

Techniques for the Analysis of Complex Oil, Water and Surfactant Mixtures

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Contents

Executive Summary	E-1
Introduction	1
Methods	2
Model Fuels and Oils	2
Extracting water miscible components from oils and fuels	2
Water Quality Analysis	2
Emulsion Preparation	3
Emulsion Stability	3
Identification of Surface Active Compounds	4
Transport of fuel additives and compounds from the oil to the aqueous phase.	4
Transport of additive surrogates in hexadecane	4
Results and Discussion	5
Fuels and Oils	5
Water Quality Analysis	7
GC-MS	8
IR Spectroscopy	11
UV Spectroscopy	12
Emulsion Stability	13
Surrogate Additive Model Tests	15
Conclusion	17
References	18

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Executive Summary

The first goal of this effort was the analysis of complex surfactant and oil mixtures, which began with making model mixtures of surfactant in water and oils/fuels in water. Water in oil (w/o) emulsions occurred during the preparation of the oil/fuel samples. The presence of these emulsions without any surfactant was unexpected and unreported in literature. Chromatographic analysis and further work was undertaken to determine the source of these emulsions. Identification of individual constituents in complex mixtures has been a challenge for a long time due to the vast differences in polarity, volatility and stability of the compounds that can be present in complex mixtures. Herein, techniques were combined to develop methods capable of identifying how various molecules present in these systems effect their stability. The techniques include but are not limited to chromatography, spectroscopy, surface tension and creaming rate.

The work revealed that components found in Navy relevant oils and fuel can contribute to the stability of emulsions. Water properties including conductivity, pH, and surface tension were altered after exposure to Navy relevant oils for 24 h. UV and GC-MS data suggested the transport of aromatic and alkane molecules with heteroatoms from the oil to aqueous phase. The analysis of the mass spectrum from GC-MS along with IR analysis revealed that aromatic and alkane molecules contain oxygen and nitrogen functional groups, which would provide 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. Finally, model oil systems with one additive showed significant decreases in creaming rate, stabilization of emulsions, with only 1-20 ppm in the water phase. This highlights how impactful a small amount of these compounds can be at low concentration.

The insights from this work have potential to not only contribute to improved methods for characterization of w/o emulsions and help preventing emulsion stabilization in water, 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 cause by fuel compounds will likely play a large role in the effectiveness of foams. Similarly, understanding the transport of various compounds into the environment is important for oil spill remediation. Additionally, the work done under this Karles Fellowship has fostered discussions with others in the field, including NWCCD and University of Minnesota, potentially leading to future collaboration and proposals.

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Techniques for the Analysis of Complex Oil, Water and Surfactant Mixtures

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Introduction

Identification of individual constituents in complex mixtures has been a challenge for a long time due to the vast differences in polarity, volatility and stability of the compounds that can be present in complex mixtures. Herein, new techniques were combined to develop methods capable of identifying components and understand complex water, oil and surfactant mixtures.

In this effort, Navy relevant oils and fuels were investigated. Navy Standard Bilge Mix #4 (NSBM #4) and its individual components were selected as surrogate oils for this study due to that it and its components represents common fuels and oils found on ships. NSBM #4 is comprised of 50% Diesel Fuel Marine (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 Navy Standard Bilge Mix #4. NSBM and its components were used to make model water in oil emulsions with surfactants, which were used to determine the compounds from fuels, and oils that stabilize water in oil (w/o) emulsions. Following the initial effort investigation of model oil systems with known concentrations of molecules identified was undertaken. The model oil systems consisted of hexadecane as a diesel fuel and oil surrogate, commonly used for diesel and oil surrogates with known concentrations of additive surrogates added.^{1, 2}

The first goal of this effort was the analysis of complex surfactant and oil mixtures, which began with making model mixtures of surfactant in water and oils/fuels in water. A single surfactant and oil/fuel were used for the initial solutions. W/o emulsions occurred during the preparation of the oil/fuel samples. The presence of these emulsions without any surfactant was unexpected. The current consensus is that oil/water emulsions are stabilized by detergents/surfactants present in the water.³⁻⁵ In fact, the MEPC.107(49) certification of oil pollution abatement (OPA) systems require the use of detergents to simulate water w/o emulsions.⁵ The addition of additives to improve properties of fuels and oils is well known. These additives are commonly biocides, antioxidants, lubricants and other compounds that could be surface active.⁶ Furthermore, it is common for surfactants to be added to fuels to improve engine performance.⁷ 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. 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.^{8, 9} Therefore, additives in fuels could significantly contribute to the properties of an oil-water interface forming an emulsion and complex mixture. While additives may play a role further investigation is needed to identify and understand how they may be making/stabilizing w/o emulsions.

