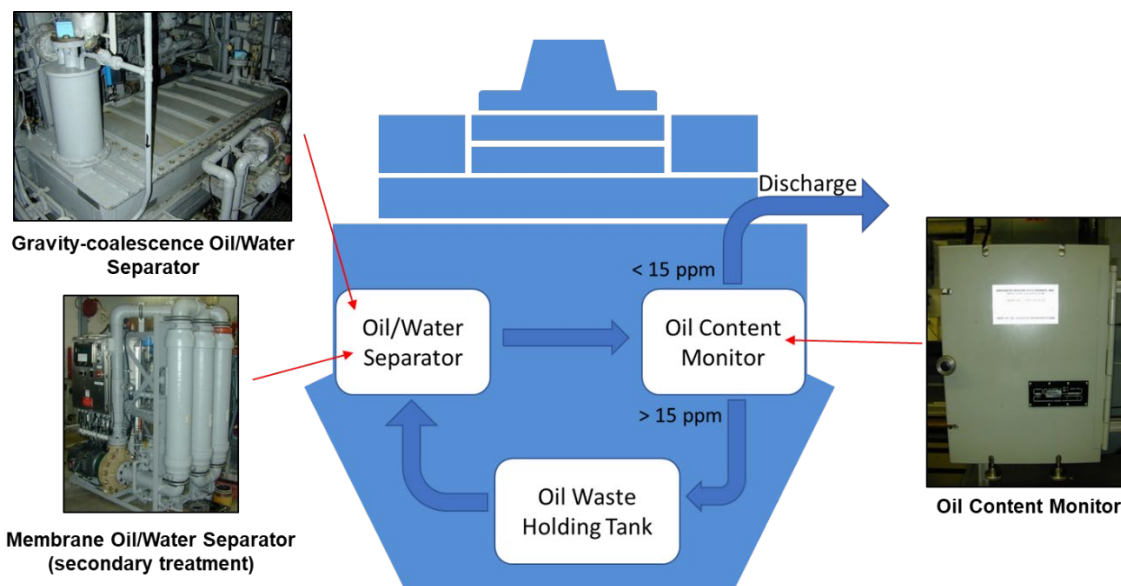


Figure 1-1 Typical oil pollution abatement systems on Navy ships

Currently, treatment methods target bilgewater as a whole and do not specifically focus on breaking emulsions into a separated oil phase for removal. Hence, current knowledge on bilgewater tends to concentrate on empirically determined treatment methods and lacks information on bilgewater emulsion characteristics. While emulsion formation and stability have been widely studied in other adjacent industries for emulsification (e.g., food science, cosmetics, agro-chemicals, paints, and pharmaceuticals), these specific properties have not been thoroughly investigated for demulsification to separate oil-in-water (O/W) emulsion, particularly, in Armed Forces bilgewater. In addition, most emulsion studies have been conducted under carefully selected conditions that help stabilize emulsions based on the dispersed or continuous phases. Given that bilgewater is extremely dynamic, making it difficult to pinpoint the major stabilizing mechanisms, thorough systematic research on bilgewater emulsion stability would enhance our understanding of this topic. A better understanding of the generation and fundamental mechanisms of emulsion stability, reliable methods of O/W emulsions treatment can assist to resolve existing bilgewater emulsion treatment challenges.

1.2 Objectives

The primary objective of this effort was to advance the current understanding of emulsion science for chemically stable emulsions formed in Armed Forces applications. While commercially available equipment can be implemented for bilgewater emulsion mitigation, there

is little knowledge surrounding the physical, chemical, and thermodynamic properties of the emulsions created in an Armed Forces vessel environment. Thus, targeted treatment and management of these fluids become conjecture and call for a deliberate and thorough understanding of fundamental emulsion stability properties. This effort focused on three segments: (1) Scoping Study for Review of Armed Forces Vessels O/W Emulsions, (2) Characterization of Prepared and Extracted Bilgewater Emulsions, and (3) Development of Emulsion Stability Guide. An illustration of the focus segments are shown in Figure 1-2.

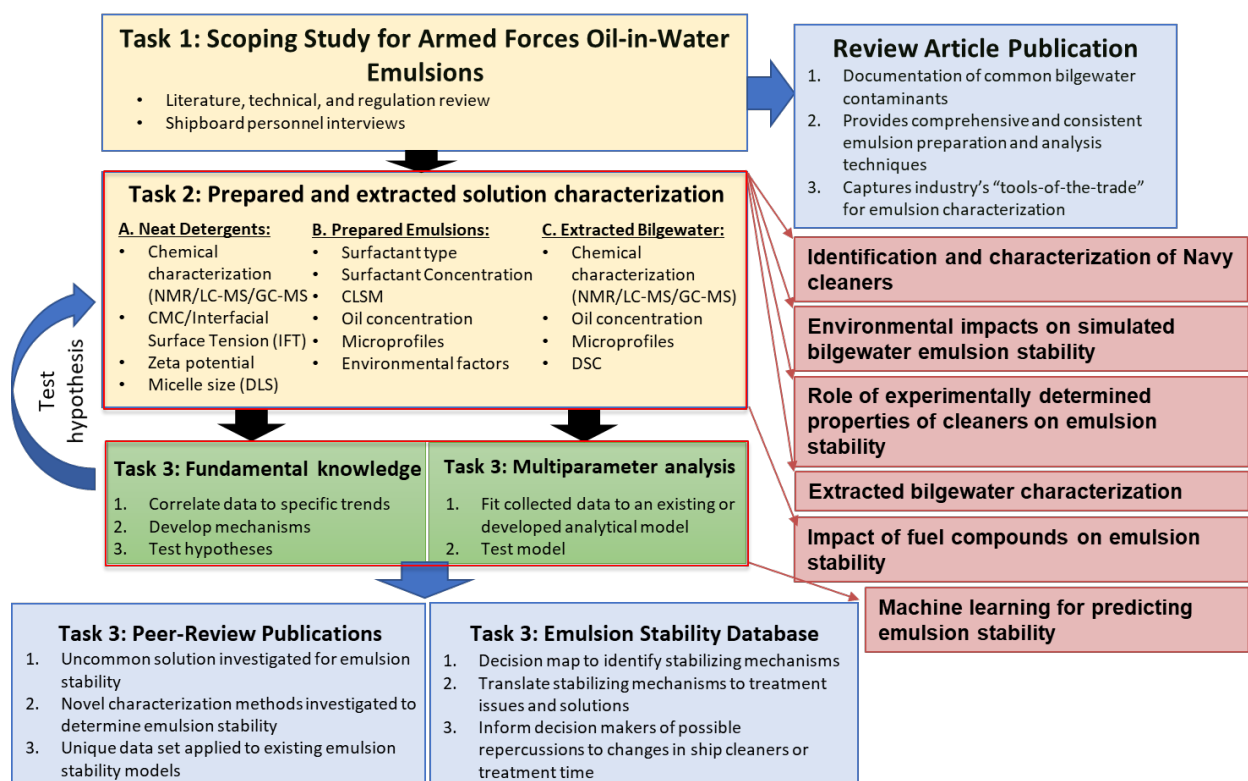


Figure 1-2 Technical approach to studying emulsions for improved bilgewater management

1.3 Organization

This report is divided into 8 Chapters where Chapters 2-7 are meant to be self-inclusive and therefore include separate methods, results, and discussion sections within each Chapter.

Chapter 2 describes the results of the scoping study for Armed Forces O/W emulsions performed under Task 1. In particular, this Chapter includes information on the formation and stability of bilgewater emulsion, as well as pertinent physiochemical properties that are known to influence emulsion stability. A survey of U.S. Navy cleaners is also presented, as well as typical bilgewater characteristics and information on standard synthetic bilgewater mixtures currently used in the validation and testing of OPA equipment. Results from this chapter were published in part in *Science of the Total Environment* (Church et al., 2019).

Chapters 3-6 describes the results of the laboratory experiments performed under Task 2. In this task, emulsion solutions were systematically investigated using identified Navy surfactants resulting from Task 1's research. Specifically, Chapter 3 lists the results of an extracted bilgewater characterization study, where bilgewater samples from three Navy ships were characterized for water quality and oil properties. Chapter 4 focuses on the impacts of environmental conditions on simulated emulsion stability, which was adapted into a manuscript that was published in *Industrial & Engineering Chemistry Research* (Diaz et al., 2021). Chapter 5 describes the role of experimentally determined properties of cleaners on emulsion stability, which was published in the *Journal of Water Process Engineering* (Church et al., 2020). And Chapter 6 gives important insights into the role of shipboard fuels on bilgewater emulsion stability.

Chapter 7 describes the data analysis effort performed under Task 3. In particular, the Chapter conveys findings of using machine learning (ML) methods to interpret data from laboratory-based experiments and to develop an emulsion stability prediction model.

Finally, important findings, lessons learned, and conclusions of the project are discussed in Chapter 8. Several recommendations for bilgewater management and possible future efforts are also included.

Chapter 2: Scoping Study for Armed Forces Oil-in-Water Emulsions

2.1 Introduction

The focus of this Chapter is to discuss emulsions that form in Armed Forces bilgewater and common approaches to study their behavior in solution. First, information on the formation and stability of bilgewater emulsions is discussed as well as pertinent physiochemical properties that are known to influence emulsion stability. Next, bilgewater emulsion characterization techniques are discussed in detail including general bilgewater analysis, droplet characterization, and emulsion stability testing methods. Subsequently, a survey of U.S. Navy surfactants is presented as well as typical bilgewater characteristics and information on standard synthetic bilgewater mixtures currently used in the validation and testing of oil pollution abatement (OPA) equipment. Overall, this review provides a description of properties that define emulsion formation and stabilization and leverage existing characterization techniques to link properties to behavior.

2.2 Formation and stabilizing mechanisms of bilgewater emulsions

When two immiscible liquids are placed together in a container, they are thermodynamically driven to form two layers to minimize the contact area between the two phases, reducing their free energy (Pichot et al., 2010; Tadros, 2009). Emulsion formation occurs through kinetically driven mechanical dispersion, which breaks up the two immiscible layers in a process called homogenization. In the context of bilgewater, the homogenization is likely to occur during the pumping and transport of bilgewater between holding tanks (Flanigan et al., 1988); however, shipboard vibrations and sea states can also influence emulsion generation. In addition, self-emulsification can generate nano-sized emulsions without the need for homogenization through a thermodynamic process called micellization self-assembly where surfactants found in bilgewater form micelles at surfactant concentrations greater than the critical micellization concentration (CMC) (Tadros, 2009). However, nano-sized emulsions produced by self-emulsification have very low volume densities and are assumed to only make up a small portion of the overall oil content of bilgewater. Therefore, nano-sized emulsions are not typically studied in a bilgewater context. Once an emulsion is formed, it could be stabilized through one or several of the mechanisms discussed below.

2.2.1 Role of emulsifiers

Emulsifiers are any substances that help stabilize a suspension of one liquid within another liquid. Any compounds that spontaneously adsorb at the oil/water interface can be used as emulsifiers (e.g. fine particles, proteins, etc.). However, surfactants are considered to be the main contributor to emulsion stabilization in bilgewater due to the large quantity of cleaners that drain into the bilge tanks during shipboard operation (Leal-Calderon et al., 2007). Surfactants, also called surface-active agents, are amphiphilic molecules comprised of a polar, hydrophilic head group attached to a non-polar, hydrophobic chain (Tadros, 2009). Surfactant molecules that are adsorbed at the oil/water interface reduce the surface free energy (interfacial tension) and allow for the formation of emulsion droplets (Pichot et al., 2010). Surfactants can also stabilize

emulsions by forming a protective layer around the droplets to prevent coalescence when two droplets collide. Depending on the charge (anionic, cationic, or nonionic) or size of the headgroup, the stabilizing layer can work using electrostatic or steric principles (Tadros, 2006; Tadros, 2009) (Figure 2-1). For example, nonionic surfactants will typically stabilize emulsions using steric mechanisms.

A surfactant's molecular structure will often govern the size and geometry of emulsion droplets. Surfactants can be characterized according to their headgroup (anionic, cationic, or nonionic), their CMC, or by their hydrophilic-lipophilic balance (HLB) (Boyd et al., 1972). A surfactant's HLB number is a semi-empirical way of determining the hydrophilic and lipophilic parts of a surfactant. It has been shown that a surfactant's HLB number can be used to determine the likelihood of a surfactant to form water-in-oil (W/O) or oil-in-water (O/W) emulsions (Tadros, 2006). It is generally considered that a surfactant with an HLB of greater than 8 is needed for the formation of O/W emulsions (Tadros, 2009).

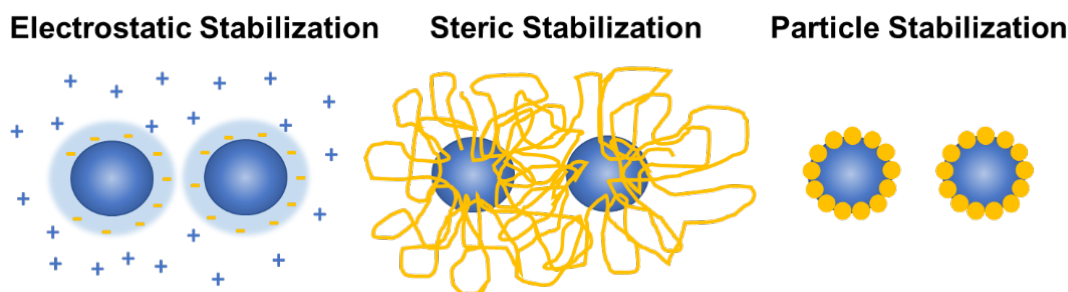


Figure 2-1 Diagram of electrostatic, steric, and particle emulsion stabilization mechanisms

2.2.2 Electrostatic stabilization

Electrostatic repulsive forces occur when charged surfactants adsorb to the surface of an oil/water interface and cause a diffuse charge cloud to form around the droplet (Adams et al., 2007). According to Gouy-Chapman and Stern theory, the charge cloud establishes a double layer. The interaction of two clouds of the same charge causes electrostatic or double-layer repulsion. The measurement of a droplet's surface charge is called zeta potential and can be used to determine whether electrostatic repulsive forces are contributing to emulsion stabilization (McClements, 2007; Stachurski and MichaŁek, 1996). The thickness of the double-layer depends on the electrolyte concentration and valency; therefore, electrostatically stabilized emulsions have poor stability in saline bilgewater (Church et al., 2017). Traditionally, electrostatic stabilization occurs in systems with ionic surfactants; however, spontaneous charging of oil/water interfaces without surfactants has also been observed (Marinova et al., 1996). However, this phenomenon is unlikely to play a major role in bilgewater emulsion stabilization considering the abundance of surfactants and fine particles found in bilgewater (Karakulski et al., 1998; U.S. EPA, 1999b).

2.2.3 Steric stabilization

Steric stabilization of emulsions is produced by using nonionic or polymeric surfactants (Adams et al., 2007; Tadros, 2009). These types of surfactants contain large bulky headgroups that

prevent the interaction of emulsion droplets by the overlapping of long hydrophilic groups associated with the surfactant (Tadros, 2006). Steric stabilization plays a major role in bilgewater stabilization because of the ability of nonionic surfactants to withstand changes in salinity and pH paired with their frequent shipboard use. Steric stabilized emulsions are considered difficult to treat considering destabilizing methods like salting-out or coagulation are generally not effective against these emulsions (Lazaridis et al., 1999).

2.2.4 Particle stabilization (Pickering emulsions)

The use of solid colloidal particles to stabilize emulsions through irreversible interaction at the oil/water interface was first realized decades ago (Binks and Lumsdon, 1999). More recently, solid nanoparticles have been developed to act as emulsion and foam stabilizers (Binks et al., 2008). Pickering emulsion stability is the result of a particle layer that forms around emulsion droplets and acts as a mechanical barrier against coalescence (Ngai and Bon, 2014). The particle barrier is related to how strongly the particle adsorbs to the oil/water interface (Pichot et al., 2010). The contact angle of a particle with the oil and aqueous layers is commonly used to predict how well a particle will adsorb to the oil/water interface (Binks et al., 2013). Particle stabilization is expected to be present in bilgewater due to the abundance of suspended particles in actual bilgewater samples (U.S. EPA, 1999b). However, the identification of Pickering emulsions in extracted bilgewater samples has not been verified. This method of stabilization has not been investigated in previous bilgewater studies and as such is of particular interest to the authors.

2.2.5 Emulsion destabilization

The term “emulsion stability” typically refers to the ability of an emulsion to maintain consistent properties over an extended period (Tadros, 2009). In general, emulsions are thermodynamically unstable and will begin to breakdown over time. Destabilization mechanisms include: creaming, sedimentation, flocculation, coalescence, and Ostwald ripening (Adams et al., 2007; Leal-Calderon et al., 2007), as displayed in Figure 2-2. Many bilgewater treatment strategies exploit these destabilization mechanisms; therefore, a general knowledge of each process is important for understanding basic bilgewater treatment design.

Creaming and sedimentation occurs when gravitational or centrifugal forces exceed the Brownian motion of the droplets and a droplet concentration gradient develops at the top (creaming) or bottom (sedimentation) of the mixture depending on the oil density. The developed creaming or sedimentation layer is comprised of closely packed emulsion droplets, which may coalesce if there is a disruption of the liquid film between two or more emulsion droplets.

Flocculation via van der Waals forces occurs when particles are within close proximity and attractive forces exceed a droplet’s electrostatic repulsion forces. When this happens, emulsions aggregate and either float or sink within container. Alternatively, introduction of cations into solution via addition of chemical coagulants or by forced oxidation of metals (e.g. aluminum or iron) through electrocoagulation can be used to neutralize repulsive electrostatic forces to allow for flocculation.

Coalescence refers to the process of thinning and disrupting the liquid film between droplets which results in the fusion of two or more droplets to form larger droplets. Coalescence typically occurs after creaming, sedimentation, or flocculation when droplets are closely packed together and van der Waals forces are preventing their separation.

Ostwald Ripening occurs due to the finite solubility of the oil phase in the aqueous phase. While oils are often referred to as immiscible with water, they often have very low solubilities which can contribute to the breakdown of an emulsion. Smaller oil droplets will have greater solubility compared to larger droplets and will completely diffuse into the water until deposited on larger oil droplets with time. The process results in an increased shift of droplet size distribution.

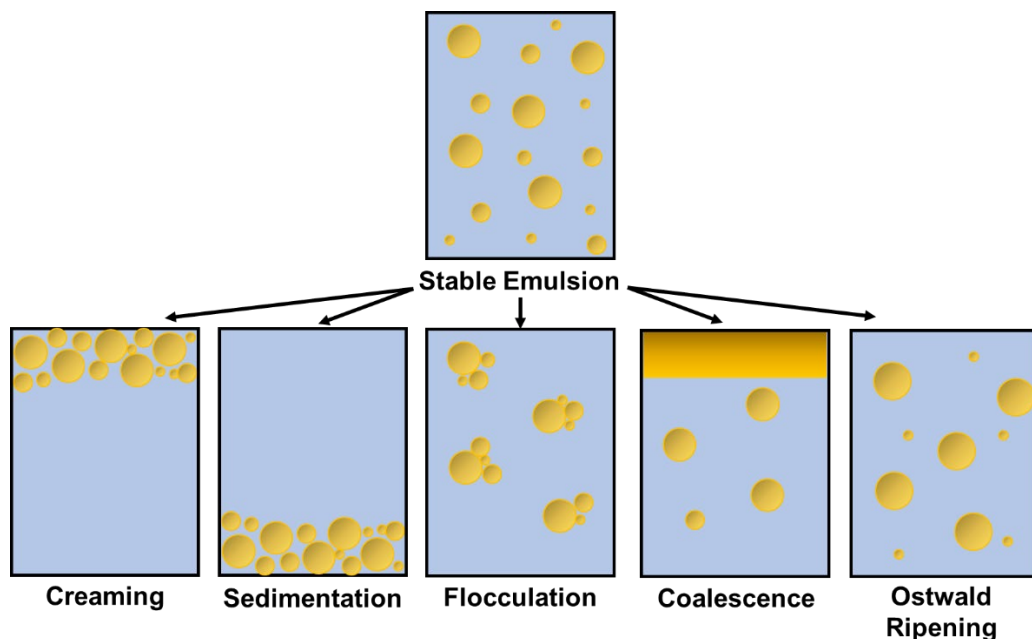


Figure 2-2 Diagram of creaming, sedimentation, flocculation, coalescence, and Ostwald ripening emulsion destabilization mechanisms

2.3 Physicochemical properties impacting oil-in-water emulsion stability

2.3.1 Temperature

Emulsion stability is affected by temperature due to its effect on the physical properties of oil, water, interfacial films, and surfactant solubility in the oil and water phases (Adams et al., 2007). As temperature increases, the thermal energy of the droplets also increases, which encourages droplet collisions and thus creaming or coalescence of the emulsion. Increased temperature also reduces the interfacial viscosity and results in a faster film-drainage rate leading to droplet coalescence. However, increased temperature can also influence surfactant adsorption kinetics, which can counteract observed coalescence behavior (Kokal, 2005). Despite the well-understood role of temperatures in emulsion stability, there is limited data on the temperature of bilgewater. Chanthamalee et al. found that the bilgewater temperature in small fishing vessels in Thailand ranged from 25- 30°C (Chanthamalee et al., 2013) and Santisi et al. reported a temperature of

21°C in a private passenger ship in Italy (Santisi et al., 2015). Without a framework through which to interpret this data, bilgewater experimentalists have typically selected a range of temperatures to explore bilgewater emulsions. For example, Ulucan and Kurt looked at temperatures ranging from 4 to 60°C (Ulucan and Kurt, 2015). Open questions remain on the relationship between bilgewater temperature and ocean temperature, which have not been reported, as well as how bilge design, i.e. the proximity of machinery or having multiple bilge tanks, impact bilgewater temperature.

2.3.2 pH

The pH of the continuous phase has a strong influence on the stability of O/W emulsions (Kimbler et al., 1966). Adding inorganic acids and bases to emulsions influences the ionization of the interfacial films, which can change the physical properties of the oil/water interface. For example, the zeta potential of an emulsion droplet can significantly change with pH. This is particularly true near a surfactant's isoelectric point, where emulsions traditionally stabilized using electrostatic mechanisms can be destabilized. Likewise, pH can influence the solubility and effectiveness of nonionic emulsifiers (Di Marzio et al., 2011); therefore, even emulsions stabilized by steric mechanisms can be impacted by pH. In this context, pH is commonly studied for its effect on emulsion stability. For example, a report by Kokal determined that a pH of approximately 10 maximizes emulsion breaking in a crude-oil and brine emulsion system (Kokal, 2005). Bilgewater pH has been reported to range from 6.8-9.0 (Chanthamalee et al., 2013; Emadian et al., 2015). As with other parameters, the pH of the bilge will likely vary while a vessel is underway. Additionally, it is likely that bilgewater emulsion generation is influenced by pH, and previously stable emulsions may be destabilized by a shift in the pH of the aqueous phase.

2.3.3 Solid particles

Fine solid particles, such as silica particles, clays, and metal oxides effect emulsion stability through the creation of Pickering emulsions. Bilgewater has significant concentrations of crystalline waxes, clays, corrosion products, and mineral scales that are known to generate very stable emulsions (Umar et al., 2018). Therefore, total suspended solids (TSS) concentration, as well as solid particle size, particle wettability, and inter-particle interactions can be analyzed to determine potential formation of particle stabilized emulsions. Reports of suspended particle concentration in bilgewater varies significantly. In one study, TSS concentration ranged from 41-2684 mg/L (U.S. EPA, 1999b). However, the wettability and types of solids were not explicitly examined. Commonly studied oil-wet solids include asphaltenes and waxes (Ali and Alqam, 2000; Yan and Masliyah, 1995). Hydrophilic, or water-wet solids, include inorganic scales (CaCO_3 and CaSO_4), clays, sand, and corrosion products.

2.3.4 Surfactant type and concentration

As mentioned in Section 2.1, surfactants play an important role in bilgewater emulsion stabilization. Surfactant type can determine whether emulsions are stabilized using electrostatic or steric principles depending on the charge (i.e. anionic, cationic, or nonionic), headgroup size, and chemical compound. However, it is difficult to predict the types of surfactants that are present in bilgewater. Unlike emulsions in food science (McClements, 2015), cosmetics (Gilbert

et al., 2013), and other fields where surfactants are selected based on specific properties, bilgewater, contains a diverse set of cleaners and detergents used in other shipboard applications. Therefore, the types of surfactants in bilgewater is largely dependent on shipboard activities, which can change daily.

Surfactant concentration can also play a major role in bilgewater emulsion stabilization. When surfactants are added into a solution in dilute amounts, they are generally less effective at stabilizing emulsions compared to when surfactant concentration is increased beyond the CMC. The CMC is the point at which micellization becomes thermodynamically favorable due to surface energy reduction and any additional surfactant goes directly to the creation of micelles. As surfactant concentration increases beyond the CMC, additional micelle geometries are possible and are guided by surfactant packing equations available in classic texts (Israelachvili, 2011; Rosen and Kunjappu, 2012). Despite the important role that surfactants play in emulsion stability, there are no reports of bilgewater surfactant characterization.

2.3.5 Ionic strength

The ionic strength of the aqueous phase is particularly important for electrostatically stabilized emulsions. When the ionic strength of a solution increases, the electrostatic shielding between droplets is reduced, which allows for increased droplet interaction. For example, Rios et al. (1998) reported the influence of electrolytes on the destabilization of O/W emulsions by breaking them using the inorganic salts calcium chloride and aluminum chloride. As expected, the addition of electrolytes lowered the zeta potential of the droplets and destabilization of the emulsion was observed (Kulmyrzaev et al., 2016; Rios et al., 1998). In addition, the presence of salts in an emulsion system can influence the solubility of nonionic surfactants (Mitra and Paul, 2005) and increase the density of the aqueous phase, which in turn impacts the stability of sterically stabilized emulsions. Given the impact of ionic strength on emulsion stabilization, electrical conductivities of bilgewater are often reported in bilgewater research. Electrical conductivity is a simple indirect method for measuring the ionic strength of a water sample. Conductivities of bilgewater have been reported to range from 679 $\mu\text{S}/\text{cm}$ to 8.4 mS/cm (Asselin et al., 2008; Santisi et al., 2015).

2.3.6 Mixing intensity

The mixing intensity, or energy input, applied to a system indirectly impacts emulsion stability by influencing the size of the oil droplets generated. The relationship between droplet size and energy input was first described by Hinze–Kolmogorov equation, which predicted that the maximum surviving droplet size in the inertial flow regime is a function of the equilibrium interfacial tension, the density of continuous phase, and the average energy dissipation per unit mass (Angle et al., 2006; Hinze, 1955). The Hinze–Kolmogorov equation has been modified multiple times to better predict droplet generation in high oil fraction systems and those with dissimilar viscosities between the dispersed and continuous phase (Angle et al., 2006). Prediction of bilgewater emulsion droplet size is complex because the oil/water interfacial tension and oil concentration is under constant flux due to varying shipboard activities. Additionally, energy sources driving droplet breakup include not only pumps but also engine vibrations and ship motion during high sea states.

2.4 Bilgewater oil-in-water emulsion characterization techniques

2.4.1 General bilgewater quality parameters

General properties of the aqueous phase, such as pH, conductivity, turbidity, chemical oxygen demand (COD), solids, and oil content can provide information on emulsion stabilizing mechanisms. These parameters are simple to measure and are generally available in bilgewater treatment literature. pH can be determined using pH test strips or a portable pH meter. Conductivity (mS/cm) can be measured using a (portable) conductivity meter and provides information on the ionic strength of a bilgewater (Canizares et al., 2007). Highly conductive O/W solutions reduce the stability of electrostatic emulsions by reducing the shielding effect. Turbidity is the quantification of the cloudiness of a water, and thus it is a proxy measurement for the concentration of emulsions, suspended particles, and other light scattering particulates found in bilgewater samples. Turbidity is measured using a nephelometer and recorded in units Nephelometric Turbidity Units (NTU). Turbidity is often used as a rudimentary method of evaluating bilgewater treatment performance. COD and soluble COD (sCOD) is the measurement of oxygen needed to decompose the organic matter and oxidize the inorganic matter of a water sample. COD is inclusive of bilgewater oil content, but requires additional analysis to isolate oil concentration contribution. A two-hour cadmium reduction assay performed in accordance to the standard methods (Method 5220B) is typically used to measure COD (Eskandarloo et al., 2018; Rice et al., 2012). However, high salinity will interfere with the COD measurement. Total solids (TS), total suspended solids (TSS), and total dissolved solids (TDS) are analyzed based on gravimetric methods per standard methods (SM 2540). Advantages and disadvantages of general water quality analyses are listed in Table 2-1.

Table 2-1 Bilgewater oil-in-water emulsion characterization techniques

Analysis	Purpose of Analysis	Methods	Pros*	Cons*
General Water Quality Parameters	Measure commonly used parameters to ensure a full description of the experimental conditions. Allows for comparison between literature reports.	pH	- Simple, portable, inexpensive, and real time - Important parameters for selecting bilgewater treatment processes (Kokal, 2005)	- Only gives general clues to emulsion stabilization mechanisms - Does not provide direct information on the stability of an emulsion or oil concentration
		Conductivity		
		Turbidity		
Droplet Characterization	Determine the droplet size distribution and, in some cases, droplet morphology. Droplet size provides clues to the emulsion mechanism, interfacial tension between the system components, and the potential for gravity driven separation.	Microscopy	- Commonly available - Gives droplet size and morphology information (McClements, 2007)	- Sample manipulation may alter droplet size - Limited working range - Low throughput
		Laser Diffraction	- Large working range (25nm – 4mm) (McClements, 2007) - Representative sample - Excellent reproducibility	- Does not distinguish between emulsions, bubbles and other particles found in bilgewater - Sample dilution required
		Dynamic Light Scattering	Able to measure very small emulsion droplets or micelles (1nm-1µm) (Bhattacharjee, 2016)	Bilgewater emulsions are too large for DLS
		Electrical Pulse Counting	- Large working range (0.1µm – 3mm) (McClements, 2007) - Representative sample - Excellent reproducibility	- Sample dilution required - Cannot distinguish between solid particles and emulsions
		Ultrasonic Spectrometry	- Can process samples with up to 40% oil (McClements and Gunasekaran, 1997) - Large working range 0.1µm-3,000µm	- Limited availability - Requires acoustic extinction curve for each type of emulsion - Not useful for emulsion mixtures
		CLSM	Able to distinguish between oil and other particles found in bilgewater (Church et al., 2017)	Sample manipulation is required for measurement (Malassange-Bulgarelli and McGrath, 2009)
		Microfluidics	- Droplet size control (Teh et al., 2008) - Used to measure droplet coalescence (Abedi et al., 2019) - Allows for individual droplet manipulation	- Extensive background knowledge is needed to perform tests - Specialty equipment is required

Interface Characterization	Provide information on the interaction between the continuous and dispersed phase	Interfacial Tension	• Gives information on how much energy is required to break up the oil phase (Tummons et al., 2016) • Simple analysis • Widely accepted methods • Quickly indicates the presence of surfactants	• Only provides one aspect of emulsion stability • Less important under high homogenization conditions
		Zeta Potential	• Provides information on the charge at the slip plane, and thus gives information on if emulsions are being electrostatically stabilized (Bhattacharjee, 2016)	• Bilgewater solids can interfere with sample measurements
Oil Characterization	Determine the type of oil in the emulsion	Density and Viscosity	• Simple tests • Standard method (ASTM D287) • Indicates likelihood of creaming	• May be time consuming to determine the viscosity
		FTIR	• Fingerprint technique that allows for the identification of individual hydrocarbons (Silva et al., 2012)	• Potential for water based inference
Emulsion Stability Characterization	Emulsion stability experiments are a good way to predict how emulsions will behave in the bilge.	Creaming Stability	• Simple test method (McClements, 2007) • Representative • Commonly reported in literature	• Long testing periods • Many bilgewater emulsion samples will not have a defined cream layer over time
		Accelerated Coalescence Test	• Simple test method • Quick test with results in less than 24 hrs (McClements, 2007)	• Not representative of real conditions • Correlation with long term coalescence stability may vary
		Microsensor Characterization	• Direct measurement of mass transport in emulsion samples (Lee et al., 2011)	• Expertise required • Does not give information in emulsion without significant mass transport of constituents from the oil to aqueous phase
		Differential Scanning Calorimetry	• Gives thermal stability information (Clausse et al., 2005)	• Not yet used for bilgewater emulsions

*The provided references contain information about a given technique but the determination of the technique as a pro or con for bilgewater measurement was made by the authors.

Literature cites a variety of methods to measure oil content including infrared (IR) spectroscopy (e.g., InfraCal O/W analyzer, Wilks), UV-Vis spectroscopy (e.g., Shimadzu MultiSpec-1501), fluorescence (e.g. TD-107, Turner Designs), and conventional light scattering (e.g. OS100, Inventive Systems Inc.) (Khan et al., 2016). However, the U.S. Environmental Protection Agency (EPA) has ruled that Method 1664 will be used for EPA's Clean Water Act Programs (U.S. EPA, 1999a) and is thus recommended for determining oil content compliance with discharge regulations. EPA 1664 uses n-hexane as the extraction solvent in both silica gel treated and non-silica gel treated samples (U.S. EPA, 2010), but is considered laborious and is therefore not recommended for small-scale laboratory-based analysis. Alternatively, ISO Method 9377-2 is specified by the US Coast Guard under 46 CFR 162.050-39 for measuring oil content in samples. ISO Method 9377-2 is used for approval testing of bilgewater separators, monitors, and alarms. Like EPA 1664, this method also uses a hydrocarbon solvent to extract oil from the water sample, but utilizes gas chromatography-flame ion detection (GC-FID) to quantify hydrocarbon oil index (HOI). ISO Method 9377 has a lower reporting limit than the EPA 1664 method (0.1 mg/L vs. 5 mg/L) and can also give information on oil characteristics; however, the method is not typically offered by commercial laboratories and can be significantly more expensive (McLaughlin et al., 2014).

2.4.2 Droplet characterization

2.4.2.1 Microscopy

The most direct approach for observing emulsions is optical microscopy (Figure 2-3). Most modern microscopes are integrated with computers, which allows for the collection of digital micrographs. Typically, emulsion images are processed to determine information about emulsion microstructures such as particle size distribution, floc microstructure, floc size, and fractal dimension (McClements, 2007). Additionally, special measurement cells can be used in conjunction with microscopes to characterize emulsion stability. For example, rheo-optic techniques have been used to provide information on the breakdown of droplets in shear fields (van der Linden et al., 2003). One drawback of microscopy is that major components of emulsions may exhibit similar contrast, making it difficult to distinguish oil droplets from air bubbles. For this reason, several approaches have been employed to help visualize the emulsion droplets. This includes chemical stains, such as confocal laser scanning microscopy (Church et al., 2017), and phase contrast or differential interference contrast microscopy (Cui et al., 2011). Droplet size information collected from microscopy is typically reported as a number distribution but may be converted to a volume distribution. Microscopy circumvents the issues caused by data transformation common in light scattering methods because the number distribution is based on the direct observation of individual droplets.

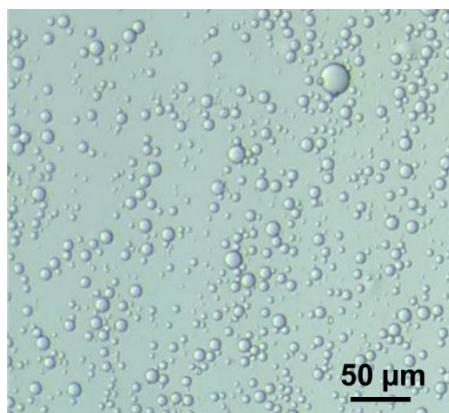


Figure 2-3 Example microscopic image of synthetic bilgewater emulsion

2.4.2.2 Laser diffraction

Laser diffraction determines the particle size distribution using the scattering pattern produced when a laser beam is directed through a diluted emulsion (McClements, 2007). The larger the particle, the smaller the scattering angle. Commercial instruments commonly come with software that calculates the particle size distribution by finding the best fit between the measured scattering pattern and the theoretically predicted fit. The user must provide the software with the refractive index of both the continuous and dispersed phases in order to obtain accurate measurements. Laser diffraction instruments are capable of determining particle diameters from 25 nm to over 1,000 μm . It is important to note that laser diffraction requires sample dilution, typically to less than 0.1 wt% to avoid multiple scattering effects (McClements, 2007). Usually, a laser diffraction flow loop, ranging in volume from 40 to 250mL, will be filled with deionized water and the sample of interest will slowly be introduced into the flow loop until the desired transmittance or absorbance is obtained. Once the sample concentration has reached an acceptable level, the diffraction pattern (measurement) will be collected. Although sample dilution can be undesirable, from the authors' experience measuring mineral oil emulsion size using both laser diffraction and microscopy, droplet size is not impacted by dilution. Additional concerns related to the use of laser diffraction are the impact of circulation speed, mechanical agitation, and sonication on emulsion stability. While each instrument and emulsions type is unique, the authors have used multiple instruments at circulation and agitation speeds that do not disturb the emulsion and provide consistent results. Laser diffraction distribution data is collected as a function of volume fraction but may be converted to a number distribution. The number distribution can provide insight on the emulsion system but should only be used as a supplement to the volume distribution because of the assumption in the data transformation.

2.4.2.3 Dynamic light scattering (DLS)

Dynamic light scattering instruments can measure droplets from 1 nm to 1 μm in diameter. The measurement ranges of DLS and laser diffraction are similar, but DLS excels in measuring the smallest droplets and micelles. Additionally, DLS instruments are typically designed for samples in cuvettes 1-3mL in volume, making DLS useful in sample-limited applications. DLS determines particle size from measuring light fluctuations occurring over time. The speed at which particles move due to Brownian motion, and thus the intensity fluctuation frequency, is a

function of particle size. DLS instruments measure intensity fluctuations over a specified time and use an autocorrelation function and the Stokes-Einstein equation to convert the fluctuations into a particle size distribution (McClements, 2007). A sample temperature (e.g., 25 °C) must be specified during DLS because temperature is directly related to the hydrodynamic diameter in the Stokes-Einstein equation (Eskandarloo et al., 2018; Tummons et al., 2016). The user must also provide the refractive index of the continuous phase, typically water ($n = 1.33$), and the dispersed phase, typically oil (hexadecane, $n = 1.434$). DLS instruments can provide droplet distribution data as a function of intensity, the measured value, or volume and number transformed values. However, Bhattacharjee and others suggest that droplet size should be deduced from the intensity data and that volume and number results should only be used as supporting information (Bhattacharjee, 2016). With respect to bilgewater, the applications of DLS are limited due to the inability in measured droplets and colloids larger than 1 μm in diameter. Bilgewater contains a wide range of droplet sizes, based on the conditions of the bilgewater. Droplets larger than 20 μm have been observed in bilgewater; therefore, laser diffraction is the recommend method for analyzing bilgewater.

2.4.2.4 Electrical pulse counting

Electrical pulse counting (i.e. electro-zone sensing or “Coulter Counter” technique) is based on measurements of changes in the electrical conductivity of a dilute emulsion as it passes across a small orifice. A variety of orifices, or apertures, are available and dictate the size of droplets that can be overserved. In a recent report looking at oil droplets in sea water, Brakstad et al., used 100 μm aperture to observe droplets 2.0-60 μm in diameter and a 280 μm aperture to observe droplets 5.6-100 μm in diameter (Brakstad et al., 2018).

When oil droplets are pulled through the aperture, the electrical current between the electrodes decreases because oil has a much lower electrical conductivity than water. Each time a droplet passes through the orifice, the instrument records a decrease in current, which is then converted into an electrical pulse. Droplet concentration is calculated by counting the number of pulses that pass through the hole per unit volume of emulsion, and particle size distribution is determined by measuring the height of each pulse, which is proportional to the volume of a particle. Electrical pulse counting can measure particles that range from 0.4 to 1,200 μm in diameter. Similar to laser diffraction, the droplet concentration must be lower than 0.1 wt% (McClements, 2007). While electrical pulse counting is suitable for measuring bilgewater, light scattering techniques and microscopy are more commonly employed to measure droplet size.

2.4.2.5 Ultrasonic spectrometry

Ultrasonic spectrometry is based on measuring the change in ultrasonic velocity as a function of frequency (MHz) as it travels through a medium (McClements, 1997; McClements, 2007). The emulsion ultrasonic spectrum depends on the particle size distribution and concentration of oil droplets. An emulsion sample is placed in a temperature-controlled chamber and its ultrasonic spectrum is measured from about 0.1 to 150 MHz (McClements, 1997; McClements, 2007). Instruments are equipped with software that determines the particle size distribution by fitting the experimental measurements to a theoretically predicted spectrum. Commercial instruments are capable of determining particle diameters within 10 nm to 1,000 μm . Compared to other

techniques, more concentrated emulsions samples (1 to 50 wt%) can be used in the instrument (McClements, 2007). It should be noted that converting the attenuation spectra into a size distribution involves a high level of mathematical complexity and many emulsions properties, such as acoustic extinction curve, thermal conductivity, heat capacity, and thermal expansion (Dukhin and Goetz, 2005). Therefore, ultrasonic spectrometry is not recommend for bilgewater characterization.

2.4.2.6 Confocal laser scanning microscopy (CLSM)

The morphology of emulsions is well studied in food sciences (McClements, 2007); however, in the context of bilgewater treatment, emulsion morphology characterization is lacking. Confocal laser scanning microscopy (CLSM) is a technique that offers an opportunity to observe distributions of emulsions by obtaining three-dimensional (3D) images of samples. It functions via extracting a series of two-dimensional (2D) slices in the vertical direction (z-stack) without the need to physically section the specimen and creates a composite 3D image from the extracted 2D images (Figure 2-4). 3D images are used to determine the spatial location of the droplets in an emulsion, so that it is possible to obtain detailed information about flocculation microstructures (Chen et al., 2013). CLSM is often used to examine the location and movement of specific components within an emulsion by using fluorescent probes to tag specific molecules or phases. For example, one study used Nile red to track the oil phase (Chen et al., 2013), because this dye has been shown to interact with the oil phase without interfering with emulsion development (Malassange-Bulgarelli and McGrath, 2009).

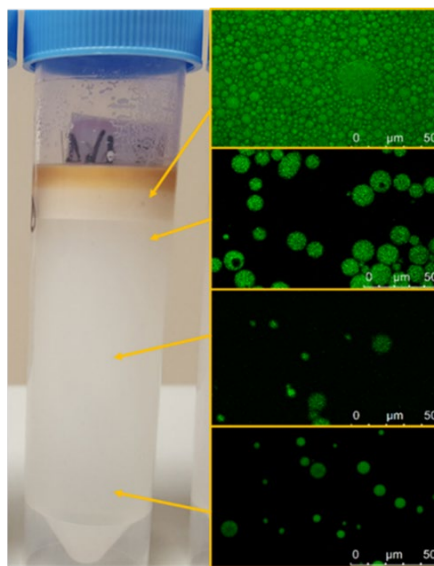


Figure 2-4 An example of CLSM images of emulsion size distribution according to the height of a prepared bilgewater sample. The sample was prepared with 100 ppm Triton X-100 solution and 10% NSBM #4 at 23 °C

2.4.2.7 Nuclear magnetic resonance (NMR)

Nuclear magnetic resonance utilizes interactions between radio waves and the nuclei of hydrogen atoms to obtain information about the microstructure of emulsions. An emulsion is placed in a

static magnetic field gradient and is exposed to a series of radio frequency pulses. The applied pulses can align or reorient hydrogen nuclei with respect to the magnetic field, generating a detectable NMR signal. A reduction in signal amplitude over time can determine molecular movement. Various NMR techniques have been used to evaluate emulsions across a range of fields. Diffusion ordered NMR spectroscopy (DOSY NMR) separates signals corresponding to diffusion coefficients, thus allowing microstructural characterization of emulsions including the type and relative distribution of oil and surfactant in emulsion droplets (Awad et al., 2018). NMR, specifically pulse-field gradient, has been extensively used in food science and crude oil emulsion characterization to size emulsions (Hollingsworth and Johns, 2003; Marques et al., 2018). Further, pulse field gradient NMR (PFG NMR) affords the observation of coalescence and sedimentation of unstable emulsions using simultaneous measurements of droplet size distribution and brine profiles (Marques et al., 2018). Lingwood et al. have applied PFG NMR at low magnetic field strength to detect and measure liquid behavior within the dispersed phase of an emulsion (Lingwood et al., 2012). Overall, the various NMR techniques provide very high sensitivity to small changes in composition and/or concentration, as well as the ability to investigate samples under dynamic conditions. Limitations of NMR analysis of emulsions result from the general need for deuterated solvents or dilution with solvent, relatively specialized equipment, and constraints based on small sample tube (e.g. transfer to NMR tube may disrupt native emulsion equilibrium).

2.4.2.8 Microfluidics

Microfluidics allows for the creation and study of well-defined emulsions. Reproducible generation of droplets of a user defined size and composition is possible using two-phase microfluidics (Teh et al., 2008). Furthermore, microfluidics allows for the control and manipulation of droplet-droplet interaction using passive and active methods in both flowing and stationary arrangements. Passive coalescence has been explored in a variety of setups such as junctions, where droplets collide (Christopher et al., 2009), and decompression chambers (Bremond et al., 2008), where droplets expand, collide, and fuse. Active methods such as electrocoalescence are also commonly employed to achieve droplet merging (Ahn et al., 2006; Gu et al., 2011). The majority of the microfluidics literature is focused on the manipulation of W/O emulsions because it allows for the manipulation of cells, proteins, DNA, and other materials of biological interest. The literature contains a handful of reports on the use of microfluidics for O/W emulsions. Krebs et al. studied the coalescence dynamics in flowing O/W emulsions using trajectory analysis (Krebs et al., 2013). In addition, a recent report from Abedi et al. describes the effect of droplet size on emulsions destabilization. The authors trapped hexadecane droplets in a chamber and tracked droplet coalescence using image analysis as the temperature was cycled (Abedi et al., 2019). Microfluidics is best suited for the creation and study of idealized bilgewater emulsions at the droplet scale. Lab-on-a-chip investigations of extracted bilgewater are feasible but have not currently been developed.

2.4.3 Interface characterization

2.4.3.1 Interfacial tension determination

Dispersion of oil droplets is facilitated when the oil/water interfacial tension is low. The presence of an emulsifier in the oil/water matrix decreases the interfacial tension and minimizes the effects

of interfacial forces (Al-Shannaq et al., 2015). The interfacial tension of emulsion samples can be measured using a pendant drop method and a standard goniometer (e.g., Model 250-F4, Rame-Hart Instrument Co.) (Figure 2-5). A microsyringe is filled with each of the test liquids and then dispensed until a hanging pendant droplet is produced. The surface tension of the sample liquid is determined based on the shape of the droplet as quantified by the software (e.g., DROPImage Advanced v2.6) (Tummons et al., 2016). Interfacial tension can also be measured using a Du Noüy ring tensiometer where the force it takes to pull a platinum ring through a liquid-liquid interface is precisely recorded. This method is established in the literature (McClements, 2015). The preferred method for measuring oil/water interfaces with very low interfacial tensions is the spinning drop method. This method correlates the interfacial tension with the distortion of a droplet under centrifugal forces and has a measurement resolution of 10^{-4} mN/M (Drelich et al., 2002).

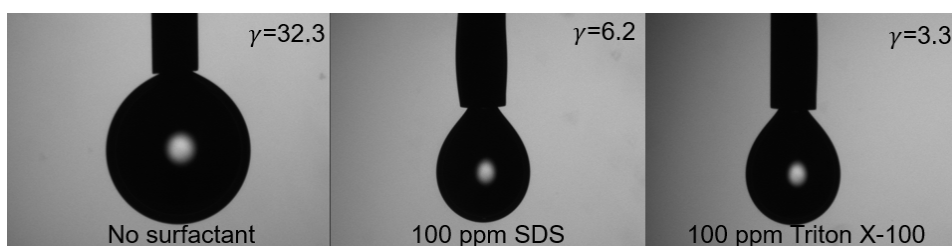


Figure 2-5 Photograph of W/O pendant drops for no surfactant, 100 ppm SDS and 100 ppm Triton X-100 at 10^{-4} M NaCl.

2.4.3.2 Zeta potential (ζ) measurement

In the presence of ionic emulsifiers or when the particle is sufficiently small ($< 1 \mu\text{m}$), a double layer will form around an emulsion droplet. This double layer creates a repulsive effect between oil droplets, which can be related to the zeta (ζ) potential. Zeta potential is the measure of the electrical potential of individual particles within an emulsion. When the zeta potential is high ($\pm 25\text{mV}$ or more), repulsive forces are expected to exceed attractive forces, which keeps the oil droplets dispersed (Remington, 2006). On the other hand, if the zeta potential is below $\pm 25\text{mV}$, particles are not electrostatically stabilized which can lead to flocculation or coalesce (Roland et al., 2003). Zeta potential is most commonly measured using phase analysis light scattering or electrophoretic light scattering techniques.

2.4.4 Oil characterization

2.4.4.1 Oil density and viscosity

The properties of dispersed oils can play an important role in bilgewater emulsion stability and separation efficiency. For example, a study by Sokolovic et al. found that coalescers are more effective at removing oil with low densities (Sokolović et al., 2010). Measurements of oil density and viscosity are simple and inexpensive. To measure oil density, a hydrometer is typically used following methods outlined in ASTM D287; however, handheld digital density meters are also commercially available. Likewise, oil viscosity can be measured using a simple U-tube viscometer where the time it takes for an oil to travel between two marks of a calibrated capillary is related to viscosity. However, oil viscosity and other rheological properties can be

measured using more advanced rheometers that work on principles of shear or extensional stresses (Sun and Gunasekaran, 2009).

