RELATING THE FORMATION MECHANISMS AND KINETIC STABILITY OF COMPLEX SHIPBOARD EMULSIONS TO THE PHYSICAL AND CHEMICAL PROPERTIES OF MODEL SURFACTANT-OIL-WATER-SALT SYSTEMS

by

Cole R. Davis

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THE PURDUE UNIVERSITY GRADUATE SCHOOL STATEMENT OF COMMITTEE APPROVAL

Dr. Kendra A. Erk, Chair

School of Materials Engineering

Dr. Carlos J Martinez School of Materials Engineering

Dr. John A. Howarter

School of Materials Engineering

Dr. Inez Hua Lyles School of Civil Engineering

Approved by:

Dr. David Bahr

Dedicated to Mom and Dad

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ABSTRACT

Emulsions are advantageous in many applications including healthcare, food science, and detergency due to their ability to disperse one fluid in another, otherwise immiscible fluid. For the same reason, emulsions are also problematic when mixtures of oil and water are undesirable like in industrial wastewater pollution and fuel systems. Whether an emulsion is desirable or not, both benefit from understanding the fundamental relationship of emulsion formation and stability to the physical and chemical properties of the oil-water-surfactant mixture. This work identifies the formation and stability mechanisms of model emulsion systems through the perspective of emulsion prevention for applications in shipboard wastewater (bilge water) treatment. Although experiments in this study were designed to model bilge water systems, their fundamental approach makes them practical for many different applications like food science, pharmaceuticals, and detergency.

The impact of salts on emulsion formation and stability to coalescence were studied to understand how emulsions stabilized by ionic surfactant behave in saltwater environments. Droplet size analysis revealed that emulsion stability to coalescence improved with salt concentration. Through interfacial tension and zeta potential measurements, it was found that the addition of salt promoted close surfactant packing and faster surfactant adsorption kinetics at the oil-water interface. This aided in preventing coalescence and created conditions favorable for the formation of a stable Newton black film. Extended DLVO calculations were used to model the interaction energy between droplets and suggested that hydration forces play an important role in stabilizing these systems. These emulsions were then studied under dynamic ageing conditions to observe the impact of motion on emulsion stability. While statically aged emulsions were stable to coalescence, dynamic ageing induced coalescence (increased droplet size) or emulsified the oil droplets (decreased droplet size) depending on the surfactant concentration and energy input during ageing.

Formation mechanisms and stability of spontaneous emulsion systems were also investigated. Low molecular weight oils (e.g., toluene, xylenes, and cyclohexane) were found to spontaneously emulsify with nonylphenol polyethoxylated (NPE) and sodium dodecylbenzene sulfonate (SDBS). NPE emulsions spontaneously emulsified via diffusion and micelle swelling and displayed limited

stability due to Ostwald ripening. SDBS emulsions also spontaneously emulsified with toluene but only in saltwater environments. As the concentration of salt in the aqueous phase increased, the spontaneity of these emulsions also increased. These systems were analyzed using the hydrophilic lipophilic difference (HLD) theory to evaluate its efficacy for predicting the conditions favorable for spontaneous emulsification. Limitations and practicality of using the HLD model for these systems were also explored.

CHAPTER 1: INTRODUCTION

1.1: Motivation and Applications

Wastewater is often contaminated with oil-in-water (OW) emulsions that result from cleaning, maintenance, and production operations. These emulsions are stabilized against phase separation by a mixture of surfactants, which increases the time and energy needed to destabilize or "break" the emulsions and separate the oil contaminants from the water prior to discharge. Significant time and energy costs are attributed to the treatment of OW emulsions using conventional and occasional novel unit operations to comply with discharge regulations. However, a simpler strategy that could reduce total treatment costs is to avoid the creation of hard-to-break emulsions through a more complete understanding of the key chemical and physical parameters that influence OW emulsion formation, phase behavior, and stability. Specifically, shipboard bilge water, as an example of oily wastewater, is an area of major concern due to both its large worldwide volume and additional challenges of managing complex water treatment processes onboard a ship.

Bilge water has been shown to be a significant source of pollution discharge into the world's oceans.^{1–4} Currently, 457,000 tonnes of oil is being released each year into the oceans from ship activity.⁵ This includes 13,500 tonnes of oil released per year from discharges that meet regulations.⁵ In fact, it is estimated that more oil is discharged that is in compliance with regulations than in accidental oil spills.^{3,5}

A ship's bilge is responsible for holding all waste fluids that are produced onboard while at sea including freshwater and seawater. Leaks and spills of engine oil, diesel fuel and other lubricants used onboard act to pollute the bilge water with various hydrocarbons. Adding to the problem are detergents and other surfactants that get introduced to the bilge after cleaning procedures. Once the bilge is full, it is pumped out into the ocean to make room for more waste fluids. Before the bilge water is released into the ocean, it must pass through an oil content monitor, shown in **Figure 1.1**, and meet regulations set by the International Maritime Organization which states that bilge water effluent must have an oil concentration less than 15 ppm.⁶ To meet this requirement, bilge water is treated through a number of different methods.



Figure 1.1: Cross-section schematic of a ship displaying the flow path (blue arrows) of onboard waste fluids. Waste fluids collect in bilge well and are pumped to bilge water holding tanks. Oil is removed during water treatment and released back into the ocean if it contains less than 15 ppm oil.

Treatment is typically performed in two stages: primary treatment followed by a secondary treatment. Primary treatments implement gravitational separation followed by skimming to separate the oil and water. However, this process does not remove enough oil to meet the 15 ppm regulation because gravitational separation becomes ineffective if the size of the oil droplets are below 20 μ m.³ Surfactants in bilge water help to form and stabilize these small oil droplets, creating an emulsified oil. Many secondary treatments have been and are currently being developed to remove emulsified oil. Few of these techniques are capable of reliably meeting regulations. In addition to being inefficient at removing oil, many of these techniques are expensive, time consuming, require routine maintenance and skilled operators, and can even add other pollutants into the water. With pollution regulations likely becoming stricter in the future,³ secondary treatment methods will become even more obsolete. One possible solution is to achieve a fundamental understanding of bilge water composition and the emulsions formed within it to prevent its formation and eliminate the need for treatments.

1.2: Bilge Water Composition

Bilge water contains many components including water, oils, surfactant, salts, metals, and other particulates. When mixed inside the bilge of a ship, these components partially separate into phases based on the density of each component. **Figure 1.2** shows a schematic representation of the possible phases in bilge water and their relative proportions along with a schematic of the oil-water-surfactant emulsion phase. An oil phase is located at the top of bilge water and makes up between 1 and 20% of the total volume.^{7–9} Approximately 70% of bilge water is composed of an aqueous phase containing emulsified oils, surfactants, and other pollutants. The remaining volume of bilge water contains oily sludge and solid particulates^{7,8}



Figure 1.2: Phases of bilge water and their relative proportions. Oil-water-surfactant emulsion schematic showing oil droplets stabilized by surfactant molecules in an aqueous continuous phase.

Within the emulsified layer, oil droplets are stabilized by surfactant molecules in a continuous phase of freshwater and seawater. Oil concentrations in this emulsion phase range from 100 to 500 ppm in bilge water.^{3,6–12} However, some studies show that oil levels can reach up to 2500 and even 45000 ppm.^{13,14} Synthetic bilge water studies have typically used higher oil concentrations ranging from 100 to 6000 ppm with an average concentration of 2300 ppm.^{15–27} Stabilizing these oil droplets, surfactants are present in concentrations ranging from 17 to 2500 ppm with an average

concentration of 600 ppm.^{15-17,20-27} Surfactant to oil ratios (S/O) range from 1:2 (0.5) to 1:200 (0.005) but are more commonly 1:5 (0.2).

The following subsections discuss the composition of the water, surfactant, and oil found in bilge water and other wastewater systems.

1.2.1: Water Chemistry

The aqueous phase of bilge water contains a mixture of freshwater and seawater. Freshwater is needed aboard ships for use by crew members and is commonly produced while at sea via shipboard desalination plants. Desalination is used to remove salt from seawater to produce freshwater by distillation or reverse osmosis.^{28,29} In addition to freshwater, seawater is collected in the bilge from cleaning and other onboard operations. It is important to understand the ions present in seawater and their respective concentrations as they have an impact on the solubility of organics and can alter the properties of surfactants in aqueous solutions by altering the structure of water.

Seawater contains many different salts at various concentrations and is dependent on the specific location.²¹ **Table 1.1** shows the composition of four different seawaters that were used to determine emulsion stability in saltwater environments.³⁰ There is an ASTM D1141-98 standard for synthesizing seawater and this can be found in **Table 1.2**.³¹ Synthetic seawater has also been used in other emulsion stability studies at salinities of 40.75 ³², 37.60 ³³, 35.93 ³⁴, and 35 g/L.³⁵

Body of Water	NaCl	Na ₂ SO ₄	MgCl ₂	CaCl ₂	KCl	NaHCO ₃	Salinity
	(g/L)	(g/L)	(g/L)	(g/L)	(g/L)	(g/L)	(g/L)
Persian Gulf	28.4	4.49	5.43	1.38	0.8	0.1	40.6
Red Sea	32.39	4.5	2.91	0.6	0.4	0.1	40.9
Mediterranean	26.44	4.32	5.5	1.16	0.88	-	38.3
Sea							
North Sea	24.12	2.9	5.36	1.18	0.88	-	34.4

Table 1.1: Composition of major salts from various bodies of natural water and their salinities.³⁰

Salt	Concentration (g/L)	Concentration (mol/L)
NaCl	24.53	0.420
MgCl ₂	5.20	0.0546
Na ₂ SO ₄	4.09	0.0288
CaCl ₂	1.16	0.0105
KCl	0.695	0.00932
NaHCO ₃	0.201	0.00239
KBr	0.101	0.000849
H ₃ BO ₃	0.027	0.000437
SrCl ₂	0.025	0.000158
NaF	0.003	0.0000714
Heavy Metal Salt	Concentration (g/L)	Concentration (mol/L)
Ba(NO ₃) ₂	9.94x10 ⁻⁵	3.80x10 ⁻⁷
Mn(NO ₂) ₂	3.40x10 ⁻⁵	2.31x10 ⁻⁷
Cu(NO ₃) ₂	3.08x10 ⁻⁵	1.64x10 ⁻⁷
Zn(NO ₃) ₂	0.96x10 ⁻⁵	0.507x10 ⁻⁷
Pb(NO ₃) ₂	0.66x10 ⁻⁵	0.199x10 ⁻⁷
AgNO ₃	0.049x10 ⁻⁵	0.0288x10 ⁻⁷

Table 1.2: ASTM D1141-98 standard composition of salts in water for synthetic seawater. This solution contains a salinity of 36.03 g/L, a chlorinity of 19.38 g/L, and a pH of 8.2.³¹

Bilge water filtration studies often use a diluted version of seawater to account for the freshwater that is used onboard that eventually enters the bilge tank. Salinity levels of bilge waters can range between 15 and 30 g/L but is typically near the high end of this range.^{14,21,36} Some studies mix equal parts of the ASTM standard synthetic seawater with freshwater, diluting the salt concentration by a factor of two to reach a salinity of 18.01 g/L.^{24,25} Other bilge water treatment studies have used NaCl, MgCl₂, Na₂SO₄, CaCl₂, and KCl to make a seawater solution with a salinity of 34.77 g/L. This was then diluted in equal parts to create a salinity of 17.39 g/L.^{22,23} Brackish water conditions were used to study bilge water biodegradation by preparing 18 g of NaCl and 6 g of MgSO₄·7H₂O in 1 L of water to produce a salinity of 20 g/L. Salinities of 34, 36,

38 and 40 g/L were also used in this study to replicate different proportions of seawater and freshwater.²⁶

Salinity and chemistry of real and artificial seawater vary throughout literature. Salinity values range from 40.9 g/L in artificial seawater to 15 g/L in diluted seawater. More importantly, the ions used to synthesize seawater differ; however, trends can be made. **Figure 1.3** compiles salt concentration data from 10 different non-dilute seawater solutions to show the average molarity of each ion present.^{22,23,26,30,31,33–35} The most abundant monovalent cation and anion were Na⁺ and Cl⁻ respectively, with chloride salts being more common than sodium salts. Although the divalent magnesium cation and sulfate anion are relatively low in concentrations, they were the most concentrated divalent ions and were found in nearly all studies.³⁷



Figure 1.3: Average ion molarity compiled from 10 different synthetic seawater solutions.^{22,23,26,30,31,33–35} Cations are displayed in black while anions are displayed as grey. Average molar concentrations of each ion are labelled above their respective points.

Water molecules naturally form self-associated networks called "flickering clusters" giving them a polymerized structure via water-water hydrogen bonding.^{38–41} Equation 1.1 shows water in the monomer state (left) self-associating into a polymeric state (right).

To hydrate and solubilize surfactants and oils, water must be dissociated into its monomer state. If water becomes self-associated or form a hydration sphere around a salt ion, there are less hydrogen bonds available to hydrate the solutes, resulting in phase separation or a decrease in solubility.^{38,41} Salt ions play a major role in the structure of water by shifting **Equations 1.1** to dissociate or self-associate water.³⁸

1.2.2: Surfactant Chemistry

Bilge water typically consists of two types of surfactants; ionic and non-ionic which differ by their hydrophilic head group chemistry. Ionic surfactants contain a salt group that dissociates in water, leaving the surfactant with a positive (cationic) or negative (anionic) net charge. Non-ionic surfactants do not contain salts but instead have a polar moiety usually composed of ethylene oxide (EO) that creates the hydrophilic region of the surfactant molecule. Head group chemistry is a distinguishing factor when observing surfactant properties in aqueous solutions. Ionic and non-ionic surfactant properties are influenced differently by their environment including other surfactants, salts, solvents, and temperature changes. When studying emulsions, such as the ones found in bilge water, it is important to understand the chemical and physical properties of the surfactants being used.