Depending on the fuels and lubricating oils that end up in the w/o emulsions, several additives could play an important role in stabilization. Diesel fuels typically have oxygenated additives to help the fuel burn more cleanly and reduce smoke emissions.⁶ 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, but it is unclear how they might impact emulsion stability.⁸ 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.⁹ 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 most likely be surface active and could help stabilize w/o 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.⁷ 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 various water treatments and the lack of studies done in the literature on the effect additives and/or minor substituents in oils and fuels have on emulsions, 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 water, oil and surfactant mixtures and how water exposed to these compounds can develop more stable emulsions. Additionally, steps were made to identify types of compounds that may stabilize w/o emulsions. Overall, results from this work provides important insights into how w/o emulsions are stabilized, classes of compounds contributing to w/o emulsions, and a suite of techniques to characterize and identify w/o emulsion and their constituents; which can help guide future research, development of treatment methods and inform on additives/compounds that cause emulsion stability.

Methods

Model 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 along with hexadecane. NSBM #4 is conventionally used to test oil pollution abatement equipment, and its components represent common oils and fuels found on Navy ships and in bilgewater³. NSBM #4 is comprised of 50% Diesel Fuel Marine (MIL-DTL-16884), 25% TEP Steam Lube Oil 2190 (MIL-PRF-17331), and 25% Diesel Lube Oil 9250 (MIL-PRF-9000), shown in Table 1. 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. Hexadecane was used as a surrogate for fuel and oil due to its similar density, viscosity, ease of chromatographic analysis, and C₁₆ compounds are near the average carbon length for fuels used on Navy vessels.

Extracting water miscible components from oils and fuels

80 mL of deionized water and 20 mL of oil sample (e.g. NSBM #4, DFM, 9250, 2190, or hexadecane samples) were added to a clean 250 mL separatory funnel and allowed to rest undisturbed under ambient conditions (20-22°C) for 24 h. This time was selected to provide ample equilibration time. Based on previous surface tension measurements, equilibrium was typically reached after 8 hours. 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.

Water Quality Analysis

After water samples were exposed to various oils and fuel 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.

Emulsion Preparation

Aqueous samples exposed to different oils and fuel 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).

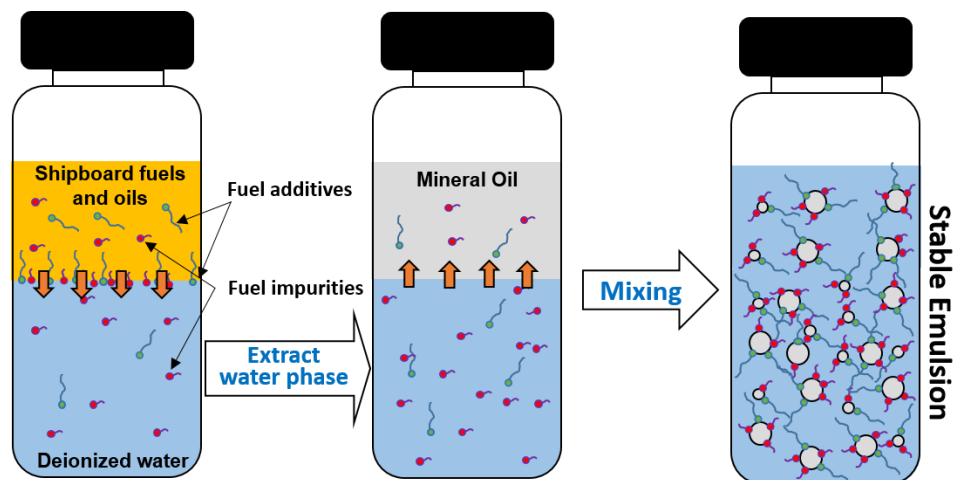


Figure 1: Diagram of emulsion preparation

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 treatment systems. Creaming results from gravitational forces between the oil and aqueous phases with different densities.³

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.¹⁰

Identification of Surface Active Compounds

To identify compounds in Navy relevant 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 per minute increase to 250 °C, and then a 10 °C per minute 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.

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.¹¹ 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.

Transport of additive surrogates in hexadecane

Surface active molecules that were identified through GC-MS analysis of extracts were categorized into several main groups. High purity molecules that have similar chemical structures and the same functional groups were purchased as surrogates for identified molecules. The surrogates, 2-ethylpyridine, 2-tert-butylpyrazine, ethyl heptanoate and ethyl-m-tolylacetate, were dissolved in hexadecane at 500 ppm and then expose to DI water using the same procedure as was done with NSBM #4 and other oils/fuels. Utilizing hexadecane allowed for direct analysis of the oil phase in determining the concentration of surrogate additives. By knowing the exact concentration of the additives, the partition coefficient was calculated providing insight into how the various types of molecules enter the water phase in oil/water systems. Additionally the emulsion stability of the exposed water was also determined to provide insight into how a single molecule with the appropriate chemical structure can effect w/o emulsions.