2.4.4.2 Fourier transform infrared spectroscopy (FTIR)

Transmission fourier transform infrared spectroscopy (FTIR) spectroscopy is based on the observation of IR that passes through an emulsion sample; both the absorbed and transmitted radiation is observed (Silva et al., 2012). Each sample presents characteristic absorption peaks that correspond to the frequencies of vibration between the bonds of the atoms in the material. Therefore, FTIR can identify the chemical composition of different materials. In addition, the size of the peaks can provide information on the relative amount of material present in the sample (Silva et al., 2012). FTIR spectra can also determine transformation (or degradation) of organic compounds present in bilgewater (Eskandarloo et al., 2018). Typically, FTIR spectra are collected at the mid-IR region, 4000–400 cm^{-1} .

2.4.5 Bilgewater emulsion stability testing methods

Emulsion stability is generally defined as the ability to resist changes in properties over time. This can be measured differently depending on the field of study. Most commonly, emulsion stability is measured based on changes in droplet size distribution, turbidity, oil separation, viscosity, and creaming rate. In a bilgewater context, emulsion stability can be defined in two ways, 1) kinetic stability and 2) coalescence stability; each with their unique impacts on bilgewater treatment processes.

Kinetic stability is defined as the ability for emulsion droplets to stay suspended in the bulk phase. Emulsions that are kinetically stable are difficult to process because the droplets are not easily separated by gravimetric methods, requiring secondary treatment (e.g., membrane filtration). Kinetically stable emulsion may quickly foul membranes or absorbents adding to the cost of bilgewater treatment.

Coalescence stability is defined as the ability for emulsion to resist coalescing. Emulsions that have coalescence stability may separate into a cream layer but will not coalesce into a separate oil phase. Understanding how to mitigate coalescence stability is important for reducing the volume of stored waste oil and to avoid fouling sensors and other OPA equipment with cream. In fact, interviews with in-service engineering agents (ISEAs) responsible for OPA have revealed that coalescence stability is a significant concern for bilgewater treatment processes.

These types of emulsion stability are not mutually exclusive. Figure 2-6 demonstrates bilgewater emulsions can be kinetically stable without showing coalescence stability or vice versa. This is because each type of stability can depend on different factors. For example, surfactant transport and absorbance kinetics can be very important to coalescence stability but less important for kinetic stability. Likewise, interfacial tension and homogenization energy are very important for kinetic stability but may not have a large influence on coalescence stability.

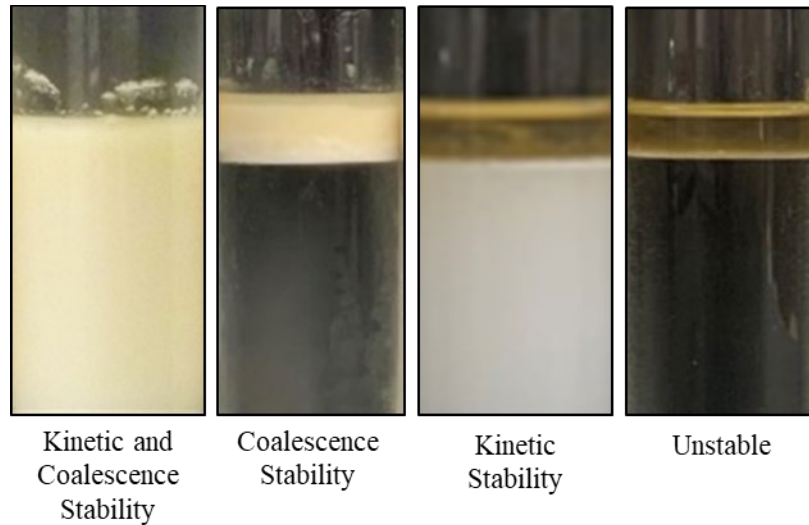


Figure 2-6 Examples of different types of emulsion stability in simulated bilgewater emulsions

2.4.5.1 Creaming stability measurement

Creaming (or sedimentation) is a reversible process driven by density differences between the oil and aqueous phases. Creaming index (CI) is a method of determining creaming visually and is described by Eq. 1-1 (McClements, 2007),

$$CI (\%) = H_L/H_E \times 100 \quad \text{Eq. (1-1)}$$

where H_L is the height of lower serum layer and H_E is the height of total liquid consisting of upper creaming, the middle emulsion, and lower serum part (H_L). For the test, the emulsion to be analyzed is placed in a transparent test-tube, gently agitated to ensure homogeneity, and then the heights of boundaries formed between layers are measured at regular time intervals until the CI is constant at which point $CI = CI_{\text{final}}$ (McClements, 2007). The slope of CI over time can be used to determine the rate of creaming (creaming velocity) ($v = dCI/dt$) in order to characterize the creaming stability of an emulsion (assuming no changes in particles size) (McClements, 2007).

Light scattering, or turbidity, can also be used as a quantitative approach to measuring creaming rate. Commercial products can detect destabilization phenomena such as particle migrations (sedimentation and creaming) and particle size variations (coalescence and flocculation) 20 to 50 times faster than visual observation. For example, the Turbiscan Lab (Formulation, Worthington, Ohio) quantifies emulsion stability using backscattering for samples with up to 60% v/v oil and droplets between 0.1 μm and 1 mm in diameter. By scanning an emulsion sample many times over a 24 hours period, it is possible to obtain a rate of emulsion stability or instability (Roland et al., 2003).

2.4.5.2 Coalescence stability and accelerated coalescence test

One of the most common ways of determining coalescence stability of an emulsion sample is measuring the height of separated oil phase over time. This can be done using image analysis or by measuring the separated oil gravimetrically. In food science, coalescence stability is often measured using the accelerated coalescence test (McClements, 2007). This is done by monitoring the change in droplet size distribution after the emulsion is centrifuged at a specific speed (>25,000 rpm) and time. The coalescence stability is characterized in terms of the minimum centrifugal force that the emulsion can tolerate and the duration it will endure at a particular speed before coalescence occurs. Initially, droplets form a cream layer where they are forced into close proximity. However, if the centrifugal force is sufficiently high, the droplets will be forced into even closer proximity and the interfacial layers will be ruptured (McClements, 2007). A critical osmotic pressure (P_{OSM}^{CR}) can be measured experimentally (Eq. 2-2),

$$P_{OSM}^{CR} = \frac{\Delta\rho g (V_{Total} - V_{Released})}{A} \quad \text{Eq. (2-2)}$$

where $\Delta\rho$ is the difference in the mass density between the continuous and dispersed phases, g is the acceleration, V_{Total} is the total volume of dispersed phase in the emulsion, $V_{Released}$ is the volume of dispersed phase released during centrifugation, and A is the cross-sectional area of the centrifuge tube. The accelerated coalescence test is commonly used to monitor the coalescence stability of food emulsions but should be used with caution as the correlation with long-term coalescence stability could vary (Tcholakova et al., 2005).

Droplet size characterization can also be used to determine the coalescence stability of a bilgewater emulsion. The most direct approach is to place an emulsion sample on a microscope slide and monitor the droplet size distribution over time using computer software or manually. Additionally, an oil droplet can be released into the aqueous phase of a sample toward the oil layer and the time from when the droplet contacts the oil layer to the time coalescence occurs can be measured to determine time of coalescence (Llamas et al., 2018).

2.4.5.3 Electrochemical microsensors for in situ monitoring of chemical compounds

Needle-type electrochemical microsensors (e.g., microelectrodes) have been used for constructing one-dimensional microprofiles of chemical compounds in many soft samples (e.g., sediments, biological tissues, and biofilms). By penetrating the electrode sensor tip into the samples, the technology can provide non-destructive and *in situ* measurements of chemicals of interest. Such measurements include pH, oxygen, free chlorine, oxidation-reduction potential (ORP), conductivity, heavy metals (e.g., Zn^{2+} , Cd^{2+} , and Pb^{2+}), and other ions (e.g., NH_4^+ , NO_2^- , NO_3^- , and Na^+) (Lee et al., 2017). Using the microsensors, various kinetic parameters including net specific consumption or production rates (k) and fluxes (J) can be estimated using Fick's law (Eq. 2-3),

$$J = -D \frac{\partial C}{\partial z} \quad \text{Eq. (2-3)}$$

where J is a flux rate (mol/cm²·sec or mg/cm²·sec), D is substrate diffusion coefficient (cm²/sec), C is a concentration (mol or mg/L) at a given depth (μm), and z is the depth (μm). Additional microsensor applications include studying biofilms, corroded materials (Ma et al., 2018), photocatalytic metal surfaces (Islam et al., 2017), and plants (Church et al., 2018). Recently, Church et al. (2017) applied needle type pH microsensors to understand dynamics of pH at the interface between oil and water via vertical pH microprofile measurements. The study revealed pH gradients approaching the oil/water interface, which can be used to determine how mass transport across on oil/water interface affects emulsion stability (Church et al., 2017).

2.4.5.4 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is a common and relatively straightforward thermal characterization technique used to determine physiochemical properties of undiluted samples by monitoring thermal exchanges between a sample and reference either (i) with time during a constant temperature or (ii) during a heating or cooling program. DSC has been used to characterize the morphology of emulsions. In a classical DSC test, an emulsion is subjected to regular cooling and heating cycles and the freezing and melting of the dispersed oil droplets are observed (e.g., surfactant emulsion stabilization test at -40°C/40°C) (Clausse et al., 2005a). Using the thermogram obtained by a DSC experiment and microscopic analysis, it is possible to correlate droplet size and crystallization temperature for emulsions (Clausse et al., 2005b). It was observed that the starting freezing point increased with increasing water content in the emulsion, and the crystallization temperature decreased with decreasing particle size (Clausse et al., 2005a). DSC of emulsions, and by comparison with the thermogram of each individual starting component, allows for the identification of emulsion type, amount of water, presence of a solute, stability, and droplet size (Dalmazzone et al., 2009). Droplet size determination from very concentration crude oil emulsions were elucidated by comparison of DSC and microscopy to identify a correlation between freezing point temperature and droplet size (Clausse et al., 2005a). Evolution of water content in W/O emulsions is often monitored by freezing point deviation (Lignel et al., 2014). In fact, DSC has recently been demonstrated to follow the evolution of W/O emulsion behavior in microgravity environments on board the international space station (Drelich et al., 2018). The crystallization of aqueous droplets in water-in-crude oil emulsions were determined via DSC such that crystallinity rate increased with decreasing temperature (Derkach et al., 2018).

2.4.5.5 Other emulsion stability testing methods

In addition to the methods already discussed, there are several emulsion stability tests focused on W/O emulsions, which could be modified for bilgewater water emulsion characterization. These tests are outlined in Table 2-2.

Table 2-2 Physical experimental methods for emulsion characterization

Method	Purpose of Analysis	Methodology	Pros	Cons	References
Field bottle test	Observe phase separation and measure emulsion stability over a given time	Dilution of an emulsion with a solvent mixed with a demulsifier to observe phase separation	• Simple and commonly-used field technique • Standard American Society for Testing Materials (ASTM) method (ASTM 4007) available for determining sediments and water content in a crude oil emulsion • Screening test for potential demulsifiers	• Requires elevated temperatures and centrifugation to enhance separation. • Not designed for oil in water bilgewater emulsions • Bottle tests are typically performed under static conditions that contrast with the dynamic environments emulsions occur	• ASTM D4007
Environmental stress tests	To determine the effect of environmental stresses on emulsion stability	Vary pH, ionic strength, solution composition, temperature, and joint-mechanical forces to expand on emulsion parameters	Many methods are available: • Storage in temperature/light-controlled environments • Determination of resistance to mechanical forces by way of shakers, vibration, and mixing • Thermal processing easily accessible	• Other factors may influence analysis of adjusted parameters because not all methods can be quantitatively isolated from other environmental factors	• Niu et al. 2015 • Gu et al. 2005
Emulsion microstructure analysis using freeze-fracture electron microscopy	Characterize emulsion microstructures	Use transmission electron microscope (TEM) and scanning electron microscope (SEM) to produce high-resolution images of molecule	• Obtains high-resolution observations of microstructure, crystalline state, and projection of specimen	• Sample preparation is time-consuming and proper pre-experiment procedures must be followed to prevent sample alteration • Expensive instrumentation	• Palanuwech and Coupland 2003 • Sakai et al. 2001 • Soppe et al. 2012

2.5 Characteristics of bilgewater emulsions

A complete understanding of bilgewater components and their behavior is required to improve treatment strategies. Therefore, this section presents a review of bilgewater characteristics based on data from several bilgewater studies conducted in locations around the world, as well as data from a major sampling event in the 1990's to support the Uniform National Discharge Standard rule development (U.S. EPA, 1999b). Furthermore, a survey was conducted to identify commonly used emulsifiers on U.S. Armed Forces' ships. Challenge solutions used for testing oil/water separators are also presented. Variability in bilgewater quality from ship to ship makes accurate representation of bilgewater quality very difficult; therefore, the goal of this review is not to provide quantitative characteristics of bilgewater, but to demonstrate the range of bilgewater composition using actual data points.

2.5.1 General bilgewater characteristics

A literature survey was performed to identify general characteristics of bilgewater. A majority of bilgewater treatment studies used artificial bilgewater to allow for more controlled experiments; however, a handful of studies have reported pH, oil content, chemical oxygen demand (COD), total organic carbon (TOC), total suspended solids (TSS) and conductivity of actual bilgewater samples (Table 2-3). The pH of bilgewater in these studies were fairly neutral and ranged from 6.8 to 9.0. Oil content, on the other hand, displayed large variation from study to study, ranging from 36 to 2,953 ppm. Suspended solids and conductivity also varied greatly between studies.

Several studies that highlights the variability of bilgewater were conducted in the 1990's to support the development of the Uniform National Discharge Standard (UNDS) for the U.S. Armed Forces. This information is available in Appendix A of the Final Rule and Technical Development Document of Uniform National Discharge Standards (EPA-842-R-99-001). The data shows tremendous variability in bilgewater quality. For example, bilgewater from five different ships during a sampling event in 1991 contained total suspended solids concentrations that ranged from 34 mg/L to 2,684 mg/L. Likewise, oil and grease concentrations ranged from 37 mg/L to 2,593 mg/L and COD concentration ranged from 660 to 2,800 mg/L. Perhaps the best representation of the variability of bilgewater characteristics is from a 2 year sampling event from 1993 to 1995, which analyzed 45 samples for oil and grease and found a minimum concentration of 5 mg/L and a maximum of 12,900 mg/L with a standard deviation of 2,234 mg/L. Large variability in bilgewater characteristics makes predicting emulsion stability difficult. Therefore, it is important to develop a firm fundamental understanding of factors which contribute to bilgewater emulsion stabilization so effective treatment technologies can be developed.

Table 2-3 General Characteristics of Bilgewater

Reference	(Ulucan and Kurt, 2015)	(Asselin et al., 2008)	(Vyrides et al., 2018a)	(Tomaszewska et al., 2005)	(Chanthamalee et al., 2013)	(Emadian et al., 2015)	(Gryta, 2020)	(Santisi et al., 2015)	(U.S. EPA, 1999b)
pH	6.95	7.09	7.5-8.5	Not reported	6.8-7.4	8.0-9.0	Not reported	6.9	Not reported
Oil content (PPM)	338	800	Not reported	107	58-976	-	124-360	36	10-2953
Organics (mg/L)	COD: 1033	COD: 3400	COD:2,900-12,800	TOC: 1765	Not reported	COD:20-200	TOC: 138-400	Not reported	COD: 520-2800 TOC: 39-570
TSS (mg/L)	295	543	800-1200	Not reported	Not reported	220-1760	NR	Not reported	41-2684
Conductivity (mS/cm)	31.7	0.67	38.1	1.8	4.22-6.25 ^{a)}	Not reported	5.8-5.9 ^{a)}	8.4 ^{a)}	Not reported
Sample description	Stabilization tanks Haydarpasa port waste acceptance plant	Washings of bilges in Quebec Canada	Bilgewater from Ecofuel Ltd in Zygi, Cyprus	Ship bilgewater sample	Bilgewater from small fishing vessels in Sing Amnuai Port, Thailand	Bilgewater from cargo ships at Amirabad port, Iran	Bilgewater collected from Szczecin harbor, Poland	Bilgewater from passenger ship, Milazzo harbor, Italy	U.S. Navy ship bilge water

^{a)} Reported in TDS

2.5.2 Identification of bilgewater surfactants

As discussed earlier (Chapter 1), identification of surfactants in bilgewater is crucial to understanding emulsion stabilizing mechanisms and determining effective treatment methods. However, no studies have reported the type or concentration of surfactants found in actual bilgewater. Therefore, synthetic bilgewater mixtures have been developed based on qualitative data collection, such as personnel interviews and maintenance observations.

In addition to personnel and expert interviews, shipboard procurement information has recently been identified as a method to determine potential bilgewater surfactants. Procurement information was queried to determine surfactants and cleaners available for purchase and the volume procured. A primary assumption of this approach was that the larger the quantity of surfactant procured, the more likely it will be found in bilgewater. The top ten cleaners identified through this analysis accounted for 73% of the total procurement volume, which are provided in Table 2-4. For those cleaners with military specifications (MIL-F and MIL-PRF), the primary surfactants are subject to change considering military specifications are performance based, thus not necessitating specific composition but rather performance properties. Therefore, the surfactants and their combinations may vary. While aqueous film forming foam (AFFF) and laundry detergent are currently included in some standard bilgewater challenge mixtures (e.g., U.S. Navy), this analysis indicated that surface cleaners and gas path cleaners should also be included in future challenge mixtures and warrants investigation in bench scale emulsion studies.

Another important finding from the surfactant procurement information is that majority of the most procured cleaners contained nonionic surfactants; a significant finding because emulsions stabilized by nonionic surfactants tend to be more resilient to changes in salinity and certain types of treatment (e.g., electrocoagulation, coagulation/flocculation). Therefore, surfactants used in challenge bilgewater mixtures should also contain nonionic surfactants.

Table 2-4 Most Procured Cleaners and Detergents by Volume

NIIN	Description	Specification	Primary Surfactant ^{a)}
010560883	AFFF 6% (Chem Guard)	MIL-F-24385	Proprietary flourosurfactant Proprietary hydrocarbon surfactant
013647375	Super Blast Off (Elsco Inter. Inc.)	N/A	Cocamide diethanolamine
010568343	AFFF 3% (Chem Guard)	MIL-F-24385	Proprietary flourosurfactant Proprietary hydrocarbon surfactant
001817594	B&B™ 3100 (Vantage)	MIL-PRF-85704	Cocamide diethanolamine 1-buoxylethanol
13738849	Power Green ^{b)} (LHB Industries)	N/A	Proprietary surfactant blend
13738848	Power Green ^{b)} (LHB Industries)	N/A	Proprietary surfactant blend
014368050	Ecolab Solid Surge Plus NP (Ecolab # 6117905)	N/A	Alcohol ethoxylate (C12-16)
009265280	Clean All Purpose Cleaner (Skilcraft)	P-D-1747	Triton CG-110 1-(2-butoxy-1-methylethoxy) propan-2-ol Lauryl glucoside Cocamidopropyl betaine
012350872	Calla 855 (Zip-Chem Products)	MIL-PRF-85570	Alcohol ethoxylate (C10-14) Cocamide diethanolamine Capriloamphorionate
014472527	PRC Deck Cleaner (Werth Sanitary Supply Co. Inc.)	N/A	Alcohol ethoxylate (C12-14)

^{a)} Surfactant information is based on the cleaner safety data sheets and may not include all surfactant components.

^{b)} This cleaner was duplicated within the top ten list and is associated with a different issue volume

2.5.3 Standard synthetic bilgewater for OPA system testing

Due to the complexity and variability of bilgewater, control mixtures are prepared synthetically in order to reduce variability for laboratory scale testing. Insights for bilgewater composition can be derived from publicly available bilge characterization efforts and mixtures developed for equipment challenge testing. The data collected to develop these mixtures are from a wide variety of sources and is not readily comparable. Qualitative rather than quantitative data have played the largest role in developing the standard bilgewater mixtures. In fact, variability in bilgewater composition observed from historic characterization data was so severe, as indicated by the 1990's EPA data collection effort, no statistically significant conclusions could be made from existing data to elucidate difficult to treat bilgewater.

The MEPC.107(49) test fluid “C” is commonly used as a synthetic bilgewater to test pollution prevention equipment. Test fluid “C” contains a ratio of 947.8 g fresh water, 25 g of a marine residual fuel in accordance with ISO 8217, 25 g of a marine distillate fuel in accordance with ISO 8217, 0.5g of SDS, and 1.7 g of iron oxides with 90% of the particle size distribution less than 10 µm. Alternatives to the MEPC.107(49) test fluid “C” protocol have also been reported. Peng et al. and Korbahti and Artut used a synthetic bilgewater, based on the reports from the Canadian Navy, which composed of 1,000 mg/L diesel fuel, 800 mg/L lubricating oil, 200 mg/L hydraulic oil and 500 mg/L detergents and surfactants (Körbahti and Artut, 2010; Peng et al., 2005). Benito et al. used a synthetic bilgewater with 2,000 mg/L fuel and 200 mg/L diesel with 20 mg/L sodium dodecylbenzenesulfonate (SDBS) as a surfactant (Benito et al., 2007). In the commercial marine industry, synthetic bilgewater studies have used mixtures of deionized water, polysorbate (Tween 40®), motor oil SAE 30, acrylic paint, sodium chloride, metallic salts (Zn^{2+} , Cu^{2+} and Ni^{2+}) (Aswathy et al., 2016), and heavy metals (Durak et al., 2016). The standard challenge mixes used by the U.S. Navy to measure OPA system treatment performance are listed in Tables 2-5 and 2-6. These solutions use a variety of surfactants or a mixture of surfactants and chemicals that are likely to be found shipboard (Maribo, 2004).

Table 2-5 Composition of current standard challenge mixes for testing OPA system treatment performance in the U.S. Navy

Class	Standard Mix	Composition
Oil	Navy Standard Bilge Mix (NSBM) #4	50% v/v Diesel Fuel Marine, MIL-DTL-16884 25% v/v 2190 TEP Steam Lube Oil, MIL-PRF-17331 25% v/v 9250 Diesel Lube Oil, MIL-PRF-9000
Contaminants	Detergent Mix #4	50% v/v Type 1 General Purpose Non-Ionic Detergent, MIL-D-16791 25% v/v Commercial Detergent 2X “Ultra Tide” Original Scent (liquid) 25% v/v Degreasing Solvent, MIL-PRF-680, Type III
	Other	Aqueous Film-Forming-Foam (AFFF), 6%, MIL-F-24385 Arizona Test Dust, ISO-12103-1, A4 Coarse “Clorox” Bleach, 260 mg/L NaOCl Cloth Fibers, lint mostly 25-150 microns in length Acetone, “Barr Klean Strip” Product NO. GAC18 Degreasing Solvent, MIL-PRF-680, Type III Simulated Seawater: Salinity - 35,000 ppm (by mass) +/- 5% (Solar Salt, Medium Size)

Compositions of standard challenges mixes for OPA system performance tests were adapted from Maribo, 2004.

Table 2-6 Standard Bilgewater Influent Composition for Performance Testing

Test	Influent Mixture
Oily Water	200 ppm v/v NSBM #4
Oily Water	1,000 ppm v/v NSBM #4
Oily Water & Mixed Detergent	1,000 ppm v/v NSBM #4 100 ppm v/v Detergent Mix #4
Oily Water & Detergent	1,000 ppm v/v NSBM #4 100 ppm v/v Type 1 Detergent
Oily Water & Seawater	1,000 ppm v/v NSBM #4 35,000 ppm m/v Solar Salt, Medium Size
Oily Water & AFFF	1,000 ppm v/v NSBM #4, 100 ppm v/v AFFF
Oily Water & Mixed Chemicals	1,000 ppm v/v NSBM #4 0.17% v/v “Clorox” bleach (100 mg/L NaOCl) 0.17% v/v Acetone 0.17% v/v Paint Thinner
Oily Water, Mixed Detergent, & Particles	1,000 ppm v/v NSBM #4 100 ppm v/v Detergent Mix #4 100 ppm m/v Arizona Test Dust (coarse) 0.70 ppm m/v Cloth Fibers (lint 25-150 μ m in length)

Compositions of standard challenges mixes for OPA system performance tests were adapted from Maribo, 2004.

2.6 Conclusions

Currently, studies have only reported general bilgewater characteristics and treatment efficiencies. However, a comprehensive characterization of bilgewater emulsion stability is required for better treatment design and preventative bilge management practices. In particular, it has been found that emulsion stability depends strongly on the droplet size, type and concentration of surfactants, the viscosity of the continuous phase, and other environmental conditions. In fact, tight control of these parameters is necessary to promote emulsion destabilization mechanisms such as flocculation, creaming, Ostwald ripening, and coalescence.

In general, water quality parameters, like pH and conductivity, are useful for bilgewater characterization and is often reported in literature because of the simplicity, availability, and portability of the methods. However, water quality parameters only give clues to emulsion stabilization mechanisms and do not provide direct information on the stability of an emulsion. Droplet size distribution is essential for understanding emulsion stability and is well established in food, cosmetic, and pharmaceutical science. Yet, there is little information reported on emulsion droplet sizes in bilgewater due to the cost and immobility of methods like laser diffraction and dynamic light scattering. Also, the large amounts of solid particles found in bilgewater makes it difficult to distinguish between emulsion droplets and solid particles. Similarly, interface characterization is necessary for understanding emulsion generation and stability but is lacking in bilgewater research. Therefore, one of the key impediments to understanding bilgewater emulsions on a fundamental level is the difficulty of characterizing bilgewater emulsions under the ever-changing environment of a bilgewater tank.

In addition, bilgewater characteristics reported in literature were found to be highly variable. For example, oil concentrations in bilgewater has been reported as low as 5 ppm and as high as 12,900 ppm. The variability of bilgewater composition was mostly attributed to the variability of shipboard activities. In an effort to better understand the types of surfactants that might be present in bilgewater, a survey of U.S. Navy cleaners was conducted. As presented in Table 2-4, the cleaners were found to mostly contain nonionic surfactants. Additionally, the standard synthetic bilgewater mixtures used in the testing of OPA equipment was reviewed and reported. Therefore, this work will serve as an important reference for ongoing and future bilgewater research that aims to better understand emulsion behavior and to develop models that describe and predict these systems.

In summary, this review has provided a consolidated source for: bilgewater emulsion properties, common techniques for emulsion characterization, types of cleaners likely to be found in the bilge of ships, compositions of synthetic bilgewaters, and properties of extracted bilgewater. As the field continues to build a better understanding of the many factors that affect emulsion stability in these highly variable bilgewater systems, key analytical techniques and standard practices to measure bilgewater emulsions will emerge and ultimately provide insight for improvements in separation and remediation technologies.

Chapter 3: U.S. Navy Cleaner and Extracted Bilgewater Characterization

3.1 Introduction

Common bilgewater constituents and their behavior in solution is first required to achieve a complete understanding of Armed Forces emulsions and to design improved treatment approaches. Likewise, it is important to understand general trends in bilgewater composition to better simulate bilgewater emulsions for laboratory experimentation. In Chapter 2, a survey of U.S. Navy surfactants was presented as well as typical bilgewater characteristics based on literature and information on standard synthetic bilgewater mixtures currently used in the validation and testing of Oil Pollution Abatement (OPA) equipment. In this Chapter, cleaners identified in Chapter 2 were characterized for properties related to emulsion stabilization, including; critical micelle concentration (CMC), interfacial tension (IFT), micelle size, and zeta potential. In addition, extracted bilgewater samples were collected from three U.S. Navy vessels in late Spring 2019 and characterized using standard water quality procedures.

Historically, incomparable data collected from a wide variety of sources has hindered Armed Forces surfactant identification in the Navy. These include subjective interviews with shipboard personnel and technical experts, as well as objective, though varied, maintenance and bilgewater characterization data. Of these sources, qualitative rather than quantitative data have played the largest role in synthetic bilgewater composition development. In fact, variability in bilgewater composition observed from historic bilgewater characterization data is so severe, no statistically significant conclusions could be made from existing data to elucidate difficult to treat surfactants. Therefore, results from the extracted bilgewater was not used to develop a new simulated bilgewater composition but rather to validate existing formulations. Overall, the results from the analysis of U.S. Navy Cleaners and bilgewater demonstrated the variable and complex nature of shipboard emulsions.

3.2 Materials and Methods

3.2.1 Characterization of Surfactant Properties

3.2.1.1 Interfacial and Surface Tension Measurements

Interfacial tensions of the surfactant solutions were measured using a du Noüy Ring tensiometer (Sigma 701, Attension). Measurements were collected for each surfactant at 9 different concentrations ranging from 10 ppm to 10,000 ppm. 40 mL of mineral oil was carefully added to 80 mL of a surfactant solution to create a clean interface without any bubbles. A stainless steel ring was lowered into the oil portion of the sample and the tensiometer was blanked. Next, the interface was left undisturbed for 5 min to allow surfactant absorption at the interface to reach equilibrium. The tensiometer then automatically determined the location of the oil/water interface by lowering the ring through the sample until a change in force of 0.03 mN/m was detected. Next, the tensiometer measured the force required to pull the ring back through the oil/water interface and recorded the interfacial tension in mN/m. Since the ring disturbed the oil/water interface during the measurement, new samples were prepared for each replicate. The

du Noüy ring was cleaned with isopropanol and dried between each measurement and measurements were performed in duplicate.

Surface tension was measured using the same method as interfacial tension except that the measurement was made between the air-water interface rather than an oil-water interface. Surface tension measurements were made continuously until the surface tension reached equilibrium (generally within 10 min). Equilibrium was defined as 10 consecutive surface tension measurements with less than a 0.5 mN/m deviation. Experiments were conducted at room temperature (18-20°C).

3.2.1.2 Critical Micelle Concentration (CMC)

To calculate CMC, the equilibrium surface tension of a series of surfactant solutions were plotted against the surfactant concentration on a semi-log plot. The data was then fit with two linear regressions. One regression was used to fit the data below CMC, a regime where the IFT and surface tension are dependent on surfactant concentration. The second regression was fit to the data above CMC, where the surface tension are independent of surfactant concentration. The CMC was then calculated by determining the intersection between the concentration dependent and independent regions using Origin 2018b.

3.2.1.3 Micelle size and zeta potential

A Brookhaven's NanoBrook Omni instrument was used to perform dynamic light scattering (DLS) and phase analysis light scattering (PALS). To determine micelle size, a solution of surfactant or cleaner in water was prepared at a concentration above the CMC, transferred to a disposable 3 mL cuvette, and placed into the instrument for analysis. 10 measurements (5 min) were performed for each sample and reported as an average micelle size. For PALS measurements, the same surfactant solution was filtered with 0.25 µm syringe filter and introduced into the zeta potential measurement cell. A total of 10 replicates were collected and the average zeta potential was reported.

3.2.2 Characterization of Extracted Bilgewater Samples

3.2.2.1 Sample Collection

Bilgewater samples analyzed in this study were collected from three different cruisers in the U.S. Navy, stationed in Mayport, Florida late Spring 2019. 5 gallon samples were collected from the oily waste holding tank of each ship and stored in a plastic cubitainer (21YK28, Grainger). The samples were shipped over night to Naval Surface Warfare Center Carderock Division (NSWCCD). Upon arrival samples were inspected for leaks and stored in a dark refrigerator at 4°C to ensure sample preservation prior to analysis. Water quality was investigated within 1 week after samples were received and the experiments were run in triplicate to guarantee the accuracy and reliability of the data collected.

3.2.2.2 Water quality testing

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, UV₂₅₄, 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 (APHA) as shown in Table 3-1. N-Hexane Extractable Material (HEM) was also measured using EPA method 1664.

Table 3-1 Test procedures used for the water quality analysis of bilgewater samples

<i>Test</i>	<i>Procedure</i>
<i>Turbidity</i>	Nephelometric method
<i>Alkalinity</i>	Titration using 0.1 N HCl
<i>UV₂₅₄</i>	Absorption at 254 nm wavelength
<i>Total Nitrogen (TN)</i>	Persulfate digestion (HACH 10072)
<i>Total Phosphorus (TP)</i>	Molybdovanadate with acid sulfuric digestion (HACH 10127)
<i>Chemical Oxygen Demand (COD)</i>	USEPA reactor digestion method (HACH 8000)
<i>Solids analysis (TS and TSS)</i>	Samples dried at 104°C and 550°C
<i>EPA 1664 (HEM)</i>	Samples mixed with hexane, separated, and weighed

3.2.2.3 Oil analysis

For gas chromatography-mass spectroscopy (GC-MS) analysis, the oil layer was separated using a separatory funnel and centrifuged at 10,000 rpm for 5 minutes to remove any solid particles. The 0.1 mL of the extracts were then placed into a 2 mL GC vial and diluted in acetonitrile. These samples were then analyzed on an Agilent 7890B3 GC connect to a 5977C MS. The inlet temperature was 250 °C with a 1 mL per minute of He flow and a Restek Rxi-5ms column. An initial oven temperature of 50 °C was held for 3 min followed by a 5 °C/min increase to 250 °C, and then a 10 °C/min increase to 325 °C. The MS was used in electron ionization (EI) mode with a scan range of 45-500 amu, source temperature of 230 °C, and quadrupole temperature of 150 °C. Mass spectra from chromatographic peaks were compared against the NIST Mass Spectral Library and analyzed for common fragments to either fully identify or provide the class of molecule observed.

3.3 Results

3.3.1 Cleaner properties

Shipboard cleaners purchased in the largest volumes were identified from Navy procurement data (Chapter 2). Of the top ten cleaners, one cleaner was repeated (Powergreen, LHB industries) and one cleaner (all-purpose cleaner, Skilcraft) was deemed unsuitable for experimentation. The

8 detergents were characterized and properties relevant to emulsion formation were measured: CMC, IFT, micelle size and zeta potential (Table 3-2). Results showed that the composition and properties of the cleaners varied significantly. The primary surfactants listed on the cleaner's safety data sheet (SDS) revealed that all the cleaners contained nonionic surfactants; a significant finding because emulsions stabilized by nonionic surfactants tend to be more resilient to changes in salinity. Therefore, surfactants used in challenge bilgewater mixtures should also have an appropriate representation of nonionic surfactants. Many of the cleaners used alcohol ethoxylates or cocamide diethanolamines. Most of the cleaners also included builders like EDTA, tetrapotassium pyrophosphate, sodium citrate, and sodium carbonate to help buffer the water and prevent interaction between the ionic species within the water and the surfactants. However, despite the similarity of primary surfactants among the cleaners, the properties of each cleaner was significantly different.

The CMC of the cleaners varied from 87 to 3,824 ppm. The cleaners with the lowest CMCs contained large concentrations of pure surfactants based on their safety data sheets. For example, Type 1 detergent is >99% alkyl aryl polyether alcohol and had a CMC of 87. This indicates the CMC may be more influenced by the amount of surfactant used in each cleaner rather than the surfactant itself. Equilibrium surface tension above CMC was also determined for each cleaner. With the exception of Aqueous Film Forming Foam (AFFF) 6% (Chemguard), all cleaners had a similar surface tension, ranging between 25 and 30.5 mN/M. This could be due to the similarity of primary surfactants used in the cleaners. Micelle size and zeta potential were all very different between the cleaners, this is likely because these properties are influenced by the presence of builders within the cleaner.

Overall, cleaner characterization provided insight into the variability of cleaners used on Navy ships. Data collected informed the Chapter 5 study investigating the impact of a cleaners' IFT and CMC on emulsion stability as well as training a machine learning model for predicting bilgewater emulsion stability, as outlined in Chapter 7.

Table 3-2 Properties of cleaners used on U.S. Navy Ships

Cleaner	Primary surfactants	CMC (ppm)	Surface tension (mN/M)	IFT with NSBM #4 (mN/M)	Micelle size (nm)	Zeta Potential (mV)
AFFF 6% (Chem Guard)	• Fluorosurfactant (e.g., Capstone 1157)	3,399	15.2 ± 0.2	2.3 ± 0.6	55 ± 2	-24 ± 5
B&B™ 3100 (Vantage)	• Cocamide diethanolamine • 1-buoxxyethanol (alcohol ethoxylate)	361	25.0 ± 0.5	7.8 ± 0.1	21 ± 1	-28 ± 6
Super Blast Off (Elsco Inter. Inc.)	• Cocamide diethanolamine	934	27.7 ± 0.5	3.4 ± 0.1	111 ± 7	-63 ± 3
Calla 855 (Zip-Chem Products)	• Alcohol ethoxylate (c10-c14) • Cocamide diethanolamine • Caprioloamphorionate	328	27.3 ± 0.3	5.7 ± 1.1	5 ± 2	-39 ± 8
Power Green (LHB Industries)	• Surfactant blend	3,824	26.1 ± 0.7	3.5 ± 0.4	7 ± 5	-13 ± 3
PRC Deck Cleaner (Werth Sanitary Supply Co. Inc.)	• Alcohol ethoxylate	1,871	30.5 ± 0.1	7.7 ± 0.3	6 ± 1	-13 ± 2
Ecolab Solid Surge Plus NP (Ecolab # 6117905)	• Alcohol ethoxylate (c12-16)	98	27.4 ± 0.3	7.3 ± 0.1	23 ± 5	-15 ± 4
Type 1 Detergent (MILSPEC: MIL-D-16791)	• Alkyl aryl polyether alcohol	87	30.2 ± 0.4	2.5 ± 0.3	18 ± 1	-28 ± 6

3.3.2 Water Quality Characterization of Collected Bilgewater Samples

Table 3-3 presents the results for water quality characterization of the collected bilgewater samples. As expected, the physicochemical characteristics of bilgewater were highly varied between vessels. Bilgewater samples vary in pH from 5.1 to 8.4. Parameters such as conductivity, COD, and TSS also 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 (Church et al., 2019). 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 60 mg/L N and 120 mg/L P reported in Vyrides et al (2018) (Vyrides et al., 2018b). UV₂₅₄ is a water quality parameter used to measure dissolved organic matter. The UV₂₅₄ was the highest for bilgewater #1 and #2, which also had the greatest concentration of oil, demonstrating a significant amount of oil is able to solubilize within the water phase.

Table 3-3 Water quality characterization of collected bilgewater samples

Parameter	Bilgewater #1	Bilgewater #2	Bilgewater #3
pH	7.0 - 7.2	5.1	7.8 - 8.4
Conductivity ($\mu\text{S}/\text{cm}$)	16.3 ± 0.1	1.74 ± 0.05	24.0 ± 0.4
Turbidity (NTU)	$1,104 \pm 104$	$10,402 \pm 20$	52 ± 2.3
COD (mg/L)	1279 ± 87	$42,800 \pm 1,500$	547 ± 11
TS (mg/L)	$13,793 \pm 146$	$3,043 \pm 502$	$20,320 \pm 500$
TSS (mg/L)	$4,248 \pm 212$	$1,848 \pm 58$	256 ± 16
UV₂₅₄(cm^{-1})	0.22 ± 0.02	0.381 ± 0.00	0.08 ± 0.01
Alkalinity (mg/L CaCO_3)	230 ± 4.1	5 ± 0.0	92 ± 2.4
TN (mg/L N)	12 ± 3.6	18 ± 13.7	12 ± 1.3
TP (mg/L PO_4^{3-})	3.8 ± 0.1	12.6 ± 0.5	0.3 ± 0.1
HEM (ppm)	50,000	50,000	3,000

Figure 3-1 shows the collected bilgewater for the three ships. Bilgewater #1 and #2 were turbid with discrete oil phases on top of the bulk water; Bilgewater #3 presented a clear aqueous appearance. Bilgewater #1 also appears to have a darker oil phase. Another interesting observation is that the turbidity was ten times greater for bilgewater #2 compared to bilgewater #1; however, the bilgewater #2 contained less than half the amount of TSS. Therefore, emulsions were likely the cause for turbidity in bilgewater #2. This demonstrates how both the variability and variety of components might result in stable emulsion.

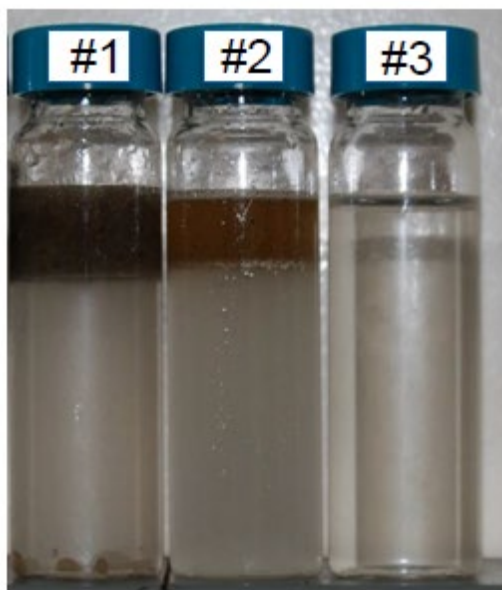


Figure 3-1 Photograph of bilgewater samples collected

3.3.3 Oil analysis

Figure 3-2 shows the GC chromatographs of the oil phase for bilgewater #1 and bilgewater #2. bilgewater #3 was not included because there was no detectable oil. Chromatographs of diesel fuel marine (DFM) (MIL-F-16884) and Navy Standard Bilge Mix #4 (NSBM #4) (composition discussed in Chapter 2) are also included in Figure 3-2 as a reference for the oils used in testing and validating OPA systems. The peaks found in DFM closely correspond to the peaks found in NSBM #4. This is due to the 50% composition of DFM in NSBM #4. It also shows other components of NSBM #4 contain hydrocarbons of similar chain length.

Bilgewater #1 corresponded closely with the chromatographs of DFM and NSBM #4, which contains DFM. This finding validated the use of NSBM #4 for simulated bilgewater emulsions for bench-scale investigations and full-scale system performance testing. Bilgewater #2 had similar peaks as NSBM #4 between 10-30 min. However, there were also a significant number of peaks with retention times larger than 30 min that were not found in NSBM #4, corresponding to compounds that are non-polar such as longer chain alkanes or alkenes.

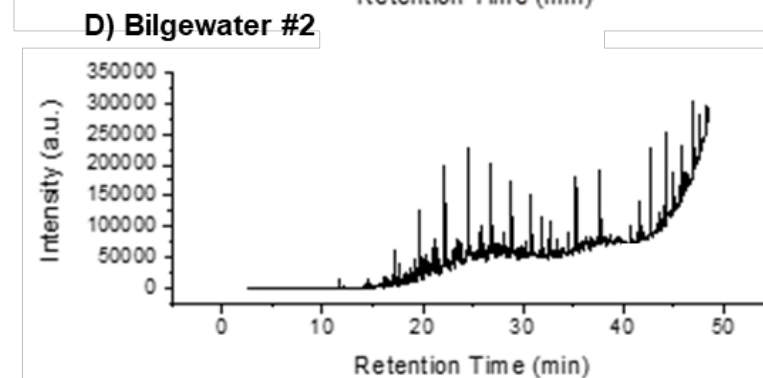
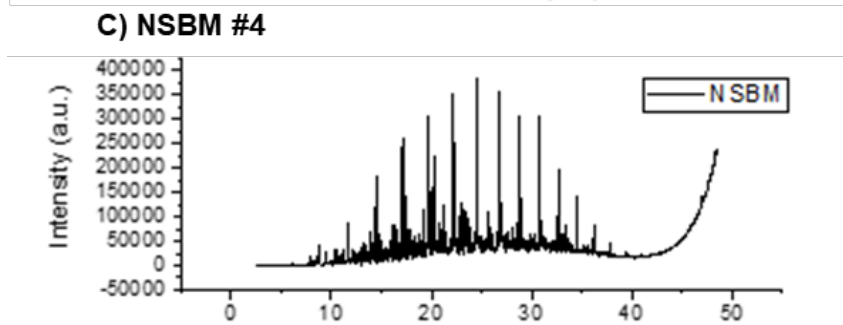
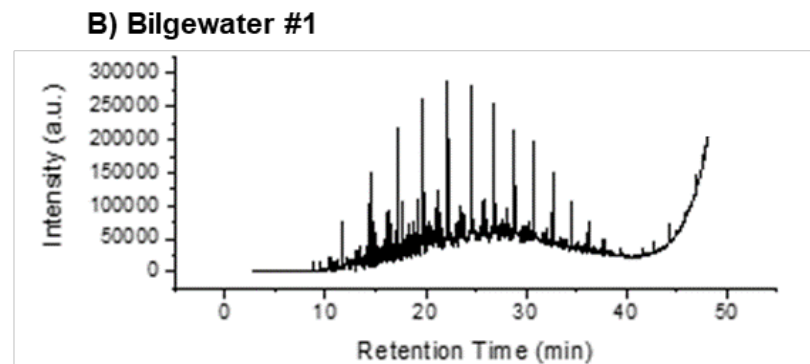
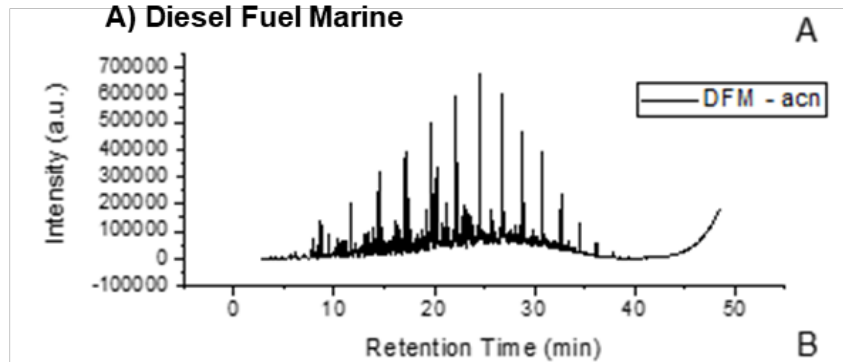


Figure 3-2 GC chromatographs of a) diesel fuel marine, b) bilgewater #1, c) NSBM #4, and Bilgewater #2 in acetonitrile. These samples were analyzed on an Agilent 7890B3 GC connect to a 5977C MS.

3.4 Conclusions

Cleaners identified in Chapter 2 were characterized for properties related to emulsion stabilization, including CMC, IFT, micelle size, and zeta potential. It was found that the primary surfactant between the cleaners were similar, mostly composed of alcohol ethylates or cocamide diethanolamines. However, cleaner properties varied significantly, likely due to the presence of builders and other compounds in the cleaners. The variability of cleaner properties are investigated in detail in Chapters 5 and 7 for correlation to emulsion stability.

Extracted bilgewater samples were collected from three U.S. Navy vessels in late Spring 2019 and characterized using standard water quality procedures. From the water quality characterization of the collected samples, it was possible to determine the physicochemical properties of bilgewater prior to collection and treatment on OPA systems. The variability of bilgewater quality has been reported in literature and the properties of the tested samples fall within the values summarized in Chapter 2. 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 TSS 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.

Results from the cleaner and extracted bilgewater analysis validated the use of detergent mix #4 and NSBM #4 for the preparation of simulated bilgewater emulsions. The cleaners used in detergent mix #4 were found among the highest procured by the Navy. In addition, the tested cleaners were found to only include nonionic surfactants, which is also the primary surfactant type in detergent mix #4. This is noteworthy because the current bilgewater standard used to test commercial oil-water separators, MEPC.107(49) test fluid “C”, uses a anionic surfactant that employs different emulsion stabilizing mechanisms (e.g. electrostatic vs steric). In addition, bilgewater #1 and #2 both had GC chromatographs similar to NSBM #4.

Chapter 4: Impacts of Environmental Conditions on Simulated Emulsion Stability

4.1 Introduction

In many disciplines, it has been demonstrated that the stability of oil-in-water (O/W) emulsions strongly depends on the physicochemical and thermodynamic properties of the mixtures (Church et al., 2019; Tadros et al., 2004). However, information related to the formation of bilgewater emulsions and the role of environmental parameters on emulsion formation and stability are 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 suspended solids (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 O/W emulsions under various environmental conditions and identify the governing parameters for O/W emulsion formation and separation in simulated bilgewater mixtures. Bilgewater emulsions were prepared using a Navy Standard Bilge Mix (NSBM) #4, 8 commercial off the shelf (COTS) cleaners identified in Chapter 2, and 2 neat surfactants. These surfactants were selected as representative emulsifiers commonly found in bilgewater. The effects of environmental parameters such as salinity (NaCl), SS (Arizona dust), temperature, and pH on emulsion formation and stability were analyzed; these parameters were selected based on the findings outlined in Chapters 2 and 3. These parameters were evaluated within common ranges found in bilgewater. 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).

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 work provided a data set for developing an emulsion stability prediction model (Chapter 7) 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.

4.2 Materials and methods

4.2.1 Emulsion preparation

Emulsion samples were prepared using 40 mL glass vials (GLC-01020, Qorpak, PA, USA) carefully cleaned to remove possible contamination that could affect result consistency. Prior to

sample preparation, vials were rinsed multiple times with hot water and soap (Dri-clean, Decon Labs, King of 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, NSBM #4 and DI water were used as immiscible phases. NSBM #4 constituents are 50% v/v Diesel Fuel Marine (DFM) (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 (discussed in Chapter 2): Type 1, Solid Surge plus, Calla, B&B 3100, Super Blast-off, PRC Deck Cleaner, 6% AFFF, and Power Green, Triton X-100, and sodium dodecyl sulfate (SDS). Emulsions were prepared by adding 10% (v/v) NSBM #4 to a seven times critical micelle concentration (CMC) solution (Table 4-1), and DI water in a vial for a total sample volume of 30 mL. Surfactant dosage used was significantly above CMC (7 times) in order to ensure micelle formation and complete coverage of the oil-droplet surface (Hsu and Nacu, 2003). 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 turned 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.