Ionic surfactants found in bilge water and other oily wastewater treatment studies are commonly anionic sulfates.^{16,21,25,34,42–45} **Figure 1.4** shows the chemical structures for sodium lauryl ether sulfate (SLES) and sodium dodecylbenzene sulfonate (SDBS) and can be found in bilge water studies. Sodium counterions are the most common counterion in this class of surfactant.



Figure 1.4: Chemical structures for (A) SLES and (B) SDBS.

The counterion for an anionic surfactant plays an important role in its ability to reduce surface tension and stabilize an emulsion. Counterions that are strongly bound (Cs^+) to the surfactant molecule in aqueous solutions create a lower surface tension than counterions that are not strongly bound (Li^+ and Na^+). If the salt on the surfactant molecule does not dissociate into its ionic form, then the surfactant molecules are able to pack more tightly at an interface because the surfactant head groups are shielded by the counterion and do not repel each other. However, if the counterion is completely dissociated from the surfactant molecules then the head groups become anionic and repel each other which restricts their ability to pack at an interface. A counterion that has a large hydrated radius (proportional to its ability to complex with water) has a weak binding force to the surfactant molecule and vice versa.⁴⁶ In addition to the counterion, surfactant molecules are sensitive to the presence of salt in aqueous solutions.

Salt effects on anionic surfactants has been well studied in literature. Anionic surfactant micelle size and aggregation number (number of surfactant molecules per micelle) are limited by the electrostatic repulsion between surfactant head groups. This repulsion is reduced upon the addition of salt ions which act to shield the charged head groups⁴⁷ and creates salt bridges between two neighboring head groups.⁴⁸ Upon shielding, the surfactant molecules are able to pack more densely, increasing the micelle size and aggregation number and reducing surface tension.⁴⁹ Increasing the cation valence or salt concentration will increase the screening of the negatively charged head groups as well as the salt bridge lifetime and stability.⁴⁸ This leads to an even further increase in micelle size and aggregation number.^{48,50–54} Eventually, increasing the salt concentration leads to precipitation of anionic surfactant micelles.^{48,53} Increasing surfactant concentration has shown

similar effects as salt does by increasing the aggregation number.⁵⁴ Anionic micelle size and aggregation number can also be controlled by changes in temperature.

At temperatures below the critical micelle temperature (CMT), anionic surfactants have very low solubility in water and precipitate. Increasing the temperature above the CMT results in solubilization of the surfactant. When reducing the temperature of a surfactant solution below its CMT, supercooling has been observed and the surfactant solution can remain stable for long periods of time.⁵³ Adding salt to a surfactant solution shifts the CMT to an increased temperature. Increasing the temperature past the CMT decreases the micelle size and aggregation number, making anionic surfactants more soluble.^{52,53}

Nonionic surfactants found in bilge water and other oily wastewater studies are commonly nonylphenol ethoxylates (NPEs) or polysorbates; both of which contain ethylene oxide (EO) groups as their polar moiety.^{17,18,26,27,32,44,45} **Figure 1.5** shows the chemical structure for NPE and the EO group inside the parentheses where n can range from 4 to 70 depending on the desired surfactant type.



Figure 1.5: Chemical structure of representative NPE molecule.

Unlike anionic surfactants, nonionic surfactants, specifically polyethoxylated surfactants, become less soluble with increasing temperature. Nonionic surfactant micelle size and aggregation number increase with temperature as well.⁵⁵ Upon heating, a nonionic surfactant solution will become cloudy at a specific temperature known as the cloud point (CP). This occurs when the surfactant and water phase separate into a surfactant rich phase and a water rich phase with a surfactant concentration close to the critical micelle concentration.^{40,41,56}

Dictating nonionic surfactant solubility is the structure of the water molecules surrounding the surfactant.⁴¹ A nonionic surfactant is soluble in water due to hydrogen bonding between water and the surfactant's EO moiety causing hydration.⁴⁰ As the temperature increases, the water molecules become excited and their interaction with EO reduces. Above the CP, the water molecules do not interact with the EO moiety and can no longer solubilize the surfactant.⁴¹ In addition to temperature, salts play a large role in determining the properties of nonionic surfactants.

Similar to anionic surfactants, the addition of salt to aqueous nonionic surfactant solutions reduces surface tension⁵⁷ but unlike anionic surfactants, the micelle size and aggregation number are not highly dependent on salt but more so on temperature. However, salt does magnify the effects that temperature has on aggregation number but has little effect at temperatures far below the cloud point.⁵⁵ Salts can also shift the CP of a nonionic surfactant by altering the structure of water.

Depending on the ions present, salt solutions can either salt in or salt out nonionic surfactants resulting in an increase or decrease in CP respectively. Large, polarizable ions are structure breaking and result in the dissociation of water molecules to salt in the surfactant. However, most ions are structure making and become hydrated by water in what is called a hydration sphere.³⁹ Water molecules that are located within this hydration sphere are no longer available to act as solvent molecules and this results in salting-out of the surfactant. As water becomes more self-associated or hydration of ions occur, hydrogen bonding with the surfactant's EO moiety is reduced and phase separation of the surfactant and water occurs at a lower temperature.^{38,40,56,58–60} Salting effects on the surfactant CP are additive meaning that the addition of two different salts will have a similar effect as the combined effect that the two salts have individually.^{38,61} However, there is a minimum concentration of salt that is needed to see the effects of salting in or salting out. This is dependent on the anion and its hydrated radius which is described by its lyotropic number in the Hofmeister series (i.e. a list of ions in order of their ability to salt-in or salt-out polymers^{40,61}). For a strongly hydrated anion (a lower lyotropic number), a lower concentration of salt is needed to show its salting in or out effects.⁶²

A nonionic surfactant's CP can also be altered by the addition of other surfactants. It was found that the addition of the anionic surfactant SDS increased the CP of a nonionic surfactant more than any salt for a given concentration: 0.5 mM SDS increased the cloud point of a nonionic surfactant

by 26 °C ³⁸. Unlike salts, there is no minimum concentration of added surfactant needed to see the effects of salting in.⁶² The anionic surfactant increases the CP of a nonionic surfactant by solubilizing it when the temperature is increased above the original CP. Anionic surfactants become more soluble as temperature increases allowing it to solubilize the otherwise insoluble nonionic surfactant.³⁸

Hydrocarbon additives have also been shown to both increase and decrease the CP of a nonionic surfactant using hexadecane and xylene respectively.³⁸ **Table 1.3** shows a summary of changes in cloud point (Δ CP) for octoxynol 9 (Triton X-100) using additives relevant to bilge water.^{38,61,62}

Additive	Concentration	ΔCP
	(M)	(°C)
SDS	0.0005	26
Hexadecane	0.023	14.5
HCl	0.50	2
MgCl ₂	0.50	-9
NaCl	0.50	-10
NaOH	0.50	-16.5
NaF	0.50	-19
Na ₂ SO ₄	0.50	-37
Xylene	0.048	-42.5

Table 1.3: Cloud point changes at a given concentration of additives relevant to bilge water.^{38,61,62}

1.2.3: Oil Chemistry

Oils exist in two main classes onboard ships: lubricants and fuel oils.^{3,6,7,12,18,26,63} Bilge water filtration studies have used lubricating oils^{17,27}, fuel oils^{16,21}, and a 50/50 mixture of lubricants and fuels.^{22–25,45} Lubricating and fuel oils used onboard United States (U.S.) Navy ships require U.S. defense standards or military standards (MIL-STD) which regulate the composition of these oils. Common MIL-STD lubricants found onboard ships are 2190 TEP steam lube oil (MIL-PRF-17331K), 9250 diesel lube oil (MIL-PRF-9000L), and synthetic lube oil (MIL-PRF-23699). MIL-

STD fuel used on naval ships can vary between marine gas oil, diesel fuel marine, or naval distillate (NATO symbol F-76) (MIL-PRF-16884N). Lubricants and fuels are both composed of hydrocarbons (apart from synthetic oils) but differ in their structure and properties.

Hydrocarbons can be divided into four general classes (see **Figure 1.6**): paraffins (alkanes), olefins (alkenes), naphthenes (cycloalkanes), and aromatics. Paraffins are saturated meaning they do not contain any double bonds and can exist as straight or branched hydrocarbons. Olefins are unsaturated meaning they contain one or more carbon-carbon double bonds which is formed during the processing of crude oil. Naphthenes are saturated hydrocarbons that contain a cyclic structure like cyclohexane. Aromatics also contain a cyclic structure but are unsaturated and contain benzene structures.^{64,65} Naphthenes can also have polycyclic structures. These four structures make up the majority (approximately 75%) of petroleum hydrocarbons⁶⁶, while the remaining portion is composed of nitrogen-sulfur-oxygen compounds and asphaltenes⁶⁷ which are partially removed when refining crude oil to become a lubricant or fuel.⁶⁴



Figure 1.6: Chemical structures of (a) dodecane (paraffin), (b) 1-dodecene (olefin), (c) butylcyclohexane (naphthene), and (d) o-xylene (aromatic).

Lubricants like steam lube oil and diesel lube oil contain highly refined mineral oil which are made up of paraffins and naphthenes between 15 and 50 carbons in length.^{68–70} These lubricants may also contain additives like calcium alkyl phenate sulfide (between 0.1 and 5 wt.%) and zinc alkyl dithiophosphate (between 0.5 and 1.5 wt.%) which acts as a detergent and an antioxidant

respectively. Synthetic lube oil, mainly used as a base lubricant for jet engine lubrication⁴, is made from synthetic esters and can contain up to 1 wt.% N-Phenyl-1-naphthalamine.⁷¹

Fuels used onboard ships are mainly composed of diesel but can vary in composition. Diesel fuel contains hydrocarbons between 9 and 20 carbons in length (C9-C20). Typical marine based diesel fuels contain approximately 30% aromatics.⁷² For diesel fuel marine (diesel fuel No. 4), these hydrocarbons are approximately 44% aromatic, 44% naphthalenes (not to be confused with naphthenes), and 12% C9 to C20 paraffins.⁷³ Marine gas oil (diesel fuel No. 2) contains C10-C22 hydrocarbons which are mostly of the paraffinic, naphthenic, and aromatic type.^{64,74} Marine gas oil also contains additives like light and heavy cycle oils that can contain up to 60% aromatics.⁷⁵ Characterization of bilge waters have shown that C10-C40 paraffins, aromatics (benzene, toluene, and xylene), and polycyclic aromatic hydrocarbons (naphthalene) make up the majority of oil pollutants present in bilge water which agree with the composition of oils used onboard.^{13,14} These oils pollute bilge water in two different ways; dissolved oil and emulsified oil.

Dissolved oil occurs when an oil is soluble in water and is in solution with water at a particular concentration. Emulsified oil occurs when oil droplets are formed in an otherwise immiscible water phase. The concentration at which a hydrocarbon is soluble in water (dissolved) is dependent on which class of hydrocarbon it belongs to, the number of carbon atoms in the molecule (or its molar volume), and parameters of the water like other dissolved oils, temperature, and dissolved salts. Among the four classes of hydrocarbons, paraffins are the least soluble for a given carbon number. Ring formation, as seen in naphthenes, increases the solubility of a hydrocarbon in water. Unsaturation (olefins and aromatics) also increases a hydrocarbon's solubility.^{76–78} As the molar volume, or number of carbon atoms, increases for a given class of hydrocarbon, its solubility in water decreases.^{65,78} When hydrocarbons (diesel fuel No. 2) were mixed with seawater, it was shown that the dissolved oil was rich in aromatics due to their increased solubility.¹ Solubility values in water for some common hydrocarbons found in lubricants and fuels can be found in **Table 1.4**.

Hydrocarbon	Hydrocarbon	Number of	Solubility (S ₀) in Water at	Reference(s)
	Class	Carbon	25 °C (ppm) (average, if	
		Atoms	multiple references)	
Decane	Paraffin	10	0	65
Heptane	Paraffin	7	2.76	65,76,79
Pentane	Paraffin	5	41.7	65,76,79
Cycloheptane	Naphthene	7	30.0	76
Cyclopentane	Naphthene	5	159	76
Naphthalene	Aromatic	10	32.5	80,81
o-Xylene	Aromatic	8	189	65,76,79
Toluene	Aromatic	7	538	65,76,79
Benzene	Aromatic	6	1770	65,76,78,79

Table 1.4: Solubility of hydrocarbons in water at 25 °C.

Temperature and composition of water can alter the solubility of a hydrocarbon. As temperature increases, the solubility of a hydrocarbon in water decreases but is relatively insensitive to temperature over ambient temperature ranges (0-30 °C). However, larger polycyclic aromatic hydrocarbons' (PAHs) solubility can be significantly altered by temperature.⁷⁸ Dissolved hydrocarbons can alter the solubility of other hydrocarbons in water. For example, the addition of a relatively soluble oil (e.g., toluene) leads to an increase in solubility of a relatively insoluble oil (e.g., decane).⁸² Dissolved salts can also alter the solubility of hydrocarbons in water.