GC-MS analysis of hexadecane samples was conducted by placing 1 mL of sample in GC vials and running through 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 minute followed by a 4 °C/min ramp to 150 °C, followed by a 1 minute hold. 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. Calibration curves of the surrogates in hexadecane at concentrations of 1, 10, 30, 60, 125, 250, and 500 ppm were made to determine the concentrations of surrogates in hexadecane after exposure. Chromatographs and calibration curve for ethyl heptanoate seen in Figure 2.

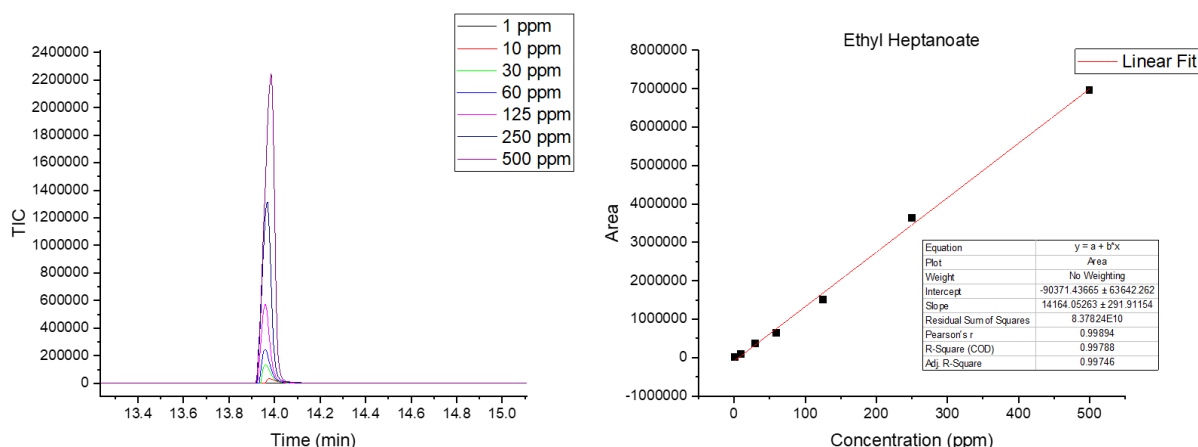


Figure 2: Chromatograph of Ethyl Heptanoate peak and calibration curve with linear fit

Results and Discussion

Fuels and Oils

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 this study, Navy Standard Bilge Mix #4 (NSBM #4) and its individual components were selected as surrogate oils. Table 1 shows the concentration and possible additives linked to each oil component, hexadecane was not included since it had no additives. NSBM #4 is comprised of 50% Diesel Fuel Marine (MIL-DTL-16884), 25% TEP Steam Lube Oil 2190 (MIL-PRF-17331), and 25% Diesel Lube Oil 9250 (MIL-PRF-9000).

Table 1: Composition of Synthetic Oils 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.¹² 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. SDSs indicate the use of up to 2.5% zinc dialkyldithiophosphate (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.¹³ Also as fuels and oils age, the oxidation and biodegradation of hydrocarbons generates significant amounts of polar compounds within the fuel.¹⁴ 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.¹⁴ 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⁻¹.¹⁵

Water Quality Analysis

Figure 3 shows the surface tension, pH, and conductivity of water exposed to NSBM #4, diesel fuel marine (DFM), Lube Oil 2190 and Lube Oil 9250 for 24 h. It is clear that exposure to oils impacted the chemistry of the aqueous solution. The conductivity of the DI water exposed to the various oils were on average 2.5 $\mu\text{S}/\text{m}$ higher than the DI control, which could indicate the transport of ionic compounds from the oil to the aqueous phase. In other systems, emulsion stability was affected only when conductivity changed by 6.5 $\mu\text{S}/\text{cm}$.⁵ It is more probable that the compounds that contribute to emulsion stabilization are nonionic and do not contribute to conductivity.

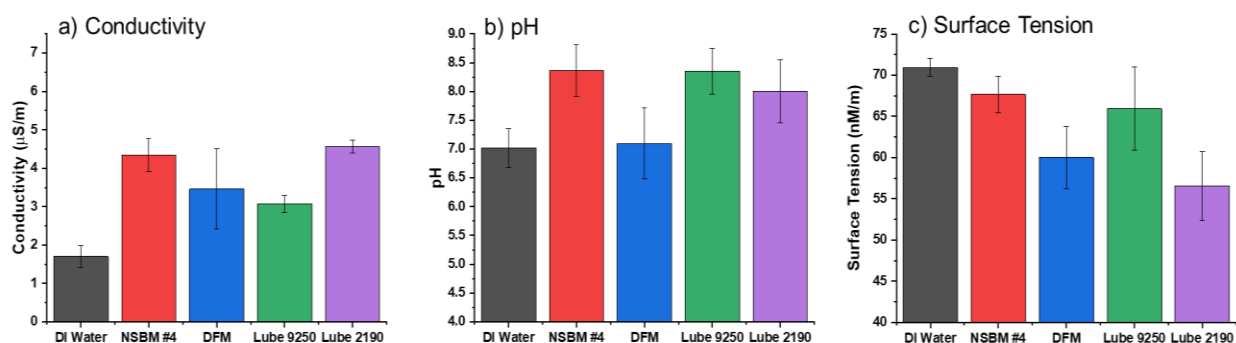


Figure 3: Changes in a) conductivity, b) pH and c) surface tension of aqueous solutions exposed to various oils after 24 h.