Table 4-1 Tested Cleaner Critical Micelle Concentrations (CMC)

Surfactant	Type	CMC (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

4.2.2 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 Chloride (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 in Chapters 2 and 3. As

shown in Table 4-2, 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 as described in section 4.2.1. 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 4-2 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

4.2.3 Bulk-water analysis

For measuring turbidity, the solution in the emulsion layer was carefully transferred into a cleaned glass cell (HACH, Product No. 2084900, CO, USA) using a pipette to avoid any possible oil mixing that could affect the final emulsion layer characteristics. Turbidity was measured after the 5 days of undisturbed conditions using a turbidimeter (HACH, 2100N, CO, USA) in accordance with Standard Methods (APHA).

4.2.4 Image-based analysis

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. Two different image-based analytical techniques were applied for investigating emulsion stability: droplet size distribution, grayscale profile, and relative oil separation (%).

Grayscale profiling is a non-destructive image analysis technique that displays a two-dimensional (2D) graph of the intensity of pixels along a line in a specific image (Ferreira and Rasband, 2012). 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 (Novales et al., 2003). For the analysis of emulsion samples, images were converted from RGB color into 8-bit grayscale using a Java-based image-processing program (ImageJ, NIH). Then, 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. 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 (Ferreira and Rasband, 2012). 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. However, low turbidity emulsions formed as a result of high emulsion destabilization also presented emulsion layers exhibiting low grayscale intensity values caused by the black background.

In addition to grayscale profiling, a time-course monitoring of changes in the oil layer height was conducted for 120 h. The relative oil layer height (%) for each emulsion sample was determined by measuring the height of the oil layer at the top of the sample using ImageJ. Oil separation (%) was calculated by dividing the height of the separated oil layer by the height of the oil before homogenization. As major changes in oil coalescence occurred within 1 day after homogenization, photos were analyzed every 2 h for the first 12 h, then every 24 h for the rest of the 5-day experiment.

4.3 Results and discussion

4.3.1 Emulsion Stability

4.3.1.1 Visual observation and relative oil layer height

Time-course visual observation was used as an initial method to evaluate the stability of emulsions by analyzing the behavior of the samples 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. Emulsion stability was highly dependent on surfactant type, temperature, and ionic strength (NaCl addition). Figure 4-1 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. Therefore, 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 produced 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 visual observations after 5 days for each cleaner/surfactant 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.

Mainly oil		Calla			PRC			Triton-X			6% AFFF			Blast Off		
Creaming + oil		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
Only creaming		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		Type 1			SDS			B&B			PG			Solid surge		
Creaming + oil		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
Only creaming		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															

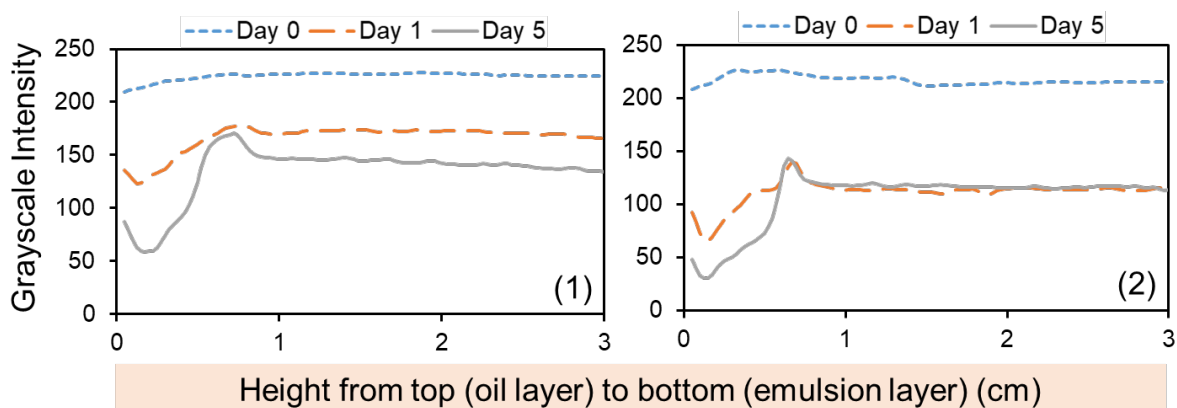
Figure 4-1 Summary of emulsion stability under all conditions Orange boxes indicate majority of oil was separated after 5 days, green boxes indicate partial oil separation, and white boxes indicate no oil separation after 5 days.

In general, the tested cleaners and surfactants 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 limited resistance of electrostatically stabilized emulsions to saline conditions. In addition, it was observed that emulsion coalescence increased with temperature. For example, 8%, 42%, and 67% of emulsions prepared with Type I detergent exhibited coalescence at 4°C, 25°C, and 35°C, respectively. Power green was more resistant to temperature changes, exhibiting similar emulsion stability for all conditions tested. Overall, visual observations indicated surfactant type, temperature, and salinity as having higher contributions to emulsion stability compared to pH and suspended solids.

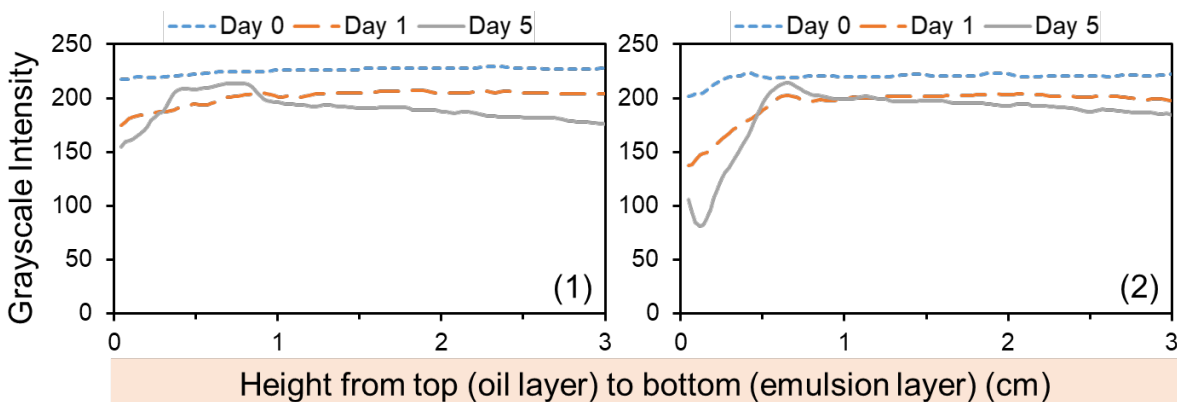
4.3.1.2 Grayscale profile analysis

Based on visual observations (Appendix B Figures B1-B3), Triton X-100, B&B, and SDS were selected for grayscale analysis as shown in Figure 4-2. For grayscale analysis, the top layer (creaming/coalescence) was considered from 0-1 cm and the bottom layer (emulsion) from 1–3 cm. At Day 0 (immediately after homogenization), all emulsion samples showed constant grayscale intensities independent of depth, approximately 225, regardless of surfactant type. For this reason, a grayscale intensity of 225 was considered to be the maximum intensity related to the highest emulsion stability. Clear oil separation was characterized by low grayscale intensities (<50) and the creaming area formed by the rising droplets presented grayscale intensities between 150 and 225, which was associated with the droplets being tightly packed together. As a result, the decrease in grayscale intensity of the emulsion layer indicates that the oil droplets raise and the bulk water becomes less cloudy (Novaes et al., 2003).

(a) 7×CMC Triton X-100



(b) 7×CMC B&B



(c) 7×CMC SDS

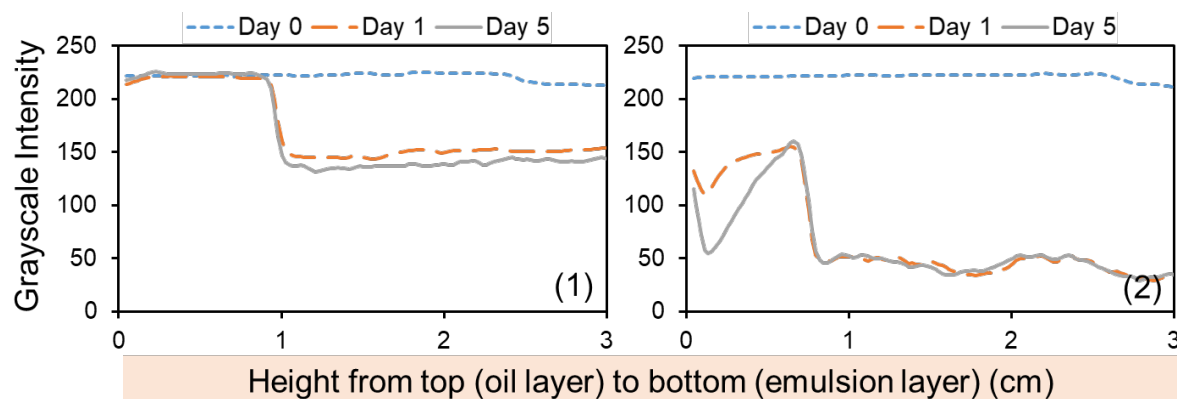


Figure 4-2 Time course evolution of the grayscale intensity profiles of emulsions prepared at 25°C with 7×CMC of (a) Triton X-100, (b) B&B, and (c) SDS using (1) DI water + surfactant (2) 35,000 ppm NaCl. 0 to 3 cm represent the depth of the sample from the surface. Zero to 250 represents the gray level intensity profile (0 – Black, 255 – White).

In Figure 4-2, the emulsion samples at Day 1 showed variations in the grayscale intensity of the oil and emulsion layers depending on the surfactant type and NaCl additions. In Triton X-100 emulsions (Figure 4-2a), the grayscale intensity of the emulsion layer decreased from 170 to 120 under NaCl addition, compared to the control sample. Additionally, the oil layer exhibited an intensity decreased from 120 to 65, indicating greater oil coalescence in high ionic strength conditions. In emulsions prepared with B&B (Figure 4-2b), the oil layer intensity decreased from 175 to 140, confirming higher oil separation by emulsion instability in saline environments. However, the intensity of the emulsion layer was not considerably changed even with the NaCl addition. For SDS emulsions (Figure 4-2c), the emulsion layer with the NaCl addition showed a grayscale intensity decrease from 145 to 50, indicating a considerably low cloudiness in the bulk water. A low grayscale intensity (< 50) in the emulsion layer can be related to a large separation of oil from water, decreasing the total oil droplet volume in suspension and can be considered a direct indication of emulsion instability. Additionally, the grayscale intensity in the top 1 cm of SDS emulsions without NaCl was 225, indicating no oil separation. After 5 days, the lowest grayscale intensities in the emulsion samples without NaCl were 145, 190, 135 (emulsion layer) and 55, 150, 225 (top layer) for Triton X-100, B&B 3100, and SDS, respectively. Under NaCl addition, the grayscale intensities were 120, 190, 50 (emulsion layer), and 30, 78, 50 (top layer), respectively. The results indicated that high salinity environments decrease emulsion stability, which was corroborated by the low intensities at the top area of the samples (e.g., increase in the tendency to coalescence).

Overall, the grayscale intensity profiles allowed the time-course monitoring of minor changes from top to bottom of the emulsion samples, which may not have been recognized with visual observation. These changes were a representation of the governing destabilization mechanism for each sample, thus providing an indication of the emulsion stability over time. Moreover, the results obtained through this method agreed with the findings from visual observation and droplet distribution.

4.3.2 Effect of Environmental Factors on Emulsion Stability

4.3.2.1 Ionic strength (NaCl)

For the tested cleaners and surfactants, the presence of high ionic strength conditions demonstrated a significant effect on emulsion stability. Figure 4-3 shows that of the 90 emulsion samples prepared with the attaching of ionic strength, 93% demonstrated a visual observation of a separated oil phase after 5 days. This is significantly greater than the 54% of the samples that showed oil separation without the addition of ionic strength. In particular, electrostatically stabilized emulsions (e.g., SDS) were observed to coalesce most rapidly. 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 4-2).

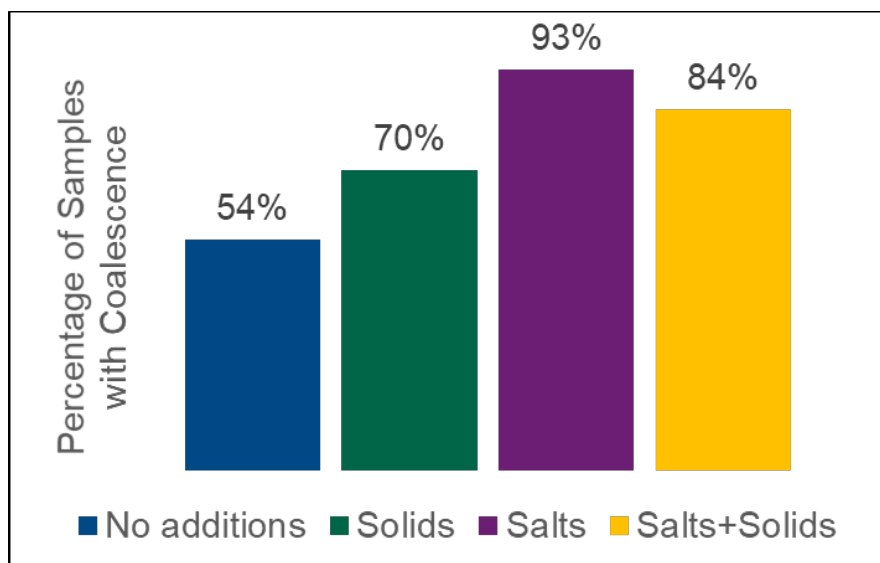


Figure 4-3 Impacts of suspended solids and salinity on emulsion stability based on coalescence

These results are in agreement with Church et al. (2017) and Moradi et al. (2010), which demonstrated the direct relationship between ionic strength and emulsion stability, concluding that salinity enhances emulsion separation (Church et al., 2017; Moradi et al., 2010).

Emulsion samples prepared at different NaCl concentrations without surfactant/cleaner was also performed to demonstrate the impact of ionic strength on emulsion stability. As shown in Figure 4-4, emulsion stability decreased with increasing NaCl concentrations, indicating that at sufficient ionic strength, major phase separation will likely occur. NaCl concentrations above 1,000 ppm resulted in coalescence and enhanced phase separation. Likewise, microscopic images showed a decreased in the droplet density of emulsion samples with high ionic strength, indicating increased oil coalescence and thus lower emulsion stability.

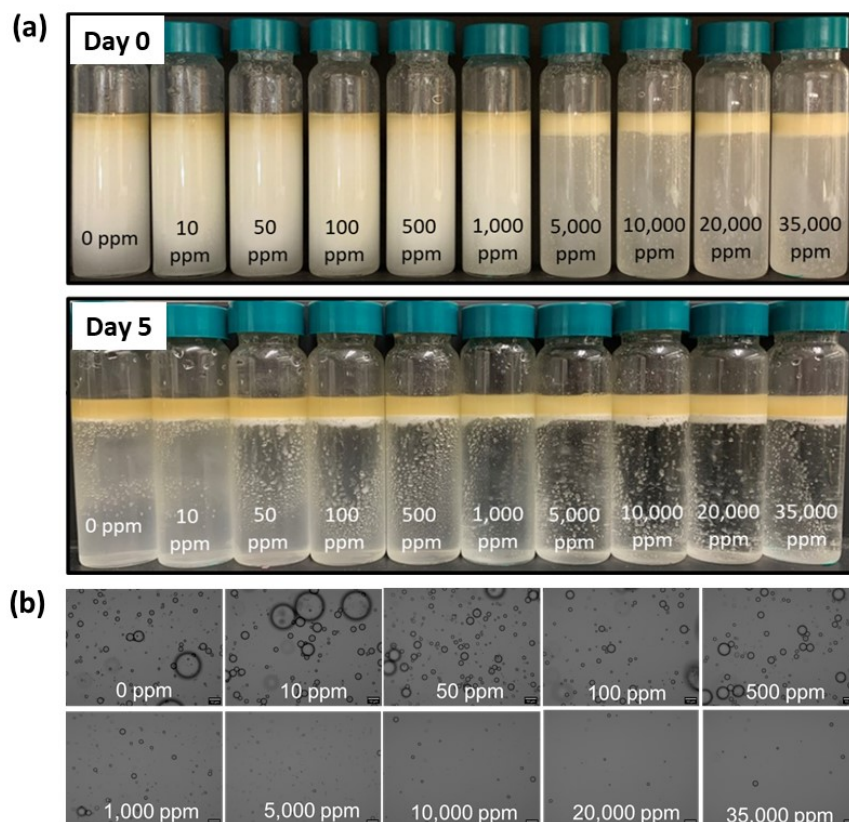


Figure 4-4 Visual observation and droplet size and density of emulsion samples prepared with different NaCl concentrations. Samples were prepared as control emulsions using DI water and NSBM #4 only. The microscopic images were taken 30 min after homogenization. (25°C).

It is widely accepted that increasing ionic strength can lower the zeta potential of the droplets, causing an increase in droplet interactions that results in the formation of larger droplets (Kulmyrzaev et al., 2016). In addition, the aqueous-phase salinity can affect the solubility of the emulsifier, which can impact the stability at the oil and emulsion interface. Among the tested cleaners, electrostatically stabilized emulsions (e.g., SDS) were less stable 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 oil droplet (e.g., electrostatic shielding) is reduced, allowing the droplets to interact and increase in size. Additionally, ionic surfactants can precipitate (i.e., salt-out) at high salt concentrations forming crystalline particles in solutions, reducing 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 (Iyota et al., 2009).

4.3.2.2 Temperature

The impact of temperature on emulsion stability was evaluated for emulsion samples prepared at 4°C, 25°C, and 35°C. The emulsion stability was clearly affected by temperature variations with more stable emulsions formed at lower temperatures (Figure 4-1). It was observed that emulsions

subjected to high temperature environments (e.g., 35°C) presented a higher tendency to form an oil layer, while a lower temperature (e.g., 4°C) often resulted in a creaming layer. Figure 4-5 shows that for emulsion samples prepared and stored at 4°C, only 60% had a separated oil phase after 5 days. However, for samples prepared and stored at 35 °C, 83% of the samples had a separated oil phase. These findings are similar to results found in the literature. It seems that increasing temperature improves interactions between emulsion droplets, enhancing oil coalescence (Chen and Tao, 2005; Kokal, 2005). In other words, increasing temperature raises the kinetic energy imparted to the droplets, which intensifies the frequency of droplet collision, thus enhancing emulsion destabilization by oil separation (Chen and Tao, 2005). In addition, temperature generally decreases the interfacial tension and oil viscosity while increasing the film-drainage rate, which when combined, can deteriorate the emulsion and decrease emulsion stability (Church et al., 2019).

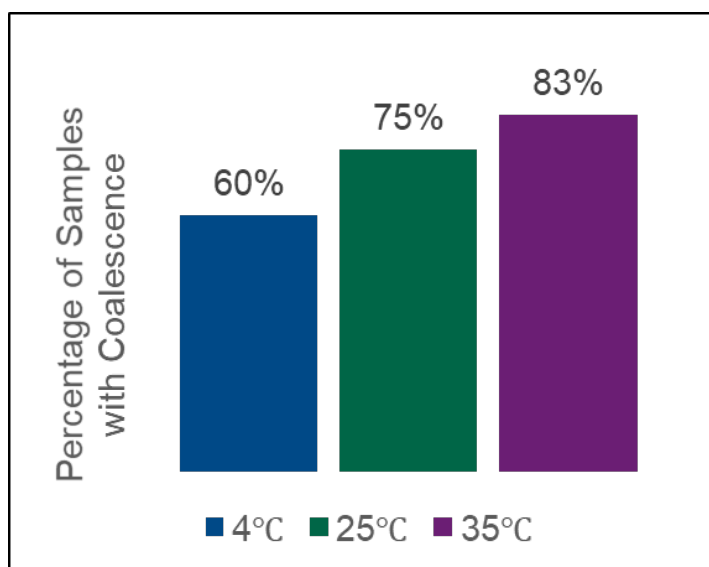


Figure 4-5 Impact of temperature on emulsion stability based on coalescence

4.3.2.3 Suspended solids (SS)

In general, the addition of SS helped destabilize emulsion samples. Results showed that 70% of the samples with SS had a separated oil layer after 5 days, while only 54% of the samples had a separated oil layer when there were no additives (Figure 4-3). However, the impact of SS was different for different cleaners. For example, the addition of SS to emulsions prepared with Triton X-100 decreased oil separation from 89% to 40%. However, for B&B emulsions, the addition of SS enhanced emulsion destabilization by increasing oil separation from 0% to 69%. On the other hand, for emulsions prepared with SDS, the addition of SS showed no major effect on emulsion stability.

In emulsion systems, solid particles have been shown to function in similar ways as surfactants, affecting the stability of emulsions through the formation of Pickering emulsions (Albert et al., 2019). 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 (Binks, 2002). It is

suggested that solid particles should be substantially smaller than the targeted droplet size to stabilize emulsions; particle sizes larger than the droplet will take longer to absorb at the interface (Albert et al., 2019). In this study, the Arizona test dust size distribution ranged from 0.97 to 176 μm , with 74% of the particles less than 22 μm in diameter. In Triton X-100 and B&B emulsions (without NaCl nor SS), the droplet sizes ranged between 10–140 μm and 0.21–70 μm , respectively. The different effect of SS on emulsion stability between Triton X-100 and B&B emulsions could be related to the ratio of suspended particles with a diameter lower than the droplet size. In Triton X-100 emulsions, more than 70% of the droplets showed a diameter greater than 20 μm , while more than 50% of droplets for B&B 3100 emulsions were found below this number. It appears that suspended solids with particle sizes larger than the droplet size could enhance flocculation or the formation of larger droplets through coalescence, thus decreasing emulsion stability as corroborated by visual observation. Overall, it can be concluded that the effect of SS on emulsion stability is dependent on the surfactant type and temperature conditions, requiring further tests of SS effects for each surfactant (e.g., emulsion sizes for each surfactant).

4.3.2.4 pH

In general, the initial pH did not have an impact on emulsion stability. Figure 4-6 shows that 70-74% of the samples had a separated oil phase after 5 days for all tested pHs. However, it could be observed that some surfactants were impacted differently by the initial bulk-water pH. In particular, Power Green was the only surfactant that demonstrated a clear impact of bulk-water pH on emulsion stability (Figure 4-1). Emulsion samples with Power Green were highly unstable for samples prepared in acidic pH (pH 4). Literature shows that pH can have a strong influence on the stability of oil-in-water emulsions. Adding inorganic acids and bases to emulsions influences the ionization of the interfacial films. Also, pH can influence the solubility and effectiveness of nonionic emulsifiers (Di Marzio et al. 2011). Therefore, it was unexpected that only one detergent was significantly impacted by pH. One explanation could be that cleaners often contain buffers to help stabilize the pH so that the surfactants work effectively. Since this study used cleaners, instead of pure surfactants, to stabilize emulsions, it is likely that there are buffers within the cleaners that helped reduce the impact of pH on emulsion stability.

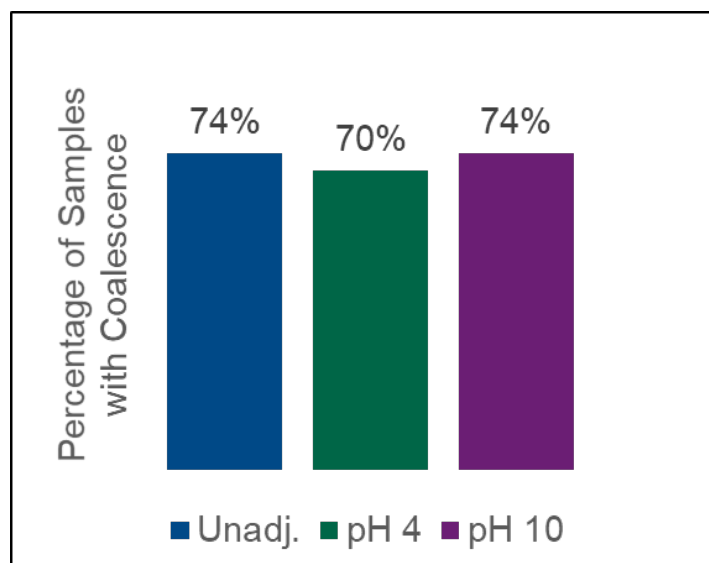


Figure 4-6 Impact of pH on emulsion stability based on coalescence

4.4 Conclusions

In this Chapter, the effects of environmental factors on emulsion stability were investigated under various environmental conditions. In particular, the effects of salinity, temperature, suspended solids (SS), and pH on the formation and stability of emulsions were evaluated using relevant model and commercial surfactants.

The findings suggest that emulsion stability is significantly affected by surfactant type, ionic strength, and temperature. The resulting emulsion stabilities based on percentage of emulsions that had visual oil separation after 5 days, from most stable to least stable, were 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%). 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 coalescence of the droplets. Ionic strength was shown to have the highest effect on emulsion destabilization, resulting in oil separation at early stage. 93% of emulsions prepared in saline conditions exhibited an oil layer formation. The addition of suspended solids helped stabilize emulsions under certain environments, and the pH effect was found be minimal for most of the cleaners tested. In conclusion, these experiments provided significant information regarding the contribution of bilgewater components to the formation and stability of emulsions in Navy bilgewater systems. Results from this work were used to help train an emulsion stability prediction model, discussed in Chapter 7.

Chapter 5: Impact of Interfacial Tension and Critical Micelle Concentration on Bilgewater Oil Separation

5.1 Introduction

The stability of oil-in-water (O/W) emulsions are widely studied in food science, cosmetics, agro-chemicals, paints, and pharmaceuticals (Gutiérrez et al., 2008; McClements and Jafari, 2018; Solans et al., 2005). In these disciplines of research, surfactants can be carefully selected to stabilize emulsions based on the dispersed or continuous phases, in addition to their robustness to environmental conditions (Gutiérrez et al., 2008). From these studies, it has been found that emulsion stability depends strongly on the droplet size, type, and concentration of surfactant used, the viscosity of the continuous phase, and other environmental conditions (Tadros et al., 2004), as identified in Chapter 2 and 4. In fact, in cases where emulsions are designed to remain stable for long periods of time (e.g. on the order of years), tight control of these parameters is necessary to prevent emulsion destabilization mechanisms such as flocculation, creaming, Ostwald ripening, and coalescence (Kale and Deore, 2017; Weiss et al., 2000). In the context of oily wastewater treatment, such as bilgewater, surfactant types and concentrations are generally unknown or highly variable (Church et al., 2019; U.S. EPA, 1999b) (as described in Chapters 2 and 3). Therefore, it is difficult to predict stability of oily wastewater emulsions on a fundamental level.

For bilgewater applications, it is desirable to relate experimentally obtained properties of common shipboard cleaners to emulsion stability. Components of commercial cleaners are often proprietary; therefore, it is important to have an empirical method for determining the stabilization imparted by commercial cleaners. Ideally, specific experimentally derived properties of the cleaners or surfactants could be used to predict their behavior in bilgewater systems. Two experimentally determined properties of surfactants that have been associated with droplet stability in traditional systems are critical micelle concentration (CMC) and interfacial tension (IFT).

CMC is the concentration of surfactant above which micellization becomes thermodynamically favorable and any additional surfactant added to the system forms micelles. CMC can be determined experimentally using several methods including surface tension, IFT, dye micellization, or conductivity (Rosen and Kunjappu, 2012). For each method, the CMC is defined as the surfactant concentration above which the measured parameter becomes independent of surfactant concentration. While some research has indicated a significant change in emulsion stability when an emulsifier concentration is above the CMC (Rehfeld, 1962; Rowe, 1965); other studies have found that CMC is not an important parameter for emulsion stability (Jafari et al., 2008; Tcholakova et al., 2004). One explanation for this discrepancy is that CMC is almost exclusively reported based on measurements in the aqueous phase (i.e. surface tension measurements); however, some studies have shown CMC can change in the presence of an oil phase when a surfactant is solubilized by the second phase (Rosen and Kunjappu, 2012). Considering oil is a major component of emulsions, CMC should also be calculated using the interfacial tension measurements between an aqueous and representative oil phase (CMC_{IFT}).

IFT is the measurement of the work (as mN/m) required to increase the size of the interface between two immiscible liquids and plays an important role in the formation of emulsion droplets during emulsification (Metaxas et al., 2021). In fact, theoretical analysis and experimental results have shown that droplet diameter depends on the power density of energy dissipation and the oil-water interfacial tension (Marquez et al., 2018; Raikar et al., 2011). Many model equations have been developed to relate IFT and emulsification energy to droplet size and emulsion stability (Håkansson et al., 2013; Liao and Lucas, 2009; Maindarkar et al., 2015).

While there are multiple examples of research relating CMC and IFT to emulsion stability (Jafari et al., 2008; Maindarkar et al., 2015; Rehfeld, 1962), these studies were performed under carefully controlled environments. In particular, it is unclear whether the CMC, CMC_{IFT} , or IFT of a shipboard cleaner (i.e. a mixture of surfactants and other compounds) can be used to predict emulsion stability. The role of CMC, CMC_{IFT} , or IFT in predicting emulsion stability is likely to differ with emulsification energy and/or oil concentration. In addition, defining emulsion stability by creaming rate rather than oil separation will also influence the impact of CMC or IFT on stability. This is because creaming rate is ultimately governed by differences in phase densities and droplet size distribution. However, oil separation requires coalescence, a mechanism that is dependent on many factors including surfactant concentration, type, and absorption. In the context of bilgewater emulsions, it is important to break the emulsions into a completely separate oil layer to reduce the volume of stored waste oil and to avoid fouling sensors with cream.

The current study investigates the relationship between CMC, CMC_{IFT} , and IFT on emulsion formation and stability using different surfactant types, oil concentrations, and homogenization energies to determine the usefulness of experimentally determined cleaner properties for predicting emulsion stability in bilgewater. Emulsions were prepared with representative nonionic surfactants, Triton X-100 and Triton CG-110, and a representative anionic surfactant sodium dodecyl sulfate (SDS) to understand how emulsions behave using pure surfactants. Then, to explore the applicability of using CMC, CMC_{IFT} and IFT to explain emulsion stability in bilgewater, emulsions were also generated with four commercial cleaners previously identified as relevant to shipboard applications (Chapter 2). Overall, the goal of this study was to provide researchers and decision makers with a tool for evaluating the likelihood of a cleaner to develop stable emulsions in bilgewater.

5.2 Materials and Methods

5.2.1 Materials

Mineral oil light (CAS # 8042-47-5) was purchased from Fischer Scientific and used as a representative control bilge oil. Triton X-100 (CAS #9002-93-1), Triton CG-110 (CAS # 68515-73-1) and sodium dodecyl sulfate (SDS; CAS #151-21-3) were selected as representative surfactants in cleaners and purchased from Sigma Aldrich. Four commercial cleaners identified from the U.S. Navy procurement system (Chapter 2) were selected as representative cleaners for study: Super Blast Off (Elsco International Inc.), PRC Deck Cleaner (Werth Sanitary Supply Co. Inc. #1100868), Ecolab Solid Surge Plus NP (Ecolab # 6117905) and Type 1 Detergent

(MILSPEC: MIL-D-16791). All materials and solvents were used as received unless otherwise noted.

5.2.2 Characterization of Surfactant Properties

5.2.2.1 Interfacial and Surface Tension Measurements

IFT of the surfactant solutions were measured using a du Noüy Ring tensiometer (Sigma 701, Attension). Measurements were conducted for each surfactant at 9 different concentrations ranging from 10 ppm to 10,000 ppm. 40 mL of mineral oil was carefully added to 80 mL of a surfactant solution to create a clean interface without any bubbles. A platinum ring was lowered into the oil portion of the sample and the tensiometer was blanked. Next, the interface was left undisturbed for at least 5 min to allow for surfactant adsorption at the interface to reach equilibrium. The tensiometer then automatically determined the location of the oil/water interface by lowering the ring through the sample until a change in force of 0.03 mN/m was detected. Next, the tensiometer measured the force required to pull the ring back through the oil/water interface and recorded the IFT in mN/m. Since the ring disturbed the oil/water interface during the measurement, new samples were prepared for each replicate. The du Noüy ring was cleaned with isopropanol and dried between each measurement. Measurements were performed in duplicate.

Surface tension was measured using the same method as IFT except that the measurement was made between the air-water interface rather than an oil-water interface. Surface tension measurements were performed continuously until the surface tension reached equilibrium (generally within 5 min). Equilibrium was defined as 10 consecutive surface tension measurements with less than a 0.5 mN/m deviation. Experiments were conducted at room temperature (20-22°C).

After finding that CMC was significantly different in the presence of mineral oil, IFT measurements were repeated using pendant drop method to monitor IFT over time and ensure that equilibrium was reached. A goniometer (Model 210, Raméhart) was used for the pendant drop analysis. Since mineral oil is less dense than water, a J-hook needle was used to suspend the mineral oil droplet in the surfactant solutions. IFT was measured every 30 secs for 1.5 hrs. In general, equilibrium was reached within 60 min (Appendix C. Fig. C1). Despite the longer time needed to reach equilibrium, the equilibrium IFT values were generally within 10% of the values obtained using the du Nouy ring method (Appendix C Fig. C2).

5.2.2.2 Critical Micelle Concentration (CMC)

While CMC values of surfactants are typically reported based on surface tension measurements, it is assumed that in the case of bilgewater emulsions, CMC measurements based on IFT measurements will be more representative due to differences in surfactant packing at an oil-water interface. Thus, in this work, CMC was determined using both surface tension and IFT measurements (Domínguez et al., 1997). The CMC derived from IFT measurements will be noted as CMC_{IFT} .

To calculate CMC and CMC_{IFT} , the equilibrium surface tension or IFT of a series of surfactant solutions were plotted against the surfactant concentration on a semi-log plot. The data was then

fit with two linear regressions. One regression was used to fit the data below CMC, a regime where the IFT or surface tension are dependent on surfactant concentration. The second regression was fit to the data above CMC, where the IFT or surface tension are independent of surfactant concentration. The CMC and CMC_{IFT} were then calculated by determining the intersection between the concentration dependent and independent regions using Origin 2018b.

5.2.3 Preparation of Emulsions

Emulsion samples were prepared with mineral oil light, deionized (DI) water, and a single surfactant or cleaner. Mineral oil was used due to its viscosity and density being similar to that of collected bilge oil. Mineral oil is also present in common shipboard lubricating oils (i.e. Lube Oil 2190). Many bilgewater treatment studies reporting use of standard bilge mixes were composed of diesel fuel and lubricating oils (Chapter 2); however, aromatic compounds and fuel additives found in these mixtures make it difficult directly relate emulsion stability to properties of cleaners. All samples were prepared with the same 10 surfactant concentrations: 0, 10, 50, 100, 500, 1,000, 2,000, 4,000, 8,000, and 10,000 ppm, in order to observe emulsion stability above and below CMC for each surfactant. Emulsions were generated with either 10 or 20% (v/v) mineral oil. To generate the oil fraction of interest, an appropriate volume of mineral oil was added to the surfactant solutions such that the total volume was 20 mL. Samples were then emulsified using either a high or low intensity homogenization to understand the impacts of CMC, CMC_{IFT} , and IFT under different homogenization regimes. High intensity homogenization samples were homogenized using a high shear homogenizer (Omni Tissue Master, Model 125, 10 mm generator probe) at 20,000 rpm for 2 min in a 50 mL centrifuge tube (Fisher Sci., 14-959-49A) and poured into a 50 mL glass flat bottom vials with Teflon-lined screw caps (Qorpak GLC01020). Low intensity homogenization samples were placed in glass sample vials, capped and then inverted 10 times. Bulk emulsion stability experiments were performed at room temperature (20-22°C).

5.2.4 Characterization of Bulk Emulsion Stability

5.2.4.1 Bulk Emulsion Stability

Immediately after emulsion preparation, samples were placed on a shelf where energy input from vibrations and changes in temperature (20-22°C) were limited. Photos of the samples were taken using a digital camera (Nikon D80) every 30 min for the first 4 h, then every 24 h up to 72 h. Changes in the appearance of the emulsion, cream, and oil layers were recorded and used to qualitatively indicate emulsion stability. A full experimental flight, emulsions at all 10 concentrations, was performed in triplicate to ensure reproducibility. In addition, triplicate samples of each model surfactant and cleaner were prepared at CMC and $7 \times$ CMC. Photographs of macro-phase separation from these samples showed the results to be highly reproducible (Appendix C Fig. C3, Table C1).

5.2.4.2 Macro-phase Oil Separation

During the bulk emulsion stability experiments, the creaming layer obscured the view of the separated oil phase (Appendix C Fig. C4). Therefore, a separation technique was employed to quantify the oil separation. After the emulsion samples reached equilibrium (> 72 h), samples were poured into a 100 mL separatory funnel and settled for 5 min to allow the sample to

separate into its emulsion, cream, and oil layers. A pre-weighed vial was then used to collect the separated oil layer and weighed to determine the amount of oil separation for each sample. The oil separation, termed macro-phase oil separation, was presented as a percentage of the total oil used in the emulsion generation.

5.2.5 Determination of Droplet Size Distribution

Optical microscopy (Zeiss Axio Imager M2m) and laser diffraction (Horiba LA-950 Particle Size Analyzer) were both employed as complementary methods to measure droplet size. Droplet size was measured after the emulsions reached equilibrium (>72 h). The low homogenization samples tended to have larger droplets and thus were more suited for microscopy. The high homogenization samples contain smaller droplets and laser diffraction allowed for more explicit quantification of the droplet size distribution.

5.2.5.1 Microscopy

The emulsion samples were gently inverted to suspend the cream layer, transferred to a glass microscope slide, and protected by a cover glass. All measurements were collected on a Zeiss Axio Imager M2m with transmitted light using a 5× (Numerical Aperture (NA) = 0.13), 10× (NA = 0.25) and, if appropriate, 20× (NA = 0.50) objective. Three images were collected of each sample in order to generate a representative droplet size distribution. All images were processed using MIPAR™ (V3.2, MIPAR™, Worthington, OH), a commercially available software that uses adaptive thresholding to automatically differentiate features in an image for quantification (Sosa et al., 2014).

5.2.5.2 Laser Diffraction

Laser diffraction data was collected on a Horiba LA-950 Particle Size Analyzer. Samples were added to a flow loop containing deionized water until the transmittance was within the proper range, as specified by the instrument. Three measurements were performed for each sample. If necessary, additional sample was added between measurements to maintain the proper transmittance. The refractive index of water, the continuous phase, was specified as 1.333 and the refractive index of light mineral oil was specified as 1.4. All laser diffraction data were imported and processed in Matlab (R2018b).

5.3 Results

5.3.1 Experimentally Determined Properties of Surfactants and Cleaners

5.3.1.1 Model Surfactants

The CMC, CMC_{IFT}, equilibrium surface tension above CMC ($\gamma_{\text{cmc(air)}}$), and equilibrium IFT above CMC_{IFT} ($\gamma_{\text{cmc(oil)}}$), were measured for the three model surfactants, Triton X-100, Triton CG-110, and SDS. These results are shown in Table 5-1. SDS had the largest CMC at 1,983 ppm, followed by Triton CG-110 with a CMC of 1,748. Triton X-100 had the lowest CMC at 102 ppm.

Table 5-1 CMC and IFT of model and commercial cleaners found in bilgewater

Surfactant	CMC (ppm)	CMC_{IFT} (ppm)	γ_{cmc} (air) (mN/M)	γ_{cmc} (oil) (mN/M)
Triton X-100	102	324	29.6 ± 0.4	3.0 ± 0.1
Triton CG-110	1,748	3,352	26.9 ± 0.2	2.2 ± 0.4
SDS	1,983	5,130	35.4 ± 0.8	9.8 ± 0.5
Blast Off	934	5,381	27.7 ± 0.5	3.4 ± 0.1
PRC	1,871	6,832	30.5 ± 0.1	7.7 ± 0.3
Solid Surge	98	396	27.4 ± 0.3	4.1 ± 0.1
Type 1	87	105	30.2 ± 0.4	2.1 ± 0.1

While CMC is typically defined by surface tension, IFT measurements can also be used to determine CMC (Rosen et al., 1999). Table 5-1 shows that the CMC calculated using the two different datasets can be significantly different. For example, the CMC_{IFT} for Triton X-100 was more than three times the CMC. Rosen and Kunjappu reported a similar finding with CMC values up to 20 $\times$ greater for IFT-based CMC measurements compared to surface tension-based CMC measurements and attributed the difference to surfactant partitioning into the oil phase (Rosen and Kunjappu, 2012). In fact, they were able to estimate partition coefficients for the surfactants (K) based on difference in CMC values. Other studies have also observed larger CMC values for oil-water interfaces compared to air/water interfaces, but attributed the difference to how surfactants pack at each interface (Rehfeld, 1962; Rowe, 1965).

The equilibrium surface tension for SDS above CMC was found to be larger than Triton X-100 and Triton CG-110, which is in agreement with (Kimura et al., 1990). While surface tension gives some indication of surfactant properties, IFT is more relevant for describing emulsion systems and understanding emulsion formation and stabilization. It is widely accepted that emulsion droplet size will decrease with decreasing IFT (Llamas et al., 2018; Oh and Shah, 1993; Tcholakova et al., 2004). SDS had a much larger equilibrium IFT with mineral oil compared to Triton X-100 and Triton CG-110. The IFT for SDS, Triton X-100, and Triton CG-110 with mineral oil were 9.8, 2.2, and 3.0 mN/m, respectively. Therefore, emulsions prepared with SDS should have larger droplet diameters compared to Triton X-100 and Triton CG-110.

This was experimentally confirmed and is discussed in Section 5.3.4. IFTs determined in this study were similar to those listed in literature (Campanelli and Wang, 1999; Llamas et al., 2018).

Using the measured IFT for the three model surfactants, the maximum surface concentration and Langmuir constant of the surfactants were determined. First, the maximum surface concentration, Γ_{∞} , indicates the maximum molar packing density of the surfactant molecules being adsorbed into the interface (Jin et al., 2004). Γ_{∞} can be obtained through fitting the Gibbs adsorption energy equation to the data of IFT as a function of the surfactant bulk concentration for concentrations just below the CMC (He et al., 2015):

$$\Gamma_{\infty} = -\frac{1}{nRT} \left(\frac{\partial \gamma}{\partial \ln C} \right)_T \quad \text{Eq. (5-1)}$$

where n depends on the surfactant type. For instance, $n=1$ for nonionic and $n=2$ for anionic surfactant, respectively. R is the gas constant, T is the ambient temperature, C is the bulk surfactant concentration and γ is the IFT. Then, the Langmuir constant, κ , gives the affinity of the surfactant molecules to the interface (Brosseau et al., 2014; Ferri and Stebe, 2000). Once Γ_{∞} is obtained for each surfactant, the Langmuir isotherm is applied to obtain an equation of state (Pan et al., 1998):

$$\frac{\Gamma_{eq}}{\Gamma_{\infty}} = \frac{\kappa C}{1 + \kappa C} \quad \text{Eq. (5-2)}$$

$$\gamma = \gamma_0 + nRT\Gamma_{\infty} \ln \left(1 - \frac{\kappa C}{1 + \kappa C} \right) \quad \text{Eq. (5-3)}$$

where γ_0 is the IFT of the system with no surfactant. Eq. (5-3) is again fit to the IFT data in Figure 5-1a to extract the κ value of each surfactant. The molecular weight of each surfactant, M_w , as well as Γ_{∞} and κ are listed in Table 5-2.

Table 5-2 Adsorption properties of model surfactants at a mineral oil-water and oil-air interface

Surfactant	Triton X-100 ^{a)}		Triton CG-110 ^{a)}		SDS	
Interface	Oil-Water	Air-Water	Oil-Water	Air-Water	Oil-Water	Air-Water
M_w (g/mol)	625		1047		288	
$\Gamma_{\infty} \left(\frac{\text{mol}}{\text{m}^2} \right)$	$(2.43 \pm 0.21) \times 10^{-6}$	$(2.57 \pm 0.5) \times 10^{-6}$	$(2.52 \pm 0.25) \times 10^{-6}$	$(2.66 \pm 0.55) \times 10^{-6}$	$(2.4 \pm 0.69) \times 10^{-6}$	$(2.9 \pm 0.9) \times 10^{-6}$
κ (m ³ /mol)	$3,843 \pm 186$	$3,519 \pm 163$	623 ± 55	420 ± 95	2.6 ± 0.5	1.74 ± 0.35

a) Triton X-100 and Triton CG-110 are mixtures of similar molecules with varying polyethylene glycol (PEG) lengths. An average molecular weight was used to represent M_w . The values for the oil-water case were based on the IFT measurements shown in APPENDIX C Fig. C2.

The values of Γ_{∞} and κ listed in Table 5-2 are within the appropriate order of magnitude of typical model surfactants (Brosseau et al., 2014). In this study, the Γ_{∞} values of all three surfactants were similar for the oil-water and air-water cases, suggesting comparable surface coverage regardless of the interface. The reason for the differences in the CMC values (Table 5-1) may be due to partitioning of the surfactant in the oil phase. However, given that IFT measurements were similar between two methods that used different oil to water ratios, other mechanisms may instead be responsible for the increase in CMC. Another explanation is that potential impurities found in mineral oil may be modifying the behavior of the aqueous phase and changing entropy of micellization. Rosen (2012) discusses the impact of Class II materials (e.g. short-chain alcohols, water soluble esters, ethylene glycol, and dioxane) on CMC. Materials that decrease the solubility parameter of water may increase CMC because they increase the solubility of the monomeric form of surfactants. Likewise, compounds that reduce the dielectric constant of water would increase the mutual repulsion of ionic heads in the micelle thus opposing micellization and increase the CMC. This may also explain the higher CMC of oil-water than that of air-water interfaces.

The adsorption constant, κ , varied significantly between the surfactants. Particularly, it shows that the Triton X-100 was the most active to be adsorbed to the interface among the three surfactants. In addition, the κ values of oil-water interface were higher than that of the air-water interface, suggesting that, for a given surfactant, the adsorption of the surfactant molecules to the oil-water interface are more active than to the air-water interface. The results shown in Table 5-2 were able to provide some insight into the underlying relationship between surfactant concentration and IFT/surface tension for a given surfactant, and resultant degree of oil separation for a given measurements as discussed in Section 5.3.2.

5.3.1.2 Commercial Cleaners

Four commercial cleaners were identified as likely to be present in bilgewater tanks of Armed Forces vessels based on a previous inventory survey (Chapter 2). These include, Blast Off, PRC Deck & Floor Cleaner, Solid Surge, and Type 1 Detergent. The composition of the cleaners is proprietary and the concentration and chemical structures are unknown; however, the safety data sheets (SDS) indicate the primary surfactants for all the cleaners are nonionic (Chapter 3). Nevertheless, builders, stabilizers, and secondary surfactants, which may not be included in the SDS, will also impact how the surfactants interact with an oil-water interface, as indicated by the discrepancy in surfactant properties, for example, between Triton X-100 and Type 1 Detergent. Therefore, the only way to predict the impact that these cleaners will have on emulsion stability is to identify the properties of the cleaners experimentally.

CMC_{IFT} for the four cleaners was calculated based on data presented in Figure 5-1b, which ranged significantly. Type 1 Detergent had the lowest CMC_{IFT} at 105 ppm, then Solid Surge with a CMC_{IFT} of 396 ppm. Blast Off had a CMC_{IFT} of 5,381 ppm and PRC Deck & Floor Cleaner had the largest CMC_{IFT} at 6,832 ppm (Table 5-1). The large range of CMC_{IFT} values between the cleaners was ideal for determining the impact of CMC_{IFT} on emulsion stability. Likewise, the equilibrium IFT measurements with mineral oil above CMC_{IFT} also varied significantly between the commercial cleaners (Table 5-1). The cleaner with the lowest equilibrium IFT above CMC was Type 1 Detergent with an IFT of 2.14 mN/m. Blast Off and Solid Surge had IFTs of 3.44 mN/m and 4.08 mN/m, respectively. PRC Deck Cleaner had the largest IFT above CMC with an IFT of 7.68 mN/m. Interestingly, IFT's of the commercial cleaners above CMC were within a similar range as the model surfactants.

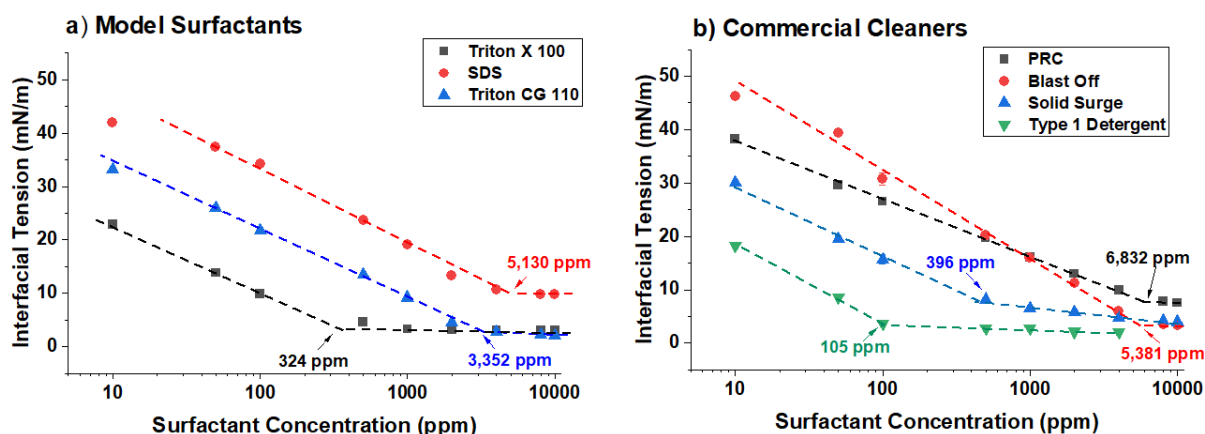


Figure 5-1 Interfacial tension measurements with mineral oil as a function of a) model surfactant and b) commercial cleaner concentration

5.3.2 Emulsion Stability: Macro-phase Oil Separation

In many cases, macro-phase oil separation was visually observed (Appendix C Fig. C5); however, the oil layer was only visible from above and could not be clearly photographed from the side. Therefore, emulsion stability was quantified by weighing the amount of oil that was separated from the creaming layer and aqueous phase using a separatory funnel. Figure 5-2

shows the quantity of oil that coalesced into a separate phase as a fraction of the initial amount of oil added with increasing surfactant concentration (shown as percentage of CMC_{IFT}). The effects of oil content, homogenization speed, and surfactant concentration were compared.