Salts, like those present in seawater, act to decrease the solubility of a hydrocarbon in water, although some salts have been shown to increase the solubility of oil. **Equation 1.2** shows how the type of salt (using the Setschenow constant or salting parameter, K_s) and its concentration (C_s) impacts the solubility of an oil in salt solution (S_s) from its solubility in pure water (S_o).

$$S_s = S_o \cdot 10^{-K_s C_s} \tag{1.2}$$

The salting parameter, K_s , expresses the amount of salting-in or salting-out that a salt has on a specific hydrocarbon. For salts with positive salting parameters, as the concentration of salt increases, oils become less soluble in water (known as "salting-out"). Salts that have negative salting parameters increase the solubility of an oil with increasing concentration (known as "salting-in").^{80,81} All salts found in seawater act to salt-out oils and have a positive salting parameter. Large organic salts like (Bu)₄NBr salt-in oils and have negative salting parameters.⁸¹ The salt's ability to bind to water molecules determines if the salt acts to salt-in or salt-out an oil. If the salt ions bind strongly to water then salting-out occurs and if they bind weakly to water then salting-in occurs.⁷⁸ When two or more salts are in solution, their salting effects are additive. **Table 1.5** shows the solubility of three hydrocarbons in seawater solutions calculated from **Equation 1.2** using a value of 0.5 mol/L for C_s .

Table 1.5: Solubility of common aromatics in pure water (S_0) and seawater (S) along with their salting parameters.

Hydrocarbon	S _o (ppm)	S (ppm)	K _s (L/mol) ⁷⁸
Naphthalene	32.5	23.5	0.28
Toluene	538	408	0.24
Benzene	1770	1410	0.20

1.3: Emulsion Types

An emulsion is a dispersion of one liquid inside of another immiscible liquid where the dispersed phase appears as spherical droplets surrounded by a continuous phase.⁸³ Surfactant is typically needed to stabilize the dispersed phase and prevent phase separation. Emulsions can form in different phases including oil-in-water (O/W), water-in-oil (W/O), and mixed emulsions (e.g., O/W/O). In an O/W emulsion, oil is the dispersed phase and forms droplets in a continuous, aqueous phase of water.^{83–86} For wastewater systems, O/W emulsions are the primary focus. Emulsions can also be categorized by their droplet size and stability. **Table 1.6** compares the droplet size and stability of macroemulsions, nanoemulsions, and microemulsions.

	Macroemulsion	Nanoemulsion	Microemulsion
	(Conventional)		
Size	1-100 µm	20-500 nm	10-100 nm
Stability	Kinetically Stable	Kinetically Stable	Thermodynamically
			Stable

Table 1.6: Categories of emulsion types based on size and stability.⁸⁷

Macroemulsions, or conventional emulsions, contain the largest droplet sizes and are common to encounter, especially in wastewater systems. Nanoemulsions may also form due to high energy inputs, ultralow interfacial tensions, spontaneous emulsification, or a combination of these things. Despite the name, microemulsions are the smallest emulsion type and also form spontaneously but should not be confused with spontaneous emulsions.⁸⁸

Wastewater emulsions are typically divided into three different categories based on droplet size and ease of removal and these are: free, dispersed, and emulsified oil. Free (> 150 μ m) and dispersed (20- 150 μ m, conventional emulsion) oil are relatively easy to remove from wastewater while emulsified (< 20 μ m, conventional and nanoemulsions) oil is considered to be more difficult.^{3,6,44,89} In general, as the droplet size of the dispersed phase decreases, emulsion stability increases.⁹⁰ Emulsion formation and stability mechanisms will be discussed in the following sections.

1.4: Emulsion Formation

For oil to be dispersed into water and form an emulsion, an energy input is typically needed. However, a specific emulsion type called a spontaneous emulsion can form without any external energy input. Both emulsion formation types will be discussed in the following two subsections.

1.4.1: Emulsification Techniques and Energy Density

Conventional emulsions are thermodynamically unfavorable and therefore, energy is required to create an emulsion from two fluids that begin at equilibrium.⁹¹ The process of dispersing one fluid into another is known as emulsification. Interfacial tension (i.e., the energy needed to increase the

surface area of a material) plays a major role in the energy required for emulsification, with larger interfacial tensions requiring more energy. This energy requirement results from the formation of new surface area during droplet formation and is described by **Equation 1.3**:

$$\Delta G = \Delta A \gamma - T \Delta S \tag{1.3}$$

where ΔG is the free energy of the system, ΔA is the change in dispersed phase surface area, γ is the interfacial tension, *T* is the temperature, and ΔS is the change in entropy. Formation of smaller droplets (i.e., large interfacial areas) or high interfacial tensions require more energy input. For example, Figure 1.7 shows how the volume mean diameter droplet size, D(4,3), decreased as the energy density during emulsification increased using a high shear mixer. Note that the interfacial tension for these two surfactants with mineral oil were similar: 3.4 and 8.3 mN/m for NPE and SLES, respectively. The presence of surfactant reduced the interfacial tension and decreases the energy required to form an emulsion. For example, the interfacial tension between mineral oil and water without surfactant was approximately 51 mN/m and would require more energy to achieve a similar droplet size.



Figure 1.7: Impact of energy density on the volume mean diameter (D(4,3)) of heavy mineral oil droplets stabilized by either SLES or NPE. The mineral oil concentration was 5000 ppm and the surfactant concentration was 500 ppm. Emulsification was performed using a high shear mixer at various speeds for 60 seconds.

Calculating energy density is useful in quantify emulsification and comparing emulsions with different processing histories. This calculation uses on the power input (P), the time of emulsification (t), and volume of the emulsion (V) to calculate the energy density (E_D) using **Equation 1.4**.

$$E_D = \frac{Pt}{V} \tag{1.4}$$

The power input for a rotor stator mixer (i.e., homogenizer or high shear mixer) can be estimated using **Equation 1.5**:

$$P = P_o \rho N^3 D^5 \tag{1.5}$$

where P_o is the power number (estimated as 3 for the data in **Figure 1.7**),^{92,93} ρ is the density of the continuous phase, *N* is the rotations per second, and *D* is the diameter of the mixer.⁹⁴ Using these equations for energy density, droplet size distributions can be compared for emulsions that were emulsified under different conditions. For example, **Table 1.7** shows the processing parameters, the calculated energy density, and emulsion droplet size parameters for three different emulsions. Each emulsion contained 5000 ppm heavy mineral oil, 500 ppm NPE, and contained a total volume of 15 mL.

	Emulsion 1	Emulsion 2	Emulsion 3
N (rpm)	13500	24000	13500
t (s)	338	60	60
E _D (J/mL)	162	162	29
D(4,3) (µm)	15.3	17.1	37.8
D ₁₀ (µm)	0.612	0.971	8.13
D50 (µm)	13.1	17.7	37.3
D ₉₀ (µm)	34.1	33.1	66.5

Table 1.7: Emulsification parameters and the resulting size distribution parameters for three different emulsions containing 5000 ppm mineral oil and 500 ppm NPE.

While all three emulsions from **Table 1.7** had different processing histories, emulsions one and two had the same energy densities during emulsification. As a result, their droplet size distributions were very similar especially when compared to emulsion three. **Figure 1.8** highlights this more clearly by showing the droplet size distributions for all three emulsions. This demonstrates how emulsions with different emulsification processes can be compared.



Figure 1.8: Volume mean size distributions for three emulsions with different processing histories. Emulsions one and two had the same energy density during emulsification (162 J/mL) while emulsion three had a much lower energy density (29 J/mL).

1.4.2: Spontaneous Emulsion Formation

While an energy input is typically needed, emulsification can occur spontaneously, without an energy input, when the two immiscible fluids do not begin at thermodynamic equilibrium.⁹⁵ When this occurs, it is called spontaneous emulsification. The rate and extent of spontaneous emulsification is known as the spontaneity. In literature, spontaneous emulsification and self-emulsification are sometimes used interchangeably.^{95,96} However, it is important to distinguish between these two terms as they are used to describe two distinct phenomena. Spontaneous emulsification refers to the emulsification of two immiscible fluids when placed in contact without the aid of any external energy source (e.g., mechanical or thermal).⁹⁷ Self-emulsification does require some energy input through gentle agitation or stirring.^{97,98} This energy input is very little when compared to conventional emulsification. The result is similar, in that nanometer-sized emulsions with kinetic stability are formed. The only difference is the mechanism in which they form.
There are three main mechanisms for spontaneous emulsification have been described in literature: ultralow interfacial tension, diffusion, and interfacial turbulence.⁹⁷ Ultralow or negative interfacial tension can be described using **Equation 1.3**. Spontaneous emulsification can occur when ΔG is negative which is achieved at negative or ultralow interfacial tensions when entropy gain is larger than the energy penalty to create new surface area.^{99–101} While ultralow interfacial tensions may play a role in spontaneous emulsification, it is often criticized as being oversimplified and fails to describe the spontaneous emulsification of many systems.^{97,102,103} For example, it has been shown that spontaneous nanometer-sized emulsions can form at appreciable interfacial tensions.^{99–102}

Diffusion is widely accepted as the predominant mechanism of many spontaneous emulsion systems.^{91,102,104} This mechanism involves the diffusion of one fluid into a separate fluid, creating regions of supersaturation. Emulsion droplets form in these supersaturated regions by means of nucleation and growth and is commonly referred to as, "diffusion and stranding".^{91,95,97,98} Diffusion can also lead to emulsification through micelle swelling which will be discussed further in Chapter 4.¹⁰¹

Interfacial turbulence, sometimes referred to as Marangoni flow, is a convective flow that forms due to Marangoni effects (i.e., interfacial or surface tension gradients). This convective flow pulls the disperse phase into the continuous phase while breaking it into small droplets as it flows.⁹⁷ While this mechanism has been observed, it is often not the sole mechanism responsible for spontaneous emulsification and only acts to increase the rate of emulsification.^{91,95,98,102,104,105} Although many mechanisms have been proposed for how spontaneous emulsification occurs, it still remains a topic of discussion as the three discussed mechanisms do not fully describe every system.¹⁰⁶

Although the driving force for spontaneous emulsification is reaching a thermodynamic equilibrium, spontaneous emulsions are only kinetically stable are not to be confused with microemulsions which are thermodynamically stable. Thermodynamic and kinetic stability of emulsions are discussed in the following section.

1.5: Emulsion Stability

Thermodynamically stable emulsions (e.g., microemulsions), have a lower free energy when emulsified and will not spontaneously phase separate over time. Most emulsions, including conventional and nanoemulsions, do not exhibit thermodynamic stability but can show appreciable kinetic stability. An emulsion that is termed kinetically stable, has the resistance to change physically and chemically over time.⁸³ This stability comes from the adsorption of macromolecules (i.e., surfactants) at the interface between oil and water. Surfactant stabilization of an emulsion can be through several mechanisms including electrostatic, hydration (ionic surfactants), and steric (non-ionic surfactants) repulsion.^{86,107,108} Although surfactants can stabilize an emulsion, given sufficient time, instabilities can arise due to many different mechanisms. There are four main instability mechanisms relevant to wastewater systems and these are: gravitational separation, flocculation, coalescence, and Ostwald ripening.

1.5.1: Gravitational Separation

Gravitational separation is the migration of the dispersed phase to the top (creaming for an OW emulsion) or bottom (sedimentation for a W/O emulsion) of an emulsion. This arises due to differences in density between the dispersed and continuous phase resulting in a net force due to gravity. The velocity at which droplets migrate follows Stokes' Law which can be seen in **Equation 1.6**.

$$v_{Stokes} = \frac{2gr^2(\rho_d - \rho_c)}{9\eta_c} \tag{1.6}$$

The migration velocity (v_{stokes}) increases with increasing droplet size (r). A large difference in density between the dispersed (ρ_d) and continuous (ρ_c) phase promotes gravitational separation. Increasing the viscosity of the continuous phase (η_c) can act to hinder creaming.⁸³ Stokes' law does not take into account droplet concentration which has been shown to decrease v_{stokes} .¹⁰⁹

As droplets decrease in size, gravitational separation becomes less significant and eventually Brownian motion dominates over gravitational forces. This can be measured by the Péclet number (P_e) which is a ratio of the Stokes' velocity to the Stokes-Einstein diffusion constant for Brownian motion and is shown in **Equation 1.7**:

$$P_e = \frac{4\pi g r^4 \Delta \rho}{3k_B T} \tag{1.7}$$

where g is the gravitational acceleration, r is the droplet radius, $\Delta \rho$ is the density difference between the dispersed and continuous phase, k_B is Boltzman's constant, and T is the absolute temperature.^{110,111}

A plot showing the Péclet number for oil droplets ($\rho = 0.8 \text{ g/mL}$) in water ($\rho = 1 \text{ g/mL}$) at different sizes can be seen in **Figure 1.9**. At a droplet size of 1.7 µm, the Péclet number is equal to 1. At droplet sizes larger than this, the Péclet number increases, and gravity (buoyancy) dominates. At droplet sizes smaller than this, diffusion dominates, and the emulsion is stabile to gravitational separation.^{110,111}



Figure 1.9: Péclet number as a function of droplet size for an oil with a density of 0.8 g/mL in water (density of 1 g/mL). The horizontal, black dashed line represents a Péclet number of 1 which is the threshold for weather gravity or diffusion dominates. The vertical, grey dotted line represents the droplet size (1.7 µm) that has a Péclet number of 1.