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.¹⁶ However, many oils contain alkalinity improvers that are used to neutralize acidic contaminants of engine oils and protect engines from wear.¹⁷ Therefore, the alkalinity additives may be responsible for the increased pH. Common alkalinity additives include calcium sulfonates, calcium phenates and magnesium sulfonates, which have potential act as emulsifiers depending on their solubility. Given that Lube Oil 9250 is advertised to contain alkalinity additives and also caused a large increase in pH of exposed water, it is possible that the additives could contribute to emulsion stability.

The change in surface tension of water exposed to the fuel samples was also analyzed to determine if components of the 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 understood that a compound's affinity to an interface will directly relate to its ability to stabilize emulsions.¹⁸ 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.^{19, 20} The surface tension of the water exposed to DFM and Lube Oil 2190 were significantly lower than the DI control (Figure 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 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 water/oil emulsion stability

GC-MS

To identify potential emulsion stabilizing compounds that leached from the oils and fuel to the water phase, GC-MS analysis was conducted on samples of water exposed to NSBM #4 components for 72 h. All of the samples had multiple peaks of interest in the chromatogram, as shown in Figure 4. Identification of 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.

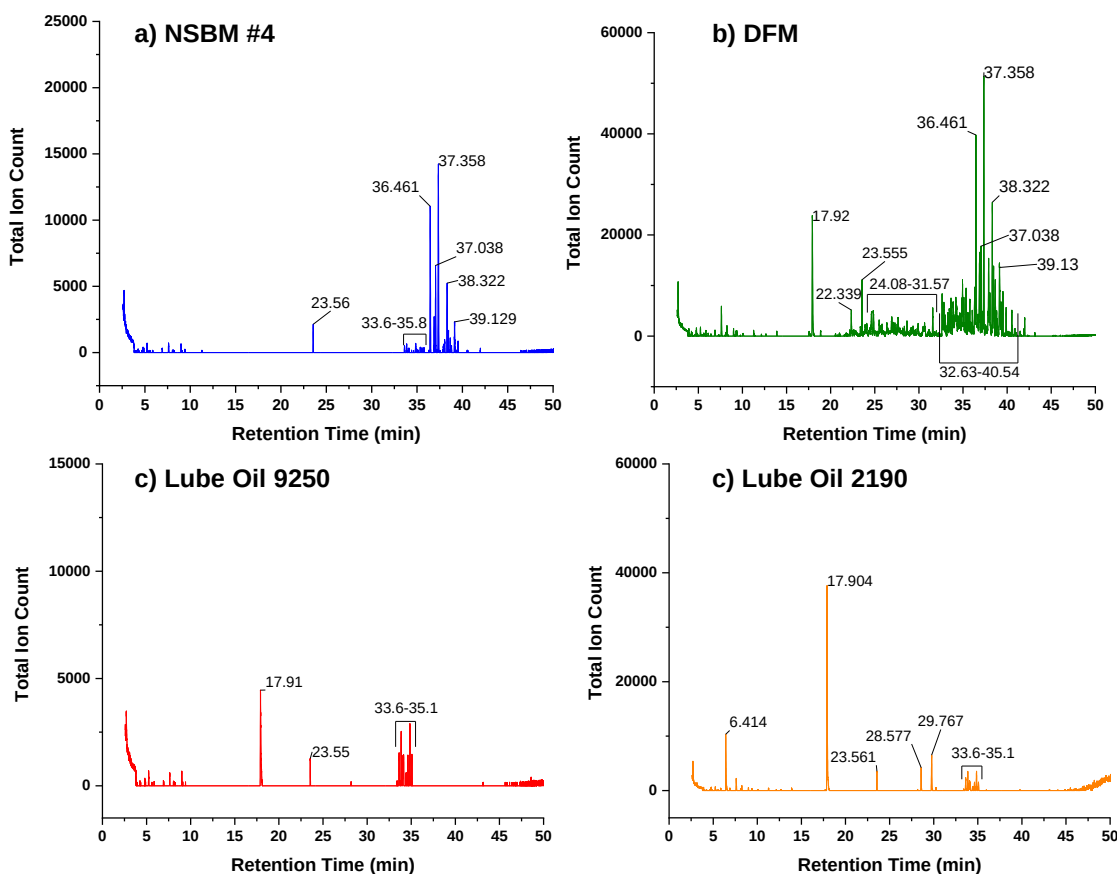
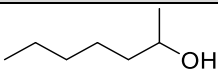
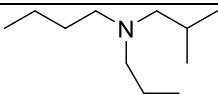
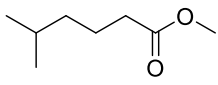
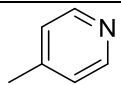
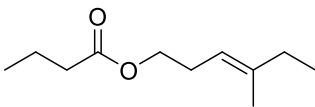
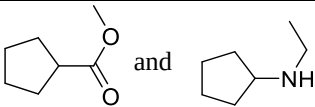
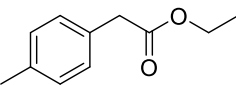
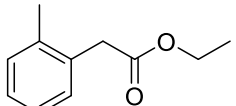
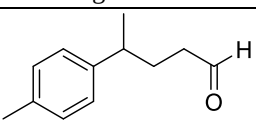
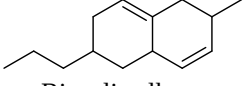
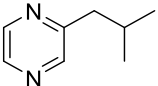