5.3.2.1 Effect of CMC on Macro-phase Oil Separation

For all surfactants in each condition, the amount of oil separation decreased with increasing surfactant concentration (Figure 5-2). At larger concentrations of surfactant, more oil was contained in the surfactant stabilized emulsions. The specific concentration at which each sample shifted from predominantly separated oil to stabilized emulsion correlated closely with CMC_{IFT} . Surprisingly, macro-phase oil separation was relatively independent of oil content. Under high and low homogenization, similar relationships of macro-phase oil separation with surfactant concentration were observed for both 10 and 20% mineral oil contents. One possible explanation for this finding is that surface area to volume ratio of droplets could have been similar between 10 and 20% mineral oil as droplet size is independent of oil content; thus, the interfacial area only doubles for the increase in mineral oil content from 10 to 20%. For example, assuming a uniform droplet size of 3 μm , the surface area would only increase from approximately 200 to 400 m^2/L for 10 and 20% oil, respectively. From the maximum surface concentrations calculated in Table 5-2, the increased surface area would only consume an extra 6×10^{-4} moles of surfactant, or a few hundred ppm, depending on the surfactant. Thus, the difference in stability with increased oil concentration may be obscured by the large increments of surfactant concentration used in this study. An even more compelling hypothesis is that droplets coalesce to a droplet size distribution with a surface area that can be supported by the surfactant's CMC_{IFT} . This could be why D50, or the droplet diameter at 50% cumulative distribution, decreases with surfactant concentration above CMC_{IFT} (Section 5.3.3); the additional surfactant can be used to stabilize the larger surface area of the smaller droplet size distribution.

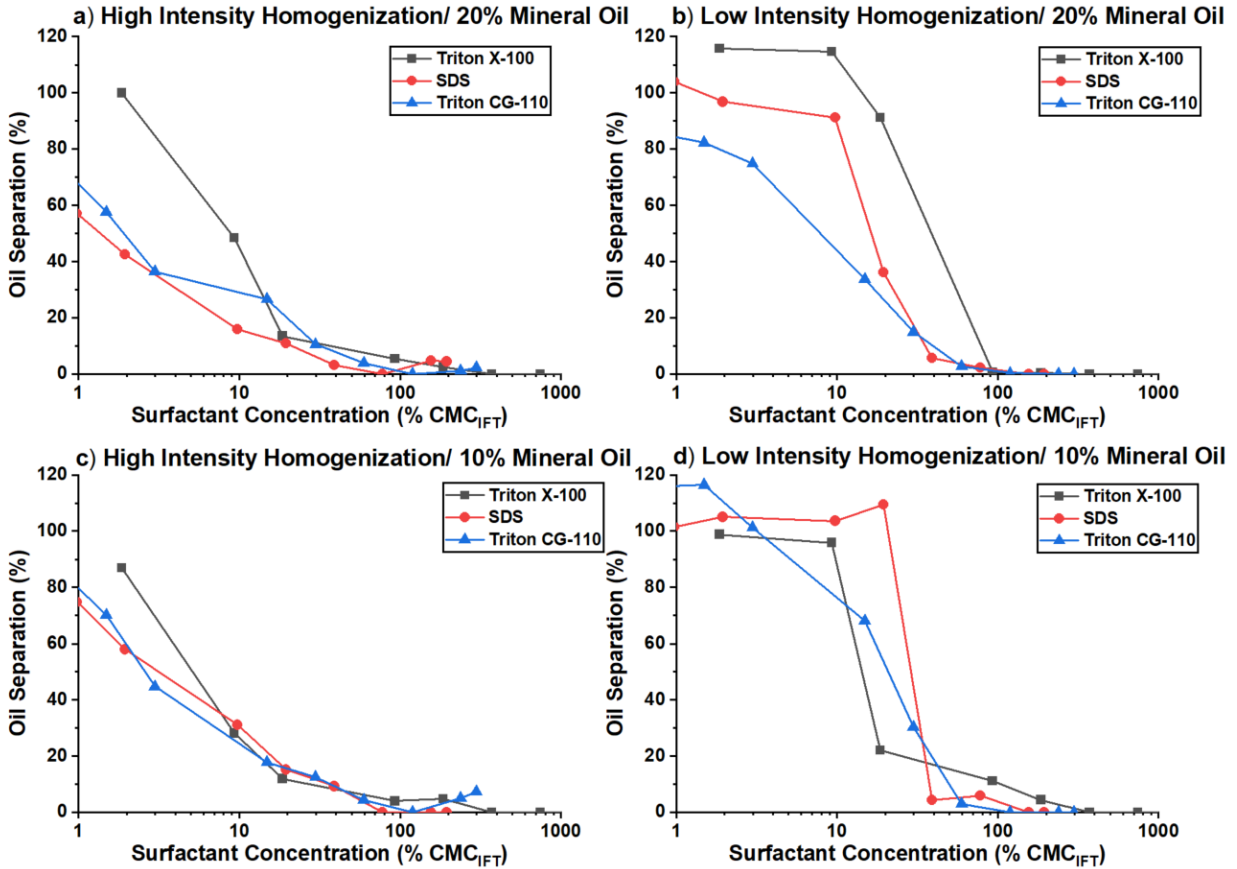


Figure 5-2 Macro-phase oil separation as a function of surfactant concentration in model O/W emulsions after 72 h for emulsions prepared with high (a,c) and low (b,d) intensity homogenization and 20% (a,b) and 10% (c,d) mineral oil

An increased dependency on homogenization intensity at low surfactant concentrations was also observed in Fig 5-2. The greater dependence on homogenization intensity at low surfactant concentrations has been observed in literature (Maindarkar et al., 2015) and occurs because at low surfactant concentrations the interfacial energy is large. Therefore, more energy is needed to disrupt the oil-water interface into droplets. Model equations have been developed to predict the relationship between homogenization intensity and emulsion stability in surfactant rich and poor regimes (Tcholakova et al., 2004; Tcholakova et al., 2003); however, it is not clear if CMC or CMC_{IFT} can be used to define whether an emulsion system is surfactant-rich or -poor. In Tcholakova et al. (2004), the authors defined surfactant rich as concentrations greater than 0.1 wt % for SDS emulsions rather than using the CMC of SDS (0.24 wt %). Likewise, Maindarkar et al. (2015) used 0.1 wt % for emulsions stabilized by Pluronic F-68 which has a CMC of 334 ppm. Maindarkar et al. (2015) also indicated that the surfactant-rich regime depends strongly on the oil concentration. In our experiments, it was clearly shown that surfactant-rich or surfactant-poor regimes can be defined by the CMC_{IFT} (Figure 5-2), rather than by a specific surfactant concentration or oil concentration.

5.3.2.2 Effect of IFT on Macro-phase Oil Separation

IFT is known to have a large impact on emulsion droplet size distribution and stability. Figure 5-3 shows the oil separation as a function of IFT for the three model surfactants with varying oil concentration and homogenization intensity. For all surfactant types, oil concentrations and homogenization intensities, oil separation increased as IFT increased. As IFT decreases, the energy required to disrupt the oil-water interface is reduced and allows for a smaller droplet size distribution. Model equations presented by Walstra et al. (1993) and Tcholakova et al. (2004) show that droplet diameter depends primarily on the oil-water IFT under surfactant-rich regimes (Tcholakova et al., 2004; Walstra, 1993). In this study, there are clear differences between the effects of IFT under high and low intensity homogenization (Figure 5-3).

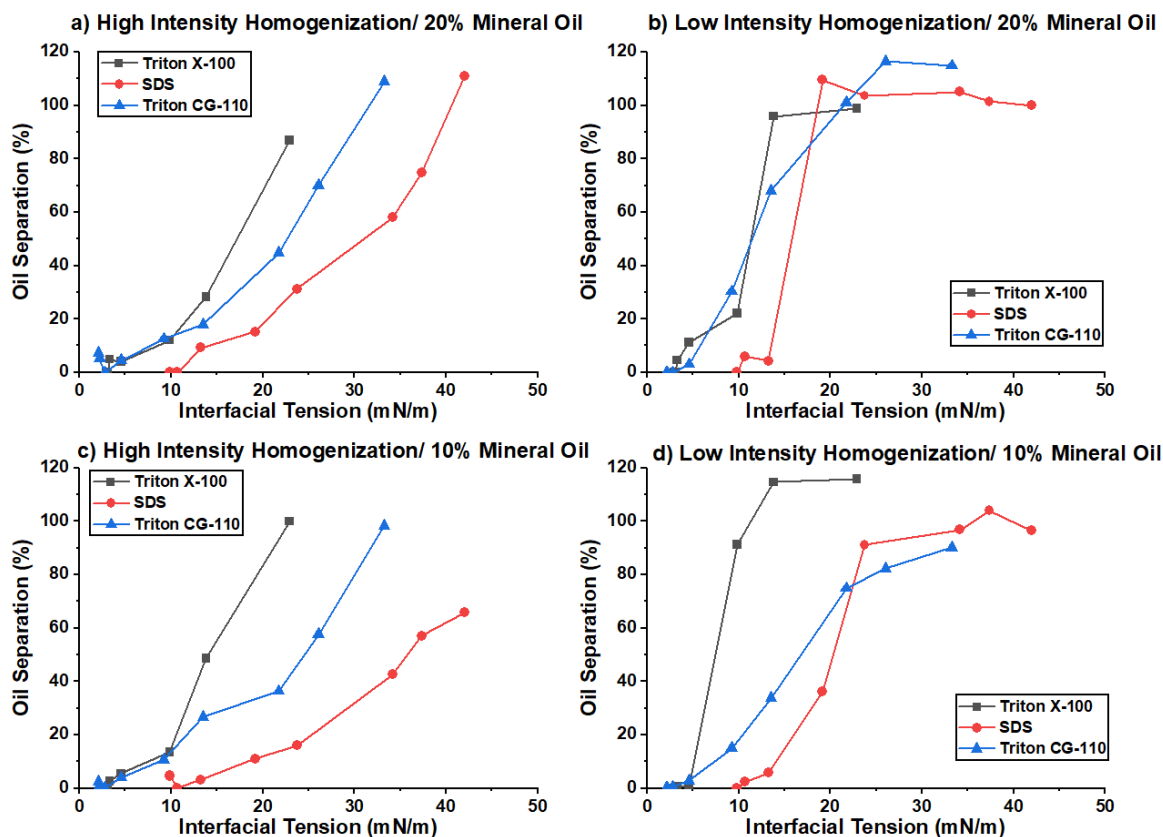


Figure 5-3 Macro-phase oil separation as a function of interfacial tension in model O/W emulsions after 72 h for emulsions prepared with high (a,c) and low (b,d) intensity homogenization and 20% (a,b) and 10% (c,d) mineral oil

For high intensity homogenization, the relationship between IFT and emulsion stability varied between surfactant types. This is likely due to the differences in Langmuir constants observed between the surfactants (Table 5-2). Larger κ values are associated with more active surfactants. Here, the κ value of Triton X-100 was two orders of magnitude larger than that for SDS, which informs why γ_{oil} for Triton X-100 is notably lower than that for SDS for a given surfactant concentration (Figure 5-1a). The Triton X-100 system also had the steepest slope in percent of oil separation for a given IFT (Figs. 5-3a and b), due to the larger κ value and resultant lower

surfactant concentration and interfacial coverage at a given IFT. Likewise, the oil separation of SDS stabilized emulsions was the least dependent on IFT, due to the lower κ value and relatively saturated surfactant coverage for a given IFT. For example, for emulsions prepared under high intensity homogenization and 20% mineral oil (Figure 5-3a), SDS demonstrated greater than 50% oil separation when IFT was above 37 mN/m; however, emulsions prepared with Triton CG-110 demonstrated similar oil separation when IFT was above 23 mN/m and 17 mN/m for Triton X-100.

Emulsions prepared using low intensity homogenization demonstrated a steep decrease in emulsion stability between 5 and 15 mN/m regardless of surfactant type (Figure 5-3b & d). This difference in oil separation for the high intensity and low intensity homogenization is likely due to the formation and stabilization of emulsion droplets. For samples prepared with high intensity homogenization, there was an excess of energy where droplets were being broken up and re-coalesced at a rate similar to the rate of surfactant mass transport (Jafari et al., 2008; Perrier-Cornet et al., 2005). For samples prepared with low intensity homogenization, mechanical energy input into the system was limited and IFT determined the fragmentation of droplets. Therefore, the homogenization intensity has an impact on the importance of IFT on emulsion stability.

5.3.3 Droplet Size Distribution

The average diameters of the emulsions (droplet size) were determined by optical microscopy and laser diffraction. The effects of homogenization speed, surfactant type, oil content, and surfactant concentration on droplet size distribution are shown in Figure 5-4, where D50 represents the droplet diameter at 50% of the cumulative distribution. As expected, emulsions prepared by high speed homogenization created droplets of much smaller diameter (10–25 μm) than those prepared by low speed homogenization (25–550 μm). Droplet size was independent of oil content for each surfactant; however, droplet size did depend on surfactant type and concentration, as well as homogenization speed.

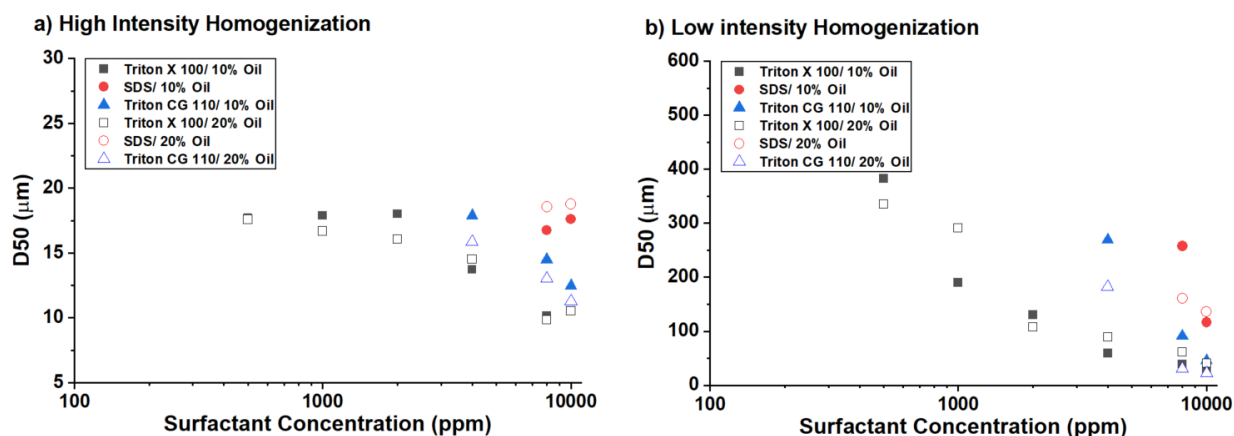


Figure 5-4 Comparison of droplet size distribution of model O/W emulsions above CMC with various surfactant and oil combinations and increasing surfactant concentrations under a) high and b) low homogenization.

For the all surfactants, droplet size decreased with increasing surfactant concentration. Considering droplet size was only measured in samples above CMC_{IFT} , this result was somewhat surprising. Ideally, IFT should be at equilibrium when the surfactant concentration is above CMC_{IFT} ; therefore, droplet size distribution was expected to be constant above CMC_{IFT} . The discrepancy could be explained by the method of IFT measurement. IFT was measured using the du Noüy ring method, which means the surfactant loss to the interface is negligible. However, in an emulsion system, the small droplets create a very large interfacial area that can adsorb a significant amount of surfactant (Llamas et al., 2018). As such, increasing surfactant concentration beyond the CMC_{IFT} effectively increases the capacity for the maximum interfacial area, without affecting measurable IFT. Therefore, with greater capacity for increased interfacial area, more droplets of smaller diameter are formed at increasing surfactant concentrations above CMC_{IFT} . In addition, droplet size was measured after 72 h; therefore, droplet size during homogenization may have been equal for emulsion systems with similar IFT and it was the coalescence over the 72 h that resulted in a change in droplet size distribution with increasing surfactant concentration.

The effect of surfactant concentration on droplet size was much larger at low intensity homogenization compared to high homogenization. The D50 of an SDS emulsion at 8,000 ppm was 300 μm , but decreased to 132 μm at SDS 10,000 ppm. Triton X-100 and Triton CG-110 both shared this relationship between surfactant concentration and droplet size. During an emulsification process, the interfacial area increases significantly and droplets are divided to form smaller droplets. Below a certain droplet size, there will not be enough surfactant to cover the interface completely; therefore, the droplet will tend to coalesce until the interfacial area is saturated with surfactant (Mittal and Vold, 1972). In this case, droplet size distribution is mostly dependent on surfactant concentration and oil volume fraction under high homogenization.

5.3.4 Commercially Stabilized Emulsions

To determine if the transition of emulsion behavior near CMC_{IFT} in emulsion samples prepared with model surfactants (Figure 5-2) can be used to predict the behavior of bilgewater emulsions, the oil separation of emulsion samples prepared using commercial cleaners was analyzed. Figure 5-5 shows the percent oil separation after 72 h for various concentrations of PRC Deck Cleaner, Blast Off, Solid Surge and Type 1 Detergent under high and low homogenization intensities. The discontinuity of oil separation at CMC_{IFT} was also apparent for the commercial cleaners. PRC Deck Cleaner, Blast Off, and Solid Surge all demonstrated an inflection of oil separation near CMC_{IFT} .

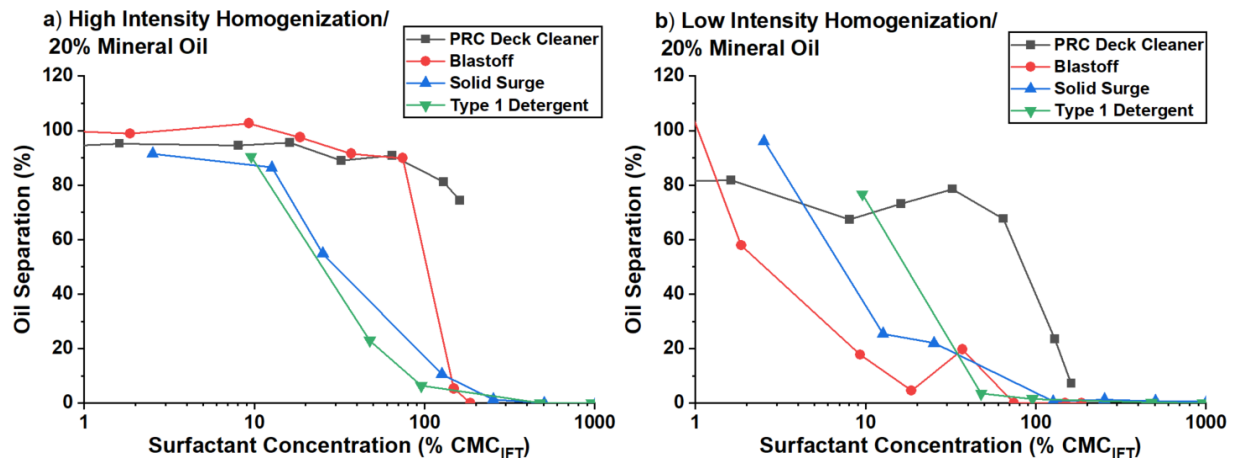


Figure 5-5 Macro-phase oil separation of commercial cleaner O/W emulsions after 72 h for emulsions prepared with a) high and b) low intensity homogenization with 20% mineral oil

Oil separation in emulsion samples prepared with commercial cleaners were also compared to CMC values determined using traditional surface tension measurements (Appendix C Fig. C6). In this case, oil separation did not correspond well to CMC. For example, emulsions prepared with PRC Deck Cleaner displayed greater than 80% oil separation for concentrations 10 times higher than CMC. Likewise, PRC Deck Cleaner emulsions prepared under low intensity homogenization did not demonstrate an inflection of oil separation until $5 \times$ CMC. The difference in relationship between oil separation as a function of CMC compared to a function of CMC_{IFT} can be explained by how surfactants adsorb at an interface. In particular, certain components of the cleaners that typically adsorb at the air/water interface may be miscible in mineral oil; therefore, they would not contribute in reducing the IFT. Thus, more cleaner would be needed to reach a maximum surface concentration. As such, CMC_{IFT} calculated based on IFT measurements were more useful for predicting emulsion stability. The trend demonstrated in Figs. 5-2 and 5-5 show how a cleaner's CMC_{IFT} can be used to predict its ability to stabilize bilgewater emulsions.

5.3.5 CMC_{IFT} as a Practical Method for Qualifying Shipboard Cleaners

Results from this study indicate CMC_{IFT} as a practical and experimental parameter for predicting a cleaner's likelihood of developing stable emulsions. Therefore, it is recommended that CMC_{IFT} be used to evaluate the risk of using a particular shipboard cleaner. For example, if a cleaner is determined to have a CMC_{IFT} of 105 ppm, as was the case for Type 1 detergent (Table 5-1), the risk of that cleaner contributing to emulsion stability would be much larger than that of a cleaner with a CMC_{IFT} of 6,832 ppm, as was observed with PRC. This is because only a small amount of Type 1 Detergent needs to be present in the bilge before the concentration reaches CMC_{IFT} . To put it in perspective, only 0.5 gals of Type 1 Detergent would need to make its way into a 5,000 gal bilge tank before the concentration exceeded the CMC_{IFT} , where 34 gals of PRC would have to be added to the same size tank before its CMC_{IFT} was reached.

However, it is important that CMC be measured under representative conditions. For example, when CMC was measured using surface tension measurements (i.e. aqueous/air interface), the

inflection point of oil separation was up to 10 times smaller than the CMC_{IFT} (Appendix C Fig. C6). The discrepancy in predicting emulsion behavior between CMC measured using surface tension (CMC) and IFT measurements (CMC_{IFT}) is likely attributable to components in cleaners that decrease surface tension but do not actually contribute to the electrostatic or steric stabilization.

While the results from this study are promising, emulsions prepared in a lab do not represent the complexity and variability of emulsions seen in ship bilges. The salinity, pH, oil composition, and temperature of bilgewater can vary significantly depending on daily shipboard activities; all of which can influence CMC and emulsion stability. Therefore, it is extremely difficult to account for all parameters that may impact emulsion stability. The goal of this study was not to use CMC_{IFT} as a quantitative predictor of emulsion stability; but instead, to understand how CMC_{IFT} impacts emulsion stability and to provide decision makers with a tool for flagging potentially problematic cleaners from being used on ships.

5.4 Conclusions

The complexity of bilgewater makes the relationship between cleaner components and emulsion stability difficult to predict. Concentration and types of oil are constantly changing, which can directly impact how different types of surfactants will interact with the oil-water interface. Also, cleaner chemical compositions are proprietary, and therefore largely unknown. In this study, we have investigated experimental properties of emulsion systems that could be used to predict emulsion stability. In particular, we evaluated how IFT, CMC, and CMC_{IFT} impact macro-phase oil separation in model surfactants and commercial cleaners.

The emulsion samples shifted from predominantly separated oil to stabilized emulsion at surfactant concentrations correlating closely with CMC_{IFT} . The change in emulsion behavior was due to the packing of surfactant at the oil-water interface. As the surfactant concentration approaches CMC_{IFT} , the amount of surfactant adsorbed at the interface approaches its highest packing density and the mechanical stability of the surfactant layer can be expected to be largest, thus improving emulsion stabilization. In addition, it was found that neither IFT nor droplet size was directly related to the breaking of a cream layer into a separate oil layer. Therefore, the stability of the emulsions prepared in this study is best explained by an electrostatic/steric stabilizing mechanism rather than the initial droplet formation. In conclusion, CMC_{IFT} has been demonstrated as a practical and experimental method to predict emulsions stability for complex systems. Cleaners developed for use on ships could be tested for CMC_{IFT} using a representative oil and flagged as having a greater potential contribution to bilgewater emulsion stability if the cleaner's CMC_{IFT} was found to be low.

Chapter 6: Stabilization of Bilgewater Emulsion by Shipboard Oils

6.1 Introduction

The current consensus is that bilgewater emulsions are stabilized by detergents found in bilge water (Bhattacharyya et al., 1979; Church et al., 2019; EPA, 2011). In fact, the MEPC.107(49) certification of oil pollution abatement (OPA) systems require the use of detergents to simulate bilgewater emulsions (Church et al., 2019). While this may be true, there is also growing evidence that fuels are capable of emulsification without the presence of detergents. In previous work, the spontaneous transport of water miscible compounds from a simulated bilgewater oil to the aqueous phase using electrochemical microsensors was demonstrated (Church et al., 2017). Also, as stated in Chapter 5, small amounts of organic materials from an oil phase may produce significant changes in the critical micelle concentration (CMC) of the aqueous phase (Church et al., 2020). For example, urea, short-chain alcohols, and water-soluble esters are known to modify the interaction of water with the surfactant molecule by modifying water's dielectric constant or solubility parameter (Rosen and Kunjappu, 2012; Schick and Gilbert, 1965).

In addition, it is well accepted that a broad variety of chemical additives are introduced to fuels and lubricating oils in order to improve their properties (Hosseinzadeh-Bandbafha et al., 2018). A fuel additive is a chemical substance that leads to better engine performance, by improving fuel properties, cleaning engine parts, and reducing greenhouse gas emissions. A total of 10,499 gasoline and diesel fuel additives are registered under Title 40 CFR part 79, as authorized by the Clean Air Act. This includes lubrication improvers, corrosion inhibitors, antioxidants, biocides, and dispersants. These additives are inherently surface active and thus may help stabilize emulsions in bilgewater. Most fuel additives have amphiphilic properties in order to interact with metal surfaces, oxidants, or acidic contaminants while also being soluble in the oil solution. Likewise, detergents and dispersants are surface active in nature in order to stabilize polar additives. Therefore, additives in fuels could significantly contribute to the properties of an oil-water interface in bilgewater.

Depending on the fuels and lubricating oils that end up in the bilges, several additives could play an important role in stabilizing emulsions in bilgewater. Diesel fuels typically have oxygenated additives to help the fuel burn more cleanly and reduce smoke emissions (Hosseinzadeh-Bandbafha et al., 2018). The most commonly used oxygenated additives are alcohols and ethers. Alkyl ethers, such as methyl tert-butyl ether (MTBE), or ethyl-tert butyl ether (ETBE), are soluble in water (Jensen and Arvin, 1990), but it is unclear how they might impact emulsion stability. Oxygenated additives like ethylene glycol monomethyl ether (EGME) and diethylene glycol monomethyl ether (DEGME) are used as an anti-icing additive in JP-5, a kerosene-type jet fuel. These compounds are also water soluble and known to be surface active (Marszall, 1980). Likewise, nitrogen based detergents are often added to gasoline and diesel fuels to help prevent the buildup of “gunk” in fuel tanks and engines. Examples include, polyether amines (Techron), polyalkylaminophenol (Chevron), and other polyalkyl amines. While the exact chemical makeup of these compounds are proprietary, these compounds will be surface active

and could help stabilize bilgewater emulsions. Lubricating oils are even more likely to contain detergent additives. Manufacturers often include detergents to help keep the engines clean, as well as inhibit corrosion and maintain alkalinity. Most commercial oils contain zinc dialkyldithiophosphate (ZDDP) as an anti-wear additive, but more detergent like sulfonates and polyalkylene succinimides are also added to lubricating oils (Ribeiro et al., 2007). ChevronTexaco 9250 Marine Engine oil advertises “an effective detergent-dispersant package to prevent ring sticking and lacquering of engine pistons”, “rust and oxidation inhibitors to prevent engine rusting and minimize oxidation of the lubricant”, and “alkaline reserves to neutralize acids which result from burned fuel gasses”.

Given the impact that emulsions have on bilgewater treatment, the objective of this work was to understand how fuel and oil compounds impact emulsion stability. In particular, this work determined how fuels and lubricating oils can alter the aqueous chemistry of bilgewater and how water exposed to these compounds can develop more stable emulsions. Additionally, preliminary steps were made to identify types of additives that may stabilize emulsions in bilgewater. Overall, results from this study give important insights into how bilgewater emulsions are stabilized, which can help guide decision makers for optimal bilgewater management.

6.2 Materials and Methods

6.2.1 Model Bilgewater Fuels and Oils

A fuel/ oil mix, called Navy Standard Bilge Mix #4 (NSBM #4) and its individual components were selected as surrogate oils in this study. NSBM #4 is conventionally used to test oil pollution abatement equipment, and its components represent common oils and fuels found in bilgewater (Church et al., 2019). NSBM #4 is comprised of 50% Diesel Fuel Marine (DFM) (MIL-DTL-16884), 25% TEP Steam Lube Oil 2190 (MIL-PRF-17331), and 25% Diesel Lube Oil 9250 (MIL-PRF-9000). Mineral oil light (CAS # 8042-47-5) was used as a control oil (without additives) due to its viscosity and density similarities to that of NSBM #4. Mineral oil is also a major component of Lube Oil 2190.

6.2.2 Extracting water miscible components from bilgewater oil and fuels

80 mL of deionized water and 20 mL of oil sample (e.g. NSBM #4, DFM, 9250, or 2190) were added to a clean 250 mL separatory funnel and allowed to rest undisturbed under ambient conditions (20-22°C) for 24 h. After which, the aqueous portion of the sample was carefully collected, avoiding any mixing or contamination from the top oil layer, and the sample was analyzed for physical and chemical properties.

6.2.3 Water Quality Analysis

After water samples were exposed to various bilgewater oils for 24 h, the pH, conductivity, and surface tension of the water samples were measured. pH was determined using a standard pH probe (IntelliCAL PHC201, Hach) following Standard Method 9040C. Conductivity was measured using a 4-pole graphite conductivity probe (IntelliCAL CDC401, Hach) following EPA Method 120.1. Surface tension was measured using the du Noüy ring method. A platinum ring was positioned just above the water sample and the tensiometer was blanked. Next, the interface was left undisturbed for 5 min to allow for any fuel compound/surfactant adsorption at the interface to reach equilibrium. The tensiometer then automatically determined the location of

the air/water interface by lowering the ring towards the sample until a change in force of 0.03 mN/m was detected. Next, the tensiometer measured the force required to pull the ring back through the water/air interface and recorded the surface tension in mN/m. Surface tension measurements were performed continuously until the surface tension reached equilibrium (generally within 5 min). The du Noüy ring was cleaned with isopropanol and dried between each sample. Experiments were conducted at ambient conditions (20-22°C). All measurements were collected in triplicate.

6.2.4 Emulsion Preparation

Aqueous samples exposed to different bilgewater oils for 24 h were used to generate emulsions with 20% (v/v) mineral oil. 16 mL of aqueous sample and 4 mL of mineral oil were added to a 50 mL centrifuge tube and homogenized at full power (30,000 rpm) using a high shear homogenizer (Omni Tissue Master) for 30 seconds. The homogenizer probe was rinsed between each sample using deionized water. After the emulsions were prepared, they were poured into 40 mL glass flat bottom vials with Teflon-lined screw caps (Qorpak GLC01020). Emulsions were prepared in triplicate at ambient conditions (20-22°C).

6.2.5 Emulsion Stability

Stability is generally defined as the ability to resist changes in properties over time. Emulsion stability can be measured differently depending on the field of study. Most commonly, emulsion stability is measured based on droplet size distribution, turbidity, oil separation, viscosity, and creaming rate. In this work, creaming rate was used to evaluate emulsion stability due to its important role in gravity separation technologies used in many bilgewater treatment systems. Creaming results from gravitational forces between the oil and aqueous phases with different densities (Church et al., 2019).

To determine creaming rate, photos of the emulsions were taken every 30 min using a digital camera (Nikon D80) over 8 h. The photos were then imported to ImageJ (NIH) for image analysis. The images were then converted to 32 bit grayscale, and the threshold was adjusted to 50% to help distinguish the lower serum layer. The height of the lower serum layer was then measured using the measuring tool in ImageJ and plotted over time to get a creaming velocity. The creaming velocity will depend on the size of the emulsions and the densities of the two phases, but emulsions with creaming velocity less than 1 mm/day are considered to be stable (Pathak, 2017).

6.2.6 Identification of Surface Active Compounds

To identify compounds in bilgewater oils and fuels that may stabilize emulsions, infrared (IR) and gas chromatography-mass spectrometry (GC-MS) analyses were conducted. 10 mL of distilled water was placed in four scintillation vials, then 10 mL of 2190, 9250, DFM, and NSBM #4 were added to each vial. After 3 days at room temperature, the water was extracted from the vials. Liquid-liquid extraction of the water was conducted using three 10 mL aliquots of dichloromethane (DCM). Room temperature rotary evaporation dried the DCM from the extractions to 1 mL. For IR analysis, the extract was placed on a salt plate (25 mm x 4 mm NaCl, Agilent) and the DCM was allowed to evaporate leaving only the extracted components from the

samples. The salt plate was then placed in an IR spectrometer (Thermo Scientific Nicolet iS50-FT-IR spectrometer) for analysis.

For GC-MS analysis, the extracts were placed into 2 mL GC vials and analyzed on an Agilent 7890B3 GC connect to a 5977C MS. The inlet temperature was 250 °C with a 1 mL per minute of He flow and a Restek Rxi-5ms column. An initial oven temperature of 50 °C was held for 3 min followed by a 5 °C/min increase to 250 °C, and then a 10 °C/min increase to 325 °C. The MS was used in electron ionization (EI) mode with a scan range of 45-500 amu, source temperature of 230 °C, and quadrupole temperature of 150 °C. Mass spectra from chromatographic peaks were compared against the NIST Mass Spectral Library and analyzed for common fragments to either fully identify or provide the class of molecule observed.

6.2.7 Transport of fuel additives and compounds from the oil to the aqueous phase.

Many “traditional” aromatic additives, such as benzene, toluene, ethylbenzene, and xylenes that have been used to boost octane ratings, are also UV absorbent (Middelburg et al., 2017). Therefore, UV-visible (UV-vis) spectroscopy was used to determine the transport rate of fuel additives from the oil to aqueous phase. 2.5 mL of DI water was added to a quartz cuvette and placed in the UV spectrophotometer (Agilent 8453 UV-Visible). The background was blanked and 0.5 mL of oil sample was carefully added to the top of the DI water, out of range of the light path. Then, the absorbance spectrum from 200-400 nm was recorded every 15 min for 2 h. The absorbance of significant peaks were plotted against time to determine the transport rate of components from the oil to aqueous phase. Samples were analyzed in triplicate and conducted at room temperature.

6.3 Results and Discussion

6.3.1 Bilgewater fuels and additives

While certain characteristics of oil are subject to some variability, the fuels brought onboard Navy ships must follow certain specifications, which gives some insights into the fuel compounds that may be found in bilgewater. In this study, NSBM #4 and its individual components were selected as surrogate oils. Table 6-1 shows the concentration and possible additives linked to each oil component. NSBM #4 is comprised of 50% DFM (MIL-DTL-16884), 25% TEP Steam Lube Oil 2190 (MIL-PRF-17331), and 25% Diesel Lube Oil 9250 (MIL-PRF-9000). Specifications associated with additives for each of the oil components are discussed below.

Table 6-1 Composition of Synthetic Bilgewater and Possible Additives

Class	Standard Mix	Composition	Description
Oil	Navy Standard Bilge Mix (NSBM) #4	50% v/v Diesel Fuel Marine, MIL-DTL-16884	Naval distillate fuel (<1% additives) • Corrosion inhibitor • Static dissipater
		25% v/v 2190 TEP Steam Lube Oil, MIL-PRF-17331	Moderate service steam turbine and gear lubricating oil (~1% additives) • Tricresyl phosphate • Proprietary additives
		25% v/v 9250 Diesel Lube Oil, MIL-PRF-9000	Lube Oil 9250 – Lubricating oil for use in shipboard internal combustion diesel engines (~30% additives) • Detergent-dispersant package • Oxidation inhibitors • Reserve Alkalinity

Diesel Fuel Marine (DFM) (MIL-DTL-16884)- DFM, also referred to as NATO F-76, is the Mil-Spec distillate fuel normally used in shipboard diesels, gas turbines, and boilers. DFM is similar to Marine Gas Oil (MGO), which is favored in the shipping industry, but has very tight specification and storage control requirements (Sermarini, 2000). Unlike MGO, which must be consumed within six weeks of receipt, DFM contains stability additives that make it acceptable for storage in DFSPs as war reserve. DFM allows for the use of metal deactivators, like *N,N'*-disalicylidene-1,2-diaminopropane or 1,2-diaminopropane. Likewise, lubricity improvers may be used, but must be approved and meet the requirements specified in MIL-PRF-32490.

TEP Steam Lube Oil 2190 (MIL-PRF-173331)- Lube Oil 2190 is primarily used as a circulating system oil for marine gear turbine sets. It is designed to provide extreme pressure protection and resistance to rust, oxidation, corrosion, and foaming. Tricresyl phosphate (TCP) is allowed for use under MIL-PRF-17331 as an antiwear additive. Additives can range in concentration, but are typically quite low. For example, a vendor (Chevron) of Lube Oil 2190 lists additives as < 1% in their safety data sheet (SDS). The SDS also showed that Lube Oil 2190 is primarily composed of mineral oil.

Diesel Lube Oil 9250 (MIL-PRF-9000)- Lube Oil 9250 is a highly refined, highly viscous paraffinic-based oil used to meet the demand of marine trunk piston-type diesel engines. MIL-PRF-9000 allows for the use of additives to meet the specification requirements. Vendors of Lube Oil 9250 market the use of “an effective detergent-dispersant package” and “rust and oxidation inhibitors”. Alkalinity improvers are also included in Lube Oil 9250. Safety Data Sheets (SDS) indicate the use of up to 2.5% ZDDP, a common fuel additive.

In addition to fuel additives, polar compounds are also inherently present in diesel fuel and lubricating oils. Short chain alcohols, thiols, and ethers are found in crude oil which may not be completely removed during the refining process (Tissot and Welte, 2013). Also as fuels and oils age, the oxidation and biodegradation of hydrocarbons generates significant amounts of polar compounds within the fuel (Lang et al., 2009). Lang et al found that weathered diesel fuel

contributed up to 98% of its water soluble fraction to polar compounds, while fresh diesel oil only had aromatic compounds that transferred to the water phase (Lang et al., 2009). Like diesel, base oils used in lubricants also contain a fraction of polar compounds that could impact bilgewater emulsion stability. The concentration of polar compounds in mineral base oils range from 2-141 mmol kg⁻¹ (Haus et al., 2001).

6.3.2 Water Quality Analysis

Figure 6-1 shows the surface tension, pH, and conductivity of water exposed to NSBM #4, DFM, Lube Oil 2190, and Lube Oil 9250 for 24 h. It is clear that exposure to bilgewater oils influenced the chemistry of the aqueous solution. The conductivity of the DI water exposed to various bilgewater oils were on average 2.5 μ S/m higher than the DI control, which could indicate the transport of ionic compounds from the oil to the aqueous phase. However, since exposure to bilgewater oil increased conductivity only $\sim$ 2.5 μ S/m, it was concluded that the increased conductivity did not have a significant role in emulsion stability. In other systems, emulsion stability was affected only when conductivity changed by 6.5 μ S/cm (Church et al., 2017). It is more probable that the compounds that contribute to emulsion stabilization are nonionic and do not contribute to conductivity.

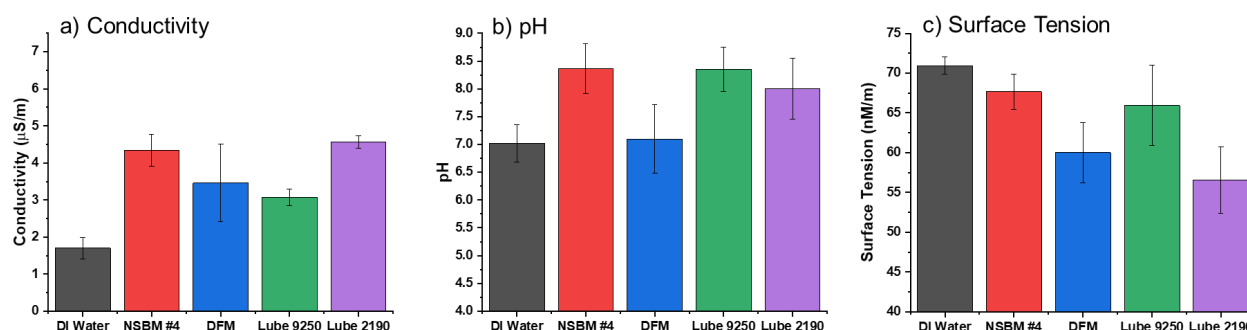


Figure 6-1 Changes in a) conductivity, b) pH and c) surface tension of aqueous solutions exposed to various bilgewater oils after 24 h.

The pH of the water exposed to NSBM #4, Lube Oil 2190, and Lube Oil 9250 were also higher than the DI control. Water exposed to both Lube Oil 9250 and NSBM #4 had a pH of 8.4 after 24 h. Water exposed to Lube Oil 2190 had a pH of 8.0, and exposure to DFM did not change the pH. Existing literature would suggest fuel and oils should decrease the pH of water due to the oxidation of alkanes within the fuel that could act as Lewis acids (Wolak, 2018). However, many lube oils contain alkalinity improvers that are used to neutralize acidic contaminants of engine oils and protect engines from wear (Pawlak, 2003). Therefore, the alkalinity improvers may be responsible for the increased pH. Common alkalinity improvers include calcium sulfonates, calcium phenates, and magnesium sulfonates, which potentially act as emulsifiers depending on their solubility. Given that Lube Oil 9250 is advertised to contain alkalinity improvers, the oil also caused a large increase in pH of the exposed water, it is possible that alkalinity improvers could contribute to emulsion stability.

The change in surface tensions of waters exposed to the fuel samples were also analyzed to determine if components of bilgewater oils are active at an aqueous air interface. Surface tension is the measurement of the work (as mN/m) required to increase the size of the interface and plays an important role in the formation of emulsion droplets during emulsification. It is well known that a compound's affinity to an interface will directly relate to its ability to stabilize emulsions (Church et al., 2019). In fact, theoretical analysis and experimental results have shown that droplet diameter depends on the power density of energy dissipation and the oil-water interfacial tension (Marquez et al., 2018; Raikar et al., 2011). The surface tension of the water exposed to DFM and Lube Oil 2190 were significantly lower than the DI control (Figure 6-1c). Specifically, water exposed to DFM and Lube Oil 2190 for 24 h had surface tensions of 56.6 and 57.3 mN/m, respectively. Considering that surfactant solutions with surface tensions as high as 60 mN/m have been shown to impact emulsion stability, it is likely that DFM and Lube Oil 2190 contain compounds that could contribute to bilgewater emulsion stability.

6.3.3 Identification of water miscible compounds

6.3.3.1 GC-MS

To identify potential emulsion stabilizing compounds that leached from bilgewater oils and fuels to the water phase, GC-MS analysis was conducted on water samples exposed to NSBM #4 components for 72 h. All of the samples had multiple peaks of interest in the chromatogram, as shown in Figure 6-2. Identifying peaks of interest involved eliminating any peaks with retention time and mass spectra that matched the blanks. The mass spectra of the peaks that remained were analyzed as well as comparing it against the NIST Mass Spectral Library to either fully identify or provide the class of molecule observed, as shown in Table 6-2.

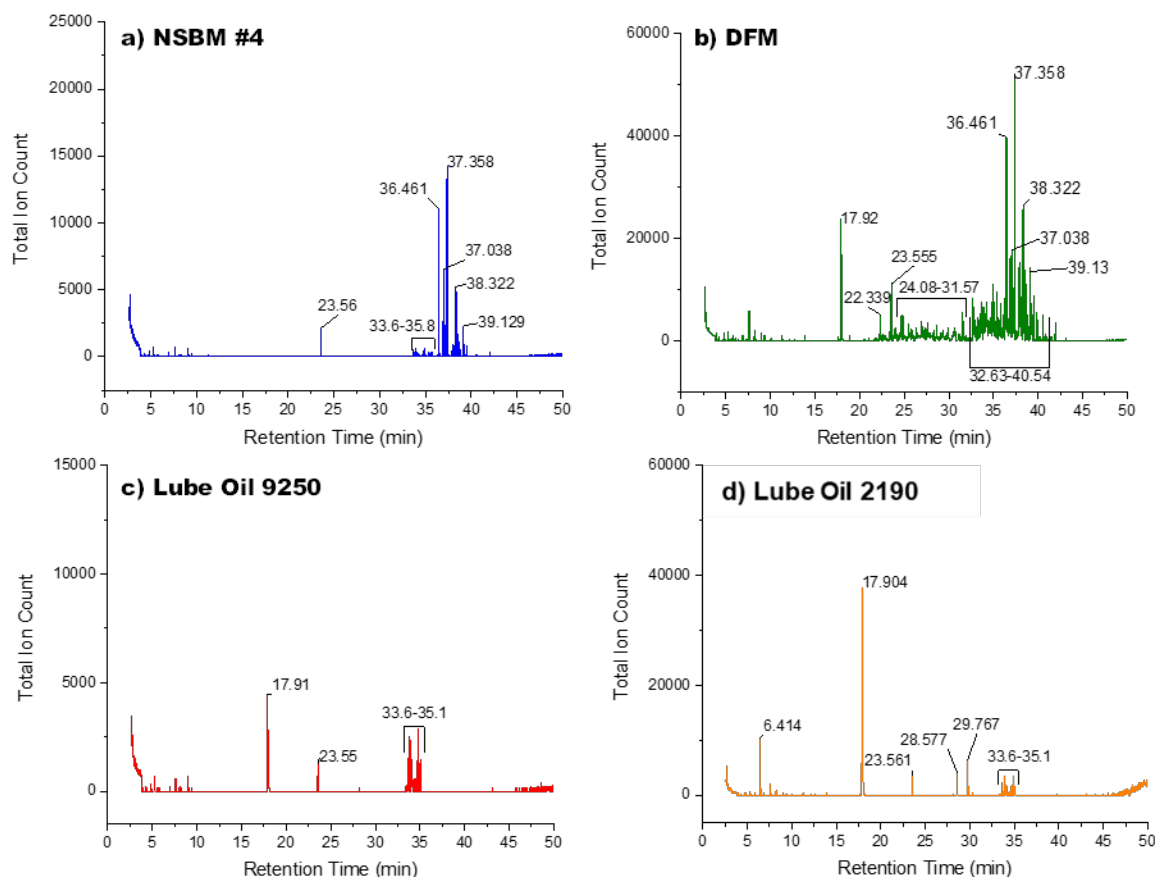


Figure 6-2 Chromatographs of water extracts from a) NSBM #4, b) DFM, c) Lube Oil 9250, and d) Lube Oil 2190 with retention time of peaks of interest

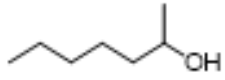
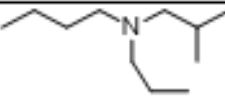
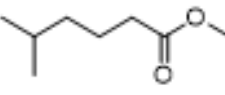
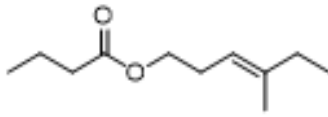
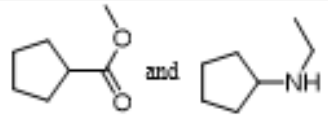
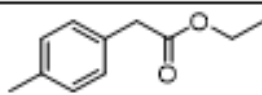
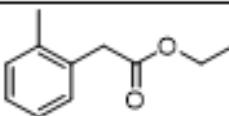
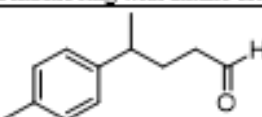
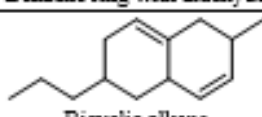
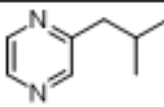
As expected, the chromatogram of water exposed to NSBM #4 (Fig. 6-2a) comprised of a compilation of peaks found in the chromatograms of its components (Fig. 6-2b-d). All the peaks in NSBM #4 were identified as components of DFM, Lube oil 9250, and Lube oil 2190. Across the three components, DFM had the most peaks/molecules with two clusters of peaks, some overlapping, at retention times 24.08-31.57 min and 32.63-40.54 min (Fig. 6-2b). Because the number of peaks was so large, only the most intense peaks were selected for identification since these would have the highest concentrations. Based on the NIST library and mass spectrum analysis, the peaks from 24.08-31.57 min were identified as C10-C12 alkane esters with thiol compounds also being potential matches. The peaks between 32.63-40.54 min were of particular interest because of their intensity and uniqueness to DFM. Identifying the mass spectrum of the peak at 36.46 min indicated aromatic, alkane, and ester fragments (Table 6-2). The peak at 37.04 min had almost the same MS spectrum as the peak at 36.46 min. Due to the similar retention time and spectra, these two peaks are likely either isomers or very similar molecules. Spectrum of the peak at 37.36 min revealed aromatic, cyclic alkane, ester, and possible aldehyde fragments. The peak at 38.32 min exhibited fragments matching cyclic alkenes and alkanes. The final peak analyzed in the set was at 39.13 min and had fragments matching pyrazine, an

aromatic containing nitrogen, and alkanes. Exact identification was not possible for most of these peaks; however, they all contained hydrophobic alkane or aromatic sections attached to oxygen and nitrogen functional groups, such as esters and amines, that provide the molecules with surface active or surfactant like properties.