1.5.2: Flocculation

Flocculation is the aggregation of two or more droplets while each droplet remains unchanged. This occurs when van der Waals forces dominate over the long-range electrostatic repulsion between droplets and allows droplets to aggregate close together.⁸³ The attractive interaction energy (W_{vdW}) between two spheres of equal radii (r) due to van der Waals interactions is described in **Equation 1.8**:

$$W_{\nu dW} = -\frac{Ar}{12D} \tag{1.8}$$

where A is the Hamaker constant and D is the distance between the two spheres.¹¹²

Acting in opposition to the van der Waals interaction is the electrostatic repulsion interaction energy ($W_{electro}$) which occurs from surface charges and the electrical double layer. The repulsion interaction energy can be seen in **Equation 1.9** for two spheres with equal radii in the presence of a monovalent salt:

$$W_{electro} = 4.61 * 10^{-11} r \tanh^2 \frac{\Psi}{103} e^{-\kappa D}$$
(1.9)

where Ψ is the surface potential in mV and κ is the inverse of the Debye length. The Debye length, or double layer thickness, is the distance from a particle's surface to where the electric potential decays by e^{-1} .¹¹² Unlike van der Waals interactions, electrostatic interactions are sensitive to electrolytes and pH.¹¹² Both, the surface potential and Debye length decrease with electrolyte concentration and reduce the electrostatic interaction energy. **Table 1.8** shows how the Debye length changes with salt concentration for different salt valences.

Table 1.8: Impact of salt valency and concentration on the Debye length.¹¹²

Salt Valency	Debye Length, $1/\kappa$ (nm)		
1:1 (NaCl)	$0.304/\sqrt{[NaCl]}$		
2:1 (MgCl ₂)	$0.176/\sqrt{[MgCl_2]}$		
2:2 (MgSO ₄)	$0.152/\sqrt{[MgSO_4]}$		

The total interaction energy between two spheres having equal radii is the sum of W_{vdW} and $W_{electro}$. This is known as the DLVO theory and can aid in predicting the stability of an emulsion to flocculation and coalescence. In bilge water systems, ions that are present in seawater can shield the electrostatic repulsion between droplets and have been shown to increase flocculation.^{33,37} This results in larger effective droplet sizes and increases the migration velocity which results in faster creaming.⁸⁶

Figure 1.10 shows plots of the interaction energy between two oil droplets (octane, $A \sim 4 \times 10^{-21}$)¹¹² with radii of 100 nm at different separation distances. **Figure 1.10A** shows the decrease in energy barrier with increasing salt at a constant surface potential. **Figure 1.10B** shows the transition from stable to unstable (energy barrier < 0) with decreasing surface potential at a constant NaCl concentration of 0.5 M. Positive and negative interaction energies represent repulsion and attraction between two droplets, respectively. All curves contain a primary minimum at small separation distances and correspond to coagulation or coalescence. However, some of the curves contain a significant energy barrier that must be overcome to reach coalescence. When the energy barrier is exactly 0, this is known at the critical coagulation concentration (CCC). If the salt concentration is large or the surface potential is small, a secondary minimum exists (identified in **Figure 1.10A**) and corresponds to flocculation. At a salt concentration of 0.5 M and surface potential of 10 mV, the interaction between the droplets is purely attractive.



Figure 1.10: Interaction energy of two particles (r = 100 nm) at different separation distances with (A) constant surface potential of 30 mV and increasing NaCl concentration and (B) constant NaCl concentration of 0.5 M and decreasing surface potential.

1.5.3: Coalescence

Coalescence is the combination of two or more droplets to form a single droplet. A reduction in interfacial area is the driving force for coalescence and reduces the free energy proportional to the interfacial tension. Lower interfacial tensions reduce the driving force for coalescence.¹⁰⁷ Droplets that are closer together (e.g., from gravitational separation or flocculation) are more susceptible to coalescence. For coalescence to occur, an energy barrier (electrostatic or steric repulsion provided by the surfactant) must be surpassed to allow the droplets to merge (as seen in **Figure 1.10**). As droplets approach each other, an area of contact is made, and a thin film exists between the droplets. This film begins to drain until a critical film thickness is achieved ($h_0 \approx 100$ nm) after which, the film ruptures. Film drainage can halt when a balance is reached between attractive and repulsive forces. Drainage time of a film between two flat interfaces is described in **Equation 1.10** and is dependent on the continuous phase viscosity (μ), the area of contact (A), the pressure forcing the interfaces together (p), and the initial separation distance when flattening occurs (h_c).¹⁰⁷

$$t_{drainage} = \frac{3\mu A}{4\pi p} \left(\frac{1}{h_c^2} - \frac{1}{h_0^2} \right)$$
(1.10)

Once the film ruptures, coalescence of two droplets occurs and the formation of a larger droplet results in a higher rate of gravitational separation. Upon further coalescence, droplets eventually are no longer present and an oil layer exists on top of the water phase.⁸³ This is known as phase separation.

1.5.4: Ostwald Ripening

Ostwald ripening is the growth of large droplets due to mass transport from smaller droplets. **Figure 1.11** depicts the Ostwald ripening process as small droplets decrease in size due to mass transfer to larger droplets.⁸³



Figure 1.11: Depiction of Ostwald ripening as small droplets transfer mass to larger droplets.⁸³

This process is highly dependent on the solubility of the dispersed phase in the continuous phase as dispersed phase molecules must transport from small droplets, through the continuous phase, and into larger droplets.⁸⁶ Solubility of the dispersed phase is dependent on droplet size; as droplet size is reduced, the dispersed phase becomes more soluble. This is due to the increase in pressure inside of the droplet as the size decreases which increases the oil's fugacity. **Equation 1.11** shows the relationship between droplet size and solubility where S_r is the solubility of a dispersed phase (e.g., oil) droplet with radius r in the continuous phase (e.g., water), S_s is the solubility of the dispersed phase in the continuous phase accounting for salt, γ is the interfacial tension between the dispersed and continuous phase, V_m is the molar volume of the dispersed phase, R is the universal gas constant, and T is the temperature.⁸³

$$S_r = S_s \cdot \exp\left(\frac{2\gamma V_m}{r_{RT}}\right) \tag{1.11}$$

Increasing solubility of the dispersed phase makes Ostwald ripening more favorable and increases droplet growth. For example, it has been shown that as the solubility of the oil in water increased, Ostwald ripening increased.^{113–115} Equation 1.12 shows how the droplet size (r) changes from the initial droplet size (r_o) where D is the diffusion coefficient and t is time.

$$r^{3} = r_{o}^{3} + \frac{8\gamma V_{m} S_{s} Dt}{9RT}$$
(1.12)

Ostwald ripening is dependent on the solubility of the dispersed phase in the continuous phase which is altered by the presence of salt (Equation 1.2). Salts in seawater decrease an oils solubility in water which decreases the rate of Ostwald ripening. Ostwald ripening rates of heptane in water emulsions decreased by two orders of magnitude when the concentration of NaCl increased up to 30 mM. At concentrations above 35 mM, Ostwald ripening was absent, but flocculation and coalescence were present due to the reduction in electrostatic repulsion.¹¹⁵ There then exists a maximum in emulsion stability with salt concentration where Ostwald ripening is inhibited without inducing coalescence.

CHAPTER 2: IMPACT OF SALTWATER ENVIRONMENTS ON THE COALESCENCE OF OIL-IN-WATER EMULSIONS STABILIZED BY ANIONIC SURFACTANT

The following chapter contains text, figures, and tables with permission from¹¹⁶ **Cole R. Davis**, C. J. Martinez, J. A. Howarter, and K. A. Erk, "Impact of Saltwater Environments on the Coalescence of Oil-in-Water Emulsions Stabilized by Anionic Surfactant," *Environmental Science and Technology Water*, (2021).

2.1: Introduction

Wastewater systems in saltwater environments can contain emulsified oils that must be removed before the water is suitable for release into the environment. As discussed in **0**, bilge water is one example of this system and requires less than 15 ppm of emulsified oil before being released into the ocean.⁶ This oil concentration is small relative to even dilute emulsions and these regulations are expected to become more stringent like those already implemented in Canada requiring less than 5 ppm of oil.³ Even when bilge water discharge limitations are satisfied or exceeded, ecological threats including mortality to marine organisms are still present.¹¹⁷ The release of oils and surfactants into the ocean also deliver sublethal risks to the marine environment, the effects of which can be seen for more than six years.¹¹⁸ These environmental risks make it apparent that the release of both oils and surfactants present in bilge water emulsions must be mitigated. Since emulsions are thermodynamically unstable, several instability mechanisms can be employed to separate emulsified oil from water like gravitational separation, flocculation, Ostwald ripening, and coalescence.^{83,119}

Coalescence is arguably the most important instability mechanism to consider for wastewater treatment because it is irreversible without a significant energy input while both flocculation and gravitational separation can be easily reversed by minor disturbances to the emulsion system.^{83,120} For example, the rocking motion of a ship or the flow and pumping of water can break apart flocs and disperse oil droplets. For coalescence to be reversed, an energy proportional to the product of interfacial tension and interfacial area must be provided to break apart a droplet into multiple.¹¹³ Therefore, in many situations, coalescence is preferred to sufficiently separate oil from water.

Driving coalescence is the reduction in the interfacial area and free energy that occurs when two droplets combine.¹⁰⁷ For coalescence to occur in surfactant stabilized emulsions, the energy barrier created by the surfactant must be surpassed to allow the merging of droplets. Film drainage occurs as neighboring droplets approach one another until a critical film thickness is achieved (~ 100 nm) after which, film rupture may occur.¹⁰⁷ However, film drainage can stop once a balance of attractive and repulsive forces between droplets is achieved. This typically occurs at smaller separations between droplets where repulsive steric and hydration forces become relevant.^{107,108,121–127} Film rupture occurs due to the presence of vacancies or holes in the interfacial film created by thermal and mechanical fluctuations of the surfactant molecules at the interface.^{121,128} In many systems, surfactant with fast adsorption kinetics can quickly fill vacancies and prevent film rupture and subsequent coalescence.^{108,129} An interface more densely populated with surfactant molecules can also reduce coalescence by decreasing the probability of vacancy formation.¹²⁸

To promote coalescence for oil separation, some techniques suggest the addition of salts to decrease emulsion stability.^{33,130,131} Salts shield surface charges and reduce the electrostatic repulsion and energy barrier between droplets.¹¹² This allows droplets to approach each other more closely, promoting flocculation and in some cases coalescence. It is frequently concluded that salt decreases the stability of an emulsion, specifically those stabilized by ionic surfactants.^{86,115,132–135} However, while salt increases flocculation, an increase in coalescence is not always observed in all emulsions.^{128,136} For example, van Aken et al. showed that the addition of NaCl to sodium dodecyl sulfate (SDS)-stabilized emulsions led to an increase in aggregation while reducing coalescence over a 24 hour period.¹²⁸

This study investigates the impact of salts on the stability to coalescence of a model oil-in-water emulsion. In this chapter, the term 'emulsion stability' is in reference to coalescence. To address increasing concerns of oily wastewaters contaminating marine environments, our model emulsion aims to replicate a similar yet simplified chemistry to those found in bilge water systems. Sodium lauryl ether sulfate (SLES) was used as a model anionic surfactant that is commonly found in detergents and similar to surfactants used in bilge water studies.^{15,21,25,132} Mineral oil was used as the oil phase to represent common lubricating oils that exist in bilge water. Salt chemistries and concentrations were chosen to represent seawater and seawater-freshwater mixtures.³¹ Higher salt

concentrations than those found in seawater were also used to provide a more fundamental understanding of salt's impact on emulsion stability and to test the strategy of adding salts for bilge water treatment. Emulsions were characterized by droplet size measurements over the course of 56 days, zeta potential measurements, interfacial techniques (interfacial tensiometry, surfactant adsorption kinetic measurements, and oscillating droplet tensiometry), and DLVO calculations. Together, these experimental techniques and calculations provide a comprehensive understanding of the impacts that salt can have on the stability of emulsions and, specifically, on the adsorption mechanisms and kinetics of surfactant at oil-water interfaces.

2.2: Materials and Methods

2.2.1: Materials

Emulsions were made with deionized (DI) water (Barnstead Nanopure Infinity, 18 Mohm·cm resistivity) as the continuous phase and heavy mineral oil (Sigma Aldrich) as the dispersed phase. Emulsions were stabilized by sodium lauryl ether sulfate (SLES, STEOL CS-170 UB, Stepan Co.) $(C_{12}H_{25} \cdot OC_{2}H_{4} \cdot SO_{4} \cdot Na, M_{w} = 332.4 \text{ g/mol})$. Sodium chloride (Sigma Aldrich) or magnesium chloride (Sigma Aldrich) were used to increase the ionic strength of the emulsions.

2.2.2: Emulsion Composition and Fabrication

All emulsions contained 500 ppm (1.50 mM) surfactant (SLES) and 5000 ppm (0.5 wt. %) mineral oil (surfactant to oil ratio (S/O) of 0.1). Emulsions were made in DI water and saltwater solutions. Emulsions made with DI water had no added salt and will be referred to as 0 M emulsions. While the addition of SLES adds sodium ions to solution, the ionic strength contributed by the surfactant is negligible (~0.00075 M at 500 ppm surfactant assuming 50% ionization¹³⁷). Concentrations of NaCl were selected to represent the 0.42 M NaCl concentration in substitute ocean water (ASTM D1141-98) as well as dilutions of this (0.05 and 0.21 M). A concentration of 0.42 M MgCl₂ was also used to study the impact of valency and ionic strength on emulsion properties. A concentrated solution of 1.25 M NaCl was also used to study the impact of valency and ionic strength of valency at an equivalent ionic strength to 0.42 M MgCl₂. Each component of the emulsion was added to a 50 mL centrifuge tube

(Corning, Centristar) to make an emulsion with a total volume of 15 mL. Salt was added to the aqueous solution before emulsification. Prior research has shown that the salt order-of-addition does not change the resulting emulsion stability but would need further investigation to confirm this.¹¹⁵ A high shear mixer (VWR, VDI 25 Homogenizer) was used for emulsification at a rate of 24000 rpm for 60 seconds. The centrifuge tubes were placed in a water bath during emulsification to minimize temperature increases. After emulsification, the emulsions were aged for approximately 90 min, 5 days, 10 days, 20 days, and 56 days. Emulsions were made in triplicate for each composition and age.