Figure 4: Chromatographs of water extracts from a) NSBM #4, b) DFM, c) Lube Oil 9250, and d) Lube Oil 2190 with retention time of peaks of interest.

As expected, the chromatogram of water exposed to NSBM #4 (Fig. 4a) comprised of a compilation of peaks found in the chromatograms of its components (Fig. 4b-c). 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 4b). Because the number of peaks was so large, only the most intense peaks were selected for identification since these would thus have the highest concentration. Based on 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. Identification of mass spectrum of the peak at 36.46 min indicated aromatic, alkane, and ester fragments, shown in Table 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 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.

Table 2: Identified Compounds in Aqueous Solutions Exposed to NSBM #4, DFM, Lube Oil 9250 and Lube Oil 2190

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 alkene
39.13	- NSBM #4 - DFM	 Benzene with nitrogen and alkane

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 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. 4d) that were identified as benzene ring compounds containing nitrogen. The group of peaks between 33.6 and 35.1 mins., 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.²¹ 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. Desse et al. recently reported up to 475 mg N/L total nitrogen in DFM.²² 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.⁶ Oxygenated additives like ethylene glycol monomethyl ether (EGME) and diethylene glycol monomethyl ether (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.

IR Spectroscopy

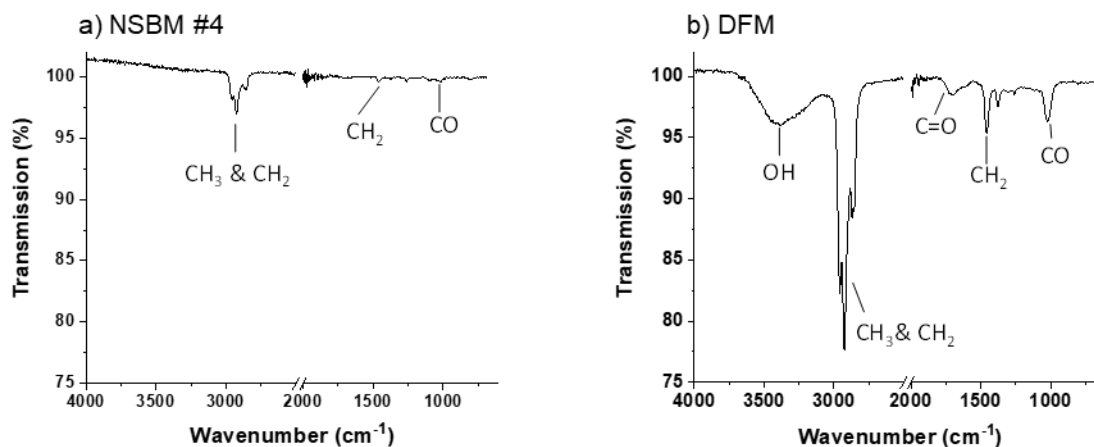


Figure 5: Infrared transmission of extracts from water exposed to a) NSBM #4 and b) DFM will labeled prominent functional groups

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. These peaks are expected in any type of oil or fuel. In addition to the peaks found in the lube oil spectra, Figure 5 shows the spectra of the DFM peaks at 3200 cm^{-1} , which is indicative of alcohol OH stretching and 1650 cm^{-1} from esters. 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 both nitrogen and alkene containing compounds in water exposed to DFM, the presence of this peak further confirms the results. 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 while preparing the sample 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.

UV Spectroscopy

The presence of aromatic compounds provides an opportunity to determine the transport of compounds into the water phase. The UV absorbance spectra of the samples are shown in Figure 6a. 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. 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.