Both lube oils had very similar chromatograms, with relatively few peaks over the first 30 min retention time and a group of peaks from 33.6-35.1 min. Both lube oils had relatively intense peaks at 17.9 min and 23.6 min. These were identified as tributylamine and octyl- or heptyl-ethers, respectively. Lube oil 2190 also had significant peaks at 28.6 and 29.8 min (Fig. 6-2d) that were identified as benzene ring compounds containing nitrogen. The group of peaks between 33.6 and 35.1 min found in both lube oils, had matches with cyclic alkenes with ethers and esters. Overall, the molecules found in the extractions were alkanes or aromatic species with heteroatom substituents, including ethers, thiols, and amines, all of which exhibit increased water solubility.

It is difficult to determine whether the ethers, thiols, amines, or aromatic compounds observed in the GC-MS analysis are additives or inherent to the base fuel. In particular, DFM is known to naturally contain up to 28% of aromatic compounds (Striebich et al., 2014). Likewise, it is well known that DFM contains significant amounts of nitrogen compounds, typically in the forms of alkyl pyrroles, alkyl pyridines, benzoquinolines, benzamines, indoles, and carbazoles. Dese et al. recently reported up to 475 mg N/L total nitrogen in DFM (Deese et al., 2019). Oxygenated compounds are also expected in fuels, as fuels and oils interact with the atmosphere, they become more oxidized, forming ethers and alcohols. Furthermore, these same compounds are also used as fuel additives. For example, diesel fuels typically have oxygenated additives to help the fuel burn more cleanly and reduce smoke emissions (Hosseinzadeh-Bandbafha et al., 2018). Oxygenated additives like EGME and DEGME are used as an anti-icing additive in JP-5. Likewise, nitrogen-containing compounds are often added to gasoline and diesel fuels to help prevent the build-up of solid deposits in fuel tanks and engines. Examples include polyether amines (Techron), polyalkylaminophenol (Chevron), and other polyalkyl amines.

Table 6-2 Identified Compounds in Aqueous Solutions Exposed to NSBM #4 Components

Peak Retention Time (min) ^a	Source Oil or Fuel	Peak Identification ^b
6.41	Lube Oil 2190	 Alkane alcohol
17.91	- DFM - Lube Oil 9250 - Lube Oil 2190	 Tri(butyl or propyl)alkane amine
23.55	- NSBM #4 - DFM - Lube Oil 9250 - Lube Oil 2190	 Alkane ester
29.77	Lube Oil 2190	 Nitrogen containing benzene or toluene
24.08-31.57	DFM	 Alkane and alkene esters C11-C12
33.6-35.1	- NSBM #4 - Lube Oil 9250 - Lube Oil 2190	 Cyclic alkanes with ester or nitrogen
36.46	- NSBM #4 - DFM	 Benzene ring with alkane ester
37.04	- NSBM #4 - DFM	 Benzene ring with alkane ester
37.36	- NSBM #4 - DFM	 Benzene ring with aldehyde
38.32	- NSBM #4 - DFM	 Bicyclic alkane
39.13	- NSBM #4 - DFM	 Benzene with nitrogen and alkane
a) All samples are run with the same method, therefore matching retention time implies same molecule b) Peak identification was not 100%, classes of compounds are shown with description underneath		

6.3.3.2 IR

IR spectra of the water exposed to various oil samples confirmed observations in the GC-MS analysis. Lube oil 2190 and 9250 had similar peaks at 2700 and 1450 cm^{-1} , which corresponds to CH_3 and CH_2 bending (Appendix D Fig. D1). These peaks are expected in any type of oil or fuel. In addition to the peaks found in the lube oil spectra, Figure 6-3 shows the spectra of the DFM peaks at 3200 cm^{-1} , which is indicative of alcohol OH stretching. The IR spectra of DFM also had a small peak at 1600 cm^{-1} , which could be weak $\text{C}=\text{C}$ or an imine group. Given that GC-MS analysis indicated the presence of nitrogen containing compounds in water exposed to DFM, the presence of an imine group is possible. Interestingly, IR of the DFM sample did not have strong peaks in the aromatic regions (1600-1400 cm^{-1}), which was expected given the typical composition of DFM. However, aromatics are known to be volatile and could have been lost due to evaporation prior to analysis. Importantly, the IR results complemented the findings from GC-MS and identified heteroatom functionalities, such as alcohol and imine (or other nitrogen-containing groups), which contributed to increased water solubility and can potentially function as surface active compounds (surfactants) to stabilize emulsions.

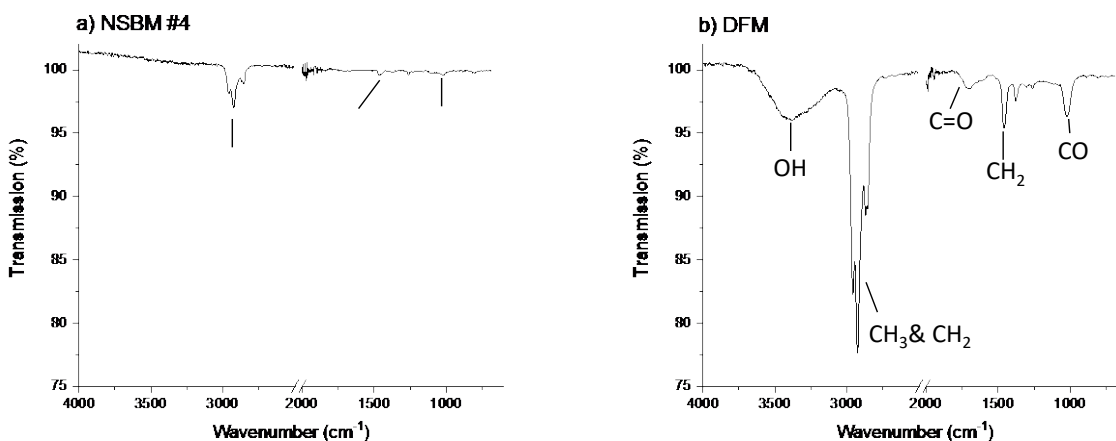


Figure 6-3 Infrared transmission of extracts from water exposed to a) NSBM #4 and b) DFM revealing prominent functional groups

6.3.3.3 UV Spectroscopy

UV spectroscopy was performed on water samples exposed to NSBM #4, DFM, Lube Oil 9150, and Lube Oil 2190 in order to better understand the types of compounds that are migrating from the fuel to the aqueous phase. The UV absorbance spectra of the samples are shown in Figure 6-4a. DFM had a large, broad peak at 192 nm that contained a small shoulder at 220 nm. Lube Oil 2190 and Lube Oil 9250 also showed an increased absorbance near 192 nm, but their peaks were less distinguished. Lube Oil 9250 also had a peak at 235 nm. Both the absorbance peaks at 192 and 235 nm were present in the NSBM #4 sample. Aromatic molecules are known to absorb near 200 nm. In particular, benzene and naphthalene both have significant absorption in the 200-300 nm region, providing further verification that these classes of molecules are partitioning into the water upon exposure.

6.3.4 Transport of fuel components

UV-vis spectra of the water samples after exposure to bilgewater fuels and oils revealed that UV active compounds are entering the water from both lube oils and DFM. The water sample exposed to DFM had the largest absorbance at 192 nm, significantly greater than that of the lube oils, indicating that DFM contains a higher concentration of water miscible UV active compounds (Fig. 6-4a). The peak at 192 nm was significantly less intense in the NSBM #4 exposed water, than in the DFM exposed water, indicating that there was no synergistic effect from the combination of the fuel and oils. Figure 6-4b shows the change in absorbance at 192 nm over time. All samples showed a linear change in absorbance, indicating a diffusive transport into the aqueous phase. The increase in intensity of the peak at 192 nm was fastest in DFM, followed by NSBM #4, Lube oil 2190, and then Lube oil 9250. Release rate of a compound from one phase to another is directly proportional to concentration, based on diffusion release kinetics. Therefore, DFM exhibited the highest concentration of water-soluble, UV active compounds.

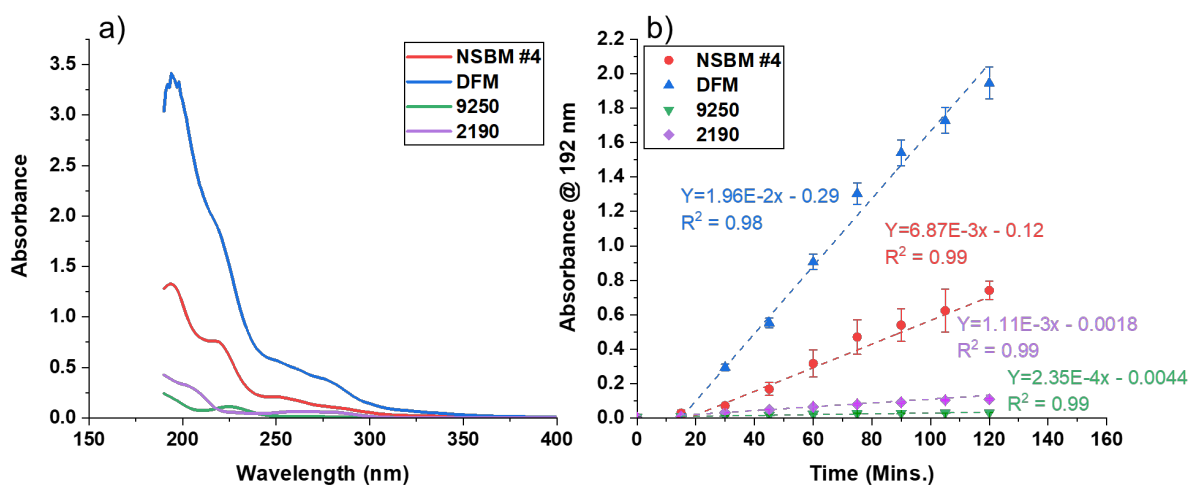


Figure 6-4 a) UV absorbance of water exposed to surrogate bilge oil samples and b) change in absorbance at 192 nm of water exposed to oil samples over time.

Considering the large concentration of additives in the lubricating oil, it was surprising to find that water exposed to DFM showed the quickest increase in UV absorbance and the most peaks in the GC-MS (Fig. 6-2). There is currently no literature precedent on the transport of fuel compounds into bilgewater; however, research on the transport of monoaromatic hydrocarbons (benzene, toluene, ethylbenzene, and xylene BTEX) into groundwater could provide clues into the interphase mass transfer of fuel compounds in bilgewater. In groundwater systems, cosolvency plays an important role in the transport of monoaromatic hydrocarbons into the aqueous phase (Heermann and Powers, 1998; Powers et al., 2001). Oxygenated hydrocarbons, like ethanol, reduce the polarity of the aqueous phase, allowing higher concentrations of hydrophobic compounds in the aqueous phase. Likewise, the cosolvent effect will also increase the rate of mass transfer into the aqueous phase (Powers et al., 2001). Therefore, the oxygenated compounds found in DFM may help facilitate the transport of larger hydrophobic compounds into bilgewater.

6.3.5 Emulsion Stability

For this study, creaming rate was used to evaluate emulsion stability. This is because creaming rate measures how effectively oil droplets are able to stay suspended in the bulk layer and is ultimately governed by differences in phase densities and droplet size distribution. In a bilgewater context, creaming rate is important because most treatment systems rely on gravimetric separation (Church et al., 2019). Emulsion stability was evaluated for emulsions prepared with mineral oil and water exposed to bilgewater fuels for 24 h. Figure 6-5 shows the change in cream height over time and the associated creaming rate. Emulsion stability is inversely related to creaming velocity, i.e. larger creaming velocity corresponds to emulsion instability. The DI control was the least stable emulsion (Fig. 6-5). The average creaming velocity for mineral oil in DI was 22 mm/h. Emulsion samples prepared with water exposed to various NSBM #4 components all demonstrated increased emulsion stability compared to the control. The average creaming rate over 3 replicate experiments was 2.6 ± 1.3 mm/h for DFM, compared to 6.18 ± 0.9 mm/h for NSBM #4, 6.7 ± 0.9 mm/h for Lube Oil 2190, and 12.9 ± 3.4 mm/h for Lube Oil 9250 (Fig. 6-5b).

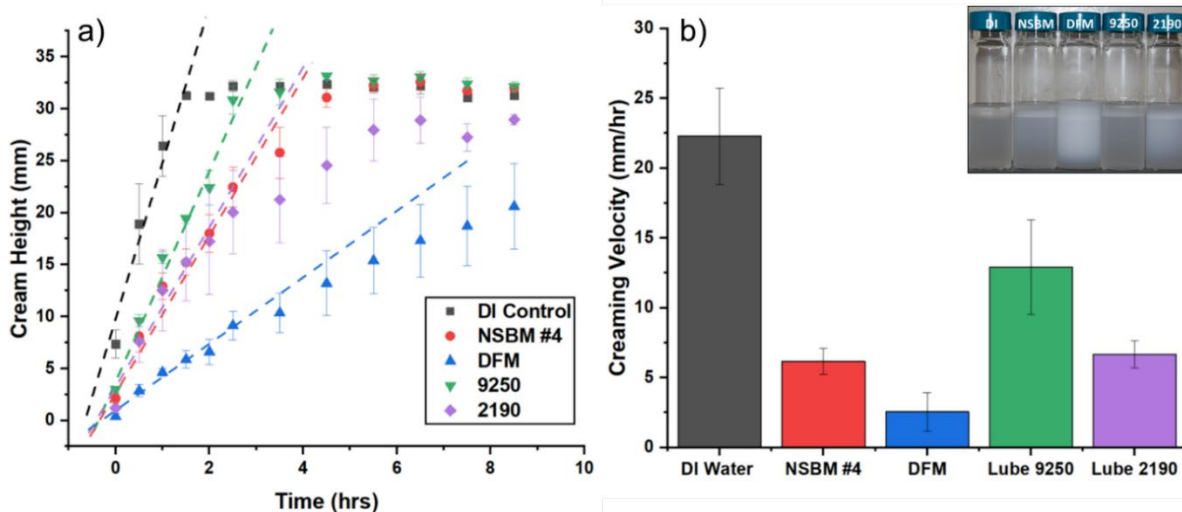


Figure 6-5 Mineral oil emulsion stability expressed as a) change in cream height over time and b) initial creaming velocity (mm/h) (Inset: Photograph of emulsions after 1 h)

The change in cream height over time provided insight on the interactions between oil droplets during the creaming process (Fig. 6-5a). Initially, all samples exhibited linear increases in cream height with time, which indicates Stokes Law kinetics with no interactions between the droplets. However with increased time, all samples exhibited non-linear behavior in cream height over time, indicating that coalescence or flocculation also occurs during the creaming of the emulsion sample. The linear Stoke's separation likely occurred from the larger droplets in the polydisperse emulsion population, which is then followed by flocculation or coalescence of the smaller droplets to facilitate their separation and creaming. A photograph of the emulsion samples after remaining undisturbed for 1 week is shown in the inset of Fig. 6-5b. Only the emulsion sample prepared with water exposed to DFM was able support a cream layer for more than 1 week. Likewise, DFM demonstrated a significantly decreased creaming rate compared to the DI

control. Stoke's Law creaming kinetics are dependent on density differences between the phases, viscosity of the continuous phase, and droplet diameter (Chanamai and McClements, 2000). It is assumed here that the phase densities and continuous phase viscosity were unaffected by additives. Therefore, the differences in the linear increase in cream height between samples were attributed to droplet size differences. Slow creaming rate in DFM samples indicated minimal initial droplet interaction that was likely due to additives from the DFM that were able to support smaller, more stable, droplets. Indeed, the trend in creaming rate shown in Fig. 6-5a corresponded well with the release of UV-active compounds demonstrated in Fig. 6-4. Specifically, there was a direct relationship between the emulsion stability of the samples and the amount and rate of release of UV-active compounds that were leached in to the water. Aromatics are known to absorb in the UV and to stabilize both water-in-oil, as well as oil-in-water emulsions through π - π interactions (Jian et al., 2017). For water-in-oil emulsions, it has been shown that coalescence rate decreases with increasing asphaltene and polyaromatic hydrocarbon concentrations (Zhang et al., 2020). Therefore, it is suggested that aromatic, UV-active compounds that partitioned from the oil phase, particularly DFM, into the aqueous phase functioned as surfactants to stabilize the emulsions.

The creaming rate of the emulsions was closely related to the surface tension of the water exposed to the oil samples (Fig. 6-1). DFM and Lube Oil 2190 demonstrated the lowest surface tensions and the most stable emulsions. This is due to the relationship between droplet size and the interfacial tension. Theoretical analysis and experimental results have shown that droplet diameter depends on the power density of energy dissipation and the oil-water IFT. Given homogenization energy was fixed for this study, the IFT is expected to have the largest impact on droplet size and emulsion stability. Droplet-droplet interactions are also important for emulsion stability; however, the creaming rate of the mineral oil emulsion generated in this study was high enough where coalescence or flocculation may have not had a large role (Krebs et al., 2012).

Naphthenic acids (or petroleum-derived carboxylic acids) and their corresponding naphthenates are relatively hydrophilic compounds found in oils that contribute to the formation and stability of oil-in-water emulsions (Kiran et al., 2009). Indeed, diesel fuels contain relatively high levels of naphthenic acids compared to other distillate fuels (Wang et al., 2007). The capability of naphthenic acids to stabilize crude oil-in-water emulsions is greatly enhanced when bulky secondary amines are also present (Saliu and Della Pergola, 2018).

6.3.6 Impact of fuel components on emulsion stability and bilgewater treatment

The goal of this study was to determine the impact of fuel components on the stability of bilgewater emulsions. Based on safety data sheet information, Lube Oil 9250 had the largest concentration of fuel additives among the NSBM #4 components. Yet, it is clear from the results of this study that these additives did not migrate into the aqueous phase (Figs. 6-1 & 6-2). Therefore, solubility of the fuel additives plays an important role in determining bilgewater emulsion stability. For example, the mineral oil emulsion prepared with water exposed to Lube Oil 9250 did not show significant emulsion stability (Fig. 6-5); however, the Lube Oil 9250 oil layer did have the most visible water-in-oil emulsions (Appendix D Fig. D2). Likewise, Lube Oil

2190 contains antiwear additives that are known to be surface active, yet the emulsion stability was significantly less than that of the emulsions prepared with water exposed to DFM. It is also uncertain if the compounds that stabilized the emulsions are fuel additives or natural to the distillate. Water exposed to DFM generated the most stable emulsions, which potentially resulted from the large concentration of water soluble monoaromatic compounds found in diesel distillates as identified by GC-MS.

Based on the mineral oil emulsion stability of water exposed to DFM, it is clear that components in DFM may impact bilgewater treatment. Many of these compounds were determined to be aromatic or cyclic alkane, ester, and possible aldehyde fragments; however, given the relationship between UV absorbance (Fig. 6-4) and emulsion stability (Fig. 6-5), it is likely that aromatic compounds have a significant impact on emulsion stability. Aromatic compounds are known to absorb to an oil-water interface (Kunieda et al., 2010), a behavior which stabilizes emulsions. Various intermolecular interactions, such as dipole-dipole, H-bonding, π - π , and cation- π , are responsible for the initial adsorption and aggregation of aromatic molecules at the oil-water interface (Teklebrhan et al., 2014). These interactions have been well studied in the oil and gas industry because of the role of asphaltene in stabilizing water-in-oil emulsions. Still, the literature is less clear on the role of more soluble monoaromatic compounds on the stability of oil-in-water emulsions. However, it is expected that the monoaromatic compounds would exhibit greater water solubility than asphaltenes and polyaromatics (McAuliffe, 1966), thus increasing transport into the aqueous phase to facilitate the stabilization of oil-in-water emulsions through similar dipole and π - π interactions.

In general, the emulsions observed in this study were considerably less stable than emulsions previously prepared using commercial cleaners and detergents that contain high concentrations of water soluble surfactants (Chapter 5). For example, bilgewater emulsions prepared with Type 1 detergent revealed a creaming rate that was more than 3 times slower than that of the emulsions generated in this study. However, the emulsion stabilization from fuel additives was still significant, particularly considering the potentially large volumes of bilgewater fuels, and components in fuels can have a major impact on bilgewater treatment in several ways. First, bilgewater containing emulsions stabilized by fuel compounds, similar to those shown in this study, will still need to be removed through a treatment system prior to discharge, which contributes to increased maintenance requirements and labor costs. Second, fuel additives in Lube Oil 9250 stabilize water-in-oil emulsions (Appendix D Fig. D2), which could lead to increased storage requirements for waste oil on ships and its pierside disposal costs. Third, many compounds that migrated into the aqueous phase were IR or fluorescence active. Therefore, oil content monitors that function based on these detection principles will encounter greater interference and noise during in situ oil content measurements, reducing accuracy and efficiency of water treatment. Therefore, the insights from this work have potential to not only contribute to improved methods for preventing emulsion stabilization in bilgewater, but also aid in improving other fields where surface-active compounds are prevalent. For example, the transport of compounds between fuel and aqueous phases have large implications in other areas of research. As fluorine-free firefighting foams are being developed to replace Per- and polyfluoroalkyl substances (PFAS) laden foams, the impact of cosolvents and interfacial turbulence caused by fuel

compounds will likely play a large role in the effectiveness of foams. Similarly, understanding the transport of BTEX compounds into the environment is important for oil spill remediation.

6.4 Conclusions

This work shows that components found in bilgewater oils and fuel can contribute to the stability of emulsions. The conductivity, pH, and surface tension of water were significantly altered after exposure to bilgewater oils for 24 h. Likewise, UV and GC-MS data suggested the transport of aromatic compounds from the oil to aqueous phase. The analysis of the mass spectrum from GC-MS along with IR analysis revealed that aromatic compounds contain oxygen and nitrogen functional groups, which exhibit surfactant-like behavior, leach into water. Emulsion stability experiments showed compounds found in DFM are most likely to stabilize emulsions, followed by Lube Oil 2190 and then by Lube Oil 9250. Further research is needed to provide exact identification of the compounds involved in bilgewater emulsion stabilization and determine the full impact of these additives on emulsion stability and bilgewater treatment.

Chapter 7: Implementing image processing and machine learning for predicting bilgewater emulsion stability

7.1 Introduction

Physicochemical properties such as temperature, pH, solid particles, surfactant type and concentration, ionic strength (e.g., salinity), and mixing intensity, can impact oil-in-water (O/W) emulsion stability due to their interaction with the interfacial film between oil and water (Church et al., 2019; Church et al., 2020), as explored in Chapters 2 and 4. Thus, a better understanding of the physical and thermodynamic properties of emulsions and surfactant transport behavior is critical to help improve bilgewater treatment and management. A broad assessment of bilgewater emulsion characterization techniques has been developed and used from general water quality analysis (e.g., pH, temp, viscosity, and alkalinity) to advanced droplet stability characterization methods (e.g., pendant drop measurement for dynamic interfacial tension (IFT)) (Chen et al., 2020; Church et al., 2019; Church et al., 2017; Gašperlin, 2000). However, due to the time-consuming and laborious experimental determination of emulsion stability as well as inherent system complexity, collating data into a stability prediction model would be beneficial.

Several studies have reported a variety of machine learning (ML)-based emulsion stability models. For example, Abubakar et al. (Umar, 2018) introduced several support vector machine (SVM) classifiers with different kernels (e.g., linear, quadratic, and cubic) that predict emulsion stability and investigated the effects of emulsification using three main variables (a laponite clay, nonionic surfactant, and time). Among several different kernels, cubic and medium Gaussian kernels provided high overall accuracies. Likewise, an artificial neural network (ANN) was used for predicting emulsion stability. Ubiratan et al. (de Souza, 2007) developed an ANN-based model using six physicochemical properties (e.g., an octanol-water partition coefficient [K_{ow}] and molar volume). Gašperlin et al. (Gašperlin, 1998; Gašperlin, 2000) predicted viscosity in a lipophilic semisolid emulsion system using simple ANN models which are statistically acceptable. Kumar et al. (Kumar et al., 2011) introduced ANN models to predict four properties (i.e., particle size, zeta potential, conductance, and viscosity) of emulsion stability with the average mean absolute error (MAE) of 0.093. Katsouli et al. (Katsouli et al., 2017) analyzed the effects on nano-emulsion properties using a nonlinear regression method, investigating the effects of emulsions-mean droplet diameter on an oxidation index. The ML approach was also used to accelerate the emulsion phase diagram construction by predicting microemulsion region boundaries (Djekic et al., 2008; Gašperlin, 2008; Richardson, 1997). While these studies established the practicality of ML for predicting emulsion stability, most of the emulsion studies were conducted using a well-controlled emulsion system, such as drug-delivery and commercial products in the form of emulsions (de Souza, 2007; Richardson, 1997). ML for predicting emulsion stability in wastewater environments adds another level of complexity due to the many interactions between the components of a highly variable wastewater. ML-based emulsion stability prediction for the purpose of treatment (e.g., o/w emulsion separation) has not yet been explored.

While this study recognizes the challenges of the highly variable nature of bilgewater emulsion stability under various conditions (e.g., surfactant and environmental factors), the novel aspect of this paper was the use of image processing and ML for emulsion characterization. The objective of this study was to develop a ML-based emulsion stability simulation and prediction model using experimentally determined data from Chapter 2 to understand behavior of shipboard bilgewater emulsions. Various environmental and material conditions (e.g., pH, temperature, and types of surfactant) were included to construct a model that predicts bilgewater emulsion stability, which can enable more intentional bilgewater treatment system recommendations for bilgewater management. This subject has not been investigated in relation to emulsion characterization for bilgewater treatment and management. In this study, a bilgewater emulsion stability model was newly developed by the following four steps (Fig. 7-1): (1) choosing candidate inputs and conditions influencing emulsion stability, (2) performing laboratory experiments by applying such inputs and conditions to bilgewater emulsion samples, (3) classifying emulsion stability levels using image processing, and (4) developing an emulsion stability prediction model using machine learning. Various classification and regression models (e.g., random forest and artificial neural network) were tested to evaluate predictive models representing emulsion stability along with sensitivity analysis of each descriptor and one predictor variable removal test.

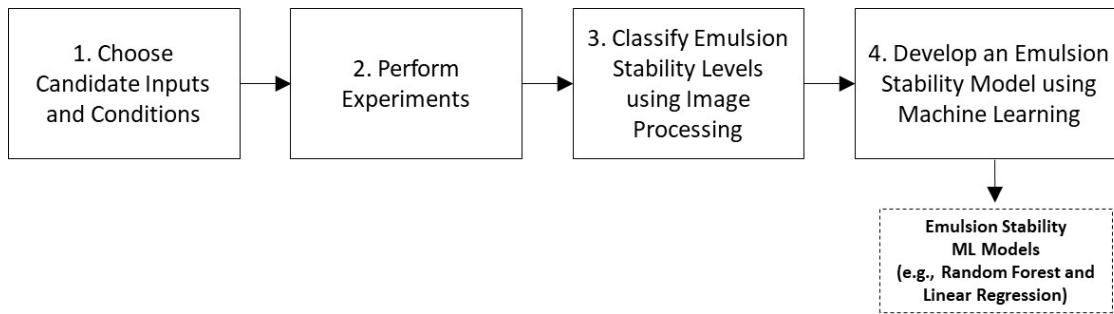


Figure 7-1 A novel approach for bilgewater emulsion stability analysis using image processing and machine learning

7.2 Materials and methods

7.2.1 Determination of emulsion stability

In this study, emulsion stability for bilgewater was evaluated in two ways: 1) observing oil layer formation and determining oil separation (coalescence emulsion stability) and 2) measuring the turbidity of the bulk solution (kinetic emulsion stability) (Fig. 7-2). Kinetic emulsion stability was defined as the ability for emulsion droplets to stay in suspension in the emulsion layer, while coalescence emulsion stability is the ability for emulsion droplets to coalesce and form a separated oil layer. As shown in Figure 7-2, the layers for coalescence stability are located at the top area of bilgewater samples, while the layers for kinematic stability are found below the coalescence stability layers. In practice, the creaming layer can foul oil sensors, while kinetically stable emulsions can pass through the gravity separator (e.g., oil water separator (OWS)).

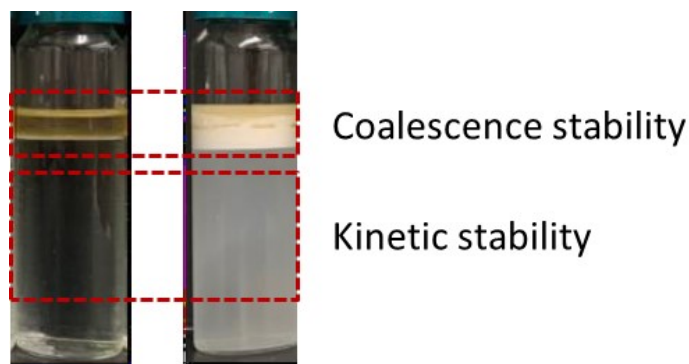


Figure 7-2 Two variables for determining emulsion stability: coalescence stability (OS or OV) and kinetic stability (turbidity)

Two target variables of coalescence emulsion stability, oil separation (OS)(%) and oily value (OV)(%), were determined differently and compared for determining the levels of coalescence stability. OS(%) values were measured experimentally (Section 7.2.2), while OV(%) values were determined by image processing (Section 7.2.3). For kinetic stability, the turbidity (NTU) of bilgewater was measured after 5 days of undisturbed conditions using a turbidimeter (HACH, 2100N, CO, USA) following a standard method (APHA). The relationship between coalescence stability (OS or OV) and kinetic stability (turbidity) was also evaluated.

7.2.2 Determination of OS(%) of prepared bilgewater emulsion samples

In our previous study on bilgewater emulsion stability (Diaz, 2020), over 1,000 emulsion samples were prepared in a laboratory under varying types and concentrations of surfactant and environmental conditions such as pH, temperature, suspended solids (SS), and salinity. A total of 10 cleaners/surfactants were used to prepare the emulsion samples: 8 commercial off-the-shelf (COTS) cleaners found on ships (Type 1, B&B 3100, Solid Surge plus, Power Green, Calla, PRC Deck Cleaner, 6% AFFF and Blast Off) and 2 neat surfactants (Sodium dodecyl sulfate [SDS] as an anionic surfactant] and Triton X-100 as a nonionic surfactant). Four different environmental conditions were included for the experiments: pH (unadjusted, pH 4, and pH 10), SS (0 and 1,000 ppm Arizona dust), salinity (0 and 35,000 ppm NaCl) and temperature (4, 25, and 35 °C). 10% of Navy Standard Bilge Mix (NSBM) #4 was used as a model bilge mix for preparing bilgewater emulsions with a fixed homogenization intensity (33,000 rpm and 2 min) (Church et al., 2017). NSBM #4 is an oil mix composed of 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). Laboratory experiments were then conducted using the candidate inputs and conditions, characterizing emulsion stability by the formation of an oil layer after 5 days (Diaz et al., 2021). OS(%) were then determined by researchers via visual observation or by measuring the weight of the separated oil layer in a separatory funnel (Church et al., 2020) (Appendix E Fig. E1).

7.2.3 Determination of OV(%) using image processing

To obtain images of oil-creaming layers from bilgewater mixture samples, glass vials containing emulsions of total sample volume of 30 mL were placed in front of a digital camera (PowerShot A480, Cannon) and images were recorded every 30 min for the first 24 h and every 3 h over 5

days. A total of 360 images taken at 5 days were processed to determine OV(%) for developing emulsion stability models using ML (Appendix E Fig. E2).

For image processing, an image processing code using OpenCV (Bradski, 2000), a library of programming functions aimed at real-time computer vision, was created to identify the status of oil coalescence in an oil and creaming layer by recording its corresponding color for the oil and creaming layer. Accordingly, the perfect creaming state can be determined as 0% of OV, while the perfect oily state can be determined as 100% of OV (Fig. 7-3(a)). Non-target layers were not considered for image processing and black color was used as a background color (Fig. 7-3(b)).

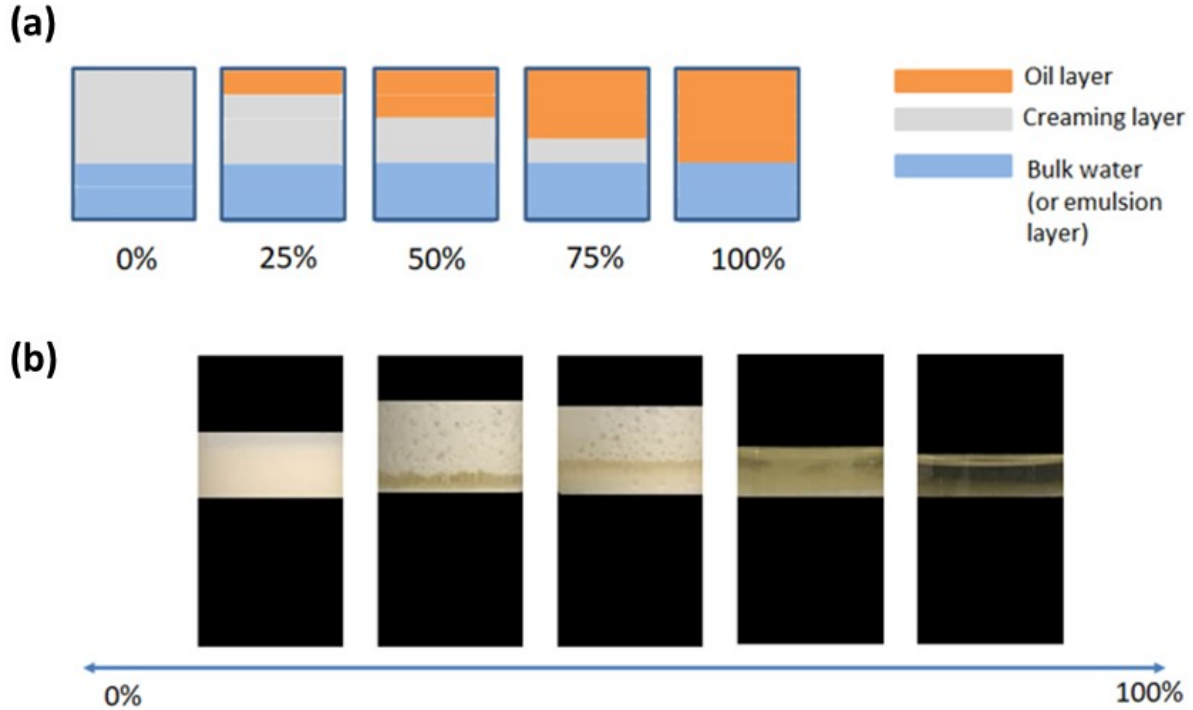


Figure 7-3 (a) Illustrative example of OV(%) determination and (b) oil and creaming layers with different OV(%). Non-target layers (i.e., bulk or emulsion layers) were not included in the image processing and black color was used as a background color.

To determine OV(%) from the collected images, it was normalized that the RGB color for perfect creaming is (255, 255, 255), while the RGB color for perfect mainly oil is (0, 0, 0). The OV (%) was calculated followed by Eq. (7-1).

$$\text{Oily Value (OV) (\%)} = \frac{(255 - \frac{R+G+B}{3})}{255} \quad \text{Eq. (7-1)}$$

where R , G , and B are the averages of the total values of red, green, and blue, respectively. For example, the 1st photo in Fig. 7-3(b) has a total of 5,763 pixels (113 pixels of height and 51

pixels of width). In these pixels, the RGB values are extracted as a list structure containing values R , G , and B such as $[(r_1=198, g_1=185, b_1=163), (r_2=234, g_2=218, b_2=192), \dots, (r_n=234, g_n=218, b_n=192)]$, where $n = 5,763$. For each color value, the sum of the values from the 5,763 pixels is averaged (e.g., $(198+234+\dots+234)/5,763$). Then, the average colors for R , G , and B were used in Eq. (7-1).

7.2.4 Development of ML-based emulsion stability models

Two different ML-based emulsion stability models for predicting coalescence stability were constructed using oil separation (OS or OV (%)). Another model for predicting kinetic stability in bulk water was also developed using turbidity. Both regression and classification ML algorithms were applied to develop these models.

7.2.5 Data preprocessing and feature selection

Table 7-1 shows the physicochemical properties of surfactants used for the experiments. 7 times critical micelle concentration (CMC) was used to prepare the emulsions to ensure complete coverage of the oil-droplet surface (Hsu and Nacu, 2003). Table 7-2 lists selected factors that were used as predictor variables. For cleaners/surfactant information, instead of using cleaner/surfactant name or type as one of the variables, their physicochemical properties (total 8) which represent each cleaner/surfactant (Table 7-1, Table 7-2) were included in ML modeling. For the selected factors, data normalization was applied by scaling between zero and one (0–1). A preliminary test on the analysis for normalization showed the data normalization improves the accuracy (Appendix E Table E1).

Table 7-1 Physicochemical properties of surfactants used for model development

Cleaner/Surfactant	CMC ^{a)} (ppm)	Equilibrium ST ^{b)} above CMC (air) (mN/M)	Equilibrium IFT ^{c)} above CMC with NSBM #4 (mN/M)	Micelle Size (nm) ^{d)}	Zeta Potential (mV) ^{e)}	Alkalinity (mg CaCO ₃ /L)	Surfactant's pH at 7×CMC
AFFF 6%	3,399	15.2	2.3	55	-24	68.9	6.8
B&B	361	25.0	7.8	21	-28	21	8.8
Blast Off	934	27.7	14.6	111	-63	171	10.5
Calla	328	27.3	5.7	5	-39	27.1	8.6
Power Green	3,824	26.1	3.5	7	-13	366.5	9.9
PRC	1,871	30.5	1.3	6	-13	6.4	6.9
SDS	1,547	35.4	2.75	1.3	-40	7.4	6.3
Solid Surge	98	27.4	7.3	23	-15	412.5	12.2
Triton X-100	102	29.6	2.1	9.1	-16	3.5	6.7
Type 1	87	30.2	2.5	18	-28	3.3	6.4

^{a)} CMC: critical micelle concentration

^{b)} ST: surface tension

^{c)} IFT: interfacial tension

^{d)} determined using dynamic light scattering (DLS). The cleaner/surfactant solutions were prepared at various concentrations (serial dilutions) and no oil present.

^{e)} determined at a concentration which is close to CMC

Table 7-2 Selected factors for ML

Factor category	Factors
Cleaners/surfactants information (8)	Test surfactant concentration ($7 \times \text{CMC}$) (ppm)
	Critical micelle concentration (CMC) (ppm)
	Equilibrium surface tension (ST) above CMC (air) (mN M^{-1})
	Equilibrium interfacial tension (IFT) above CMC with NSBM #4 (mN/M)
	Micelle size (nm) ^{a)}
	Zeta potential (mV) ^{b)}
	Alkalinity ($\text{mg CaCO}_3 \text{ L}^{-1}$)
	Surfactant's pH at $7 \times \text{CMC}$
Environmental factors (4)	pH (4, 10, and unadjusted)
	Suspended solids (SS) concentration (0 and 2,000 ppm)
	Salinity (0 and 35,000 ppm)
	Temperature (4, 25, and 35°C)

^{a)} determined using dynamic light scattering (DLS). The cleaner/surfactant solutions were prepared at various concentrations (serial dilutions) and no oil present.

^{b)} determined at above CMC

7.2.6 ML for emulsion stability models

Two types of ML algorithms, regression and classification, were used to identify the model which provides better emulsion stability prediction. 9 regression algorithms were tested in this study: Deep learning regressor, Bayesian ridge regressor (MacKay, 1992), Random forest regressor, Decision tree regressor (Quinlan, 1986), Gradient boosting regressor, Multilayer perceptron regressor (Hinton, 1989), Linear regressor (Galton, 1886), Gaussian process regressor (Williams and Rasmussen, 1995), and Support vector regressor (Chang and Lin, 2011). 9 classification algorithms were tested in this study: K-Nearest neighbor classifier, Gaussian process classifier, Decision tree classifier, Random forest classifier (Ho, 2002), Multilayer perceptron classifier, Adaptive boost classifier (Breiman, 1998), and Gaussian naive Bayes classifier (Maron, 1961). Except for the deep learning regressor, Scikit-learn, a Python-based ML library, was utilized to develop the regression and classification models. For the development of the deep learning regressor, Keras (Chollet, 2015), a Python-based deep learning library, was used. A deep learning architecture was selected as this can provide a better prediction result among other architectures. We performed a preliminary experiment to determine an appropriate deep learning architecture among several candidate architectures. The preliminary experiment

explored such architectures within the context of exploiting the diverse numbers of layers and nodes, the different types of activation functions (relu, sigmoid, and tanh), and the different number of epochs (Goodfellow et al., 2016). The selected architecture used in this study contains the 5 layers, 12 input variables, 192 hidden variables (with Relu activation functions), and one output variable (Appendix E Table E2).

For the ML step, the following experimental settings were conducted. The total data size was 360 after data preprocessing (over 1,000 data) and it was split into 80% in the training set and 20% in the test set by being randomly taken from the original data. For the 80% training set, cross-validation with 10 folds was applied for model validation, in which nine-tenth of the training set was randomly selected for developing prediction models and the remaining data from the training set (i.e., one-tenth) were used for model validation. The final cross-validation scores were averaged. For regression, mean absolute error (MAE) was used as an evaluation metric (i.e., prediction score). For classification, F1-score was used as an evaluation metric, while the target variables were converted to categorical variables with three states (Low, Mid, and High with 33.3% per each category) for OS, OV, and turbidity. Due to imbalanced data (e.g., the number of the low-labeled data is higher than the number of the high-labeled data), the synthetic minority over-sampling technique, called SMOTE (Chawla et al., 2002), was applied to the data for the classification experiment. SMOTE generated more samples using the original data to ensure the balance of the data. These experiments were run on a 3.40 GHz Intel Core i7-3770 processor.

7.2.7 Sensitivity analysis for predictor variables for OS, OV, and turbidity

To understand the effects of predictor variables on the target variables (OS and OV), an *F-value* test for the sensitivity analysis was performed on the 12 predictor variables to evaluate statistically significant factors. The F-value test aims to identify parameters that are important for governing emulsion stability. The identified parameters can be used to control and manage the coalescence stability in bilgewater in practice. The high score of the F-value indicates the high correlation between predictor and target variables.

F-value is a positive numeric value indicating a correlation (p_i) between a predictor variable and target variable (Eq. 7-2) (Pedregosa, 2011).

$$p_i = \frac{(X[i] - \text{mean}(X[i])) \times (y - \text{mean}(y))}{\text{std}(X[i]) \times \text{std}(y)} \quad \text{Eq. (7-2)}$$

where X is an input matrix for values of the predictor variables and y is a vector for values of the target variables. For each predictor variable i , we can compute the correlation p_i . Mean(.) and std(.) are the functions for mean and standard deviation, respectively.

F-value (F_i) can be computed as shown in the following equation (Eq. 7-3) (Pedregosa, 2011).

$$F_i = \frac{p_i^2}{1-p_i^2} \times (n - 2) \quad \text{Eq. (7-3)}$$

where n denotes the number of samples of y .

7.3 Results and discussion

7.3.1 Determination and comparison between OS and OV

The resulting emulsion stability using the averaged OS(%) based on surfactant type from most stable to least stable was Type 1 (29%) > B&B (38%) > SDS (41%) > Power Green (44%) > Solid Surge (52%) > PRC (60%) > Triton X-100 (62%) > Calla (63%) > 6% AFFF (69%) > Blast Off (80%) (Appendix E Fig. E1) (Diaz, 2020). Figure 7-4 shows the OV(%) values that were determined using image processing and the associated classification with the order of emulsion stability. The resulting emulsion stability using the averaged OV (%) from most stable to least stable was Type 1 (22%) > B&B (47%) > SDS (53%) > Power Green (55%) > Triton X-100 (63%) > Calla (66%) > Solid Surge (67%) > PRC (67%) > 6% AFFF (69%) > Blast Off (87%). There was a good agreement between OS(%) and OV(%) in terms of emulsion stability for the selected cleaners/surfactants tested (Appendix E Fig. E3). Among 10 cleaners/surfactants, Type 1 showed to produce the most stable emulsion, while Blast Off resulted in the most unstable emulsion (highest tendency to coalescence). Anionic surfactant (e.g., SDS) resulted in less oil separation with great emulsion stability (i.e., more creaming layers were formed) compared to nonionic surfactants (e.g., Triton X-100). It was found that emulsion stability was highly dependent on surfactant type, temperature, and ionic strength (NaCl). For most of the surfactants, emulsion coalescence increased with salinity and temperature.

OV		Type 1			B&B			SDS			Power Green			Triton X			Calla			Solid Surge			PRC			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	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 addition	Unadj.	0	0	0	0	14	15	0	14	10	0	7	18	17	78	57	0	6	14	0	16	88	29	78	30	0	22	23	100	43	41
	pH 4	0	0	0	0	15	8	6	11	8	100	99	100	1	31	0	0	6	0	27	52	68	26	99	5	0	22	16	100	100	100
	pH 10	0	0	43	0	21	6	2	14	8	0	7	21	7	37	0	100	46	58	11	21	89	99	77	28	43	26	17	100	54	15
SS	Unadj.	0	0	0	44	82	52	50	20	11	0	14	38	18	60	77	90	97	43	29	32	61	76	37	83	47	60	83	54	96	31
	pH 4	0	0	100	36	42	48	40	21	14	100	100	100	12	88	91	22	70	45	92	80	58	70	38	100	42	59	69	100	100	95
	pH 10	0	0	41	33	82	43	49	25	17	0	20	48	34	76	84	66	90	30	45	58	40	100	42	100	47	67	39	100	96	30
Salinity	Unadj.	72	100	100	19	71	39	60	90	100	0	20	100	100	100	100	100	100	84	100	100	94	100	8	100	100	100	100	100	100	99
	pH 4	0	100	72	36	44	33	56	97	89	100	100	100	56	100	100	69	100	100	48	63	93	100	0	100	90	96	100	100	100	100
	pH 10	0	0	56	85	76	56	44	93	95	25	26	87	99	92	100	47	63	100	52	91	100	100	26	83	100	100	100	100	100	100
SS+Salinity	Unadj.	0	81	12	100	54	66	100	100	99	38	36	100	84	100	100	100	100	99	100	100	100	100	14	100	100	100	100	100	100	100
	pH 4	0	19	0	95	66	57	85	100	99	100	100	100	43	100	100	46	97	100	94	82	92	100	33	100	100	100	100	100	100	70
	pH 10	13	0	0	100	92	62	96	87	100	47	36	98	49	84	8	100	77	99	50	94	100	99	35	94	100	100	100	100	100	94

Oil separation		
	mainly oil	over 66.6%
	Creaming + oil	33.3-66.6%
	Only creaming	<33.3%

Figure 7-4 OV(%) determined using image processing and associated classification with the order of emulsion stability from stable (left) to unstable (right).

7.3.2 Oil coalescence prediction model using OS and OV: regression and classification

Using the OS(%) and OV(%), regression and classification models were constructed to predict the emulsion stability and compared each other. For regression models, nine regression algorithms were compared with the MAE scores as shown in Table 7-3, which lists two results (i.e., validation and test results) for each algorithm. The validation results were the averaged MAEs for the cross-validations with 10 folds. For OS(%), the random forest (RF) regressor achieved the most accurate result (0.1804) compared to other algorithm models which showed results in the range between 0.1946 and 0.2609 (Table 7-3). For OV(%), the decision tree (DT) regressor shows the most accurate results (0.1611) among other algorithms. Gradient boosting (GB) regressor and random forest (RF) regressor was the next selection for the prediction for OS (0.1888) and OV (0.1834), respectively. Both RF and DT regressor algorithms are based on ensemble learning, in which simple predictive models (e.g., decision trees) collaborate to predict a target value. Since the data used in this study was small (total 360), and only characterized by a small number of predictor variables (twelve), it seems that these characteristics were suitable for the random forest and decision tree regressors. For two models with accurate results (GB and RF for OS and DT and RF for OV), the comparison between the actual and predicted values showed that the OS and OV showed a relatively good matching and naturally dispersed although there are two extreme cases for the actual values of zero (completely creaming layer) and one (completely oil layer) (Appendix E Fig. E4).

Table 7-3 Regression and classification results for OS, OV, and turbidity

ML Algorithms		Validation results ^{a)} (Averaged MAE or F1)			Test results ^{b)} (MAE or F1)		
		OS	OV	Turbidity	OS	OV	Turbidity
Regression	Deep learning regressor	0.2109 (0.0366) ^{c)}	0.1919 (0.0288)	0.0853 (0.0120)	0.2131	0.2166	0.0676
	Bayesian ridge regressor	0.2892 (0.0248)	0.2561 (0.0291)	0.1287 (0.0182)	0.2609	0.2652	0.1074
	Random forest (RF) regressor	0.2002 (0.0281)	0.178 (0.0233)	0.0637 (0.0134)	0.1804	0.1834	0.0559
	Decision tree (DT) regressor	0.2417 (0.0627)	0.1871 (0.0535)	0.0735 (0.0144)	0.1947	0.1611	0.0681
	Gradient boosting (GB) regressor	0.2080 (0.0296)	0.1843 (0.0235)	0.0749 (0.0179)	0.1888	0.1998	0.0664
	Multilayer perceptron regressor	0.2073 (0.0310)	0.1997 (0.0235)	0.0825 (0.0125)	0.2007	0.2082	0.0732
	Linear regressor	0.2752 (0.0261)	0.2435 (0.0226)	0.1284 (0.0178)	0.2382	0.2625	0.1065
	Gaussian process regressor	0.2783 (0.0263)	0.2437 (0.0251)	0.1282 (0.0177)	0.2475	0.2626	0.1062
	Support vector regressor	0.2003 (0.0395)	0.1873 (0.0222)	0.0880 (0.0150)	0.1946	0.2002	0.0710
Classification	K-Nearest neighbor classifier	0.7085 (0.0470)	0.6792 (0.0583)	0.8655 (0.0467)	0.6759	0.6822	0.8212
	Gaussian process classifier	0.6763 (0.0717)	0.686 (0.0619)	0.8307 (0.0587)	0.6944	0.7196	0.8742
	Decision tree (DT) classifier	0.7293 (0.0708)	0.7192 (0.0758)	0.8853 (0.0617)	0.7685	0.8037	0.8874
	Random forest (RF) classifier	0.7803 (0.0540)	0.8172 (0.0659)	0.9185 (0.0501)	0.8611	0.8224	0.9338
	Multilayer perceptron classifier	0.7017 (0.0603)	0.7001 (0.0742)	0.8588 (0.0533)	0.6759	0.6542	0.8079
	Adaptive boost classifier	0.6070 (0.1108)	0.6137 (0.0652)	0.7142 (0.0750)	0.6574	0.7196	0.7483
	Gaussian naive bayes classifier	0.5280 (0.0740)	0.5432 (0.0638)	0.6528 (0.0783)	0.5185	0.6262	0.6291

a) Averaged MAE for regression and averaged F1 for classification

b) MAE for regression and F1 for classification

c) Standard deviation

For classification models, three categories that are equally divided (less than 33.3%, between 33.3 and 66.6%, greater than 66.6 %) have been used both for OS and OV, and seven classification algorithms were compared with the F1 scores as shown in Table 7-3. The validation results were the averages of F1 scores for the cross-validations with 10 folds. In validation results, the test results of OS (0.8611) were better than the results of OV (0.8224) with RF classifier, but almost similar, indicating that the use of OS and OV also showed a good prediction of the classification of emulsion stability. Overall, the ML models using experimentally determined values (OS) showed acceptable prediction in coalescence stability with the RF regressor for the regression model and RF classifier for classification. The ML models using image processed values (OV) also showed a good agreement in the prediction of emulsion stability with the DT regressor for the regression model and the RF classifier for classification. The result of modeling showed that OV can be substituted instead OS.