2.2.3: Optical Microscopy

A rectangular, borosilicate capillary tube (VitroCom, Cat. # 3524) was used to collect emulsion samples via capillary action. These capillaries were then sealed using an epoxy resin to reduce evaporation. Optical micrographs (Olympus BX41 equipped with AM Scope camera and software) were taken at 90 minutes (labeled as 0 days) and 20 days.

2.2.4: Laser Diffraction

Laser diffraction (Malvern Mastersizer 3000) was used to measure emulsion droplet volume size distributions using Mie theory. Before measuring droplet size, emulsions were aged for approximately 90 minutes to remove air bubbles formed during the emulsification process. After aging, the emulsions were gently agitated by hand to reverse any segregation of droplets caused by gravity. Once the droplets were evenly dispersed, a sample of the emulsion was pipetted into the dispersion unit of the Mastersizer. DI water was used as the dispersant for all laser diffraction measurements. Experiments were also done with dispersants that matched the continuous phase of the emulsion (e.g., 500 ppm surfactant), but there were no measurable differences between these measurements and ones using DI water. This suggested that any effects due to solvent shock did not play a significant role in droplet size at the time scales of the measurements (minutes). A stirrer speed of 1500 rpm was used to circulate the sample through the measurement cell without emulsifying and reducing droplet size. Five measurements were made for 10 seconds each. This process was repeated in triplicate for each composition and age. Volume mean diameters (D_{4,3})

and volume size distributions are reported as an average of three different samples for a total of 15 measurements.

2.2.5: Zeta Potential

Zeta potential measurements were made at approximately 90 minutes of aging for each emulsion with a Malvern Zetasizer Nano ZS using the Smoluchowski equation. Zeta potential was measured over the 56-day aging period but did not vary outside of the 0-day standard deviation. Emulsion sampling for zeta potential measurements followed the same procedure as for laser diffraction. Values are reported as the averages of three or more measurements with an error of one standard deviation.

2.2.6: Interfacial Tension and Surfactant Adsorption Kinetics

Interfacial tension (IFT) measurements were performed using pendant drop tensiometry using a DSA30 (KRÜSS Inc., Germany). KRÜSS Advance software was used to calculate the IFT by fitting the Young-Laplace equation to the droplet profile which has been described elsewhere.^{138,139} Aqueous droplets were formed in a glass cuvette filled with mineral oil. For IFT measurements, salt concentrations of 0, 0.005, 0.05, 0.21, 0.30, 0.42, 0.50, 0.60, 0.84, 1.0, and 1.25 M NaCl and 0.42 M MgCl₂. To ensure accuracy, droplets were formed as large as possible without detaching from the needle¹³⁸ and the dimensionless shape factor, β , always exceeded 0.4 as recommended by the manufacturer. This shape factor represents the ratio between drop deformation due to gravity and the interfacial tension.¹⁴⁰ Dynamic IFT measurements were recorded until an equilibrium in surfactant adsorption was obtained. This was repeated in triplicate for each sample and the equilibrium IFT are reported as an average IFT for three separate droplets. Error bars represent the accuracy of the tensiometer (0.3 mN/m) because the standard deviation between measurements was less than the accuracy of the machine.

Dynamic IFT measurements were performed at shorter timescales (up to 300 seconds) with higher measurement resolution (10 measurements per second). Drops between 2 and 10 μ L were dispensed rapidly (15 μ L/s) using needle sizes between 0.518 and 1.825 mm in diameter to resolve the early time dynamic IFT. For solutions containing 0, 0.0005, 0.05, 0.21, 0.42, 0.60, 0.84, 1.00,

and 1.25 M NaCl, a droplet volume of approximately 10, 10, 10, 10, 8, 3.5, 3.5, 3.0, and 2.0 μ L was used, respectively. Smaller drop volumes were used for systems with relatively low IFTs (< 3 mN/m) to prevent the drop from detaching from the needle. IFT kinetics are independent of drop size for millimeter-scale drops and this effect is more pronounced at higher surfactant concentrations (e.g. > 100 ppm).¹⁴¹ Therefore, the differences in drop volume between experiments is not expected to play a significant role in measuring the surfactant adsorption kinetics. To confirm this, dynamic IFT tests were conducted for 0.84 M NaCl samples using 3.5 and 6 μ L drops and 0.60 M NaCl samples using 1.5 and 3.5 μ L drops and no significant difference in surfactant adsorption kinetics were observed (see **Figure A1** in **Appendix A**).

2.2.7: Interfacial Rheometry

Interfacial rheometry measurements were made using a Ramé-Hart tensiometer equipped with an automated drop volume dispenser, motor-driven oscillator, and DROPimage Advanced software. The interfacial viscoelastic properties were calculated using **Equation 2.1** which relates the complex surface dilatational modulus (E^*), the elastic storage modulus (E'), and the viscous loss modulus (E'') each of which are dependent on the oscillation frequency (f). The storage and loss moduli are calculated using the amplitude in IFT ($\Delta \gamma$), the amplitude in surface area (ΔA), the initial surface area (A_0), and the phase shift or loss angle (φ) between the area oscillation and IFT response.^{142–144}

$$E^* = E' + iE'' = \frac{\Delta\gamma}{\Delta A/A_0} \cos\varphi + i\frac{\Delta\gamma}{\Delta A/A_0} \sin\varphi$$
(2.1)

From the elastic and viscous moduli, the interfacial dilatational modulus (*E*) can be calculated using Equation 2.2.^{145,146}

$$E = \sqrt{E'^2 + E''^2}$$
(2.2)

Droplets were brought to their equilibrium IFT before harmonically oscillating them at frequencies of 0.01, 0.05, and 0.1 s⁻¹ with relative area amplitudes ($\Delta A/A_0$) between 6 and 14%. Low oscillation frequencies, together with small changes in the area amplitude, ensured mechanical equilibrium of the system.^{140,147} Drop sizes were between 2 and 2.5 mm in diameter at the apex and had a shape factor between 0.3 and 0.5. Viscoelastic responses to oscillations were not purely dilatational but also had a shear component that was not accounted and is a limitation in these measurements.^{148,149} Each oscillation experiment was performed in triplicate.

2.2.8: Extended DLVO Theory

Classical DLVO theory and an extended DLVO theory including hydration repulsion were used to calculate the interaction energies between mineral oil droplets in water and saltwater. Classical DLVO theory uses the sum of the van der Waals attraction (W_{vdW}) and electrostatic repulsion energies ($W_{electro}$) to calculate the total interaction energy (W) between two spherical particles and is summarized using **Equations 2.3**, **2.4**, and **2.5**:¹¹²

$$W = W_{vdW} + W_{electro} \tag{2.3}$$

$$W_{vdW} = -\frac{Ar}{12D} \tag{2.4}$$

$$W_{electro} = 4.61 * 10^{-11} r \tanh^2 \frac{\Psi}{103} e^{-\kappa D}$$
(2.5)

where A is the Hamaker constant $(4x10^{-21})$; r is the droplet radius; D is the separation distance between the interacting droplets; Ψ is the droplets' surface potential estimated here as the measured zeta potential;¹²² and κ is the inverse Debye length calculated by **Equation 2.6** for a monovalent salt and divalent salt, respectively.¹¹²

$$\kappa = \frac{\sqrt{[NaCl]}}{.304}; \kappa = \frac{\sqrt{[MgCl_2]}}{.176}$$
(2.6)

Hydration forces are not considered in classical DLVO calculations but are important to consider in aqueous systems containing salt and ionic surfactant and where droplets become close together (1 to 4 nm).^{108,112} Hydration repulsion has only been estimated by empirical models and fitted to exponential decay functions.^{112,127} However, Ivanov et al. introduced **Equation 2.7** for the hydration repulsion energy (W_{hydr}) between two deformable droplets:¹⁰⁸

$$W_{hydr} = \pi \gamma [R^2 + r\lambda] * exp(-D/\lambda)$$
(2.7)

where γ is the interfacial energy between the droplet and surrounding fluid, estimated here as the measured equilibrium interfacial tension; λ is the decay constant typically between 0.6 and 1.1 nm^{108,112,150} and estimated here as 0.8 nm; and *R* is the radius of the thin film between the droplets created by the flattening of the droplets when approaching each other. The film radius can be estimated by the external forces (non-interaction forces) pushing the droplets together (*F*) and their interfacial energies using **Equations 2.8** and **2.9**.¹⁰⁸

$$R^2 = \frac{Fr}{2\pi\nu} \tag{2.8}$$

The external force acting on the droplets can be estimated by the buoyancy force which represents droplets in the creamed layer of an emulsion:

$$F = \Delta \rho g V_d \tag{2.9}$$

where $\Delta \rho$ is the density difference between the droplet and continuous phase; *g* is the acceleration due to gravity; and *V_d* is the volume of a droplet.¹⁰⁸ Calculating the total interaction energy using extended DLVO theory then be written as **Equation 2.10**.

 $W = W_{vdW} + W_{electro} + W_{hydr}$

(2.10)

2.3: Results and Discussion

2.3.1: Emulsion Stability

Figure 2.1A and **Figure 2.1B** show the mean droplet size (volume mean diameter, D(4,3)) and percent change in diameter for each salt concentration from 0 to 56 days, respectively. Individual droplet size distributions for each composition and time can be found in **Figure A2** of **Appendix A.** Salt-free emulsions displayed a significant decrease in droplet size after 10 days of ageing due to droplet coalescence and migration beyond the detection window, displaying a known limitation of laser diffraction measurements.^{83,115} **Figure 2.2** shows millimeter-sized oil drops at the surface of the salt-free emulsion after 56 days, clear evidence that droplet diameter decreases in **Figure 2.1A** were caused by the coalescence and creaming of larger drops, leaving behind only the smaller droplets. This conclusion is supported by the optical micrographs in **Figure 2.3** which show the disappearance of large droplets after 20 days.



Figure 2.1: (A) Volume mean droplet diameter (D(4,3)) for emulsions containing 0, 0.05, 0.21, 0.42, and 1.25 M NaCl and 0.42 M MgCl₂ between 0 (90 minutes) and 56 days of aging. (B)
Percent increase in droplet diameter (D(4,3)) from the initial size 90 minutes after emulsification. Error bars represent one standard deviation from the mean.

The initial droplet size (0 days) decreased as salt increased from 0 to 0.05 M NaCl. This was likely due to a decrease in IFT when salt was added,^{115,134} allowing for the formation of smaller droplets for a given emulsification energy density. Increasing the salt concentration above 0.05 M NaCl led to an increase in the 0-days droplet size and this behavior was likely due to coalescence within the first 90 minutes^{86,115,134} until the surface concentration at the interface (i.e., the surface load, Γ) reached equilibrium.¹⁵¹ The addition of salt reduced the electrostatic repulsion between anionic surfactants resulting in more surfactant adsorption at the interface (larger Γ). The minimum droplet size (*d*) and the surface load are directly proportional ($d = \frac{6\varphi\Gamma}{c}$).^{83,151} Therefore, the minimum droplet size that could be formed increased (i.e., the maximum oil-water interfacial area was reduced) with salt as the oil volume fraction (φ) and surfactant concentration (*C*) were constant. Once sufficient surfactant adsorption was achieved, further coalescence was prevented indicated by the plateau after 20 days for high salt concentrations (≥ 0.21 M) in **Figure 2.1**.

To observe the relative changes in droplet size with time for each composition, volume mean diameters were normalized by their respective initial droplet size to obtain a percent change in

diameter and can be seen in **Figure 2.1B**. As salt concentration and valency increased, the total change in droplet diameter from 0 to 56 days decreased. Emulsions containing 0.05 M NaCl showed the largest increase in droplet size (331%, 6.96 to 30.0 μ m) while 0.42 M MgCl₂ showed the smallest increase in droplet size (11.6%, 23.6 to 26.3 μ m). Although the droplet size increased significantly for 0.05 M NaCl, **Figure 2.2** shows that the addition of small salt concentrations significantly reduced the amount of mm-sized coalesced oil drops at the surface of the emulsion when compared to salt-free emulsions. Increases in droplet size for these emulsions were likely the result of coalescence indicated by the multimodal size distributions seen in **Figure A2**.^{83,152}

At 1.25 M NaCl there was a large positive change in droplet size at 20 days followed by a reduction at 56 days. Droplet size distributions in **Figure A2** show that this large increase can be explained by the peaks that appear between 100 and 300 μ m starting at 5 days of aging and are likely due to the formation of aggregates rather than the coalescence of droplets. Aggregate formation was likely due to the coagulation of droplets, in contrast to weaker flocculation, promoted by the high salt concentrations and could not be separated during measurement.^{112,120} Optical micrographs in **Figure 2.3** show an increase in the aggregation number and, therefore, aggregate size (~100 to 200 μ m) for 1.25 M NaCl due to the salt's reduction of the electrical double layer thickness^{112,115,153} but shows no significant change in the individual droplet sizes. In the presence of a divalent salt (0.42 M MgCl₂), the emulsion droplet size showed little change over time and were similar to the 1.25 M NaCl emulsions which had an equivalent ionic strength. Additionally, at high salt concentrations (\geq 0.21 M NaCl), **Figure 2.2** shows that macroscopic coalescence was not observed, and only creamed oil droplets were present at 56 days. Optical micrographs of all emulsions at 0 and 20 days can be found in **Figure A3** and **Figure A4** of **Appendix A**.