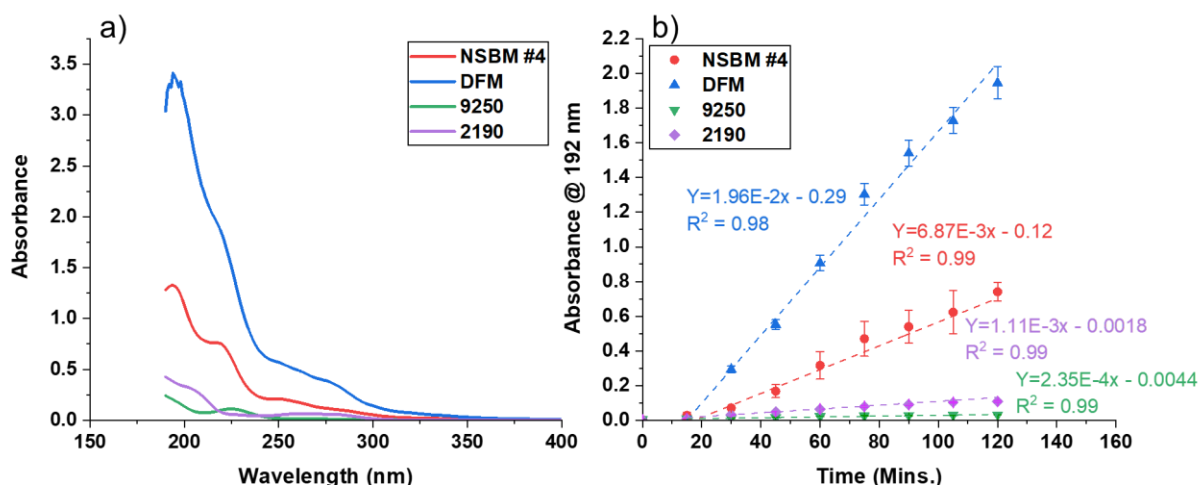


Figure 6: a) UV absorbance of water exposed to surrogate bilge oil samples after 24 h exposure and b) change in absorbance at 192 nm of water exposed to oil samples over time.

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. 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 6b 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.

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, Figure 6. There is currently no literature precedent on the transport of fuel compounds into w/o emulsions; 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 w/o emulsions. In groundwater systems, cosolvency plays an important role in the transport of monoaromatic hydrocarbons into the aqueous phase.^{23, 24} 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.²³ Therefore, the oxygenated compounds found in DFM may help facilitate the transport of larger hydrophobic compounds into water.

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 water purification context, creaming rate is important because most w/o treatment systems rely on gravimetric separation³. Emulsion stability was evaluated for emulsions prepared with mineral oil and water exposed to bilgewater fuels for 24 h. Figure 7 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. 7). 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. 7b).

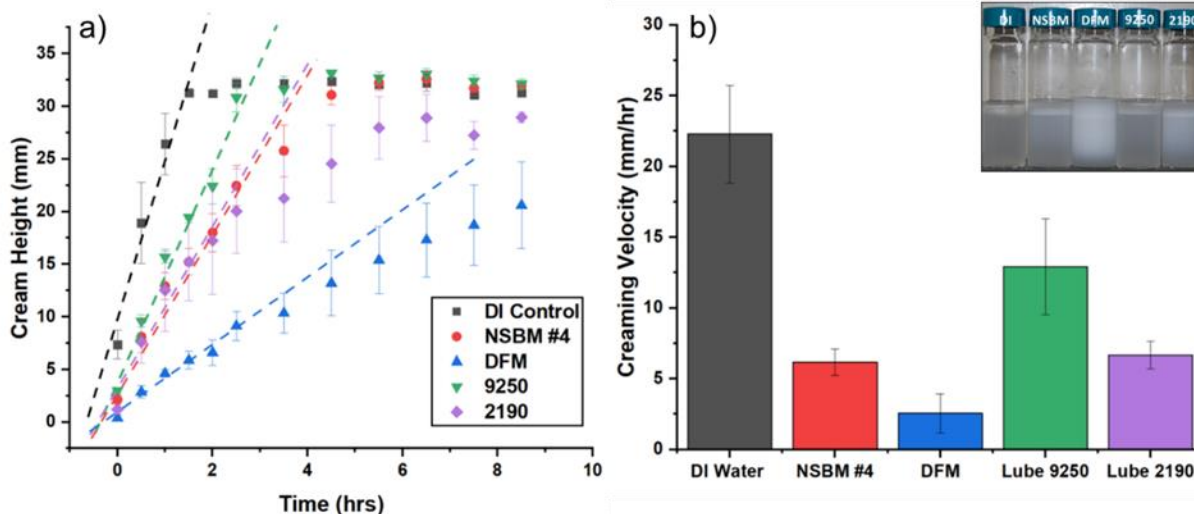


Figure 7: Mineral oil emulsion stability expressed as a) change in cream height over time and b) initial creaming velocity (mm/h) (Inset: Photograph of emulsions)

The change in cream height over time provided insight on the interactions between oil droplets during the creaming process (Fig. 7a). 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. 7b. Only the emulsion sample prepared with water exposed to DFM was able to 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.²⁵ 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. 7a corresponded well with the release of UV-active compounds demonstrated in Fig. 6. 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.²⁶ For water-in-oil emulsions, it has been shown that coalescence rate decreases with increasing asphaltene and polyaromatic hydrocarbon concentrations.²⁷ 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 3). 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 interfacial tension (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.²⁸