7.3.3 Turbidity prediction model: regression and classification

Prediction models for kinetic stability using turbidity values were developed using regression and classification algorithms. For this, the same set of regression and classification algorithms with coalescence stability analysis was used. For the regression test, the RF regressor achieved the highest MAE score of 0.0559, while for the classification test, the RF classifier obtained the highest F1 score of 0.9338 among tested algorithms (Table 7-3). Both regression and classification tests showed that the ML approach is applicable to predict the turbidity value with high accuracy.

7.3.4 The effect of predictor variables on the prediction of OS, OV, and turbidity

Table 7-4 lists the results of the F-value test for 12 predictor variables for OS, OV, and turbidity. In both OS and OV, salinity showed the strongest correlation with the target variables with the F-value of 48 for OS and 112 for OV, respectively. Temperature showed the next highest correlation with the F-value of 41 for OS. The results agreed with the previous studies where salt concentration was found to be the most critical factor in controlling the coalescence stability of emulsions (Church et al., 2017; Diaz, 2020). For turbidity, micelle size showed the highest correlation with the F-value of 46 and the salinity showed the next correlation with the kinetic stability (Table 7-4). Variables other than salinity, temperature, and micelle size showed a relatively low impact on the emulsion stability prediction. For example, the effects of pH and SS concentration were not significant for both OS and OV compared to salinity and temperature in this sensitivity analysis. This is possible because sensitivity analysis provides a rough correlation considering their linearity and thus it may be difficult to determine whether the parameter is sensitive when the F-value is in the middle or low range. Therefore, additional sensitivity analysis, a one predictor variable removal test, was performed for further analysis on the effect of an individual variable on OS, OV, and turbidity prediction.

Table 7-4 Sensitivity analysis (F-test) for 12 predictor variables for OS, OV, and turbidity

OS		OV		Turbidity	
Predictor variables	F-value	Predictor variables	F-value	Predictor variables	F-value
Salinity	48.1611	Salinity	111.8622	Micelle size	46.4228
Temperature	41.6371	Micelle size	19.9932	Salinity	27.7239
Micelle size	21.9660	IFT	15.3829	IFT	15.0081
IFT	8.6671	Surfactant's pH	11.8255	Temperature	9.8801
Surface tension	6.8291	SS	8.8851	Zeta potential	9.3253
Zeta potential	6.5790	Zeta potential	5.5881	Surface tension	9.1339
Surfactant's pH	2.3006	Alkalinity	4.8326	Alkalinity	8.0607
SS	0.8304	Surface tension	3.7573	Surfactant's pH	5.0450
Surfactant conc.	0.4627	Temperature	3.6465	Surfactant conc.	1.8664
CMC	0.4627	Surfactant conc.	2.0034	CMC	1.0238
Alkalinity	0.1142	CMC	2.0033	SS	0.8436
pH	0.0322	pH	0.6269	pH	0.3976

a) Equilibrium interfacial tension (IFT) above CMC with NSBM

b) Surface tension (ST) above CMC (air)

7.3.5 One predictor variable removal test for OS, OV, and turbidity

Although the F-value test provides meaningful information in correlation for each predictor variable, one may be more interested in understanding how each predictor variable affects the emulsion stability prediction model in order to include or remove the variables in/from the models for future efforts. For this, we performed another sensitivity analysis, called a *one predictor variable removal test*, in which one of the predictor variables is removed one by one from the set of the 12 predictor variables and the remaining predictor variables are used for ML and each prediction test. Then, the results of the original prediction test are compared with the results from the one predictor variable removal test.

Table 7-5 shows the results of the one predictor variable removal test for OS, OV, and turbidity in regression models. The first row of each OS, OV, and turbidity denotes the MAE results from each original prediction test. The following rows present each variable that is removed for the test. For example, in the second row of OS, the variable “Surfactant concentration” was removed from 12 predictor variables and the remaining 11 predictor variables were used for ML for OS

prediction, followed by each regression test. The values in the cells below the first row denote the differences between the original prediction test and each test. Therefore, the positive value in each cell means that the value may positively influence the prediction result, while the negative value in each cell means that the value may negatively influence the prediction result and should be removed from the consideration to improve the prediction. For example, in the column of the RF regressor which was the most accurate model for OS prediction, when the predictor variable “Salinity” was removed from the model, the model accuracy went down from the original 0.1804 to 0.3235 with a difference of 0.1431, indicating that salinity is the most influencing parameter among 12 predictor variables to improve the accuracy. There were no negative values in the one predictor variable removal tests with the selected ML models for OS, OV, and turbidity, indicating that all 12 variables affect the emulsion stability for both coalescence and kinetic stability. In the DT regressor with OV which was the best prediction regression model for coalescence stability, salinity and temperature were identified as the most influencing factors for emulsion stability prediction. pH and SS concentration also positively affected the model, indicating that they also are important parameters in emulsion prediction. In the RF regressor model for turbidity, salinity was the most influencing factor for the kinetic stability, then pH and temperature were the next ones.

Table 7-5 Results of one predictor variable removal test for OS, OV, and turbidity

ML algorithms		OS	OV	Turbidity
		RF regressor	DT regressor	RF regressor
Ave. MAE in original prediction		0.1804	0.1611	0.0599
Removed variable	Surfactant conc.	0.016	0.0411	0.0137
	CMC	0.0242	0.0458	0.0086
	Surface tension	0.0185	0.0248	0.0047
	IFT	0.0092	0.0309	0.0112
	Micelle size	0.0126	0.0244	0.0064
	Zeta potential	0.0114	0.0283	0.0059
	Alkalinity	0.0233	0.0219	0.0022
	Surfactant's pH	0.0172	0.0198	0.0071
	pH	0.0616	0.027	0.0355
	SS concentration	0.0401	0.057	0.008
	Salinity	0.1431	0.2531	0.0667
	Temperature	0.0575	0.0655	0.0195

*Note that the values are difference in average MAE values between original prediction and one variable removal tests

The results of the *one predictor variable removal test* are in agreement with findings observed in literature. In general, salinity and temperature are known to play significant roles in emulsion stability (Zolfaghari et al., 2016). Many studies have reported the effect of salinity or ionic strength on the o/w emulsion stability due to surfactant adsorption behavior and a reduction in the IFT (Hezave et al., 2013). Water salinity is known to be an important parameter for spontaneous emulsification for o/w systems (Davis et al., 2020). In our previous study, it was observed that emulsion samples with high concentrations of NaCl were found to be less stable (Church et al., 2017). This is because of an effect called “salting out” which reduces hydrophilicity of surfactants and diminishes the solubility of surfactant in the aqueous phase, thus decreasing an o/w emulsion stability (Martínez-Palou et al., 2013; Zolfaghari et al., 2016). Rostami et al (2019) also reported a decrease in the IFT at low water salinity but an increase in the IFT with a higher salt concentration (Rostami et al., 2019). On the other hand, as temperature increases, the interfacial viscosity decreases, and thermal energy of the droplets increases,

resulting in droplet coalescence (Church et al., 2019). We also observed the oil coalescence behavior with the increased temperature at 35 °C (Appendix E Fig. E1).

Figure 7-5 shows the results with scatter plot charts for the selected models using OS, OV, and turbidity. The values of each predictor were more than zero, indicating higher effects on the prediction of emulsion stability. In particular, the effect of salinity, temperature, SS concentration, and pH on the prediction model was considerably significant compared to others. The other one predictor variable removal tests with other ML algorithms also showed similar results (Appendix E Table E3). Overall, in this study, environmental factors like salinity, temperature, SS concentration, and pH were found to be the highly affecting parameter for the emulsions stability compared to the thermodynamic properties of cleaners/surfactants.

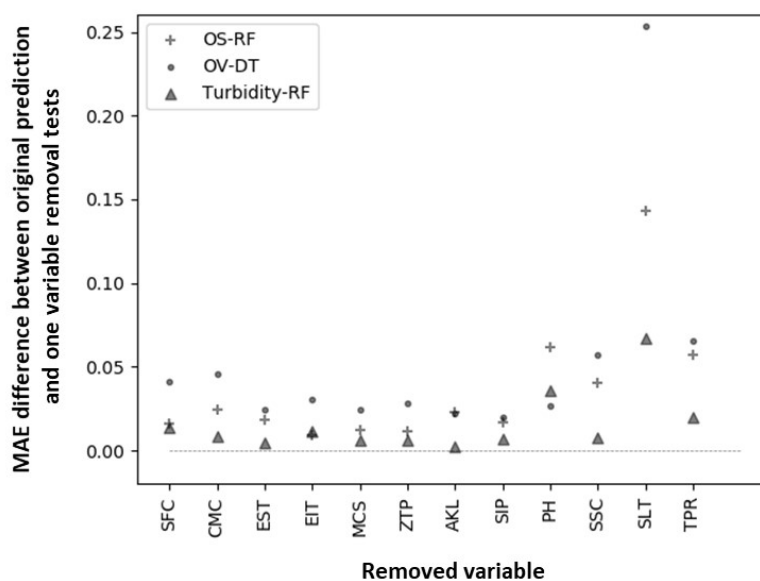


Figure 7-5 Summary of one predictor variable removal test for OS, OV, and turbidity (RF: Random forest regressor, DT: Decision tree regressor) (SFC: Surfactant concentration, CMC: Critical micelle concentration (CMC), EST: Equilibrium surface tension (ST) above CMC (air), EIT: Equilibrium interfacial tension (IFT) above CMC with NSBM #4, MCS: Micelle size, ZTP: Zeta potential, ALK: Alkalinity, SIP: Surfactant's pH at 7CMC, PH: Initial pH, SSC: Suspended solids (SS) concentration, SLT: Salinity, TPR: Temperature)

We also explored an alternative to the RGB-based image processing, by drawing an oil line (Appendix E Fig. E6). However, it was found that, in a preliminary test, determining the oil line between the oil and creaming layers was challenging when a creaming layer is mixed with oil droplets and coalescence oils. Although the image processing using oil lines was not further tested in this study, the possible solution would be to create a proper assumption for defining the oil lines (e.g., oil line should be over 80% of the separation line) and crosscheck with the experimental results. With well-defined rules of image analysis, the use of oil lines would be a good alternative to the current method of using RGB color from collected images.

7.3.6 Practical implications and improvement of emulsions stability prediction models

This study demonstrated emulsion stability prediction models using 10 cleaners/surfactants as a whole data and showed well-predicted coalescence stability and turbidity models. An individual model for each cleaner/surfactant can also be developed to predict the emulsion stability from the use of a specific surfactant. A preliminary test of the regression with separated data according to surfactant type showed a relatively good prediction of oil separation (OS or OV) and turbidity depending on the selected algorithms (Appendix E Table E4). However, due to lack of data of individual cleaner/surfactant, in this study, information from 10 cleaners/surfactants was incorporated into a single analysis for OS (or OV) and turbidity to improve model accuracy and develop a prediction model. With more data, modeling both for classification and regression can be improved to consider the individual type of surfactant and determine specific emulsion stability for an individual surfactant. Additional properties and experimental data obtained with different environmental parameters can be included in the developed ML model for broader applicability to other non-tested surfactants as well as different oils.

Using the ML results, a public and free webpage prototype for bilgewater emulsion stability prediction was created where users enter the information of environmental factors (e.g., pH, SS concentration, salinity, and temperature) along with surfactant type, then the predicted emulsion stability is shown with the number of OV (%) and turbidity (NTU) (Appendix E Fig. E7). The best prediction models of regression for OV (DT regressor) and turbidity (RF regressor), and classification for OV (RF classifier) were utilized on this web page. For the classification, three categories were used: 1) Only creaming: “Only creaming” represents the samples with less than 33.3% oil separation, 2) Creaming + oil: “Creaming + oil” represents the sample between 33.3–66.6% oil separation, and 3) Mainly oil: “Mainly oil” represents the samples with higher than 66.6% oil separation. The web page was configured to provide a user-friendly interface for easy and quick prediction, and the source code used for this study was published in Github for public access.

The feasibility test using the image process to improve oil separation determination showed a good agreement with the experimentally determined OS values. Various ML algorithms were used to prediction of bilgewater emulsion stability using the experimental data and image processed data. Although the use of the proposed ML models for the emulsion prediction may be limited to the set of existing experimental data (e.g., one concentration of cleaner/surfactant), the work can be extended with more data sets of parameters which are found in literature for better understanding of emulsion stability. For example, some of the physicochemical properties used in this study (e.g., micelle size and zeta potential) does not include the effect of NSBM #4 on the system. The inclusion of more realistic and diverse data would improve the emulsion stability prediction models of non-tested surfactants.

ML is a method whereby one can predict discrete and numeric values, find relationships and clusters, and optimize inputs and conditions. In the process of emulsion stability analysis, as shown in Figure 7-1, there are a variety of applications to which ML can be applied. For example, we can use ML for optimizing input and condition values to maximize or minimize emulsion stability. On the other hand, in laboratory experiments, it is critical to quickly and

accurately find optimal input values and their range (e.g., salinity concentrations) that may maximize a target performance (e.g., determining the best oil separation). However, investigating all possible values is a time-consuming, labor-intensive, and expensive process. Experiments considering total ranges of a combination of input values can increase experiments to be conducted exponentially along with the number of the input variables. However, in most cases, performing experiments on the entire scale is infeasible. In this case, Bayesian Optimization (BO) can be used as a possible solution of an ML approach that automatically recommends candidate input values to achieve optimal input values, maximizing a target performance, significantly reducing the experimental time and cost (Appendix E Fig. E8). Recently, materials scientists have applied BO to their laboratory experiments in order to perform effective and accurate determination for complex materials (Frazier, 2016; Mizoguchi, 2018; Packwood, 2017). In a further study of emulsion stability analysis, it is expected that the use of BO may help find optimum input values (e.g., the properties of surfactants, pH, and temperature) which maximize or minimize emulsion stability even in a small number of experiments.

7.4 Conclusion

In this study, ML was successfully used to interpret emulsion data and to develop a bilgewater emulsion stability prediction model. Various regression and classification models were evaluated to develop an emulsion stability prediction model using the experimentally obtained data which present coalescence stability and kinetic stability. Two different coalescence stability parameters (OS and OV) were used to predict the emulsion stability and compared to improve accuracy. It was found that both experimentally determined OS data and image processed OV showed relatively good agreement in coalescence stability. Overall, the developed emulsion stability models are successful in determining and predicting conditions where the emulsion is stable or unstable. It is expected that the models developed in this study will aid other researchers, as well as those in the field, to improve emulsion science and address field-related bilge purification issues after modification with more data sets. By utilizing the models, better conditions to maximize the oil separation can be recommended under varying scenarios, thus benefitting emulsion treatment process selection in practice.

Chapter 8: Conclusions and Implications for Future Research

8.1 Conclusions

Until now, there has been very little knowledge surrounding the physical, chemical, and thermodynamic properties of the emulsions created in an Armed Forces vessel environment. Thus, targeted treatment and management of these fluids becomes conjecture and calls for a deliberate and thorough understanding of fundamental emulsion stability properties. The results described in this report helped fill this knowledge gap by focusing on three segments: (1) Scoping Study for Review of Armed Forces Vessels Oil-in-Water Emulsions, (2) Characterization of Prepared and Extracted Bilgewater Emulsions, and (3) Development of Emulsion Stability Guide.

First, a review of literature was conducted to determine common approaches for studying emulsions. Information on the formation and stability of bilgewater emulsion was discussed as well as pertinent physiochemical properties that are known to influence emulsion stability. Bilgewater emulsion characterization techniques were also discussed in detail, where the importance of kinetic and coalescence emulsion stability on bilgewater processes was outlined. The review also investigated bilgewater characteristics reported in literature, which was found to be highly variable. For example, oil concentrations in bilgewater has been reported as low as 5 ppm and as high as 12,900 ppm. In an effort to better understand the types of surfactants that might be present in bilgewater, a survey of U.S. Navy cleaners was conducted. In total, 10 cleaners were identified as likely to be found in bilgewater based on the total procurement of each cleaner. Overall, the review helped define the analytical techniques, definition of emulsion stability, types of cleaners, and environmental conditions used for experimental testing.

Cleaners identified in the review were then characterized for properties related to emulsion stabilization, including: critical micelle concentration (CMC), interfacial tension (IFT), micelle size and zeta potential. It was found that the primary surfactant between the cleaners were similar; mostly composed of alcohol ethoxylates or cocamide diethanolamines. However, the properties of the cleaners varied significantly; likely due to the presence of builders and other compounds in the cleaners. Extracted bilgewater samples were highly variable but were within water quality ranges that have been reported in literature. Results from the cleaner and extracted bilgewater analysis validated the use of detergent mix #4 and Navy Standard Bilge Mix (NSBM) #4 for the preparation of simulated bilgewater emulsions. The cleaners used in detergent mix #4 were found among the highest cleaners procured by the Navy. In addition, the tested cleaners were found to only include nonionic surfactants; which is also the primary surfactant type in detergent mix #4. This is noteworthy because the current bilgewater standard used to test commercial oil-water separators, MEPC.107(49) test fluid “C”, uses an anionic surfactant, which uses different emulsion stabilizing mechanisms (e.g. electrostatic vs steric). In addition, bilgewater samples taken from Navy ships in Spring 2019 (Bilgewater #1 and #2) both had gas chromatography mass spectroscopy (GC-MS) chromatographs similar to NSBM #4.

After establishing relevant properties of cleaners and bilgewater, the effect of environmental factors on emulsion stability was investigated. In particular, the impact of salinity, temperature, suspended solids (SS), and pH on the formation and stability of emulsions was evaluated. The findings suggested 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 > SDS > B&B > Power Green > solid surge > Calla = PRC > Triton X-100 > 6% AFFF = Blast-off. For all cleaners tested, except Power Green, it was found that increasing temperature accelerated emulsion separation by enhancing coalescence of the droplets. Ionic strength was shown to have the largest influence on emulsion destabilization, resulting in oil separation at early stage. Overall, the experiments provided significant information regarding the contribution of bilgewater components to the formation and stability of emulsions in Navy bilgewater systems. Results from this work were also used to help train an emulsion stability prediction model.

Experimental properties of emulsion systems that could be used to predict emulsion stability were also investigated. The impact of IFT, CMC, and CMC in the presence of oil (CMC_{IFT}) on macro-phase oil separation in model surfactants and commercial cleaners was evaluated. The emulsion samples shifted from predominantly separated oil to stabilized emulsion at surfactant concentrations correlating closely with CMC_{IFT} . The change in emulsion behavior was due to the packing of surfactant at the oil/water interface. As the surfactant concentration approached CMC_{IFT} , the amount of surfactant adsorbed at the interface approached its highest packing density and the mechanical stability of the surfactant layer was expected to be largest, thus improving emulsion stabilization. In addition, it was found that neither IFT nor droplet size was directly related to the breaking of a cream layer into a separate oil layer. Therefore, the stability of the emulsions was best explained by an electrostatic/steric stabilizing mechanism rather than the initial droplet formation. Overall, CMC_{IFT} was demonstrated as a practical method for predicting emulsions stability in complex systems. Cleaners developed for use on ships could be tested for CMC_{IFT} using a representative oil and flagged as having a greater potential contribution to bilgewater emulsion stability if the cleaner's CMC_{IFT} was found to be low.

Based on changes in CMC observed in the presence of NSBM #4, the impact of fuels on bilgewater emulsion stability was also investigated. It was found that components in bilgewater oils and fuel can contribute to the stability of emulsions. The conductivity, pH, and surface tension of water was significantly altered after exposure to bilgewater oils for 24 h. Likewise, UV and GC-MS data suggested the transport of aromatic compounds from the oil to aqueous phase. It was found that aromatic compounds, containing oxygen and nitrogen functional groups leached into the water phase and helped stabilize emulsions. Emulsion stability experiments showed compounds found in DFM were most likely to stabilize emulsions, followed by Lube Oil 2190 and then by Lube Oil 9250. Further research is needed to provide exact identification of the compounds involved in bilgewater emulsion stabilization and determine the full impact of these additives on emulsion stability and bilgewater treatment.

Finally, various regression and classification machine learning (ML) models were evaluated for predicting emulsion stability using experimentally obtained data from previous studies. Image

processed oil values (OV) showed better prediction compared to visually determined oil separation (OS). In regression ML models, the gradient boosting regressor achieved the most accurate prediction for OV (0.093), while in classification models, the random forest classifier showed the highest prediction of emulsion stability with 0.8868 for OV. Sensitivity analysis showed that salinity and temperature were dominant factors in predicting emulsion stability for the conditions tested. The developed ML models were used for creating a website prototype for bilgewater emulsion stability prediction. Overall, ML-based bilgewater emulsion stability models may benefit future the emulsion treatment process selection.

8.2 Transition and Future Research

Knowledge gained from this research has already helped inform bilgewater management decisions within the Armed Forces. Currently, the U.S. Navy is developing recommendations for bilge cleaners that prevent the generation of stable bilgewater emulsions or negatively impact bilge treatment processes. Insights from this study, on how to best evaluate bilgewater emulsion stability, was transitioned to a Naval Sea Systems Command (NAVSEA) funded investigation of commercial bilge cleaners (NSWCCD-63-TR-2020/38) (Church and Park, 2021) and will be used to develop a commercial item description for future use of bilgewater cleaners aboard Navy ships. Likewise, the improved understanding of bilgewater composition and the role of environmental factors on emulsion stability has validated the selection of the most challenging and representative test conditions for evaluations of oil pollution abatement (OPA) equipment.

Future work, looking at fundamentals mechanisms of bilgewater emulsion stability, should focus on how emulsions are impacted by different treatment technologies. While important insights into how cleaner and fuel properties can influence bilgewater emulsion stability was realized under stationary bilgewater environments, no work was done looking at how conventional bilgewater treatment can break emulsions. For example, it is currently unknown how emulsions interact with the surface of ceramic membranes that are currently employed by many Navy ships for bilgewater treatment. This information is critical for both the selection and operation of bilgewater treatment technologies.

The insights from this work have potential to not only contribute to mitigating emulsions in bilgewater, but also aid in improving other fields where surface active compounds are prevalent. The transport of compounds between fuel and aqueous phases also have large implications in other areas of research. As fluorine free firefighting foams are being developed to replace per- and polyfluoroalkyl substances (PFAS) laden foams, the impact of cosolvents and interfacial turbulence caused by fuel compounds will likely play a large role in the effectiveness of foams. Expertise gained from this project is being used to support an additional SERDP project looking at the transport of surfactants at liquid-liquid interfaces in the presence of fuels (WP19-1407). Similarly, understanding the transport of benzene, toluene, ethylbenzene, and xylene (BTEX) compounds into the environment is important for oil spill remediation. The Bureau of Safety and Environmental Enforcement (BSEE) is currently involved in several areas of research where knowledge in emulsion science and treatment can be utilized. Research findings developed under WP18-1114 has transitioned to support a FY21-FY23 BSEE investigation to better understand the role of emulsions in *in situ* incineration for oil spill response. The techniques reported here

will be used to characterize crude oil emulsions and provide insights into their impact on *in situ* incineration. Similarly, NSWCCD is currently pursuing proposal development in collaboration with Carderock's computation fluid dynamics (CFD) branch. The proposal will address another BSEE need for CFD modeling of water-in-oil emulsion behavior to simulate oil capture with novel boom designs. The fundamental understanding of emulsions gained in this project supports this modeling work.

References

- Abedi S, Suteria NS, Chen C-C, Vanapalli SA. Microfluidic production of size-tunable hexadecane-in-water emulsions: Effect of droplet size on destabilization of two-dimensional emulsions due to partial coalescence. *Journal of Colloid and Interface Science* 2019; 533: 59-70.
- Adams F, Walstra P, Brooks B, Richmond H, Zerfa M, Bibette J, et al. Modern aspects of emulsion science: Royal Society of Chemistry, 2007.
- Ahmad A, Sumathi S, Hameed B. Coagulation of residue oil and suspended solid in palm oil mill effluent by chitosan, alum and PAC. *Chemical Engineering Journal* 2006; 118: 99-105.
- Ahn K, Agresti J, Chong H, Marquez M, Weitz DA. Electrocoalescence of drops synchronized by size-dependent flow in microfluidic channels. *Applied Physics Letters* 2006; 88: 264105.
- Al-Shannaq R, Farid M, Al-Muhtaseb S, Kurdi J. Emulsion stability and cross-linking of PMMA microcapsules containing phase change materials. *Solar Energy Materials and Solar Cells* 2015; 132: 311-318.
- Albert C, Beladjine M, Tsapis N, Fattal E, Agnely F, Huang N. Pickering emulsions: Preparation processes, key parameters governing their properties and potential for pharmaceutical applications. *J. Controlled Release* 2019.
- Ali MF, Alqam MH. The role of asphaltenes, resins and other solids in the stabilization of water in oil emulsions and its effects on oil production in Saudi oil fields. *Fuel* 2000; 79: 1309-1316.
- Angle CW, Dabros T, Hamza HA. Predicting sizes of toluene-diluted heavy oil emulsions in turbulent flow. Part 1—Application of two adsorption kinetic models for σE in two size predictive models. *Chemical Engineering Science* 2006; 61: 7309-7324.
- APHA. Standard Methods for the examination of water and wastewater. Vol 20th ed. Washington, DC: American Public Health Association, AWWA.
- Asselin M, Drogui P, Brar SK, Benmoussa H, Blais J-F. Organics removal in oily bilgewater by electrocoagulation process. *Journal of Hazardous Materials* 2008; 151: 446-455.
- Aswathy P, Gandhimathi R, Ramesh ST, Nidheesh PV. Removal of organics from bilge water by batch electrocoagulation process. *Separation and Purification Technology* 2016; 159: 108-115.
- Awad TS, Asker D, Romsted LS. Evidence of coexisting microemulsion droplets in oil-in-water emulsions revealed by 2D DOSY ^1H NMR. *Journal of Colloid and Interface Science* 2018; 514: 83-92.
- Benito J, Sánchez M, Pena P, Rodríguez M. Development of a new high porosity ceramic membrane for the treatment of bilge water. *Desalination* 2007; 214: 91-101.
- Bhattacharjee S. DLS and zeta potential – What they are and what they are not? *Journal of Controlled Release* 2016; 235: 337-351.
- Bhattacharyya D, Jumawan A, Grieves R, Harris L. Ultrafiltration characteristics of oil-detergent-water systems: membrane fouling mechanisms. *Separation Science and Technology* 1979; 14: 529-549.
- Binks BP. Particles as surfactants—similarities and differences. *Curr. Opin. Colloid Interface Sci.* 2002; 7: 21-41.
- Binks BP, Isa L, Tyowua AT. Direct measurement of contact angles of silica particles in relation to double inversion of pickering emulsions. *Langmuir* 2013; 29: 4923-4927.

- Binks BP, Liu W, Rodrigues JA. Novel stabilization of emulsions via the heteroaggregation of nanoparticles. *Langmuir* 2008; 24: 4443-4446.
- Binks BP, Lumsdon SO. Stability of oil-in-water emulsions stabilised by silica particles. *Physical Chemistry Chemical Physics* 1999; 1: 3007-3016.
- Bradski G. The OpenCV Library. *Dr. Dobb's Journal of Software Tools* 2000.
- Brakstad OG, Farooq U, Ribicic D, Netzer R. Dispersibility and biotransformation of oils with different properties in seawater. *Chemosphere* 2018; 191: 44-53.
- Breiman L. Arcing Classifiers. *The Annals of Statistics* 1998; 26: 801-824.
- Bremond N, Thiam AR, Bibette J. Decompressing emulsion droplets favors coalescence. *Physical Review Letters* 2008; 100: 024501.
- Brosseau Q, Vrignon J, Baret J-C. Microfluidic dynamic interfacial tensiometry (μ DIT). *Soft matter* 2014; 10: 3066-3076.
- Campanelli JR, Wang X. Dynamic interfacial tension of surfactant mixtures at liquid-liquid interfaces. *Journal of colloid and interface science* 1999; 213: 340-351.
- Canizares P, Martinez F, Lobato J, Rodrigo M. Break-up of oil-in-water emulsions by electrochemical techniques. *Journal of Hazardous Materials* 2007; 145: 233-240.
- Chanamai R, McClements DJ. Creaming stability of flocculated monodisperse oil-in-water emulsions. *Journal of Colloid and Interface Science* 2000; 225: 214-218.
- Chang C-C, Lin C-J. LIBSVM: A library for support vector machines. *ACM Trans. Intell. Syst. Technol.* 2011; 2: Article 27.
- Chanthamalee J, Wongchitphimon T, Luepromchai E. Treatment of oily bilge water from small fishing vessels by PUF-immobilized *Gordonia* sp. JC11. *Water, Air, & Soil Pollution* 2013; 224: 1601.
- Chawla NV, Bowyer KW, Hall LO, Kegelmeyer WP. SMOTE: synthetic minority over-sampling technique. *J. Artif. Int. Res.* 2002; 16: 321-357.
- Chen G, Tao D. An experimental study of stability of oil-water emulsion. *Fuel Process. Technol.* 2005; 86: 499-508.
- Chen QJ, Cao XT, Liu H, Zhou W, Qin LJ, An ZS. pH-responsive high internal phase emulsions stabilized by core cross-linked star (CCS) polymers. *Polymer Chemistry* 2013; 4: 4092-4102.
- Chen Y, Narayan S, Dutcher CS. Phase-Dependent Surfactant Transport on the Microscale: Interfacial Tension and Droplet Coalescence. *Langmuir* 2020: <https://dx.doi.org/10.1021/acs.langmuir.0c02476>.
- Chollet Fao. Keras. 2020, 2015.
- Christopher G, Bergstein J, End N, Poon M, Nguyen C, Anna SL. Coalescence and splitting of confined droplets at microfluidic junctions. *Lab on a Chip* 2009; 9: 1102-1109.
- Church J, Armas SM, Patel PK, Chumbimuni-Torres K, Lee WH. Development and Characterization of Needle-Type Ion-Selective Microsensors for in situ Determination of Foliar Uptake of Zn^{2+} in Citrus Plants. *Electroanalysis* 2018.
- Church J, Lundin JG, Diaz D, Mercado D, Willner MR, Lee WH, et al. Identification and characterization of bilgewater emulsions. *Science of The Total Environment* 2019.
- Church J, Paynter DM, Lee WH. In Situ Characterization of Oil-in-Water Emulsions Stabilized by Surfactant and Salt Using Microsensors. *Langmuir* 2017; 33: 9731-9739.
- Church J, Willner MR, Renfro BR, Chen Y, Diaz D, Lee WH, et al. Impact of Interfacial Tension and Critical Micelle Concentration on Bilgewater Oil Separation. *Journal of Water Process Engineering* 2020: 101684.

- Clausse D, Gomez F, Dalmazzone C, Noik C. A method for the characterization of emulsions, thermogravimetry: application to water-in-crude oil emulsion. *Journal of colloid and interface science* 2005a; 287: 694-703.
- Clausse D, Gomez F, Pezron I, Komunjer L, Dalmazzone C. Morphology characterization of emulsions by differential scanning calorimetry. *Advances in Colloid and Interface Science* 2005b; 117: 59-74.
- Cui Y, Threlfall M, van Duijneveldt JS. Optimizing organoclay stabilized Pickering emulsions. *Journal of Colloid and Interface Science* 2011; 356: 665-671.
- Dalmazzone C, Noik C, Clausse D. Application of DSC for emulsified system characterization. *Oil & Gas Science and Technology-Revue de l'IFP* 2009; 64: 543-555.
- Davis CR, Martinez CJ, Howarter JA, Erk KA. Diffusion-Controlled Spontaneous Emulsification of Water-Soluble Oils via Micelle Swelling. *Langmuir* 2020.
- de Souza UFAQ, Frank H and Guardani, Roberto. Prediction of emulsion stability via a neural network-based mapping technique. *Industrial & engineering chemistry research* 2007; 46: 5100--5107.
- Deese RD, Morris RE, Metz AE, Myers KM, Johnson K, Loegel TN. Characterization of Organic Nitrogen Compounds and Their Impact on the Stability of Marginally Stable Diesel Fuels. *Energy & Fuels* 2019; 33: 6659-6669.
- Derkach SR, Kolotova DS, Simonsen G, Simon SC, Sjöblom J, Andrianov AV, et al. Kinetics of crystallization of aqueous droplets in water-in-crude oil emulsions at low temperatures. *Energy & fuels* 2018; 32: 2197-2202.
- Di Marzio L, Marianecchi C, Petrone M, Rinaldi F, Carafa M. Novel pH-sensitive non-ionic surfactant vesicles: comparison between Tween 21 and Tween 20. *Colloids and Surfaces B: Biointerfaces* 2011; 82: 18-24.
- Diaz D. Emulsion Characterization Study for Improved Bilgewater Treatment and Management Civil, Environmental, and Construction Engineering. Master. University of Central Florida, Orlando, FL, 2020.
- Diaz D, Church J, Willner MR, Sarnyai S, Lundin JG, Paynter DM, et al. Evaluation of bilgewater emulsion stability using nondestructive analytical methods. *Industrial & Engineering Chemistry Research* 2021; 10.1021/acs.iecr.0c04814.
- Djekic L, Ibric S, Primorac M. The application of artificial neural networks in the prediction of microemulsion phase boundaries in PEG-8 caprylic/capric glycerides based systems. *Int J Pharm* 2008; 361: 41-6.
- Domínguez A, Fernandez A, Gonzalez N, Iglesias E, Montenegro L. Determination of critical micelle concentration of some surfactants by three techniques. *Journal of chemical education* 1997; 74: 1227.
- Drelich A, Dalmazzone C, Pezron I, Liggieri L, Clausse D. DSC (Differential Scanning Calorimetry) used to follow the evolution of W/O emulsions versus time on ground and in space in the ISS. *Oil & Gas Sciences and Technology–Revue d'IFP Energies nouvelles* 2018; 73: 16.
- Drelich J, Fang C, White C. Measurement of interfacial tension in fluid-fluid systems. *Encyclopedia of surface and colloid science* 2002; 3: 3158-3163.
- Dukhin A, Goetz P. Ultrasound for characterizing emulsions and microemulsions. *Emulsions and Emulsion Stability*. CRC Press, 2005, pp. 331-374.
- Durak SG, Acar TO, Kahraman C, Balcioglu EB, Tüfekci N. Assessment Of Treatment Methods For Ship Originated Wastewaters. *Proceedings Book* 2016: 832.

- Emadian SM, Rahimnejad M, Hosseini M, Khoshandam B. Investigation on up-flow anaerobic sludge fixed film (UASFF) reactor for treating low-strength bilge water of Caspian Sea ships. *Journal of Environmental Health Science and Engineering* 2015; 13: 23.
- EPA US. Oily Bilgewater Separators. In: Management OoW, editor, Washington, DC, 2011.
- Eskandarloo H, Selig MJ, Abbaspourrad A. In situ H₂O₂ generation for de-emulsification of fine stable bilge water emulsions. *Chemical Engineering Journal* 2018; 335: 434-442.
- Ferreira T, Rasband WJIF. ImageJ user guide. 2012; 1: 155-161.
- Ferri JK, Stebe KJ. Which surfactants reduce surface tension faster? A scaling argument for diffusion-controlled adsorption. *Advances in Colloid and Interface Science* 2000; 85: 61-97.
- Flanigan D, Stolhand J, Scribner M, Shimoda E. Droplet size analysis: a new tool for improving oilfield separations. SPE Annual Technical Conference and Exhibition. Society of Petroleum Engineers, 1988.
- Frazier PIaW, Jialei. *Information Science for Materials Discovery and Design*: Springer, 2016.
- Galton F. Regression Towards Mediocrity in Hereditary Stature. *The Journal of the Anthropological Institute of Great Britain and Ireland* 1886; 15: 246-263.
- Gašperlin MaP, F and Šibanc, R. Evolutionary artificial neural networks as tools for predicting the internal structure of microemulsions. *Journal of Pharmacy & Pharmaceutical Sciences* 2008; 11: 67-76.
- Gašperlin MaT, L and Tušar, M and Kristl, J and Šmid-Korbar, J. Lipophilic semisolid emulsion systems: viscoelastic behaviour and prediction of physical stability by neural network modelling. *International journal of pharmaceutics* 1998; 168: 243-254.
- Gašperlin MaT, Livija and Tušar, Marjan and Šmid-Korbar, Jelka and Zupan, Jure and Kristl, Julijana. Viscosity prediction of lipophilic semisolid emulsion systems by neural network modelling. *International journal of pharmaceutics* 2000; 196: 37-50.
- Gilbert L, Picard C, Savary G, Grisel M. Rheological and textural characterization of cosmetic emulsions containing natural and synthetic polymers: relationships between both data. *Colloids and Surfaces A* 2013; 421: 150-163.
- Goodfellow I, Bengio Y, Courville A. *Deep Learning*: The MIT Press, 2016.
- Gryta M. Bilge water separation by membrane distillation. *Separation and Purification Technology* 2020; 237: 116332.
- Grzechulska J, Hamerski M, Morawski AW. Photocatalytic decomposition of oil in water. *Water Research* 2000; 34: 1638-1644.
- Gu H, Duits MH, Mugele F. Droplets formation and merging in two-phase flow microfluidics. *International journal of molecular sciences* 2011; 12: 2572-2597.
- Gutiérrez J, González C, Maestro A, Solè I, Pey C, Nolla J. Nano-emulsions: New applications and optimization of their preparation. *Current opinion in colloid & interface science* 2008; 13: 245-251.
- Håkansson A, Innings F, Trägårdh C, Bergenståhl B. A high-pressure homogenization emulsification model—Improved emulsifier transport and hydrodynamic coupling. *Chemical Engineering Science* 2013; 91: 44-53.
- Haus F, German J, Junter G-A. Primary biodegradability of mineral base oils in relation to their chemical and physical characteristics. *Chemosphere* 2001; 45: 983-990.
- He Y, Yazhgur P, Salonen A, Langevin D. Adsorption–desorption kinetics of surfactants at liquid surfaces. *Advances in colloid and interface science* 2015; 222: 377-384.

- Heermann SE, Powers SE. Modeling the partitioning of BTEX in water-reformulated gasoline systems containing ethanol. *Journal of Contaminant Hydrology* 1998; 34: 315-341.
- Hezave AZ, Dorostkar S, Ayatollahi S, Nabipour M, Hemmateenejad B. Dynamic interfacial tension behavior between heavy crude oil and ionic liquid solution (1-dodecyl-3-methylimidazolium chloride ([C12mim][Cl]⁺ distilled or saline water/heavy crude oil)) as a new surfactant. *Journal of Molecular Liquids* 2013; 187: 83-89.
- Hinton GE. Connectionist learning procedures. *Artificial Intelligence* 1989; 40: 185-234.
- Hinze J. Fundamentals of the hydrodynamic mechanism of splitting in dispersion processes. *AIChE Journal* 1955; 1: 289-295.
- Ho TK. A Data Complexity Analysis of Comparative Advantages of Decision Forest Constructors. *Pattern Analysis & Applications* 2002; 5: 102-112.
- Hollingsworth K, Johns M. Measurement of emulsion droplet sizes using PFG NMR and regularization methods. *Journal of Colloid and Interface Science* 2003; 258: 383-389.
- Hosseinizadeh-Bandbafha H, Tabatabaei M, Aghbashlo M, Khanali M, Demirbas A. A comprehensive review on the environmental impacts of diesel/biodiesel additives. *Energy Conversion and Management* 2018; 174: 579-614.
- Hsu J-P, Nacu A. Behavior of soybean oil-in-water emulsion stabilized by nonionic surfactant. *Journal of Colloid and Interface Science* 2003; 259: 374-381.
- Islam MA, Church J, Han C, Chung HS, Ji E, Kim JH. Noble metal-coated MoS₂ nanofilms with vertically-aligned 2D layers for visible light-driven photocatalytic degradation of emerging water contaminants. *Scientific reports* 2017; 7: 14944.
- Israelachvili JN. Intermolecular and surface forces: Academic press, 2011.
- Iyota H, Krastev RJC, science p. Miscibility of sodium chloride and sodium dodecyl sulfate in the adsorbed film and aggregate. 2009; 287: 425-433.
- Jafari SM, Assadpoor E, He Y, Bhandari B. Re-coalescence of emulsion droplets during high-energy emulsification. *Food hydrocolloids* 2008; 22: 1191-1202.
- Jensen HM, Arvin E. Solubility and degradability of the gasoline additive MTBE, methyl-tert-butyl-ether, and gasoline compounds in water. *Contaminated soil'90*. Springer, 1990, pp. 445-448.
- Jian C, Liu Q, Zeng H, Tang T. Effect of model polycyclic aromatic compounds on the coalescence of water-in-oil emulsion droplets. *The Journal of Physical Chemistry C* 2017; 121: 10382-10391.
- Jin F, Balasubramaniam R, Stebe KJ. Surfactant adsorption to spherical particles: The intrinsic length scale governing the shift from diffusion to kinetic-controlled mass transfer. *The journal of adhesion* 2004; 80: 773-796.
- Kale SN, Deore SL. Emulsion micro emulsion and nano emulsion: a review. *Systematic Reviews in Pharmacy* 2017; 8: 39.
- Karakulski K, Morawski W, Grzechulska J. Purification of bilgewater by hybrid ultrafiltration and photocatalytic processes. *Separation and Purification Technology* 1998; 14: 163-173.
- Katsouli M, Polychniatou V, Tzia C. Influence of surface-active phenolic acids and aqueous phase ratio on w/o nano-emulsions properties; model fitting and prediction of nano-emulsions oxidation stability. *Journal of Food Engineering* 2017; 214: 40-46.
- Khan MF, Singh MK, Sen S. Measuring size, size distribution, and polydispersity of water-in-oil microemulsion droplets using fluorescence correlation spectroscopy: comparison to dynamic light scattering. *The Journal of Physical Chemistry B* 2016; 120: 1008-1020.

- Kimbler OK, Reed R, Silberberg I. Physical characteristics of natural films formed at crude oil-water interfaces. *Society of Petroleum Engineers Journal* 1966; 6: 153-165.
- Kimura M, Komaki M, Nakajima T, Nakahara H, Fukuda K. Influence of detergent builders on surface properties of sodium dodecyl sulfate solutions under dynamic and static conditions. *Journal of the American Oil Chemists' Society* 1990; 67: 698-704.
- Kiran SK, Acosta EJ, Moran K. Evaluating the hydrophilic-lipophilic nature of asphaltenic oils and naphthenic amphiphiles using microemulsion models. *Journal of colloid and interface science* 2009; 336: 304-313.
- Kokal S. Crude-oil emulsions: A state-of-the-art review. *Spe Production & Facilities* 2005; 20: 5-13.
- Körbahti BK, Artut K. Electrochemical oil/water demulsification and purification of bilge water using Pt/Ir electrodes. *Desalination* 2010; 258: 219-228.
- Krebs T, Schroën C, Boom R. Separation kinetics of an oil-in-water emulsion under enhanced gravity. *Chemical Engineering Science* 2012; 71: 118-125.
- Krebs T, Schroen CGPH, Boom RM. Coalescence kinetics of oil-in-water emulsions studied with microfluidics. *Fuel* 2013; 106: 327-334.
- Kulmyrzaev A, Chanamai R, McClements DJ. Influence of pH and CaCl₂ on the stability of dilute whey protein stabilized emulsions. *Food Research International* 2016; 33: 15-20.
- Kumar KJ, Panpalia GM, Priyadarshini S. Application of artificial neural networks in optimizing the fatty alcohol concentration in the formulation of an O/W emulsion. *Acta Pharm* 2011; 61: 249-56.
- Kunieda M, Nakaoka K, Liang Y, Miranda CR, Ueda A, Takahashi S, et al. Self-accumulation of aromatics at the oil-water interface through weak hydrogen bonding. *Journal of the American Chemical Society* 2010; 132: 18281-18286.
- Lang DA, Bastow TP, Van Aarssen BG, Warton B, Davis GB, Johnston CD. Polar compounds from the dissolution of weathered diesel. *Groundwater Monitoring & Remediation* 2009; 29: 85-93.
- Lazaridis N, Alexopoulos A, Chatzi E, Kiparissides C. Steric stabilization in emulsion polymerization using oligomeric nonionic surfactants. *Chemical engineering science* 1999; 54: 3251-3261.
- Leal-Calderon F, Schmitt V, Bibette J. *Emulsion science: basic principles*: Springer Science & Business Media, 2007.
- Lee WH, Pressman JG, Wahman DG. Three-dimensional free chlorine and monochloramine biofilm penetration: correlating penetration with biofilm activity and viability. *Environmental Science and Technology* 2017.
- Liao Y, Lucas D. A literature review of theoretical models for drop and bubble breakup in turbulent dispersions. *Chemical Engineering Science* 2009; 64: 3389-3406.
- Lignel S, Drelich A, Sunagatullina D, Clausse D, Leclerc E, Pezron I. Differential scanning calorimetry analysis of W/O emulsions prepared by miniature scale magnetic agitation and microfluidics. *The Canadian Journal of Chemical Engineering* 2014; 92: 337-343.
- Lingwood I, Chandrasekera T, Kolz J, Fridjonsson E, Johns M. Emulsion droplet sizing using low-field NMR with chemical shift resolution and the block gradient pulse method. *Journal of Magnetic Resonance* 2012; 214: 281-288.
- Llamas S, Santini E, Liggieri L, Salerni F, Orsi D, Cristofolini L, et al. Adsorption of sodium dodecyl sulfate at water-dodecane interface in relation to the oil in water emulsion properties. *Langmuir* 2018; 34: 5978-5989.

- Ma X, Armas SM, Soliman M, Lytle D, Chumbimuni-Torres K, Tetard L. In Situ Monitoring of Pb²⁺ Leaching from the Galvanic Joint Surface in a Prepared Chlorinated Drinking Water. *Environmental Science & Technology* 2018; 52: 2126-2133.
- MacKay DJC. Bayesian Interpolation. *Neural Computation* 1992; 4: 415-447.
- Maindarkar SN, Hoogland H, Henson MA. Predicting the combined effects of oil and surfactant concentrations on the drop size distributions of homogenized emulsions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 2015; 467: 18-30.
- Malassange-Bulgarelli N, McGrath KM. Dynamics of oil transfer in oil-in-water emulsions. *Soft Matter* 2009; 5: 4804-4813.
- Maribo D. Performance Test Plan for Oily Waste Treatment Systems (Public). Naval Surface Warfare Center, Carderock Division, Bethesda, 2004.
- Marinova K, Alargova R, Denkov N, Velev O, Petsev D, Ivanov I, et al. Charging of oil–water interfaces due to spontaneous adsorption of hydroxyl ions. *Langmuir* 1996; 12: 2045-2051.
- Maron ME. Automatic Indexing: An Experimental Inquiry. *J. ACM* 1961; 8: 404–417.
- Marques DS, Sørland G, Less S, Vilagines R. The application of pulse field gradient (PFG) NMR methods to characterize the efficiency of separation of water-in-crude oil emulsions. *Journal of Colloid and Interface Science* 2018; 512: 361-368.
- Marquez R, Forgiarini AM, Langevin D, Salager J-L. Instability of emulsions made with surfactant–oil–water systems at optimum formulation with ultralow interfacial tension. *Langmuir* 2018; 34: 9252-9263.
- Marszall L. Effective hydrophile-lipophile balance and micelle formation of non-ionic surfactants in the presence of short-chain glycol ethers. *International Journal of Pharmaceutics* 1980; 6: 253-260.
- Martínez-Palou R, Cerón-Camacho R, Chávez B, Vallejo AA, Villanueva-Negrete D, Castellanos J, et al. Demulsification of heavy crude oil-in-water emulsions: a comparative study between microwave and thermal heating. *Fuel* 2013; 113: 407-414.
- McAuliffe C. Solubility in water of paraffin, cycloparaffin, olefin, acetylene, cycloolefin, and aromatic hydrocarbons¹. *The Journal of Physical Chemistry* 1966; 70: 1267-1275.
- McClements DJ. Ultrasonic characterization of foods and drinks: principles, methods, and applications. *Crit Rev Food Sci Nutr* 1997; 37: 1-46.
- McClements DJ. Critical review of techniques and methodologies for characterization of emulsion stability. *Crit Rev Food Sci Nutr* 2007; 47: 611-49.
- McClements DJ. Food emulsions: principles, practices, and techniques: CRC press, 2015.
- McClements DJ, Jafari SM. Improving emulsion formation, stability and performance using mixed emulsifiers: A review. *Advances in Colloid and Interface Science* 2018; 251: 55-79.
- McLaughlin C, Falatko D, Danesi R, Albert R. Characterizing shipboard bilgewater effluent before and after treatment. *Environmental Science and Pollution Research* 2014; 21: 5637-5652.
- Metaxas AE, Panwar V, Olson RL, Dutcher CS. Ionic strength and polyelectrolyte molecular weight effects on floc formation and growth in Taylor–Couette flows. *Soft Matter* 2021.
- Middelburg L, de Graaf G, Bossche A, Bastemeijer J, Ghaderi M, Wolffenbuttel F, et al. Multi-domain spectroscopy for composition measurement of water-containing bio-ethanol fuel. *Fuel Processing Technology* 2017; 167: 127-135.