Figure 2.2: Top view looking down at the emulsion surface after 56 days of aging. Salt-free emulsions contain large, coalesced oil droplets in the center of the image. Emulsions containing 0.05 M NaCl show a significant reduction in coalesced oil droplets at the surface and higher salt concentrations do not show any macroscopic coalescence. The white circles in the center of 0.42 and 1.25 M NaCl samples are the bottoms of the centrifuge tubes.



Figure 2.3: Optical micrographs for emulsions containing 0 and 1.25 M NaCl at 0 (90 minutes) and 20 days after emulsification. The droplet-free streaks in the 1.25 M NaCl micrographs are an artifact of sample preparation and display the aggregates' creaming path within the capillary tube due to their larger effective size.

From the emulsion stability data, it can be concluded that salt-free emulsions are unstable to coalescence after 20 days and that the addition of salt improves the emulsion's stability to coalescence up to 56 days. As the concentration and valency of salt increased, emulsion stability to coalescence also increased and little to no coalescence was observed at the highest ionic strengths tested. These emulsion stability results hold true for longer time periods (e.g., 455 and 700 days) and can be found in **Figure A5** and **Figure A6** of **Appendix A**. While salt reduced coalescence events, flocculation, aggregation, and creaming were still observed. For the emulsion stability tests described above, salt was added to the aqueous solution before emulsification. Adding salt after emulsification is not expected to change the emulsion stability observed here and is a characteristic of the salt and not the order of addition.¹¹⁵ To explore possible mechanisms for the increased stability to coalescence in the presence of salt, these emulsion systems were characterized by interfacial tensiometry, zeta potential measurements, surfactant adsorption kinetic measurements, and oscillating droplet tensiometry in the following sections.

2.3.2: Interfacial Surfactant Packing

To better understand the surfactant packing at the interface, equilibrium interfacial tension (γ_{eq}) and zeta potential were measured. **Figure 2.4A** shows the impact of ionic strength on γ_{eq} between oil and water containing surfactant. **Figure 2.4B** shows the 0-day zeta potential of the emulsion droplets studied in the previous section. Increasing the NaCl concentration decreased γ_{eq} ^{49,134,154} and the rate of change in γ_{eq} decreases. A plateau in γ_{eq} was achieved at approximately 0.5 M NaCl as this was within the measurement precision (0.3 mN/m) of the minimum γ_{eq} measured (1.0 M NaCl). This plateau in γ_{eq} indicates that the interface approaches a maximum in the surfactant packing at ionic strengths > 0.42 M. The γ_{eq} of 0.42 M MgCl₂ was similar to 0.42 M NaCl suggesting that γ_{eq} was more dependent on NaCl concentration than valency.

Zeta potentials of emulsion droplets were also reduced due to the screening provided by the salt ions. Without salt, a large, negative zeta potential was measured due to the dissociation of sodium ions from SLES. This negative charge acted to repel the surfactant molecules from each other and reduce their packing density at the interface. Salt screened the electrostatic repulsion between charged surfactants (indicated by the reduction in zeta potential), allowing the head groups to pack more densely at the interface (i.e., reducing γ_{eq}).^{49,154–156}



Figure 2.4: (A) Impact of ionic strength on equilibrium interfacial tension (γ_{eq}) between mineral oil and water containing 500 ppm SLES and (B) zeta potential for mineral oil droplets stabilized by 500 ppm SLES at 0 days. Error bars for IFT measurements represent the precision of the tensiometer (0.3 mN/m). Error bars for zeta potential measurements represent one standard deviation from the mean.

The data in **Figure 2.4** indicates that salt increased the amount of surfactant adsorbed at the oilwater interface. An increase in surfactant adsorption at the interface of emulsion droplets can increase their stability to coalescence.^{146,157,158} However, this was unlikely to be the only acting mechanism for enhanced stability as interfacial tension and surfactant adsorption are not always correlated with emulsion^{115,132–134} and film stability^{155,159}. Therefore, we investigated the surfactant adsorption kinetics and viscoelasticity of the oil-water interface to display additional mechanisms for the observed emulsion resistance to coalescence.

2.3.3: Surfactant Adsorption Kinetics

Surfactant adsorption kinetics at the oil-water interface were measured for solutions with and without NaCl. The initial IFT decay within 20 seconds after drop formation is shown in **Figure 2.5A** and **Figure 2.5B** for low (0 to 0.21 M NaCl) and high (0.42 to 1.25 M NaCl) salt concentrations, respectively.



Figure 2.5: Dynamic interfacial tension for (A) salt-free to 0.21 M NaCl and (B) 0.42 to 1.25 M NaCl aqueous solutions containing 500 ppm SLES against mineral oil. Dotted black line represents the equilibrium interfacial tension for 0.42 M NaCl.

As the concentration of salt increased, greater IFT decay rates likely due to accelerated surfactant adsorption were observed. An example of this can be seen in **Figure 2.5B** at γ_{eq} for 0.42 M NaCl, represented by the dotted black line. As the concentration of NaCl increased from 0.42 M to 1.25 M, less time was needed for each solution to achieve the same IFT which corresponds to approximately the same surfactant adsorption. Divalent salt (0.42 M MgCl₂) had a similar effect on surfactant adsorption as an equivalent concentration of NaCl. This suggests that SLES adsorption kinetics were more dependent on salt concentration than ionic strength which was also observed for γ_{eq} values in **Figure 2.4A**.

Faster surfactant adsorption in the presence of salt can be explained by the effective thinning of the electrical double layer by the salt ions. For a salt-free system, the adsorbed anionic surfactant molecules created a negatively charged interface that repelled other negatively charged surfactant molecules. This effectively reduced the concentration of surfactant near the interface and reduced adsorption kinetics.¹⁶⁰ When salt was added, the negatively charged surface adsorbed positive ions and the electrical double layer decreased in thickness. This increased the surfactant concentration near the interface and therefore, faster adsorption kinetics were observed.^{154,161,162} Furthermore, the addition of salt reduces the solvent quality, "salting-out" the surfactant molecules and driving them to the interface.^{163,164}

Dynamic IFT results in **Figure 2.5** are valuable for qualitatively comparing the impact of salt concentration on surfactant adsorption. However, the quantitative IFT decay timescales may not be broadly applicable to all emulsions because the droplet sizes in many emulsions are typically much smaller (micrometer-scale) than the drop size used for dynamic IFT measurements (millimeter-scale). For emulsions in the micrometer size range, the IFT decay would occur more rapidly because of the decreased diffusion boundary layer thickness. A study by Chen and Dutcher¹⁴¹ showed that surfactant adsorption timescales can increase by one to two orders of magnitude when the droplet size reduced from ~2 mm to ~80 μ m using a simulated bilge water detergent mixture.

Results from surfactant adsorption kinetics reveal additional mechanisms responsible for the observed increase in emulsion stability with salt. Faster surfactant adsorption increased the resistance to interfacial tension gradients (i.e., Marangoni effects) that prevent film drainage and create what is termed a less mobile interface.^{108,158,165} Faster surfactant adsorption can better adapt to deformations at the interface and quickly eliminate vacancies in the interfacial film, thus hindering coalescence.^{128,129}

2.3.4: Interfacial Viscoelasticity

The dilatational, elastic, and viscous moduli of the oil-water-surfactant interface were measured to identify how salt impacts the interfacial viscoelasticity, or the resistance of the interface to expansion, and are shown **in Figure 2.6A** and **Figure 2.6B**. **Figure 2.6A** shows the dilatational

modulus (*E*) at oscillation frequencies between 0.01 and 0.1 s⁻¹ for 500 ppm SLES solutions without salt, with 0.42 M NaCl, and with 0.42 M MgCl₂. As the oscillation frequency increased, the moduli increased linearly on a log-log scale. **Figure 2.6B** shows the elastic and viscous moduli at a frequency of 0.1 s⁻¹ for different ionic strengths. For all three samples, the viscous moduli are greater than the elastic moduli and were reduced with added salt and valency. Values for all elastic, viscous, and dilatational moduli can be found in

Table A1 of **Appendix A**.



Figure 2.6: (A) Dilatational modulus (*E*) at oscillation frequencies of 0.01, 0.05, and 0.1 s⁻¹ for the mineral oil-water interface using 500 ppm SLES and 0 M, 0.42 M NaCl, and with 0.42 M MgCl₂. Dashed lines represent a curve fit using Equation 6. (B) Elastic (*E'*) and viscous (*E''*) moduli of SLES as a function of ionic strength at a frequency of 0.1 s⁻¹. Lines are used to guide the eye. Error bars represent one standard deviation from the mean.

The dilatational moduli followed the scaling law relationship (plotted as dotted lines) in **Equation** 2.11 where f is the oscillation frequency and n is the relaxation exponent.

(2.11)

The relaxation exponent and the theoretical loss angle have the relationship described in **Equation 2.12** for a critical gel.^{146,166,167}

$$\varphi = n\frac{\pi}{2} \tag{2.12}$$

Equation 2.13 was used to calculate the loss angles from the elastic and viscous moduli and are reported in **Table 2.1**.^{146,166,167}

$$\varphi = \tan^{-1} \frac{E'}{E''} \tag{2.13}$$

Table 2.1 shows the measured and theoretical loss angles using **Equations 2.13** and **2.12**, respectively. As the oscillation frequency increased, there were no apparent trends in the measured loss angle over the limited frequency range that was studied. The measured loss angles were similar to the theoretical loss angles for each salt concentration.

Table 2.1: Values of measured loss angles (Equation 2.13) and theoretical loss angles (Equation 2.12) at different oscillation frequencies for the oil-water interface using 500 ppm SLES and 0 M (salt-free), 0.42 M NaCl, and 0.42 MgCl₂. Error represents one standard deviation from the

	Loss Angle, φ (°)		
Frequency (s ⁻¹)	0 M (Salt-Free)	0.42M NaCl	0.42M MgCl ₂
0.01	50.4 ± 0.11	64.3 ± 0.14	58.6 ± 0.063
0.05	53.9 ± 0.042	64.1 ± 0.035	61.3 ± 0.035
0.1	52.2 ± 0.024	59.6 ± 0.033	59.9 ± 0.036
Average <i>φ</i>	52.2 ± 1.75	62.7 ± 2.7	59.9 ± 1.4
Theoretical φ	54.0	65.7	63.0

Equations 2.11 and **2.12** were originally used to describe a gel near its gelation point^{166,168}, and have since been used to characterize the low frequency interfacial rheology of asphaltene^{146,167} and soluble nonionic surfactant¹⁶⁹ at an oil-water interface. A system that follows **Equations 2.11** and **2.12** exhibits gelation point behavior and, therefore, the system studied here has the rheological characteristics of a critical gel.

The relaxation exponent calculated using **Equation 2.11** provides useful information when characterizing the viscoelastic properties of an interface. As relaxation exponents exceed 0.5 and approach a value of one, viscous behavior is expected to dominate over elastic behavior at low frequencies^{145,166} and is in agreement with the results presented in **Figure 2.6B**. The dilatational moduli shown in **Figure 2.6A** indicate that systems containing salt have larger relaxation exponents than salt-free systems (e.g., $n = 0.73 \pm 0.03$ for 0.42 M NaCl and $n = 0.60 \pm 0.01$ without salt).

It has also been shown that larger relaxation exponents correspond to more frequent interactions between surfactant molecules at the interface.¹⁶⁹ More surfactant adsorption should lead to an increase in the dilatational modulus.^{169,170} This interpretation partially agrees with our results because systems with added salt (larger relaxation exponent) contained more adsorbed surfactant at the interface compared to salt-free systems (lower relaxation exponent) as displayed by the IFT data in **Figure 2.4**. Although surfactant-surfactant interactions at the interface were more frequent in the presence of salt, **Figure 2.6** shows that salt decreased the moduli. A decrease in the dilatational modulus is likely due to a competing effect in which salt increases the rate of surfactant adsorption leading to a decrease in the dilatational modulus at low oscillation frequencies.^{162,169–171} This is also in agreement with our results that show an increase in the rate of surfactant adsorption with salt (see **Figure 2.5**). When the surfactant adsorption rate is faster than the oscillation frequency, interfacial tension gradients ($\Delta \gamma$) are dissipated quickly by the adsorbed surfactant, thus lowering the dilatational modulus.^{172,173} From the results in **Figure 2.6**, we can conclude that the surfactant adsorption kinetics dominated the behavior of the interfacial viscoelasticity at the frequencies tested (0.01 to 0.10 s⁻¹).