A potential explanation for the slower coalescence rate observed in DFM is the presence of naphthenic acids (or petroleum-derived carboxylic acids) and their corresponding naphthenates identified via UV spectroscopy. These are relatively hydrophilic compounds found in oils that contribute to the formation and stability of oil-in-water emulsions.²⁹ Indeed, diesel fuels contain relatively high levels of naphthenic acids compared to other distillate fuels.³⁰ The capability of naphthenic acids to stabilize crude oil-in-water emulsions is greatly enhanced when bulky secondary amines are also present.³¹

The goal of the emulsion stability analysis was to determine the impact of fuel components on the stability of w/o 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.3 & 4). Therefore, solubility of the fuel additives plays an important role in determining emulsion stability. For example, the mineral oil emulsion prepared with water exposed to Lube Oil 9250 did not show significant emulsion stability (Fig. 7); however, the Lube Oil 9250 oil layer did have the most visible w/o emulsions. 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 water 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) and emulsion stability (Fig. 7), it is likely that aromatic compounds have a significant impact on emulsion stability. Aromatic compounds are known to absorb to an oil-water interface, a behavior which stabilizes emulsions.³² 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.³³ 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 w/o emulsions. However, it is expected that the monoaromatic compounds would exhibit greater water solubility than asphaltenes and polyaromatics, thus increasing transport into the aqueous phase to facilitate the stabilization of w/o emulsions through similar dipole and π - π interactions.³⁴

These points are of particular interest in bilgewater systems on ships where w/o emulsion stability and surfactant solubility is influenced by the presence of salt. The direct correlation between ionic strength and emulsion stability is well established in literature, indicating that higher ionic strengths will destabilize oil-in-water emulsions with preference to electrostatically stabilized droplets. Increased ionic strength results in the neutralization and compression of electrostatic charges around surfactant stabilized oil droplets, subsequently increasing droplet interaction and coalescence. This phenomenon was experimentally validated as a component of previous research inspecting the impact of salt on oil-in-water emulsions stabilized by surfactants and commercial cleaners.³⁵ Potentially more impactful are the implications to organic compound solubility in the presence of salt, which can result in salting out of compounds from solution and further destabilizing the system.^{36, 37}

Surrogate Additive Model Tests

The surrogates chosen all either matched a molecule identified in the GCMS analysis or had similar number of carbons with matching functional groups. The concentration of surrogates in hexadecane was 500ppm before exposure and determined by GCMS analysis after 24 hours. The concentrations in the water and the partition coefficient were calculated from this information, seen in Table 3. The partition coefficient provides an easy way to compare the molecules tendency to stay in each phase to other molecules and get an estimate of how many molecules are in each phase no matter what the initial concentration. The coefficient was calculated by taking the hexadecane concentration after 24 h over the water concentration. From lowest to highest partition coefficient the surrogates are, 2-ethylpyridine, ethyl heptanoate, 2-tert-butylpyrazine and ethyl-m-tolylacetate.

Table 3: Concentrations of 500ppm surrogate in hexadecane after 24 h exposure to water and calculated partition coefficients

Surrogate	Hexadecane Concentration (ppm)	Aqueous Concentration (ppm)	Partition Coefficient
2-Ethylpyridine	369.0	131.0	2.82
2-tert-Butylpyrazine	486.2	13.8	35.13
Ethyl heptanoate	428.0	72.0	5.95
Ethyl-m-tolylacetate	499.5	0.5	1087

2-Ethylpyridine has the lowest partition coefficient at 2.82 and contains a single heteroatom substituted aromatic ring. This helps support the initial test of DFM that showed high concentrations of similar molecules in the water after exposure. Similarly, ethyl heptanoate has a lower coefficient, 5.95, supporting the presence of alkyl esters and other heteroatom substituted alkyls seen in the initial fuel and oil analysis. Ethyl-m-tolylacetate however had a very high coefficient of 1087 indicating that aromatics with ester or similar groups have low solubility on their own. This runs slightly counter to what was seen for DFM and shows that cosolvency is responsible for the amount of similar molecules, aromatics with ester pendant groups, seen in the DFM samples. The hexadecane model provided confirmation of which types of chemical structures are entering water from fuels and oils along with confirming that cosolvency plays an important role in these complex w/o systems.

Stability studies conducted with the water after exposure to hexadecane solutions had the same procedure as the fuels and oils to provide comparisons for a single additive to many additives. The hexadecane samples tested all exhibited linear increases in cream height with time, initially; however, non-linear behavior is observed in cream height over time with increased time for all the samples, Figure 8. The creaming height change behavior has the same trend as the fuels and oils tested earlier indicating that the hexadecane model system works well to replicate the effects of the more complex system.