- Mitra RK, Paul BK. Effect of temperature and salt on the phase behavior of nonionic and mixed nonionic–ionic microemulsions with fish-tail diagrams. *Journal of colloid and interface science* 2005; 291: 550-559.
- Mittal KL, Vold RD. Effect of the initial concentration of emulsifying agents on the ultracentrifugal stability of oil-in-water emulsions. *Journal of the American Oil Chemists' Society* 1972; 49: 527-532.
- Mizoguchi SKaHOaSKaT. Bayesian optimization for efficient determination of metal oxide grain boundary structures. *Physica B: Condensed Matter* 2018; 532: 24-28.
- Moradi M, Alvarado V, Huzurbazar S. Effect of salinity on water-in-crude oil emulsion: evaluation through drop-size distribution proxy. *Energy & fuels* 2010; 25: 260-268.
- Moslehyani A, Mobaraki M, Isloor A, Ismail A, Othman M. Photoreactor-ultrafiltration hybrid system for oily bilge water photooxidation and separation from oil tanker. *Reactive and Functional Polymers* 2016; 101: 28-38.
- Ngai T, Bon SA. Particle-stabilized emulsions and colloids: formation and applications: Royal Society of Chemistry, 2014.
- Novales B, Papineau P, Sire A, Axelos M. Characterization of emulsions and suspensions by video image analysis. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 2003; 221: 81-89.
- Oh S-G, Shah D. Effect of counterions on the interfacial tension and emulsion droplet size in the oil/water/dodecyl sulfate system. *The Journal of Physical Chemistry* 1993; 97: 284-286.
- Packwood D. Bayesian Optimization for Materials Science: Springer Singapore, 2017.
- Pan R, Green J, Maldarelli C. Theory and experiment on the measurement of kinetic rate constants for surfactant exchange at an air/water interface. *Journal of colloid and interface science* 1998; 205: 213-230.
- Pathak M. Nanoemulsions and their stability for enhancing functional properties of food ingredients. *Nanotechnology applications in food*. Elsevier, 2017, pp. 87-106.
- Pawlak Z. *Tribochemistry of lubricating oils*: Elsevier, 2003.
- Pedregosa FaV, G. and Gramfort, A. and Michel, V. and Thirion, B. and Grisel, O. and Blondel, M. and Prettenhofer, P. and Weiss, R. and Dubourg, V. and Vanderplas, J. and Passos, A. and Cournapeau, D. and Brucher, M. and Perrot, M. and Duchesnay, E. Scikit-learn: Machine Learning in Python. *Journal of Machine Learning Research* 2011; 12: 2825-2830.
- Peng H, Tremblay A, Veinot D. The use of backflushed coalescing microfiltration as a pretreatment for the ultrafiltration of bilge water. *Desalination* 2005; 181: 109-120.
- Perrier-Cornet J, Marie P, Gervais P. Comparison of emulsification efficiency of protein-stabilized oil-in-water emulsions using jet, high pressure and colloid mill homogenization. *Journal of Food Engineering* 2005; 66: 211-217.
- Pichot R, Spyropoulos F, Norton I. O/W emulsions stabilised by both low molecular weight surfactants and colloidal particles: The effect of surfactant type and concentration. *Journal of Colloid and Interface Science* 2010; 352: 128-135.
- Powers SE, Hunt CS, Heermann SE, Corseuil HX, Rice D, Alvarez PJ. The transport and fate of ethanol and BTEX in groundwater contaminated by gasohol. *Critical Reviews in Environmental Science and Technology* 2001; 31: 79-123.
- Quinlan JR. Induction of decision trees. *Machine Learning* 1986; 1: 81-106.

- Raikar NB, Bhatia SR, Malone MF, McClements DJ, Henson MA. Predicting the effect of the homogenization pressure on emulsion drop-size distributions. *Industrial & Engineering Chemistry Research* 2011; 50: 6089-6100.
- Rehfeld SJ. Stability of emulsions to ultracentrifugation: Discontinuity at the critical micelle concentration. *The Journal of Physical Chemistry* 1962; 66: 1966-1968.
- Remington J. Remington: the science and practice of pharmacy. Vol 1: Lippincott, Williams & Wilkins, 2006.
- Ribeiro NM, Pinto AC, Quintella CM, da Rocha GO, Teixeira LS, Guarieiro LL, et al. The role of additives for diesel and diesel blended (ethanol or biodiesel) fuels: a review. *Energy & fuels* 2007; 21: 2433-2445.
- Rice E, Baird R, Eaton A, Clesceri L, editors. *Standard Methods for the Examination of Water and Wastewater: American Public Health Association, American Water Works Association, Water Environment Federation*, 2012.
- Richardson CaM, A and Aboofazeli, R and Lawrence, MJ and Barlow, DJ. Prediction of phase behavior in microemulsion systems using artificial neural networks. *Journal of colloid and interface science* 1997; 187: 296-303.
- Rincón GJ, La Motta EJ. Simultaneous removal of oil and grease, and heavy metals from artificial bilge water using electro-coagulation/flotation. *Journal of Environment Management* 2014; 144: 42-50.
- Rios G, Pazos C, Coca J. Destabilization of cutting oil emulsions using inorganic salts as coagulants. *Colloids and Surfaces A* 1998; 138: 383-389.
- Roland I, Piel G, Delattre L, Evrard B. Systematic characterization of oil-in-water emulsions for formulation design. *International Journal of Pharmaceutics* 2003; 263: 85-94.
- Rosen MJ, Kunjappu JT. *Surfactants and interfacial phenomena: John Wiley & Sons*, 2012.
- Rosen MJ, Mathias JH, Davenport L. Aberrant aggregation behavior in cationic gemini surfactants investigated by surface tension, interfacial tension, and fluorescence methods. *Langmuir* 1999; 15: 7340-7346.
- Rostami P, Mehraban MF, Sharifi M, Dejam M, Ayatollahi S. Effect of water salinity on oil/brine interfacial behaviour during low salinity waterflooding: A mechanistic study. *Petroleum* 2019; 5: 367-374.
- Rowe E. Effect of emulsifier concentration and type on the particle size distribution of emulsions. *Journal of pharmaceutical sciences* 1965; 54: 260-264.
- Saliu F, Della Pergola R. Organic bases, carbon dioxide and naphthenic acids interactions. Effect on the stability of petroleum crude oil in water emulsions. *Journal of Petroleum Science and Engineering* 2018; 163: 177-184.
- Santisi S, Gentile G, Volta A, Bonsignore M, Mancini G, Quatrini P, et al. Isolation and characterization of oil-degrading bacteria from bilge water. *Growth* 2015; 17: 45-49.
- Schick M, Gilbert A. Effect of urea, guanidinium chloride, and dioxane on the cmc of branched-chain nonionic detergents. *Journal of colloid science* 1965; 20: 464-472.
- Sermarini JT. *The Universal Fuel at Sea: Replacing F-76 with JP-5. NAVAL POSTGRADUATE SCHOOL MONTEREY CA*, 2000.
- Sharp T. MARPOL: how to do it: manual on the practical implications of ratifying and implementing MARPOL 73/78. *International Maritime Organization* 1993.
- Silva HD, Cerqueira MA, Vicente AA. Nanoemulsions for Food Applications: Development and Characterization. *Food and Bioprocess Technology* 2012; 5: 854-867.

- Sokolović RMŠ, Govedarica DD, Sokolović DS. Separation of oil-in-water emulsion using two coalescers of different geometry. *Journal of Hazardous Materials* 2010; 175: 1001-1006.
- Solans C, Izquierdo P, Nolla J, Azemar N, Garcia-Celma MJ. Nano-emulsions. *Current opinion in colloid & interface science* 2005; 10: 102-110.
- Sosa JM, Huber DE, Welk B, Fraser HL. Development and application of MIPAR™: a novel software package for two- and three-dimensional microstructural characterization. *Integrating Materials and Manufacturing Innovation* 2014; 3: 10.
- Stachurski J, MichaŁek M. The effect of the ζ potential on the stability of a non-polar oil-in-water emulsion. *Journal of Colloid and Interface Science* 1996; 184: 433-436.
- Stamper DM, Montgomery MT. Biological treatment and toxicity of low concentrations of oily wastewater (bilgewater). *Canadian journal of microbiology* 2008; 54: 687-693.
- Striebich RC, Smart CE, Gunasekera TS, Mueller SS, Strobel EM, McNichols BW, et al. Characterization of the F-76 diesel and Jet-A aviation fuel hydrocarbon degradation profiles of *Pseudomonas aeruginosa* and *Marinobacter hydrocarbonoclasticus*. *International Biodeterioration & Biodegradation* 2014; 93: 33-43.
- Sun C, Gunasekaran S. Effects of protein concentration and oil-phase volume fraction on the stability and rheology of menhaden oil-in-water emulsions stabilized by whey protein isolate with xanthan gum. *Food Hydrocolloids* 2009; 23: 165-174.
- Tadros T, Izquierdo P, Esquena J, Solans C. Formation and stability of nano-emulsions. *Advances in colloid and interface science* 2004; 108: 303-318.
- Tadros TF. *Applied surfactants: principles and applications*: John Wiley & Sons, 2006.
- Tadros TF. *Emulsion science and technology: a general introduction*: Wiley-VCH Verlag GmbH & Co. KGaA Weinheim, 2009.
- Talbert SG, Paul DD, Millett SM, Evers DP, Dvorsky JE, Paul EGI, et al. Thermal water treatment. Google Patents, 2004.
- Tcholakova S, Denkov N, Sidzhakova D, Ivanov I, Campbell B. Effects of electrolyte concentration and pH on the coalescence stability of beta-lactoglobulin emulsions: Experiment and interpretation. *Langmuir* 2005; 21: 4842-4855.
- Tcholakova S, Denkov ND, Danner T. Role of surfactant type and concentration for the mean drop size during emulsification in turbulent flow. *Langmuir* 2004; 20: 7444-7458.
- Tcholakova S, Denkov ND, Sidzhakova D, Ivanov IB, Campbell B. Interrelation between drop size and protein adsorption at various emulsification conditions. *Langmuir* 2003; 19: 5640-5649.
- Teh S-Y, Lin R, Hung L-H, Lee AP. Droplet microfluidics. *Lab on a Chip* 2008; 8: 198-220.
- Teklebrhan RB, Ge L, Bhattacharjee S, Xu Z, Sjöblom J. Initial partition and aggregation of uncharged polyaromatic molecules at the oil–water interface: a molecular dynamics simulation study. *The Journal of Physical Chemistry B* 2014; 118: 1040-1051.
- Tissot BP, Welte DH. *Petroleum formation and occurrence*: Springer Science & Business Media, 2013.
- Tomaszewska M, Orecki A, Karakulski K. Treatment of bilge water using a combination of ultrafiltration and reverse osmosis. *Desalination* 2005; 185: 203-212.
- Tummons EN, Tarabara VV, Chew JW, Fane AG. Behavior of oil droplets at the membrane surface during crossflow microfiltration of oil-water emulsions. *Journal of Membrane Science* 2016; 500: 211-224.
- U.S. EPA. Fact Sheet: Method 1664, Oil and Grease, Revision A. 1999a.

- U.S. EPA. Phase I Uniform National Discharge Standards for Vessels of the Armed Forces. In: Water Oo, editor, Washington DC, 1999b.
- U.S. EPA. Method 1664, Revision B: n-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated n-Hexane Extractable Material (SGT-HEM; Non-polar Material) by Extraction and Gravimetry. United States Environmental Protection Agency, Washington, DC, 2010.
- Ulucan K, Kurt U. Comparative study of electrochemical wastewater treatment processes for bilge water as oily wastewater: a kinetic approach. *Journal of Electroanalytical Chemistry* 2015; 747: 104-111.
- Uma V, Gandhimathi R. Organic removal and synthesis of biopolymer from synthetic oily bilge water using the novel mixed bacterial consortium. *Bioresource technology* 2019; 273: 169-176.
- Umar AA, Saaid IBM, Sulaimon AA, Pilus RBM. A review of petroleum emulsions and recent progress on water-in-crude oil emulsions stabilized by natural surfactants and solids. *Journal of Petroleum Science and Engineering* 2018; 165: 673-690.
- Umar AAaS, Ismail M and Sulaimon, Aliyu A. An SVM-Based Classification and Stability Analysis of Synthetic Emulsions Co-Stabilized by a Nonionic Surfactant and Laponite Clay. *Science and Technology Behind Nanoemulsions* 2018: 111.
- van der Linden E, Sagis L, Venema P. Rheo-optics and food systems. *Current opinion in colloid and interface science* 2003; 8: 349-358.
- Vyrides I, Drakou E-M, Ioannou S, Michael F, Gatidou G, Stasinakis AS. Biodegradation of bilge water: Batch test under anaerobic and aerobic conditions and performance of three pilot aerobic Moving Bed Biofilm Reactors (MBBRs) at different filling fractions. *Journal of environmental management* 2018a; 217: 356-362.
- Vyrides I, Drakou E-M, Ioannou S, Michael F, Gatidou G, Stasinakis ASJoem. Biodegradation of bilge water: Batch test under anaerobic and aerobic conditions and performance of three pilot aerobic Moving Bed Biofilm Reactors (MBBRs) at different filling fractions. 2018b; 217: 356-362.
- Waller GH, Martin CA, Jones NJ, Paynter DM. Treatment of oil-in-saltwater emulsions by in-situ production of magnetic FeOx nanoparticles. *Journal of Water Process Engineering* 2019; 31: 100851.
- Walstra P. Principles of emulsion formation. *Chemical Engineering Science* 1993; 48: 333-349.
- Wang YZ, Sun XY, Liu YP, Liu CG. Removal of naphthenic acids from a diesel fuel by esterification. *Energy & fuels* 2007; 21: 941-943.
- Weiss J, Canceliere C, McClements DJ. Mass transport phenomena in oil-in-water emulsions containing surfactant micelles: Ostwald ripening. *Langmuir* 2000; 16: 6833-6838.
- Williams CKI, Rasmussen CE. Gaussian processes for regression. *Proceedings of the 8th International Conference on Neural Information Processing Systems*. MIT Press, Denver, Colorado, 1995, pp. 514-520.
- Wolak A. Changes in lubricant properties of used synthetic oils based on the total acid number. *Measurement and Control* 2018; 51: 65-72.
- Yan N, Masliyah JH. Characterization and demulsification of solids-stabilized oil-in-water emulsions Part 1. Partitioning of clay particles and preparation of emulsions. *Colloids and Surfaces A* 1995; 96: 229-242.

- Zhang Z, Song J, Lin Y-J, Wang X, Biswal SL. Comparing the Coalescence Rate of Water-in-Oil Emulsions Stabilized with Asphaltenes and Asphaltene-like Molecules. *Langmuir* 2020; 36: 7894-7900.
- Zolfaghari R, Fakhru'l-Razi A, Abdullah LC, Elnashaie SS, Pendashteh A. Demulsification techniques of water-in-oil and oil-in-water emulsions in petroleum industry. *Separation and Purification Technology* 2016; 170: 377-407.

APPENDIX A. List of Publications and Presentations

Publications

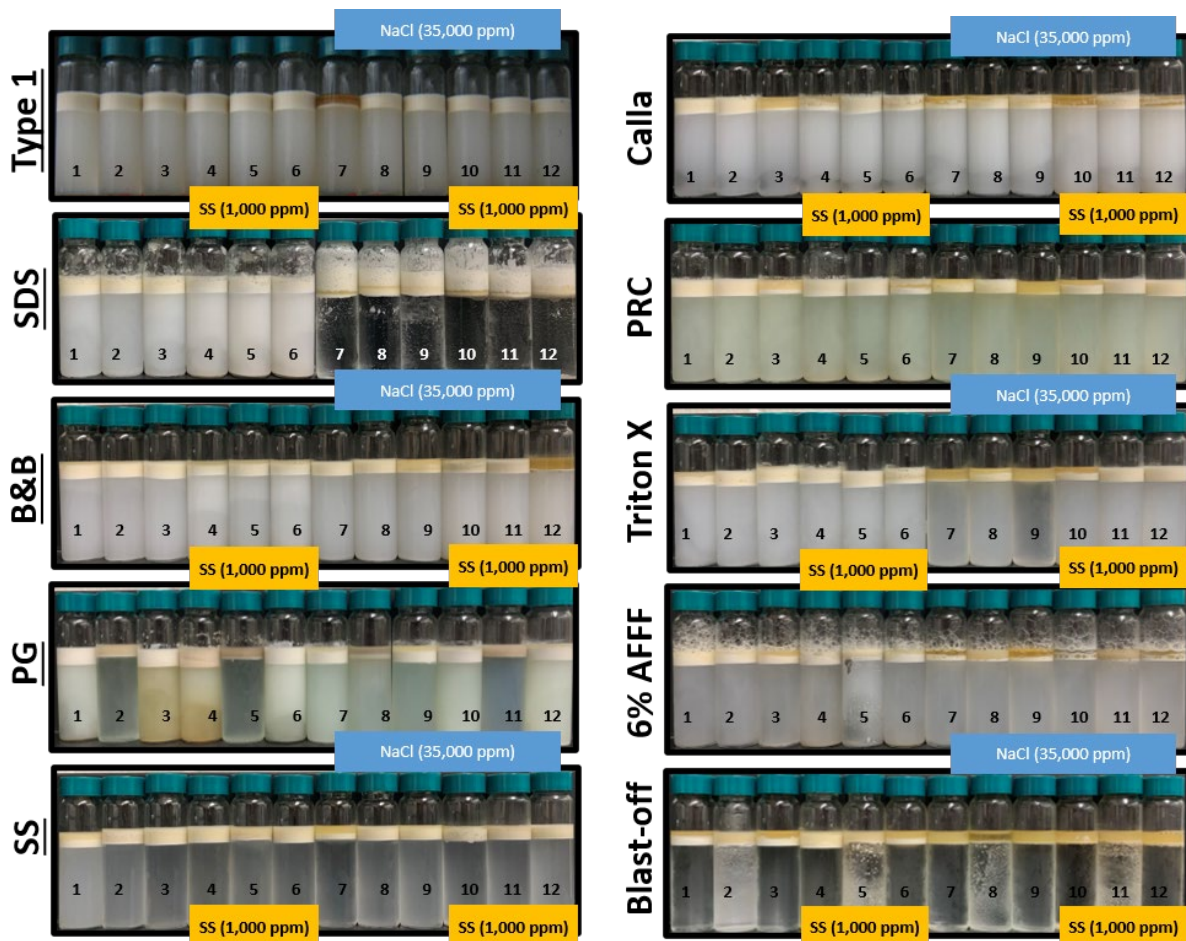
1. Daniels, G., Church, J., Chen, Y, Rodriguez, K., Lee, W.H., Paynter, D.M., & Lundin, J.G. Effects of Surface Active Impurities on Surfactant Behavior at Fuel Oil-Water Interfaces. Langmuir. (In Preparation)
2. Diaz, D., Rodriguez, K., Church, J., Sarnyai, S., Lundin, J.G., Paynter, D.M., & Lee, W.H. Characterization of Simulated Shipboard Emulsion Stability Under Varying Environmental Conditions. Colloids and Surfaces A: Physicochemical and Engineering Aspects. (In Preparation)
3. Park, C.Y., Diaz, D., Church, J., Lundin, J.G., Paynter, D.M. & Lee, W.H. Implementing Image Processing and Machine Learning for Predicting Bilgewater Emulsion Stability. Colloids and Surfaces A: Physicochemical and Engineering Aspects. (Submitted)
4. Church, J., Daniels, G.C., Lundin, J.G., Lee, W.H., & Paynter, D.M. Stabilization of Bilgewater Emulsions by Shipboard Oils. Environmental Science and Technology Water. (Submitted).
5. Diaz, D., Church, J., Willner, M. R., Sarnyai, S., Lundin, J. G., Paynter, D. M., & Lee, W. H. (2020). Evaluation of Bilgewater Emulsion Stability Using Nondestructive Analytical Methods. Industrial & Engineering Chemistry Research.
6. Church, J., Willner, M. R., Renfro, B.R., Diaz, D., Lee, W. H., Lundin, J.G., & Paynter, D. M. (2020). Impact of interfacial tension and critical micelle concentration on bilgewater oil separation. Journal of Water Process Engineering 39, 101684
7. Church, J., Lundin, J. G., Diaz, D., Mercado, D., Willner, M. R., Lee, W. H., & Paynter, D. M. (2019). Identification and characterization of bilgewater emulsions. Science of the Total Environment. (IF=5.589)

Presentations

1. Daniels, G., Church, J., Lundin, J.G., and Paynter, D.M. Identification and Role of Fuel Components on Bilgewater Emulsion Stability. *ACS National Meeting & Exposition*, Virtual, April 5-16, 2021.
2. Church, J., Daniels, G., Diaz, D., Willner, M.R., Park, C.Y., Rodriguez, K., Lundin, J.G., Lee, W.H., and Paynter, D.M., Emulsion Characterization Study for Improved Bilgewater Treatment and Management, *2020 SERDP/ESTCP Symposium*, Virtual, Dec. 1, 2020.
3. Park, C.Y., Diaz, D., Church, J., Rodriguez, K., Lundin, J.G., Paynter, D.M. & Lee, W.H. Implementing Image Processing and Machine Learning for Predicting Bilgewater Emulsion Stability. *2020 SERDP/ESTCP Symposium*, Virtual, Dec. 1, 2020.
4. Paynter, D.M. Emulsions Characterization Study for Improved Bilgewater Treatment and Management. Waste Reduction & Treatment in Armed Forces Vessels Webinar, June 12, 2020.
5. Church, J., Willner, M.R., Renfro, B.R., Chen, Y., Diaz, D., Lee, W.H., Dutcher, C.S., Lundin, J.G., Paynter, D.M. Impacts of Interfacial Tension and Critical Micelle Concentration on Emulsion Stability in Bilgewater. *259th ACS National Meeting & Exposition*, Philadelphia, PA, March. 22- 26, 2020. (Accepted/Cancelled due to COVID)

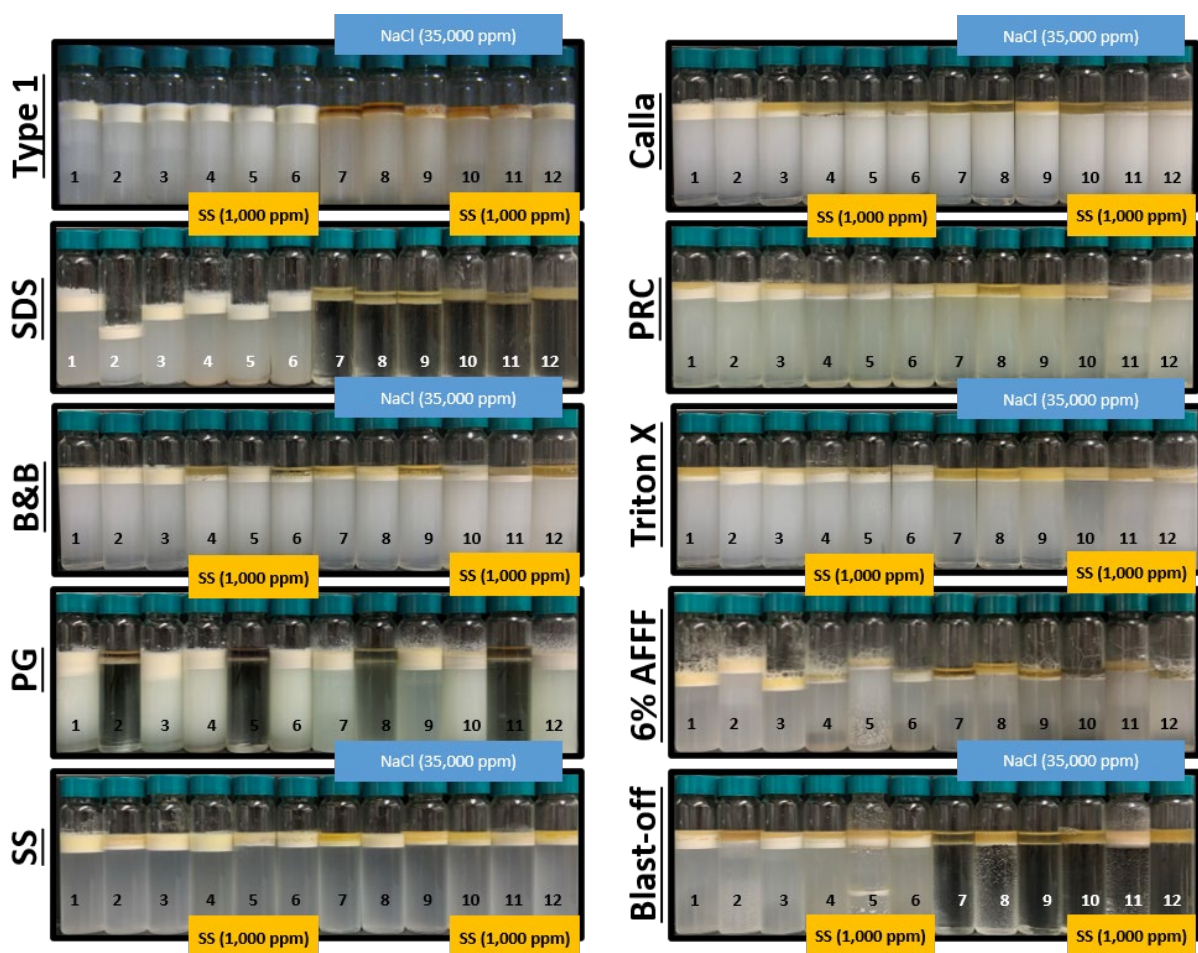
6. Church, J., Daniels, G.C., Willner, M.R., Lundin, J.G., Paynter, D.M. Impact of Fuel Additives on Oil-in-Water Emulsion Stability. *259th ACS National Meeting & Exposition*, Philadelphia, PA, March. 22- 26, 2020. (Accepted/Cancelled due to COVID)
7. Willner, M.R., Church, J., Lundin, J.G., Diaz, D., Lee, W.H., and Paynter, D.M., Emulsion Characterization Study for Improved Bilgewater Treatment and Management, *2019 SERDP/ESTCP Symposium*, Washington DC, Dec. 3–6, 2019.
8. Diaz, D., Willner, M.R., Church, J., Lundin, J.G., Diaz, D., and Paynter, D.M., and Lee, W.H. Nondestructive Stability Analysis and Characterization of Emulsions in the Presence of Suspended Solids, Salinity, and Surfactants. *2019 SERDP/ESTCP Symposium*, Washington DC, Dec. 3–6, 2019.
9. Willner, M., Church, J., Lundin, J., Diaz, D., Lee, W. H., & Paynter, D.. Structure-property relationship of commercial surfactants and bilgewater emulsions stability. *257th ACS National Meeting & Exposition*, Orlando, FL, Mar. 31–Apr. 4, 2019.
10. Willner, M.R., Church, J., Lundin, J.G., Diaz, D., Lee, W.H., and Paynter, D.M., Emulsion Characterization Study for Improved Bilgewater Treatment and Management, *2018 SERDP/ESTCP Symposium*, Washington DC, Nov. 27–29, 2018.

APPENDIX B: Supporting Data for Chapter 4



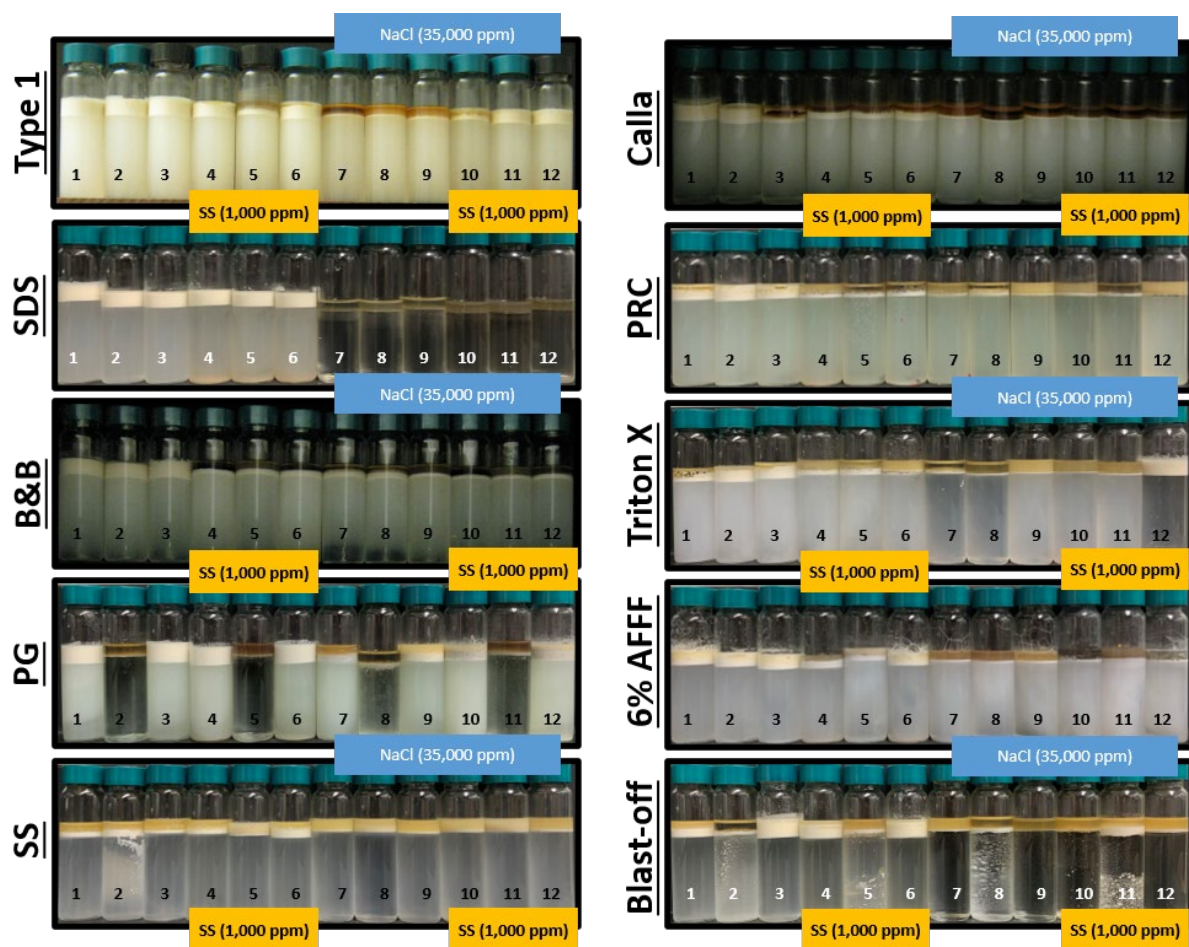
Sample	Description		
	pH	Suspended solids (SS)	Salinity
1	Unadjusted	-	-
2	4	-	-
3	10	-	-
4	Unadjusted	1,000 ppm	-
5	4	1,000 ppm	-
6	10	1,000 ppm	-
7	Unadjusted	-	35,000 ppm
8	4	-	35,000 ppm
9	10	-	35,000 ppm
10	Unadjusted	1,000 ppm	35,000 ppm
11	4	1,000 ppm	35,000 ppm
12	10	1,000 ppm	35,000 ppm

Figure B1. Emulsion samples prepared at 4°C. Photos were taken at 5 days.



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 B2. Emulsion samples prepared at 25°C. Photos were taken at 5 days.



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 B3. Emulsion samples prepared at 35°C. Photos were taken at 5 days.

APPENDIX C: Supporting Data for Chapter 5

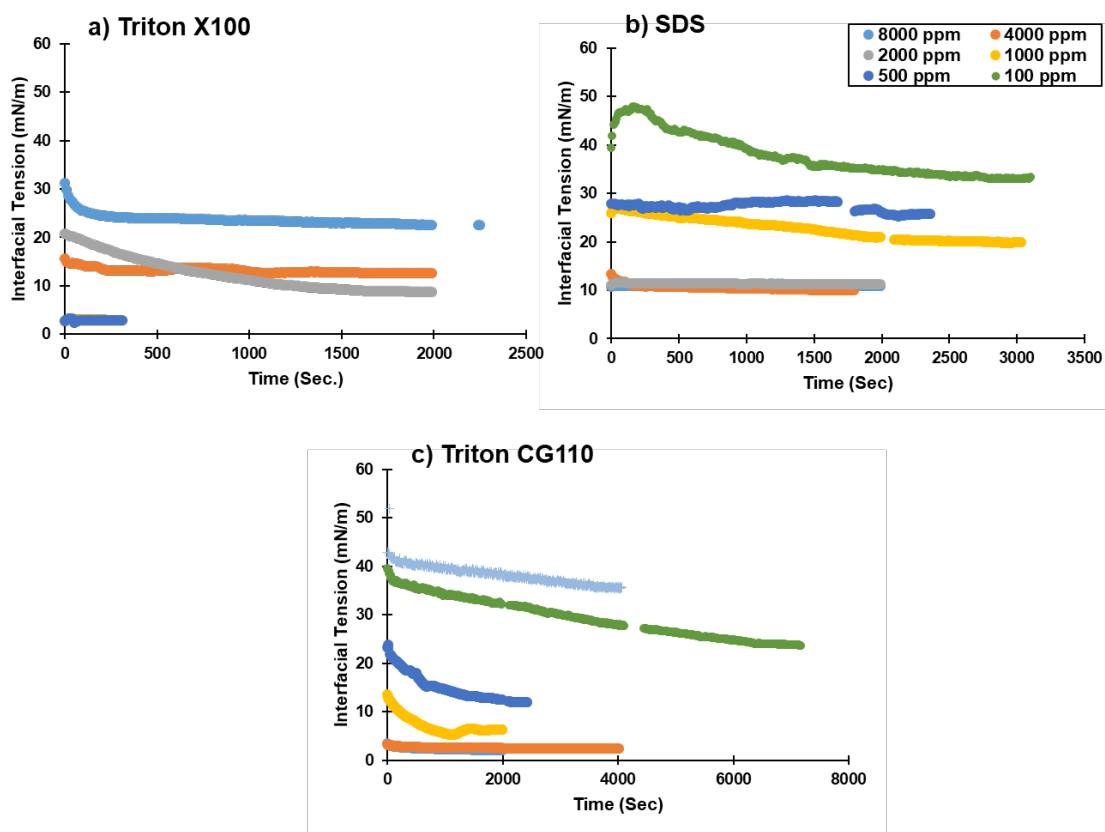


Figure C1. Interfacial tension measurements of a) Triton X100, b) SDS, and c) Triton CG110 over time using pendant drop method.

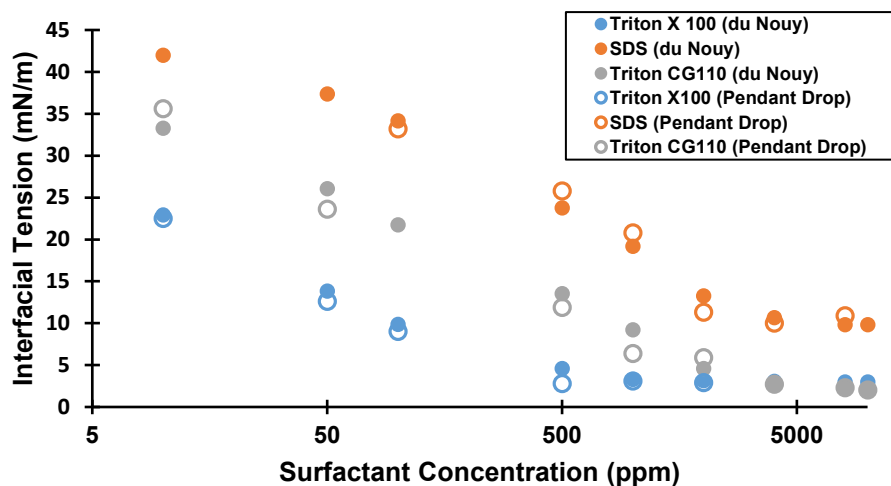


Figure C2. Differences in interfacial tension measurements using du Nouy ring method and pendant drop method for Triton X100, SDS and Triton CG110.

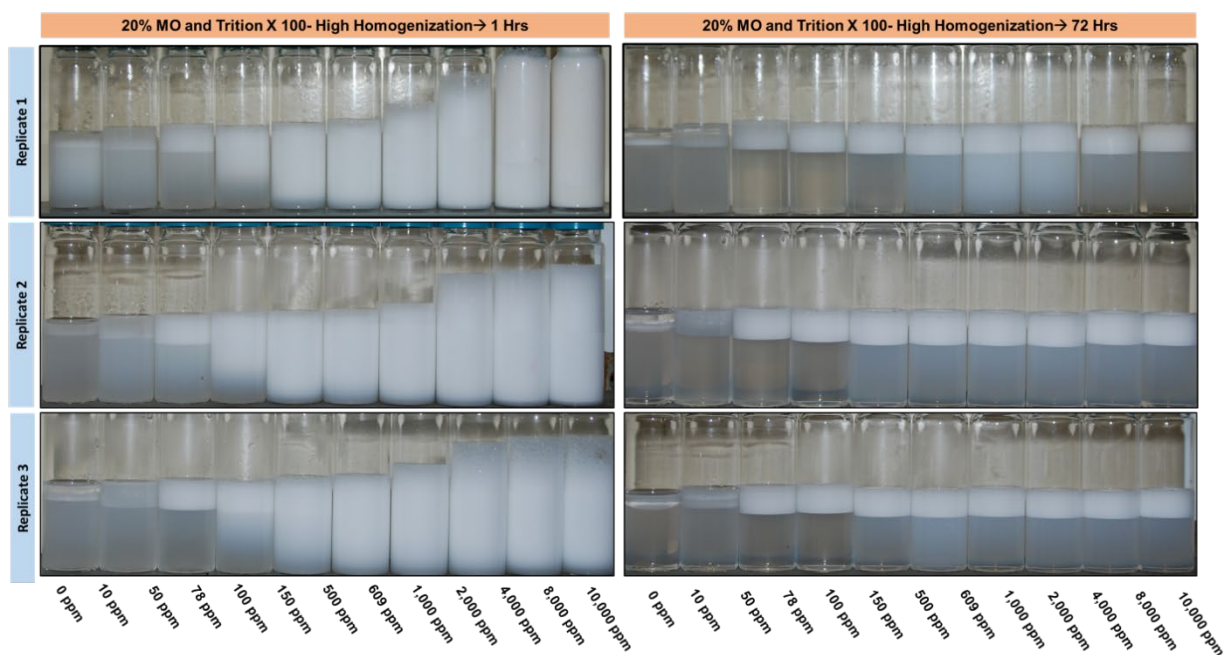


Figure C3. Reproducibility of emulsion sample generation and stability for 20% mineral oil (MO) and Triton X-100.

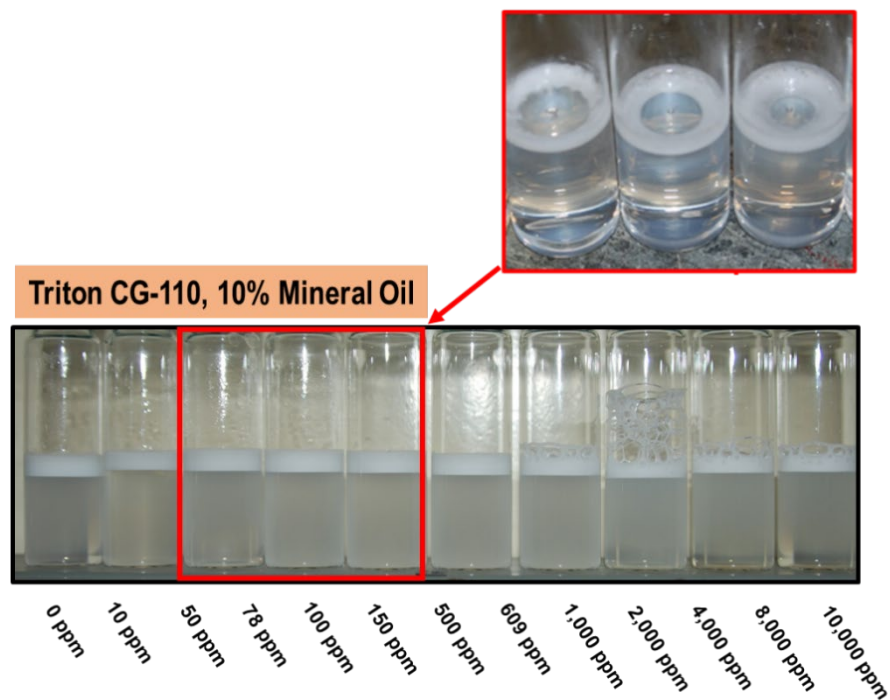
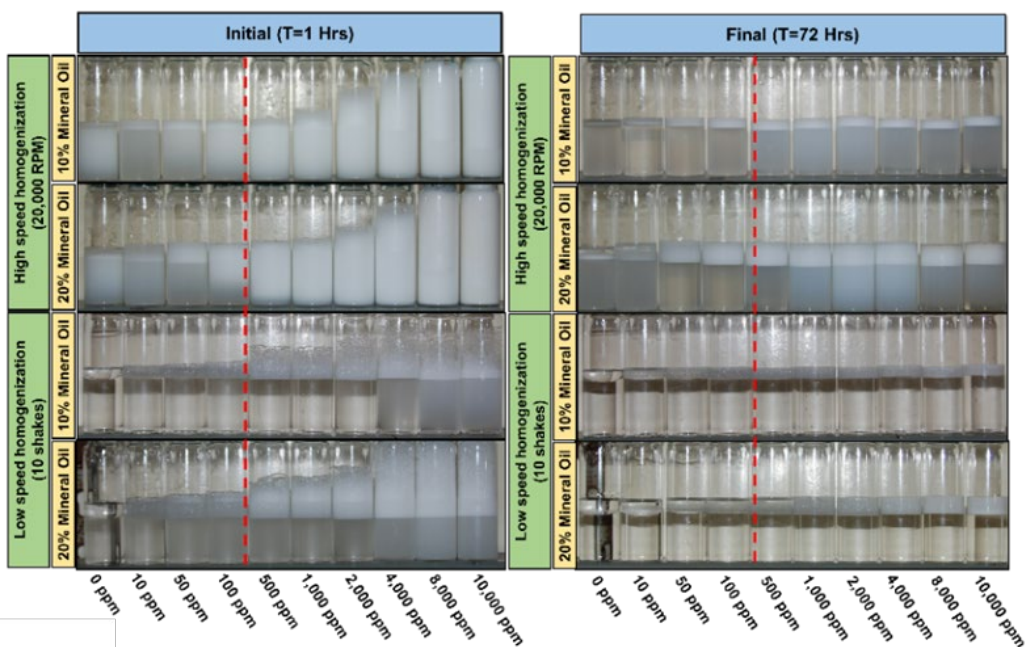
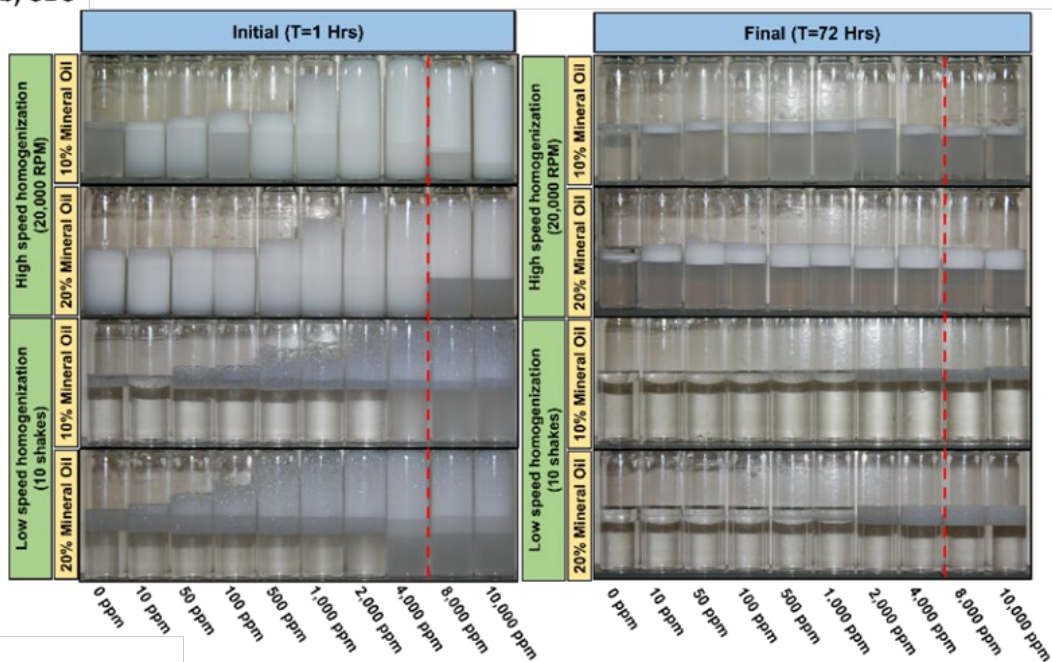


Figure C4. Example of oil separation in emulsions prepared with 10% mineral oil and Triton CG-110 after 72 hrs.

a) Triton X-100



b) SDS



c) Triton CG-110

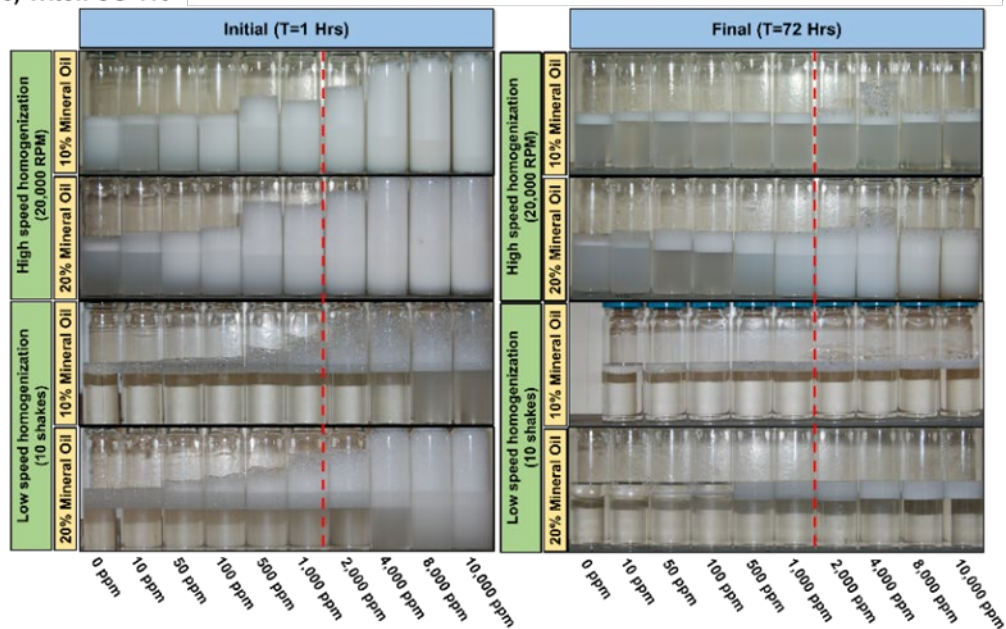


Figure C5. Photographs of model oil-in-water emulsions for each surfactant prepared at different homogenization speeds and oil fractions at 1 h (left column) and 72 h (right column) after homogenization. Red line indicates CMC.