Previous studies have shown that the low-frequency ($< \sim 1 \text{ s}^{-1}$) modulus decreases with increasing surfactant concentration (i.e., increasing film stability) whereas the high-frequency ($> \sim 1 \text{ s}^{-1}$)

modulus increases.^{172,173} Emulsion stability to coalescence is better represented by high-frequency oscillations as coalescence events occur in less than a millisecond.^{144,171} As the oscillation frequency increases, a crossover in the dilatational modulus between the salt-free and 0.42 M systems is expected so that the systems containing salt have a larger modulus than the salt-free system. This crossover would likely occur when the oscillation frequency is larger than the surfactant adsorption rate. This further supports why systems containing salt experience a greater resistance to coalescence because at high oscillation frequencies, like those experienced during coalescence, surfactant-covered interfaces containing salt are expected to have larger dilatational moduli.

Past studies have correlated improvements in emulsion stability with increases in the interfacial viscoelasticity.^{174–176} However, many emulsion systems have not exhibited a positive correlation between emulsion stability and interfacial viscoelasticity.^{129,144,146,157,177} Additionally, previous studies have observed that a more flexible interface (i.e., lower dilatational modulus) allows for the formation of a flat interfacial film between two approaching droplets which leads to an improved resistance to coalescence.^{108,165} As discussed in this section, a decrease in the dilatational modulus does not imply that the interface is more susceptible to coalescence.

2.3.5: Extended DLVO Analysis

We have observed that salt improves emulsion stability to coalescence due to an increase in surfactant adsorption and faster adsorption kinetics. However, salt increased flocculation and aggregation (see **Figure 2.3**, **A2**, and **A3**) which would increase the probability of droplet-droplet collisions and therefore coalescence. To further analyze this observed behavior, DLVO theory was used to calculate the interaction energy between two oil droplets as a function of their separation distance. DLVO calculations are useful in modeling the expected droplet-droplet separation distance and interactions that promote flocculation and aggregation. However, these calculations do not always determine droplet coalescence^{119,122} and are only used as an approximation to compare between different systems. There are several limitations to classical DLVO calculations that must be considered like short range, repulsive interactions including steric and hydration forces.^{108,122–127} Hydration forces occur between two hydrophilic surfaces separated by a thin layer

of ordered and strongly bound water.^{112,123} Therefore, we considered classical DLVO theory together with an extended DLVO theory that included hydration repulsion and compared the two.

Figure 2.7A and **Figure 2.7B** show the interaction energy (W) in units of thermal energy (kT) at room temperature (298 K) as a function of the distance between droplets (D) normalized by the Debye length (κ^{-1}) without and with the inclusion of hydration forces, respectively. Interaction energies were calculated at salt concentrations of 0.00075 (salt-free), 0.21, 0.42 and 1.25 M NaCl, and 0.42 M MgCl₂. Zeta potentials for each system were used as an approximation of the surface potential.¹²² The calculated Debye lengths are reported in the caption of **Figure 2.7**.



Figure 2.7: Interaction energy (kT) between two mineral oil droplets stabilized by SLES as a function of separation distance (D) normalized by the Debye length (κ^{-1}) for (A) classical DLVO theory, and (B) extended DLVO theory including hydration forces. A droplet size of 1 μ m was used for all calculations and the surface potential was approximated as the zeta potential. A Hamaker constant of 4x10⁻²¹ was used for all calculations. The Debye lengths were calculated to be 11.1, 0.663, 0.469, 0.272, and 0.271 nm for 0, 0.21, 0.42, 1.25 M NaCl and 0.42 M MgCl₂, respectively.

Both classical and extended DLVO theories predict that salt-free systems have a relatively large electrostatic repulsion barrier that begins repelling at separation distances of approximately 100 nm (D/ κ^{-1} ~9.0). However, this is still within the critical film thickness necessary for film rupture

and coalescence (~100 nm),¹⁰⁷ meaning that coalescence can still occur. It is important to note that the droplet size does not change the distance at which droplet-droplet repulsion begins and is only controlled by the salt concentration and surface potential for classical DLVO calculations. Similarities between calculations with and without hydration forces show that these short-range interactions do not significantly impact the droplet-droplet interaction energy in salt-free systems with highly charged (100 mV) surfaces.

DLVO calculations also show that salt and valency decrease the repulsive energy barrier (maximum *W*). For classical DLVO calculations (**Figure 2.7A**), ionic strengths of 1.25 M (e.g., 1.25 M NaCl and 0.42 M MgCl₂) exceed the critical coagulation concentration (CCC) and rapid coagulation is expected.¹¹² At salt concentrations above the CCC, one would expect to observe coalescence between oil droplets with interfaces containing little or no adsorbed surfactant. However, we have shown in previous sections that at high salt concentrations, the oil-water interface contains a layer of close packed surfactant molecules that prevent coalescence. Furthermore, repulsive hydration forces are not included in this calculation but are important to consider for ionic surfactants, high salt concentrations, and small separation distances (1 to 4 nm).^{112,124,125,158,178} When including hydration forces in extended DLVO calculations (**Figure 2.7B**), a repulsive energy barrier is present for high ionic strengths. This displays how hydration forces dominate the droplet-droplet interactions at small separations and high salt concentrations.

Extended DLVO calculations in **Figure 2.8** show that salt can reduce the electrostatic repulsion enough for droplets to approach each other within several nanometers. For example, droplets that are 1 μ m in diameter and contain 0.21 and 0.42 M NaCl begin experiencing repulsion at approximately 4.2 nm (7.2 nm for a 100 μ m droplet) and 3.6 nm (7.2 nm for a 100 μ m droplet), respectively. Compare this to a system that is salt-free or contains 0.05 M NaCl, both of which were unstable to coalescence (see **Figure 2.2**), which experience repulsion at approximately 100 nm (also 100 nm for a 100 μ m droplet) and 8.5 nm (8.8 nm for a 100 μ m droplet), respectively. This shows that increasing salt concentration and reducing droplet-droplet separation creates conditions favorable for the formation of a stable Newton black film (NBF) between two droplets. The formation of a NBF has been discussed in emulsion^{128,136} and foam^{123,155,179,180} films and demonstrates an improved resistance to coalescence. A NBF requires close packing of surfactant molecules at the interface and forms a surfactant bilayer between the two droplets. critical salt concentration between 0.15 and 0.35 M NaCl has been shown to achieve a NBF in systems with similar surfactants as in the current study.^{123,126,128,178,179,182}



Figure 2.8: Interaction energy (kT) between two mineral oil droplets stabilized by SLES as a function of separation distance (D) at salt concentrations of 0.05, 0.21, 0.42, and 1.25 M NaCl and 0.42 M MgCl₂. Calculated interaction energies include hydration forces (extended DLVO theory).

2.3.6: Implications

Many studies show that salt decreases the stability of oil-in-water emulsions stabilized by ionic surfactants,^{86,115,132–135} nonionic surfactants,^{175,183} proteins,¹²¹ and in the absence of added surfactants.^{30,130} The addition of salt to an emulsion has even been suggested as a method to help flocculate, coalesce, and remove oil from wastewater systems.^{33,130,131} Contrarily, some studies show an increase in emulsion stability with salt^{128,136,184} with some cases being water-in-oil emulsions.^{157,185} It is important to explain our current finding of increasing emulsion stability to coalescence with salt, considering that this result is different from the majority of other emulsion stability studies. To do this, we considered the following five factors: the surfactant-to-oil ratio

(S/O), the interfacial area, the length scales and timescales of observation, and interpretation of data (e.g., interfacial rheometry).

The S/O plays a critical role in the stability of an emulsion and is closely related to the total interfacial area. The recommended minimum S/O to form an emulsion that shows appreciable kinetic stability is 0.1 by mass.⁸⁶ A S/O of 0.1 was used in the current study to ensure enough surfactant was available so that any emulsion instabilities were due solely to changes in salt concentration. If the S/O is sufficiently large, there will be enough surfactant to cover the total interfacial area of an emulsion for a given oil droplet size, and this emulsion will have improved stability to coalescence. A decrease in droplet size increases the interfacial area and thus a higher S/O is needed for surfactant to cover the interface. If the S/O is too small, the resulting emulsion system will be unstable to coalescence regardless of surfactant type or salt concentration. Additionally, salt plays a critical role in the S/O needed for a stable emulsion. For ionic surfactants like SLES, salt increases the number of adsorbed molecules at the interface. Therefore, with salt, a relatively larger S/O, or a smaller interfacial area (larger droplet size) is needed to achieve maximum interfacial adsorption and an emulsion with improved stability to coalescence. This agrees with our results in that the initial droplet size increased with salt because more surfactant was consumed by the oil-water interface creating larger droplets until sufficient adsorption was achieved to prevent further coalescence.

For example, Church et al.¹³² concluded that a decrease in emulsion stability occurred when adding 0.1 M NaCl to SDS-stabilized and Triton X-100-stabilized emulsions. While emulsions containing salt did in fact phase separate more quickly, emulsions without salt were also unstable to coalescence and phase separated during the ten-day ageing period. This was most likely due to a low S/O of 0.01. After aging, the aqueous phase beneath the bulk oil appeared opaque, suggesting that an emulsion still remained; however, this remaining emulsion was not characterized or discussed.¹³² As coalescence and oil separation occur, the remaining emulsion has a lower interfacial area and the S/O subsequently increases. This means a system that is initially unstable (small S/O) can experience an increase in stability for the remaining emulsion after coalescence and partial phase separation occur. This is very relevant to wastewater systems because the remaining dilute (15 ppm) oil droplets are a major concern and difficult to remove from water,

especially in saltwater environments. This is essentially the biggest issue with wastewater treatments: removal of small, dilute oil droplets.

To the authors' knowledge, the S/O of actual bilge water has not been measured and it is likely to vary significantly over time and between ships. However, we can assume that the S/O eventually becomes sufficiently large to stabilize oil droplets due to the difficulty in emulsified oil removal. Additionally, we can also conclude that as separation processes coalesce emulsified oil and surfactant is released back into the aqueous phase, the remaining emulsified oil will be increasingly difficult to remove do to the increase in the S/O.

Length scales and timescales of observation are also important when interpreting emulsion stability. Here, if only microscale measurements were made (optical microscopy and laser diffraction) without macroscale observations, the presence of large, coalesced drops in Figure 2.2 would have been missed. The same could be true if only the bulk, macroscopic properties are observed. Therefore, all length scales - from nanoscale to macroscale - should be considered when assessing emulsion stability to avoid incorrect or misleading conclusions. Timescales must also be considered as all macroemulsions are only kinetically stable. As mentioned in the previous paragraph, an emulsion can initially be unstable and experience rapid coalescence; however, after this initial period the emulsion can become more stable due to the changes that occurred in the emulsion that can alter the S/O and interfacial area. If emulsion stability is only measured during this initial period, then one may conclude that the overall emulsion is unstable.^{86,115,134} However, the droplets that did not coalesce and phase separate could be increasing in stability as the S/O increases. To reiterate, while an emulsion can in fact be unstable during short timescales (hours to days), this may be misleading if portions of the original emulsion increase in stability over long timescales (weeks). The current study used both microscopic (optical microscopy and laser diffraction) and macroscopic observations over short (90 min) and long (56 days) timescales to fully understand the stability and evolution of the entire emulsion.

Data interpretation is also important when concluding whether an emulsion is stable or unstable, specifically when using interfacial rheometry measurements. Greater interfacial viscoelasticity has been used to explain increases in emulsion^{174–176} and film¹⁷³ stability. A positive correlation between emulsion stability and interfacial viscoelasticity may be true for specific systems, but this

is not always true for other emulsion systems^{129,144,146,157,177} including the system studied here. Additionally, emulsion stability to coalescence is more accurately represented by high frequency (> 10^3 s^{-1})^{144,171} oscillations^{158,172,177,186} that mimic the thermally driven concentration and thickness fluctuations at the interface that are responsible for coalescence.¹⁷³ In cases where emulsion stability is not directly correlated with the interfacial viscoelasticity, interfacial rheometry can still be a valuable tool for characterizing emulsion stability by considering the relaxation exponents and surfactant adsorption kinetics as done herein.

2.4: Conclusions

Salt increased emulsion stability to coalescence over the 56-day aging period for mineral oil-inwater emulsions containing sodium lauryl ether sulfate at a surfactant to oil ratio of 0.1. The following mechanisms were responsible for the observed resistance to coalescence:

- Salt reduced the electrostatic repulsion between sodium lauryl ether sulfate head groups, allowing surfactant molecules to pack more densely at the interface. This decreased the probability of a vacancy appearing at the oil-water interface leading to subsequent coalescence.
- Dynamic interfacial tension measurements showed that salt increased the rate of surfactant adsorption at the oil-water interface. This allowed interfacial tension gradients to restore more quickly during film drainage or during the formation of surfactant vacancies at the droplet surface.
- Salt decreased the dilatational modulus due to the increase in surfactant adsorption rate. This created a more flexible interface that could more easily deform and flatten when two droplets approached each other.
- Calculations using an extended DLVO theory showed that hydration forces become significant in the presence of salt and act to repel droplets at several nanometers of separation. These small separation distances and high salt concentrations created conditions favorable for the formation of a stable Newton black film.