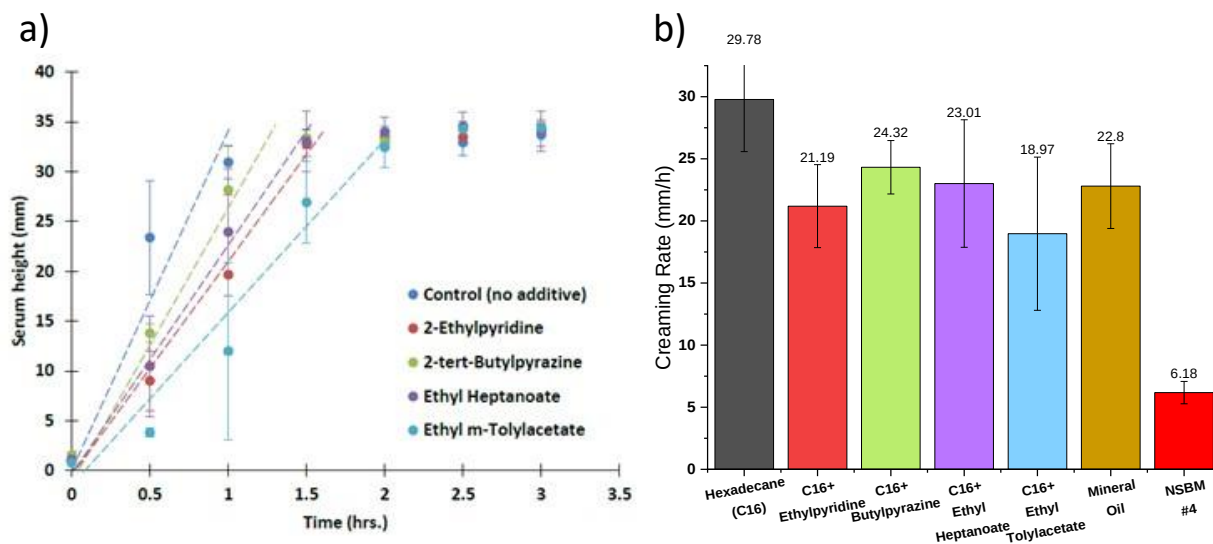


Figure 8: Mineral oil emulsion stability expressed as a) change in cream height over time and b) initial creaming velocity (mm/h) for surrogate additive samples, controls, and NSBM#4

Comparing the initial creaming velocity of water exposed to neat hexadecane with the rates seen from the surrogate additives shows a substantial reduction in the velocity for all samples. The decrease in the creaming rate velocity for the additive samples proves that these types of molecules effect the stability of w/o emulsions. While the additives had a decrease from hexadecane control, they are all within the error, from the sample exposed to just mineral oil. The lack of any differentiation between the additive samples and mineral oil reveals how changing the oil will alter the stability; however, molecules similar the ones tested appear to always increase stability of w/o emulsions. Further evidence for this trend is found in the NSBM #4 sample, Fig 8. The fuels and oils initially tested had tens to hundreds of additives or molecules with similar chemical structure to the additives. The NSBM has a much lower creaming rate velocity of 6.18 compared to the 18.97 of the best performing surrogate additive. Despite the lack of the large variety of molecules, the additives still decreased the creaming rate velocity thus improving stability. The large difference in the rates highlights the importance of the tens to hundreds of different molecules present in NSBM #4 has a dramatic effect on the resulting w/o emulsion. Further experiments are needed to confirm the trends observed and increase the complexity of the model systems to better match Navy relevant w/o emulsions. However, the knowledge gained provides insight into which molecules and functional groups effect solubility of organic molecules and their ability to create and stabilize w/o emulsions.

Conclusion

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.^{5, 38} For example, 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 and components in fuels can have a major impact on w/o emulsions and treatment systems. This is particularly true considering the potentially large volumes of fuels and oils that are present in various systems,

such as bilgewater treatment. There are several ways that fuel and oil additives can effect oil treatment systems. First, water 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 use or discharge, which contributes to increased maintenance requirements and labor costs. Second, fuel additives in Lube Oil 9250 stabilize w/o emulsions, 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 include additional compounds as part of the oil content ppm outputs as compared to other common detection methods.

The work has shown that components found in Navy relevant oils and fuel can contribute to the stability of emulsions. The conductivity, pH, and surface tension of water was significantly altered after exposure to Navy relevant 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 would provide 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. Finally, model oil systems with one additive showed significant decreases in creaming rate with only 1-20 ppm in the water phase. This highlights how impactful a small amount of these compounds can be at low concentration.

The insights from this work have potential to not only contribute to improved methods for characterization of w/o emulsions and help preventing emulsion stabilization in water, 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 cause by fuel compounds will likely play a large role in the effectiveness of foams. Similarly, understanding the transport of various compounds into the environment is important for oil spill remediation. Additionally, the work done under this Karles Fellowship has fostered discussions with others in the field, including NWCCD and University of Minnesota, potentially leading to future collaboration and proposals.

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