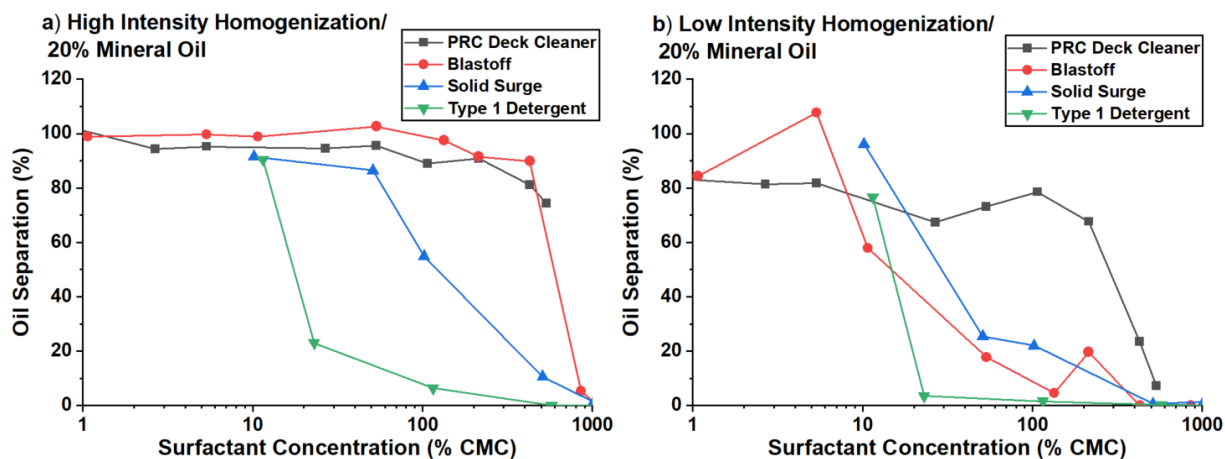


Figure C6. Macro-phase oil separation of commercial cleaner oil-in-water emulsions as a function of CMC after 72 h for emulsions prepared with a) high and b) low intensity homogenization with 20% mineral oil

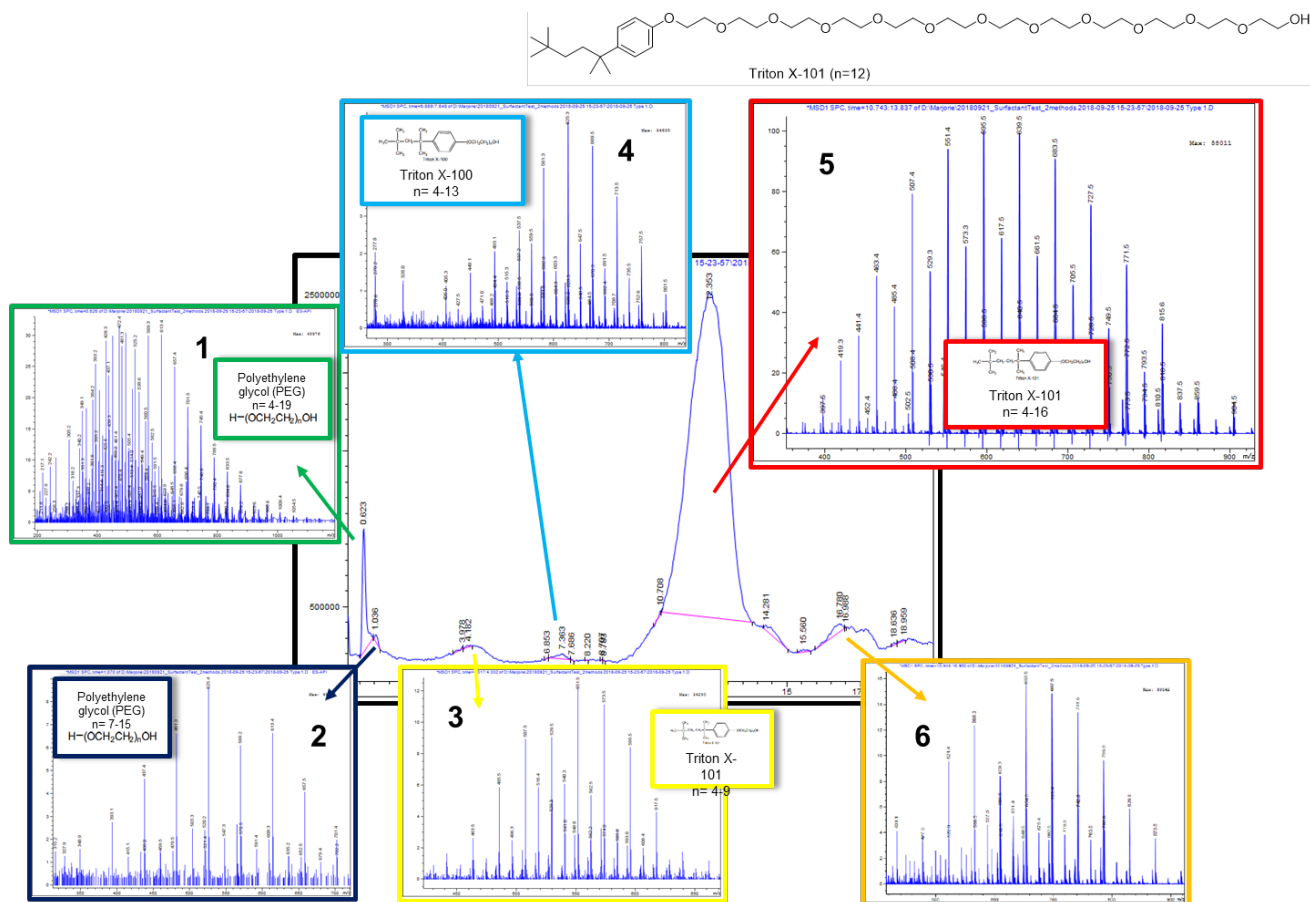


Figure C7. LC-MS analysis of Type 1 Detergent. Peaks 1 and 2 are associated with a polyethylene glycol (PEG) chain, Peaks 3 and 5 are associated with nonionic surfactant Triton X-101, and Peaks 4 and 6 are associated with nonionic surfactant Triton X-100.

Table C1. Oil Separation and Standard Deviations of Emulsions prepared with Commercial Cleaners

Commercial Cleaner	Oil Separation (g)			
	10 % Mineral Oil		20% Mineral Oil	
	CMC	7x CMC	CMC	7x CMC
Blast Off	0 ± 0	0 ± 0	0.13 ± 0.09	0.04 ± 0.01
PRC	0.66 ± 0.01	0 ± 0	2.33 ± 0.23	0.02 ± 0.05
Surge	0 ± 0	0 ± 0	0.95 ± 0.45	0 ± 0
Type 1 Detergent	0 ± 0	0 ± 0	$0.02 \pm .026$	0 ± 0

APPENDIX D: Supporting Data for Chapter 6

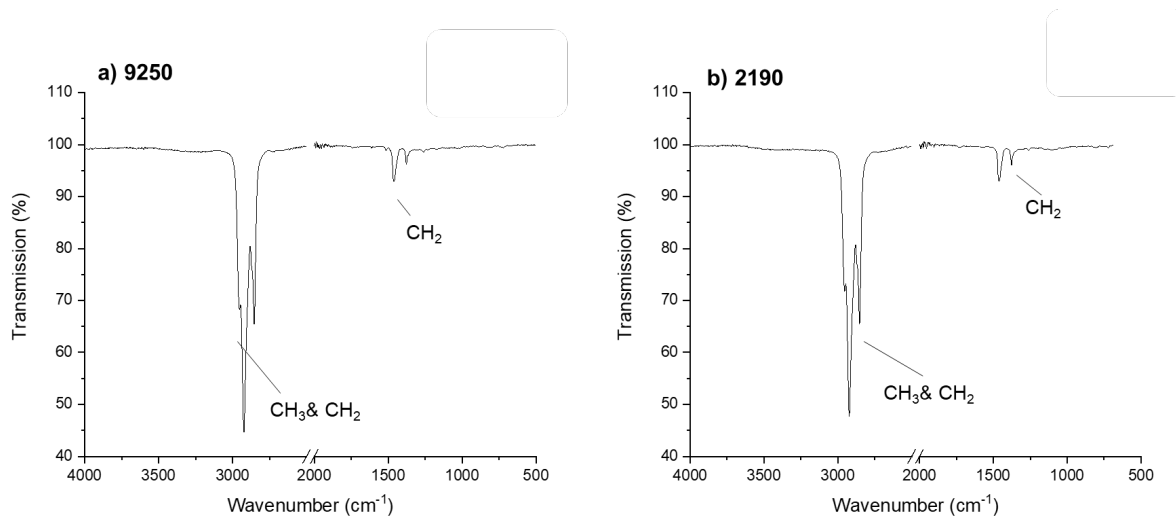


Figure D1. Infrared transmission of extracts from water exposed to a) 9250 and b) 2190 prominent functional groups

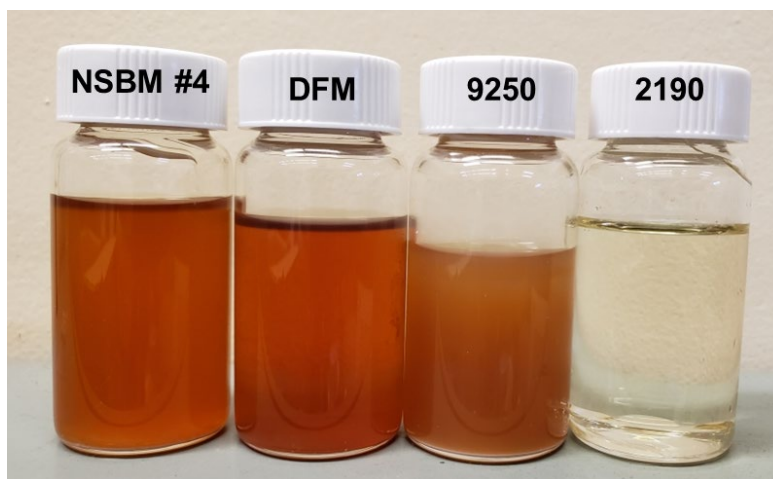


Figure D2. Oil samples after exposure to DI water for 24 hrs

APPENDIX E: Supporting Data for Chapter 7

OS		Type 1			B&B			SDS			Power Green			Solid Surge			PRC			Triton X			Calla			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	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 addition	Unadj.	0	0	0	0	0	0	0	0	0	0	0	65	0	80	0	63	84	40	76	80	0	0	0	44	59	71	56	68	68	
	pH 4	0	0	0	0	0	0	0	0	0	76	93	100	0	88	78	0	0	0	26	48	0	0	0	28	85	65	94	89	94	
	pH 10	0	0	59	0	0	0	0	0	0	0	0	0	0	0	98	92	52	84	0	42	43	100	78	80	29	64	78	60	51	28
SS	Unadj.	0	0	35	21	71	72	0	0	0	0	0	0	0	91	0	96	93	13	64	73	81	95	60	27	66	45	0	65	74	
	pH 4	0	21	66	21	0	70	0	0	0	74	97	98	87	93	100	0	80	93	0	71	86	0	58	75	60	73	70	92	81	84
	pH 10	0	0	53	19	78	63	0	0	0	0	0	0	20	75	41	84	82	91	77	89	89	78	93	50	33	74	72	45	63	25
Salinity	Unadj.	77	88	76	0	58	48	36	100	100	62	24	83	68	81	97	60	85	100	88	81	89	91	81	80	39	98	78	100	100	100
	pH 4	0	82	72	0	64	33	35	100	81	52	100	91	0	0	52	0	82	44	62	82	83	69	83	84	54	100	81	91	100	94
	pH 10	0	88	71	100	71	78	70	100	88	24	23	78	0	68	93	97	93	99	100	97	100	70	78	83	49	93	80	100	100	100
SS+Salinity	Unadj.	0	84	65	0	49	68	37	100	100	24	19	63	0	73	100	53	90	97	41	88	91	98	88	86	63	95	89	97	100	100
	pH 4	0	92	0	0	61	70	62	92	97	78	100	97	24	42	100	0	0	92	0	82	97	0	93	85	63	100	100	90	90	78
	pH 10	0	0	0	100	88	68	74	94	99	28	26	61	0	67	93	0	66	100	0	59	0	94	80	92	63	98	81	100	100	96

Oil separation

mainly oil

over 90%

Creaming + oil

10-90%

Only creaming

<10%

Figure E1. Summary of emulsion stability using OS (%) under various environmental conditions with the order of emulsion stability from stable (left) to unstable (right). “Mainly oil” was used for emulsions with more than 90% OS or samples with coalescence as the main destabilization mechanism. “Creaming + oil” was used for emulsions presenting an oil layer formation as well as a predominant creaming layer (10–90% OS). “Only creaming” was used for samples with less than 10% OS.

(a) Type 1

TI_0.35C 0.0000	TI_0.35C 0.0000	TI_0.4C 0.0000	TI_0.35NaCl.35C 1.0000	TI_0.35NaCl.35C 1.0000	TI_0.35NaCl.4C 0.7220	TI_0.35.35C 0.0000	TI_0.35.35C 0.0000	TI_0.35.4C 0.0000	TI_0.35.35NaCl.35C 0.0073	TI_0.35.35NaCl.35C 0.1161	TI_0.35.35NaCl.4C 0.0000
TI_10.35C 0.0000	TI_10.35C 0.4323	TI_10.4C 0.0000	TI_10.35NaCl.35C 0.0000	TI_10.35NaCl.35C 0.5613	TI_10.35NaCl.4C 0.0000	TI_10.35.35C 0.0000	TI_10.35.35C 0.4129	TI_10.35.4C 0.0000	TI_10.35.35NaCl.35C 0.0000	TI_10.35.35NaCl.35C 0.0000	TI_10.35.35NaCl.4C 0.1292
TI_4.35C 0.0000	TI_4.35C 0.0000	TI_4.4C 0.0000	TI_4.35NaCl.35C 1.0000	TI_4.35NaCl.35C 0.7161	TI_4.35NaCl.4C 0.0000	TI_4.35.35C 0.0000	TI_4.35.35C 1.0000	TI_4.35.4C 0.0000	TI_4.35.35NaCl.35C 0.1927	TI_4.35.35NaCl.35C 0.0000	TI_4.35.35NaCl.4C 0.0000

(b) B&B

BAR_0.35C 0.1439	BAR_0.35C 0.1500	BAR_0.4C 0.0000	BAR_0.35NaCl.35C 0.7085	BAR_0.35NaCl.35C 0.3853	BAR_0.35NaCl.4C 0.1868	BAR_0.35.35C 0.8155	BAR_0.35.35C 0.5206	BAR_0.35.4C 0.4396	BAR_0.35.35NaCl.35C 0.5351	BAR_0.35.35NaCl.35C 0.6618	BAR_0.35.35NaCl.4C 1.0000
BAR_10.35C 0.5066	BAR_10.35C 0.0559	BAR_10.4C 0.0000	BAR_10.35NaCl.35C 0.7085	BAR_10.35NaCl.35C 0.5647	BAR_10.35NaCl.4C 0.8462	BAR_10.35.35C 0.8192	BAR_10.35.35C 0.4294	BAR_10.35.4C 0.3297	BAR_10.35.35NaCl.35C 0.9223	BAR_10.35.35NaCl.35C 0.6206	BAR_10.35.35NaCl.4C 1.0000
BAR_4.35C 0.1476	BAR_4.35C 0.0794	BAR_4.4C 0.0000	BAR_4.35NaCl.35C 0.4554	BAR_4.35NaCl.35C 0.3355	BAR_4.35NaCl.4C 0.3626	BAR_4.35.35C 0.4207	BAR_4.35.35C 0.4765	BAR_4.35.4C 0.5626	BAR_4.35.35NaCl.35C 0.6568	BAR_4.35.35NaCl.35C 0.5578	BAR_4.35.35NaCl.4C 0.9451

(c) SDS

SDS_0.35C 0.1352	SDS_0.35C 0.1017	SDS_0.4C 0.0000	SDS_0.35NaCl.35C 0.8994	SDS_0.35NaCl.35C 1.0000	SDS_0.35NaCl.4C 0.5978	SDS_0.35.35C 0.2075	SDS_0.35.35C 0.1138	SDS_0.35.4C 0.5000	SDS_0.35.35NaCl.35C 1.0000	SDS_0.35.35NaCl.35C 0.9927	SDS_0.35.35NaCl.4C 1.0000
SDS_10.35C 0.1447	SDS_10.35C 0.0523	SDS_10.4C 0.0244	SDS_10.35NaCl.35C 0.5340	SDS_10.35NaCl.35C 0.9467	SDS_10.35NaCl.4C 0.4290	SDS_10.35.35C 0.2494	SDS_10.35.35C 0.1671	SDS_10.35.4C 0.4578	SDS_10.35.35NaCl.35C 0.8742	SDS_10.35.35NaCl.35C 1.0000	SDS_10.35.35NaCl.4C 0.8854
SDS_4.35C 0.1069	SDS_4.35C 0.0823	SDS_4.4C 0.0610	SDS_4.35NaCl.35C 0.9654	SDS_4.35NaCl.35C 0.8862	SDS_4.35NaCl.4C 0.5610	SDS_4.35.35C 0.2138	SDS_4.35.35C 0.1356	SDS_4.35.4C 0.4024	SDS_4.35.35NaCl.35C 1.0000	SDS_4.35.35NaCl.35C 0.9879	SDS_4.35.35NaCl.4C 0.8537

(d) Power Green

PG_1.25C 0.0091	PG_1.25C 0.1844	PG_1.4C 0.0000	PG_1.25NaCl.25C 0.2044	PG_1.25NaCl.25C 1.0000	PG_1.25NaCl.4C 0.0000	PG_1.25.25C 0.1301	PG_1.25.25C 0.3709	PG_1.25.4C 0.0000	PG_1.25.25NaCl.25C 0.3591	PG_1.25.25NaCl.25C 1.0000	PG_1.25.25NaCl.4C 0.3018
PG_1.8.25C 0.0663	PG_1.8.25C 0.2120	PG_1.8.4C 0.0000	PG_1.8.25NaCl.25C 0.2569	PG_1.8.25NaCl.25C 0.6652	PG_1.8.25NaCl.4C 0.2545	PG_1.8.25.25C 0.1909	PG_1.8.25.25C 0.4752	PG_1.8.25.4C 0.0000	PG_1.8.25.25NaCl.25C 0.3591	PG_1.8.25.25NaCl.25C 0.9767	PG_1.8.25.25NaCl.4C 0.4727
PG_4.25C 0.9862	PG_4.25C 1.0000	PG_4.4C 1.0000	PG_4.25NaCl.25C 1.0000	PG_4.25NaCl.25C 1.0000	PG_4.25NaCl.4C 1.0000	PG_4.25.25C 1.0000	PG_4.25.25C 1.0000	PG_4.25.4C 1.0000	PG_4.25.25NaCl.25C 1.0000	PG_4.25.25NaCl.25C 1.0000	PG_4.25.25NaCl.4C 1.0000

(e) Solid Surge

SS_0.25C 0.1041	SS_0.25 0.0054	SS_0.4C 0.0000	SS_0.25NaCl.25C 1.0000	SS_0.25NaCl.25 0.9412	SS_0.25NaCl.4C 1.0000	SS_0.25.25C 0.3203	SS_0.25.25 0.6134	SS_0.25.4C 0.2679	SS_0.25.25NaCl.25C 1.0000	SS_0.25.25NaCl.25 1.0000	SS_0.25.25NaCl.4C 1.0000
SS_10.25C 0.2109	SS_10.25 0.8906	SS_10.4C 0.1061	SS_10.25NaCl.25C 0.9062	SS_10.25NaCl.25 1.0000	SS_10.25NaCl.4C 0.5152	SS_10.25.25C 0.5781	SS_10.25.25 0.4034	SS_10.25.4C 0.4545	SS_10.25.25NaCl.25C 0.9375	SS_10.25.25NaCl.25 1.0000	SS_10.25.25NaCl.4C 0.5000
SS_4.25C 0.5156	SS_4.25 0.6807	SS_4.4C 0.2727	SS_4.25NaCl.25C 0.6250	SS_4.25NaCl.25 0.9328	SS_4.25NaCl.4C 0.4545	SS_4.25.25C 0.6047	SS_4.25.25 0.5798	SS_4.25.4C 0.5242	SS_4.25.25NaCl.25C 0.8203	SS_4.25.25NaCl.25 0.9244	SS_4.25.25NaCl.4C 0.8394

(f) PRC

PRC_0.25C 0.7812	PRC_0.25C 0.2970	PRC_0.4C 0.2875	PRC_0.25NaCl.25C 0.0833	PRC_0.25NaCl.25C 1.0000	PRC_0.25NaCl.4C 1.0000	PRC_0.25.25C 0.3698	PRC_0.25.25C 0.8315	PRC_0.25.4C 0.7825	PRC_0.25.25NaCl.25C 0.1354	PRC_0.25.25NaCl.25C 1.0000	PRC_0.25.25NaCl.4C 1.0000
PRC_10.25C 0.7656	PRC_10.25C 0.2869	PRC_10.4C 0.0875	PRC_10.25NaCl.25C 0.2552	PRC_10.25NaCl.25C 0.8315	PRC_10.25NaCl.4C 1.0000	PRC_10.25.25C 0.4219	PRC_10.25.25C 1.0000	PRC_10.25.4C 1.0000	PRC_10.25.25NaCl.25C 0.3490	PRC_10.25.25NaCl.25C 0.9382	PRC_10.25.25NaCl.4C 0.8875
PRC_4.25C 0.9896	PRC_4.25C 0.0506	PRC_4.4C 0.2825	PRC_4.25NaCl.25C 0.0000	PRC_4.25NaCl.25C 1.0000	PRC_4.25NaCl.4C 1.0000	PRC_4.25.25C 0.3802	PRC_4.25.25C 1.0000	PRC_4.25.4C 0.7000	PRC_4.25.25NaCl.25C 0.3333	PRC_4.25.25NaCl.25C 1.0000	PRC_4.25.25NaCl.4C 1.0000

(g) Triton X-100

TX 0.25C 0.7806	TX 0.25C 0.5714	TX 0.4C 0.1737	TX 0.25NaCl.25C 1.0000	TX 0.25NaCl.25C 1.0000	TX 0.25NaCl.4C 1.0000	TX 0.25NaCl.25.4C 0.2443	TX 0.25.25C 0.6020	TX 0.25.25C 0.7653	TX 0.25.4C 0.1798	TX 0.25.25NaCl.25C 1.0000	TX 0.25.25NaCl.25C 1.0000
TX 10.25C 0.3873	TX 10.25C 0.0000	TX 10.4C 0.0659	TX 10.25NaCl.25C 0.9184	TX 10.25NaCl.25C 1.0000	TX 10.25NaCl.4C 0.9940	TX 10.25NaCl.25.4C 0.4910	TX 10.25.25C 0.7551	TX 10.25.25C 0.8387	TX 10.25.4C 0.3413	TX 10.25.25NaCl.25C 0.8418	TX 10.25.25NaCl.25C 0.0016
TX 4.25C 0.3112	TX 4.25C 0.0000	TX 4.4C 0.0120	TX 4.25NaCl.25C 1.0000	TX 4.25NaCl.25C 1.0000	TX 4.25NaCl.4C 0.5569	TX 4.25NaCl.25.4C 0.4311	TX 4.25.25C 0.8827	TX 4.25.25C 0.9082	TX 4.25.4C 0.1198	TX 4.25.25NaCl.25C 1.0000	TX 4.25.25NaCl.25C 1.0000

(h) Calla

Calla 0.25C 0.0625	Calla 0.25C 0.1384	Calla 0.4C 0.0000	Calla 0.25NaCl.25C 1.0000	Calla 0.25NaCl.25C 0.8428	Calla 0.25NaCl.4C 1.0000	Calla 0.25.25C 0.9608	Calla 0.25.25C 0.4277	Calla 0.25.4C 0.8983	Calla 0.25.25NaCl.25C 1.0000	Calla 0.25.25NaCl.25C 0.3874	Calla 0.25.25NaCl.4C 1.0000
Calla 10.25C 0.4598	Calla 10.25C 0.5849	Calla 10.4C 1.0000	Calla 10.25NaCl.25C 0.6250	Calla 10.25NaCl.25C 1.0000	Calla 10.25NaCl.4C 0.4748	Calla 10.25.25C 0.9018	Calla 10.25.25C 0.2956	Calla 10.25.4C 0.6610	Calla 10.25.25NaCl.25C 0.7723	Calla 10.25.25NaCl.25C 0.9874	Calla 10.25.25NaCl.4C 1.0000
Calla 4.25C 0.0625	Calla 4.25C 0.0000	Calla 4.4C 0.0000	Calla 4.25NaCl.25C 1.0000	Calla 4.25NaCl.25C 1.0000	Calla 4.25NaCl.4C 0.6949	Calla 4.25.25C 0.6964	Calla 4.25.25C 0.4528	Calla 4.25.4C 0.2203	Calla 4.25.25NaCl.25C 0.9732	Calla 4.25.25NaCl.25C 1.0000	Calla 4.25.25NaCl.4C 0.4578

(i) 6% AFFF

6% 0.25C 0.2150	6% 0.25C 0.2347	6% 0.4C 0.0000	6% 0.25NaCl.25C 1.0000	6% 0.25NaCl.25C 1.0000	6% 0.25NaCl.4C 1.0000	6% 0.25.25C 0.6041	6% 0.25.25C 0.8316	6% 0.25.4C 0.4653	6% 0.25.25NaCl.25C 1.0000	6% 0.25.25NaCl.25C 1.0000	6% 0.25.25NaCl.4C 1.0000
6% 10.25C 0.2584	6% 10.25C 0.1684	6% 10.4C 0.4257	6% 10.25NaCl.25C 1.0000	6% 10.25NaCl.25C 1.0000	6% 10.25NaCl.4C 1.0000	6% 10.25.25C 0.8655	6% 10.25.25C 0.3878	6% 10.25.4C 0.4653	6% 10.25.25NaCl.25C 1.0000	6% 10.25.25NaCl.25C 1.0000	6% 10.25.25NaCl.4C 1.0000
6% 4.25C 0.2184	6% 4.25C 0.1633	6% 4.4C 0.0000	6% 4.25NaCl.25C 0.9625	6% 4.25NaCl.25C 1.0000	6% 4.25NaCl.4C 0.9010	6% 4.25.25C 0.3870	6% 4.25.25C 0.6939	6% 4.25.4C 0.4158	6% 4.25.25NaCl.25C 1.0000	6% 4.25.25NaCl.25C 1.0000	6% 4.25.25NaCl.4C 1.0000

(j) Blast Off



Figure E2. Determined oil values (OVs) of bilgewater mixture samples: (a) Type 1, (b) B&B, (c) SDS, (d) Power Green, (e) Solid Surge, (f) PRC, (g) Triton X-100, (h) Calla, (i) 6% AFFF, (j) Blast Off. Non-target layers (i.e., bulk or emulsion layers) were not considered for image processing and black color was used as a background color. A total of 10 cleaners/surfactants were used for image processing and ML modeling.

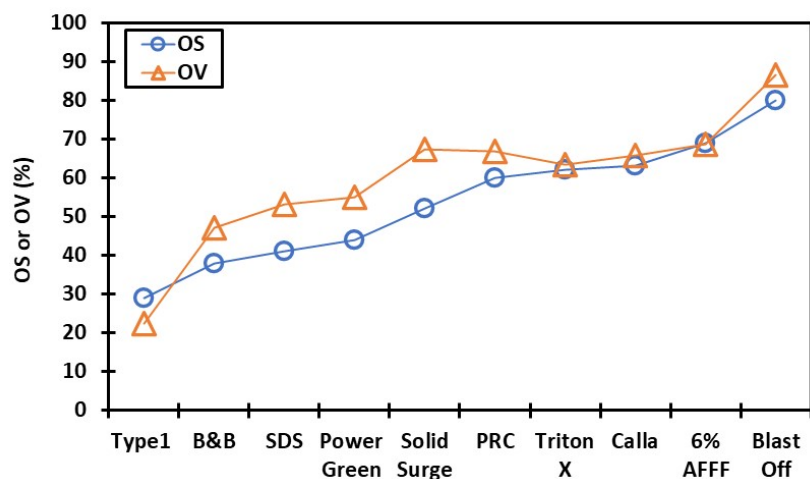


Figure E3. Comparison of averaged values between OS and OV for 10 cleaners/surfactants tested in this study.

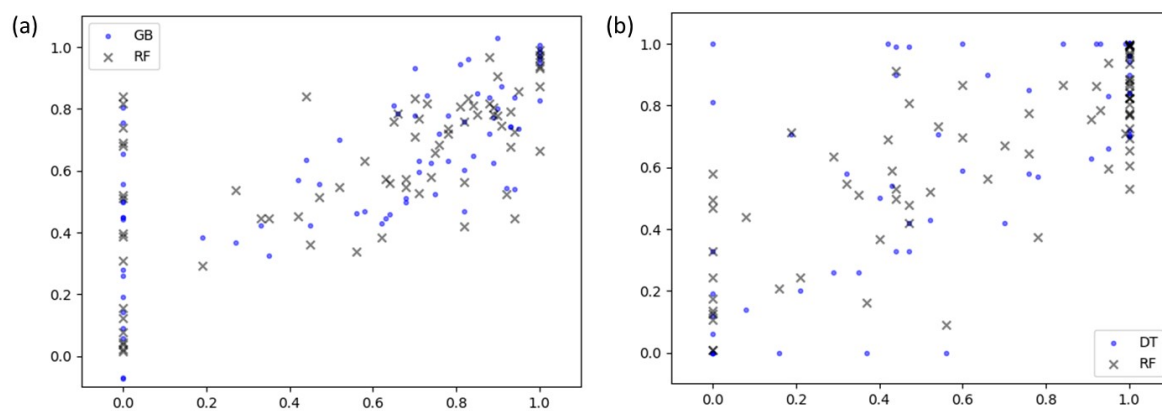


Figure E4. Actual and predicted values for (a) OS and (b) OV. (GB: Gradient boosting regressor, RF: Random forest regressor, and DT: Decision tree regressor).

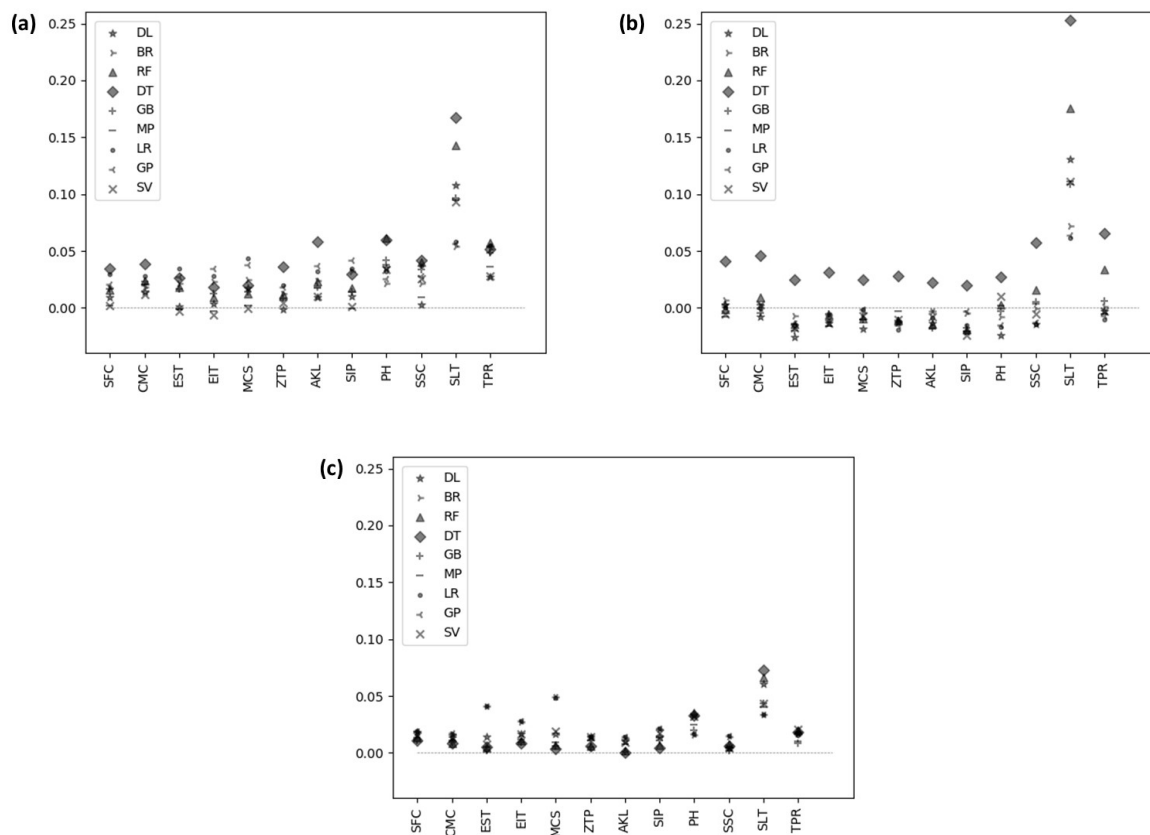


Figure E5. Results of one predictor variable removal test: (a) results for the models using OS and (b) results for the models using OV, and (c) results for the models using turbidity. Values more than zero indicate higher effects on the prediction of emulsion stability (DL: Deep learning regressor, BR: Bayesian ridge regressor, RF: Random forest regressor, DT: Decision tree regressor, GB: Gradient boosting regressor, MP: Multilayer perceptron regressor, LR: Linear regressor, GP: Gaussian process regressor, SV: Support vector regressor) (SFC: Surfactant concentration, CMC: Critical micelle concentration (CMC_{log}), EST: Equilibrium surface tension (ST) above CMC (air), EIT: Equilibrium interfacial tension (IFT) above CMC with NSBM #4, MCS: Micelle size, ZTP: Zeta potential, ALK: Alkalinity, SIP: Surfactant's pH at 7CMC, PH: Initial pH, SSC: Suspended solids (SS) concentration, SLT: Salinity, TPR: Temperature).

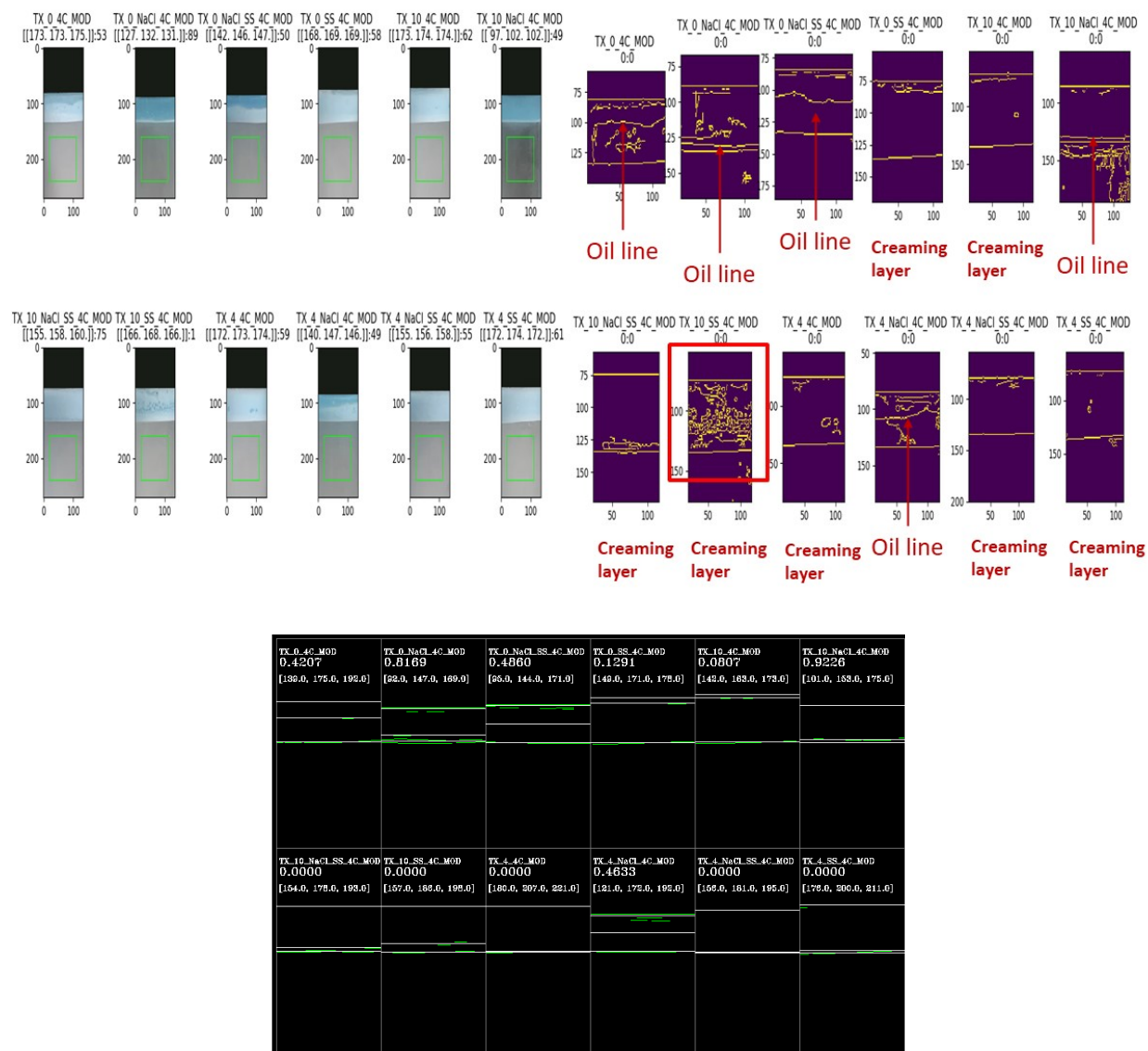


Figure E6. Alternative to image processing using oil line.

Prediction for Bilgewater Emulsion Stability

Surfactant name

Select a surfactant

Submit

Fixed surfactant information for PRC

Critical micelle concentration (CMC_{log}) (ppm)

1871.0

Equilibrium surface tension (ST) above CMC (air) (mN/M)

30.5

Equilibrium interfacial tension (IFT) above CMC with NSBM (mN/M)

1.3

Micelle size (nm)

6.0

Zeta potential (mV)

-13.0

Alkalinity (mg CaCO₃/L)

6.4

Surfactant's Initial pH at 7CMC

6.9

Editable variables for PRC

Surfactant concentration (ppm)

10000.0

pH

7.0

Suspended solids concentration (ppm)

2000.0

Salinity (ppm)

15000.0

Temperature (°C)

24.0

Oil separation (%) in Regression

88.73%

Oil separation determines the levels of coalescence stability.

Example meaning of oil separation

100%: 100%(v/v) oil separation.

60%: 60%(v/v) is separated oil layer and 40%(v/v) is creaming layer.

20%: 20%(v/v) is separated oil layer and 80%(v/v) is creaming layer.

0%: no oil separation (100% creaming layers).

Oil separation (%) in Classification

Mainly oil. "Mainly oil" represents the samples with higher than 66% oil separation.

Turbidity (NTU)

413.83

Figure E7. A website prototype for bilgewater emulsion stability prediction (<http://woohyounglee.pythonanywhere.com/>). Once surfactant name and concentration are selected, parameters related to surfactant are shown automatically as their values are predetermined by experiments. Web and software program languages used for this website include Python, Javascript, HTML, and Flask (a micro web framework). Main source files are 1) main.html: the main webpage when accessing the web, people will see, 2) flask_app.py: the web server, 3) question_set.py: the question sets (e.g., surfactant name), and 4) ML_Algo.pkl: an ML model file (e.g., a random forest model). The source code used for this study has been published in Github (https://github.com/woohyounglee/SERDP_Emulsion) for public access.

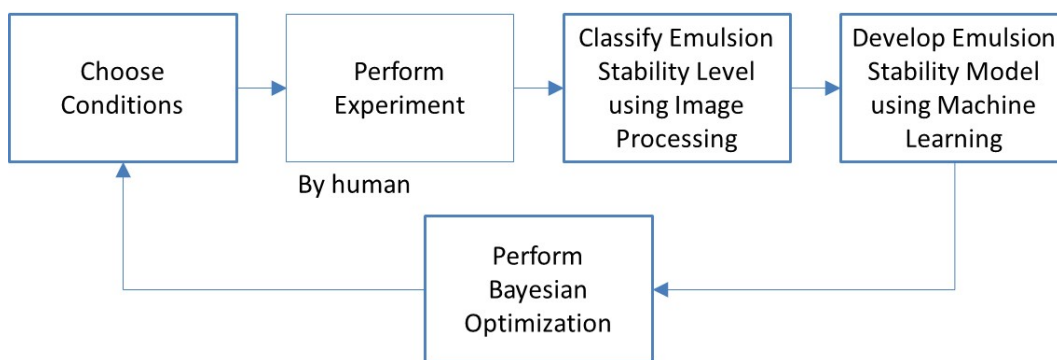


Figure E8. Experiment optimization using Bayesian Optimization.

Table E1. Analysis for normalization: normalized data vs. non-normalized data

Normalization	Target Variable	Deep Learning Regressor	Bayesian Ridge Regressor	Random Forest Regressor	Decision Tree Regressor	Gradient Boosting Regressor	Multilayer Perceptron Regressor	Linear Regressor	Gaussian Process Regressor	Support Vector Regressor
TRUE	OS	0.2131	0.2609	0.1804	0.1947	0.1888	0.2007	0.2382	0.2475	0.1946
	OV	0.2166	0.2652	0.1834	0.1611	0.1998	0.2082	0.2625	0.2626	0.2002
	Turbidity	0.0676	0.1074	0.0559	0.0681	0.0664	0.0732	0.1065	0.1062	0.0710
FALSE	OS	3.9949	0.2617	0.1845	0.1950	0.1888	3.7646	0.2382	0.2417	0.2735
	OV	1.6683	0.2714	0.1758	0.1691	0.1998	11.0361	0.2625	0.2626	0.2816
	Turbidity	1.4418	0.1086	0.0559	0.0680	0.0664	9.2049	0.1065	0.1065	0.1383

Table E2. Selected architecture of the Deep Learning model for emulsion stability prediction

Layer	# of variables	Activation function
Input	12	-
Fully-Connected	64	Relu
Fully-Connected	64	Relu
Fully-Connected	64	Relu
Output	1	Linear

Table E3. Results of one predictor variable removal test for OS, OV, turbidity

A variable will be removed		Deep Learning Regressor	Bayesian Ridge Regressor	Random Forest Regressor	Decision Tree Regressor	Gradient Boosting Regressor	Multilayer Perceptron Regressor	Linear Regressor	Gaussian Process Regressor	Support Vector Regressor
OS	Results from the Original Prediction Test	0.2131	0.2609	0.1804	0.1947	0.1888	0.2007	0.2382	0.2475	0.1946
	Surfactant concentration	0.0095	0.017	0.016	0.0344	0.0163	0.0019	0.0298	0.0209	0.0018
	Critical micelle concentration	0.0138	0.0182	0.0242	0.0387	0.0229	0.0207	0.0281	0.0198	0.0121
	Equilibrium surface tension above CMC (air)	0.001	0.0217	0.0185	0.0265	0.0163	-0.0014	0.0343	0.0274	-0.0027
	Equilibrium interfacial tension above CMC with NSBM	0.0039	0.0233	0.0092	0.0181	0.0129	-0.0026	0.0283	0.0348	-0.0062
	Micelle size	0.0178	0.0245	0.0126	0.0199	0.0142	0.0016	0.0437	0.0376	-0.0005
	Zeta potential	-0.0012	0.0129	0.0114	0.0359	0.0086	0.0064	0.0197	0.0181	0.0044
	Alkalinity	0.0091	0.0242	0.0233	0.0578	0.0185	0.0174	0.0322	0.037	0.0104
	Surfactant's pH at 7CMC	0.0097	0.0319	0.0172	0.0297	0.0139	-0.0005	0.0346	0.0416	0.0007
	pH	0.0356	0.0214	0.0616	0.06	0.0418	0.0375	0.032	0.0252	0.0335
	Suspended solids concentration	0.0024	0.0211	0.0401	0.0416	0.034	0.0096	0.0372	0.028	0.0257
	Salinity	0.1075	0.0538	0.1431	0.1677	0.0968	0.0945	0.0578	0.0568	0.093
OV	Results from the Original Prediction Test	0.2166	0.2652	0.1834	0.1611	0.1998	0.2082	0.2625	0.2626	0.2002
	Surfactant concentration	0.0026	0.0067	-0.0011	0.0411	0.0024	-0.0075	-1E-04	0.0009	-0.0057
	Critical micelle concentration	-0.0081	0.0028	0.0092	0.0458	-0.0046	0.0026	-0.0005	0.0008	0.003
	Equilibrium surface tension above CMC (air)	-0.0258	-0.0073	-0.0144	0.0248	-0.0199	-0.0144	-0.0148	0.0136	-0.0179
	Equilibrium interfacial tension above CMC with NSBM	-0.0136	-0.0059	-0.0062	0.0309	-0.0053	-0.0158	-0.0113	-0.006	-0.0137
	Micelle size	-0.0184	-0.0044	-0.0095	0.0244	-0.0102	-0.01	-0.0014	0.0016	-0.0068
	Zeta potential	-0.0126	-0.0118	-0.0112	0.0283	-0.0111	-0.0029	-0.0192	0.0156	-0.0104
	Alkalinity	-0.0138	-0.0027	-0.0141	0.0219	-0.0177	-0.0184	-0.009	-0.003	-0.0081
	Surfactant's pH at 7CMC	-0.0213	-0.0048	-0.019	0.0198	-0.0177	-0.0209	-0.0152	0.0033	-0.0245
	pH	-0.0243	-0.008	0.0025	0.027	-0.0027	0.002	-0.0169	0.0153	0.0097
	Suspended solids concentration	-0.014	-0.0003	0.0158	0.057	0.0049	0.0033	-0.0145	0.0124	-0.0056
	Salinity	0.1311	0.0718	0.1754	0.2531	0.1083	0.1108	0.0611	0.0641	0.1114
Turbidity	Results from the Original Prediction Test	0.0676	0.1074	0.0559	0.0681	0.0664	0.0732	0.1065	0.1062	0.071
	Surfactant concentration	0.0179	0.0184	0.0137	0.0107	0.0108	0.0132	0.0193	0.0194	0.015
	Critical micelle concentration	0.013	0.0166	0.0086	0.0087	0.0091	0.0112	0.0169	0.0173	0.0132
	Equilibrium surface tension above CMC (air)	0.0142	0.041	0.0047	0.005	0.0023	0.0051	0.0408	0.0409	0.0077
	Equilibrium interfacial tension above CMC with NSBM	0.0167	0.027	0.0112	0.0083	0.0096	0.0117	0.0276	0.028	0.0165
	Micelle size	0.0165	0.049	0.0064	0.0032	0.0058	0.0093	0.0482	0.0489	0.0188
	Zeta potential	0.0142	0.0131	0.0059	0.0057	0.0054	0.0107	0.0142	0.0141	0.0138
	Alkalinity	0.0098	0.0132	0.0022	0	0.0009	0.0073	0.0138	0.0141	0.0096
	Surfactant's Initial pH at 7CMC	0.014	0.021	0.0071	0.0042	0.0106	0.0134	0.0215	0.0218	0.0176
	pH	0.0329	0.0159	0.0355	0.0325	0.0199	0.0246	0.0164	0.0165	0.032
	Suspended solids concentration	0.0043	0.0145	0.008	0.0058	0.0023	0.005	0.0148	0.015	0.0043
	Salinity	0.0602	0.0334	0.0667	0.0725	0.0435	0.0406	0.0333	0.0337	0.0435
	Temperature	0.0173	0.0169	0.0195	0.018	0.0081	0.01	0.0174	0.0176	0.0207

Table E4. A preliminary regression results for a comparison between using 10 cleaners/surfactants and using separate data collected by surfactant type (Blast Off, PRC, SDS, Solid Surge, Triton X-100, and Type 1)

Target	Surfactants	Train Size	Test Size	LightGBM MAE	DeepLearningRegressor MAE	Ridge MAE	Bayesian Ridge MAE	RandomForestRegressor MAE	DecisionTreeRegressor MAE	Gradient BoostingRegressor MAE	MLPRegressor MAE	LinearRegression MAE	Gaussian ProcessRegressor MAE	SVR-MAE
OV	ALL	86	22	0.1754	0.0935	0.161	0.1636	0.1019	0.1256	0.1036	0.1086	0.1681	0.1658	0.1115
Oil_separation(%)	ALL	264	66	0.2116	0.2034	0.2434	0.242	0.1637	0.186	0.1772	0.2078	0.2421	0.2407	0.2018
Turbidity	ALL	187	47	0.0929	0.0727	0.1001	0.1005	0.0617	0.0619	0.0666	0.0774	0.101	0.1006	0.0857
OV	Blast	28	8	0.2092	0.1379	0.1407	0.1386	0.1364	0.1517	0.144	0.1393	0.1448	0.1424	0.1401
Oil_separation(%)	Blast	44	11	0.202	0.1632	0.1855	0.1891	0.1262	0.1158	0.119	0.1609	0.1932	0.1953	0.1779
Turbidity	Blast	36	9	0.2218	0.2239	0.2034	0.2034	0.1688	0.1615	0.1514	0.2134	0.2285	0.2239	0.222
OV	PRC	28	8	0.2499	0.1455	0.1622	0.1502	0.1356	0.1793	0.1579	0.1366	0.1393	0.13	0.1545
Oil_separation(%)	PRC	44	11	0.2562	0.2395	0.2338	0.2308	0.2217	0.2167	0.223	0.2357	0.2377	0.231	0.2369
Turbidity	PRC	36	9	0.1936	0.1359	0.1259	0.1192	0.1531	0.1898	0.18	0.1377	0.1233	0.122	0.1432
OV	SDS	28	8	0.2481	0.065	0.1838	0.1685	0.0345	0.0428	0.0434	0.0591	0.1647	0.1668	0.0891
Oil_separation(%)	SDS	44	11	0.2428	0.1044	0.1817	0.1417	0.0823	0.079	0.0812	0.1187	0.1405	0.1395	0.1219
Turbidity	SDS	36	9	0.1389	0.0643	0.0929	0.1055	0.0585	0.0652	0.0577	0.0581	0.1138	0.1137	0.0771
Oil_separation(%)	Surge	44	11	0.3262	0.2279	0.2734	0.2487	0.2257	0.2554	0.2422	0.2484	0.2839	0.2413	0.2571
Turbidity	Surge	36	9	0.1828	0.1154	0.1141	0.1153	0.0954	0.0986	0.1031	0.1147	0.1222	0.1221	0.139
Oil_separation(%)	Triton-X-100	40	10	0.3175	0.2507	0.2764	0.267	0.2484	0.3185	0.234	0.2935	0.2772	0.2625	0.3021
Turbidity	Triton-X-100	32	8	0.1943	0.1334	0.1528	0.1477	0.1332	0.1633	0.148	0.128	0.1481	0.1468	0.1476
Oil_separation(%)	Type 1	48	12	0.308	0.2421	0.3015	0.2808	0.1844	0.1937	0.2163	0.2383	0.2715	0.2837	0.2939
Turbidity	Type 1	11	3	0.3631	0.2557	0.3063	0.257	0.2042	0.2011	0.2125	0.4113	0.2986	0.2645	0.3945