Emulsion stability to coalescence is an important characteristic for creating or breaking an emulsion like in the removal of emulsified oils from bilge water. Observations of emulsions stability are only as precise as the techniques and interpretations used to characterize them. We have shown the importance of data interpretation and the lack of correlation in emulsion stability metrics between emulsion systems with similar chemistries. Emulsions are inherently complex, and their properties and behavior depend not only on chemistry but also the surfactant to oil ratio, interfacial area, length scale of observation, and timescale of observation. Without considering these specific parameters for each system, an emulsion may initially appear unstable but a dilute emulsion with superior stability can still exist in solution. For some systems this may not be concerning and may even be favorable. However, this raises a major concern when trying to remove oil from wastewater systems because the small, dilute (~15 ppm) droplets are difficult to remove and environmentally unfavorable. Our results demonstrate that salt, while sometimes employed to destabilize an emulsion, can at times also enhance an emulsion's stability to coalescence. Thus, oil-in-water emulsions, such as bilge water, may show an increased stability and resistance to oil removal processes in saltwater environments.
CHAPTER 3: IMPACT OF SURFACTANT CONCENTRATION AND TYPE ON O/W EMULSION STABILITY DURING STATIC AND DYNAMIC AGEING

The following chapter contains adapted text and figures with permission from Rina G. Sabatello, **Cole R. Davis**, Kendra A. Erk, John A. Howarter, and Carlos J. Martinez.

3.1: Introduction

The previous chapter studied emulsion stability to coalescence while the emulsions were undisturbed or statically aged.¹¹⁶ However, most wastewater systems are not static for long time periods and are often pumped and transported. For example, bilge water would experience mixing due to the ship movement caused by the ocean waves. This mixing, or dynamic ageing, can create different ageing conditions than static ageing and is important to consider when observing emulsion stability.

Mechanical agitation and liquid flow of an emulsion can either induce coalescence or emulsify and break apart droplets. Coalescence can be caused when the fluid motion increases dropletdroplet collisions^{187,188} or due to the differences in creaming velocities between droplets of different sizes.¹⁸⁸ This concept has been utilized to accelerate coalescence for emulsion stability measurements.⁸³ Contrarily, if the fluid motion dissipates enough energy, emulsification can occur leading to a reduction in droplet size.

Several methods have been used to study relatively low energy emulsification methods including wave tank simulators, swirling flask agitators, and baffled flask agitators.^{188–193} These techniques aim to replicate ocean wave movement to study the emulsification of oil slicks with ocean water. When the mixing energy is low (i.e., a non-breaking wave) the oil is emulsified into relatively large droplets greater than 200 μ m in diameter. However, when the mixing energy increases (i.e., a breaking wave), droplets can reduce in size to below 50 μ m in diameter.¹⁸⁹ These droplet sizes are dependent on: the amount of mixing time,^{189,193} oil viscosity,¹⁹⁰ and the surfactant-to-oil ratio (S/O).^{189,193} Of these factors, the S/O is important to understand because this can fluctuate widely (from 0.5 to 0.005) in bilge water studies (see **Section 1.2**: Bilge Water Composition). As

discussed previously, the addition of surfactant reduces the energy needed for emulsification, or in the case of a fixed energy input and oil concentration, reduces the average droplet size.¹⁹³

In this study, the impact of dynamic ageing and the S/O on emulsion droplet size over the course of 20 days was studied. Model bilge water emulsions were created using SLES, heavy mineral oil, and saltwater and emulsified using a high shear mixer. This initial, high energy, emulsification replicated the emulsification of oils prior drainage into the bilge tank (e.g., cleaning processes, pumping, etc.). Emulsions were then aged statically and dynamically to replicate different bilge conditions during ageing. Droplet sizes were monitored via laser diffraction after static and dynamic aging. These experiments provide a better understanding of how the S/O and motion during ageing can influence droplet size over time in bilge water systems.

3.2: Materials and Methods

3.2.1: Materials

Emulsions were made with deionized (DI) water (Barnstead Nanopure Infinity, 18 Mohm·cm resistivity) as the continuous phase and heavy mineral oil (Sigma Aldrich) as the dispersed phase. Emulsions were stabilized by sodium lauryl ether sulfate (SLES) (STEOL CS-170 UB, Stepan Co.) $(C_{12}H_{25} \cdot OC_{2}H_{4} \cdot SO_{4} \cdot Na, M_{w} = 332.4 \text{ g/mol})$. Sodium chloride (Sigma Aldrich) was used to increase the salinity in the aqueous phase.

2.2.2: Emulsion Formation

All emulsions were made with 5000 ppm (0.5 wt%) heavy mineral oil as the dispersed phase. The continuous, aqueous phase contained 0.42 M NaCl to mimic the salinity of seawater and SLES concentrations of 10 (0.03), 100 (0.30), 500 (1.50), and 1000 (3.01) ppm (mM). The total emulsion volume was 15 mL and was emulsified in a 50 mL centrifuge tube using a high shear mixer at 24000 rpm for 60 seconds. The calculated energy density used to form these emulsions was approximately 162 J/mL using **Equations 1.4** and **1.5**.

2.2.3: Emulsion Ageing

After emulsification, some emulsions were statically aged (i.e., without motion) as a control to compare with dynamically aged emulsions. Dynamic ageing was used to replicate shipboard movement at sea. Ships oscillate at sea due to surface waves that have a period frequency between 3 and 60 periods per minute¹⁹⁴ and has been approximated as 14 periods per minute.¹⁹⁵ To replicate this, a nutating rocker (Benchmark BenchRocker 3D) was used to age emulsions at oscillation frequencies of 12 and 30 rpm with tilt angles of 13° and 24°, respectively. A first approximation to the energy density input during dynamic ageing was derived using the kinetic energy of the emulsion falling in the centrifuge tube and can be found in **Equation 3.1**:

$$E_{Dynamic} = \frac{\rho ghNt \cdot sin(\theta)}{30} * 10^{-6} \left(\frac{J}{mL}\right)$$
(3.1)

where ρ is the density of the total emulsion and can be found using the oil volume fraction and oil density, g is the acceleration due to gravity, h is the falling height in the centrifuge tube (77 mm), N is the rocker speed (12 or 30 rpm), and θ is the tilt angle (13° or 24°). Using this approximation, the maximum energy density (i.e., 30 rpm, 24° tilt angle, and 20 days ageing) of a dynamically aged emulsion was calculated to be 0.53 J/mL.

2.2.4: Emulsion Characterization

Emulsion droplet size distributions were measured over time to monitor coalescence and emulsification during ageing. Laser diffraction (Malvern Mastersizer 3000) was used to measure emulsion droplet volume size distributions using Mie theory. Emulsions were aged for 0 (180 minutes), 5, 10, and 20 days before droplet size distributions were measured. After aging, the emulsions were gently agitated by hand to reverse any segregation of droplets caused by gravity. Once the droplets were evenly dispersed, a sample of the emulsion was pipetted into the dispersion unit of the Mastersizer. A stirrer speed of 1500 rpm was used to circulate the sample through the measurement cell without emulsifying and reducing droplet size. Five measurements were made

for 10 seconds each. This process was repeated in triplicate for each emulsion. Volume mean diameters $(D_{4,3})$ and volume size distributions are reported as an average of three different samples for a total of 15 measurements per distribution.

3.3: Results and Discussion

Statically and dynamically aged emulsion droplet size distributions can be seen in **Figure 3.1**, **Figure 3.2**, **Figure 3.3**, and **Figure 3.4** for emulsions containing 10, 100, 500, and 1000 ppm SLES, respectively. Emulsions containing 10 ppm SLES (**Figure 3.1**) were unstable to coalescence under static ageing conditions indicated by the increase in droplet size over time. Dynamic ageing accelerated the coalescence behavior of these emulsions as larger droplet sizes were achieved at earlier times. For example, at 5 days of static ageing, most droplets did not reach a diameter greater than 200 μ m. However, when aged dynamically, many of the droplets exceeded 1000 μ m in diameter after 5 days of ageing. A surfactant concentration of 10 ppm (0.03 mM) or a S/O of 0.002 was not sufficient to prevent coalescence regardless of ageing conditions.



Figure 3.1: Droplet size distributions for emulsions containing 10 ppm SLES aged between 0 (180 minutes) and 20 days under static and dynamic (12 and 30 rpm) conditions. The dotted light grey line represents the initial droplet size distribution. Lines become darker as ageing time increases.

Emulsions containing 100 ppm SLES (**Figure 3.2**) did not show evidence of coalescence over the 20-day ageing period as the droplet size distributions did not change significantly over that time.

However, when dynamically aged at 12 rpm, the droplet size distribution split into larger and smaller droplet diameters indicating coalescence and emulsification, respectively. When the energy of dynamic ageing increased to 30 rpm, more emulsification occurred than coalescence indicated by the large peaks between 0.1 and 2 μ m at 5, 10, and 20 days of ageing. A surfactant concentration of 100 ppm (0.30 mM) or a S/O of 0.02 was sufficient to prevent coalescence during static ageing. However, during dynamic ageing, this surfactant concentration was not sufficient to eliminate coalescence.



Figure 3.2: Droplet size distributions for emulsions containing 100 ppm SLES aged between 0 (180 minutes) and 20 days under static and dynamic (12 and 30 rpm) conditions. The dotted light grey line represents the initial droplet size distribution. Lines become darker as ageing time increases.

Emulsions containing 500 ppm SLES (**Figure 3.3**) were stable to coalescence under static ageing conditions for up to 20 days. When dynamically aged at 12 rpm, emulsification occurred, reducing the average droplet diameter. Although emulsification was dominant, there was a slight increase in droplet size from the initial droplet size distribution near 100 μ m. The size distribution peak between 10 and 100 μ m broadened after day zero to include droplets up to 200 μ m in diameter. Dynamic ageing at 30 rpm resulted in only emulsification as the droplet diameters reduced over time. A surfactant concentration of 500 ppm (1.50 mM) or a S/O of 0.10 was sufficient to prevent coalescence during static ageing and dynamic ageing at 30 rpm. However, this surfactant concentration was not able to prevent all coalescence during dynamic ageing at 12 rpm as the maximum droplet size did increase slightly.



Figure 3.3: Droplet size distributions for emulsions containing 500 ppm SLES aged between 0 (180 minutes) and 20 days under static and dynamic (12 and 30 rpm) conditions. The dotted light grey line represents the initial droplet size distribution. Lines become darker as ageing time increases.

Emulsions containing 1000 ppm SLES (**Figure 3.4**) behaved similarly to those containing 500 ppm SLES. Under static ageing conditions, the emulsion droplet size distribution was stable over 20 days. Dynamic ageing at 12 rpm resulted in an average droplet size reduction although the maximum droplet size increased slightly. At 30 rpm, only emulsification was observed. A surfactant concentration of 1000 ppm (3.01 mM) or a S/O of 0.2 had similar results to emulsions containing 500 ppm SLES; only slight coalescence was observed during dynamic ageing at 12 rpm.



Figure 3.4: Droplet size distributions for emulsions containing 1000 ppm SLES aged between 0 (180 minutes) and 20 days under static and dynamic (12 and 30 rpm) conditions. The dotted light grey line represents the initial droplet size distribution. Lines become darker as ageing time increases.

3.4: Conclusions

Model bilgewater emulsions were formulated using 5000 ppm heavy mineral oil, 0.42 M NaCl, and concentrations of SLES ranging from 10 to 1000 ppm. These emulsions were aged statically and dynamically at different rotation speeds to investigate the impact of motion on emulsion ageing. The main findings are as follows:

- A concentration of SLES between 10 and 100 ppm (S/O between 0.002 and 0.02) was needed to stabilize the emulsions under static ageing.
- Dynamic ageing promoted coalescence for emulsions containing 10 and 100 ppm SLES.
- At higher concentrations of SLES (500 and 1000 ppm), very little coalescence occurred, and emulsification reduced the droplet size.
- As the speed of dynamic ageing increased from 12 to 30 rpm, emulsification became more dominate over coalescence and droplet sizes decreased more rapidly for surfactant concentrations ≥ 100 ppm (S/O ≥ 0.02).

This study demonstrates the significance of motion during the ageing of emulsions. Dynamic ageing conditions can facilitate both coalescence and emulsification depending on the energy associated with the motion. This study shows that disturbances of bilge water emulsions due to

ship movement or wastewater transportation (e.g., pumping) influences the emulsion properties and ultimately the emulsion stability. If the S/O and energy density of dynamic ageing are sufficiently large, then droplets will be emulsified making oil removal increasingly difficult. Wastewater management techniques should be investigated to minimize dynamic ageing conditions that promote emulsification and complicate oil removal processes.

CHAPTER 4: DIFFUSION-CONTROLLED SPONTANEOUS EMULSIFICATION OF WATER-SOLUBLE OILS VIA MICELLE SWELLING

The following chapter contains text, figures, and tables with permission from⁸⁸ **Cole R. Davis**, C. J. Martinez, J. A. Howarter, and K. A. Erk, "Diffusion-Controlled Spontaneous Emulsification of Water-Soluble Oils via Micelle Swelling," *Langmuir*, (2020).

4.1: Introduction

Although emulsion formation typically requires an energy input, emulsions can form spontaneously without any external energy input. Since the discovery of spontaneous emulsions made by Gad in 1876⁹⁷, an effort has been made to describe and quantify these systems. The motivation for this fundamental understanding is the increased use of spontaneous emulsions in industry for pharmaceuticals,^{196,197} food science,^{198,199} enhanced oil recovery,^{97,200} detergency,²⁰¹ and more. Although spontaneous emulsification can be advantageous from an industrial standpoint, it can also be problematic when oil and water separation is desired, adding to the need for a fundamental understanding of spontaneous emulsions.

Wastewater containing emulsified oils presents difficulties in water treatment technology and raises environmental concerns. Removing oils from water becomes increasingly difficult as the oil droplet size decreases.²⁰² Spontaneous emulsification can produce nano-sized^{95,97} oil droplets and does so without any energy input. This means that even when care is taken as to not intentionally emulsify oil in water, nano-sized droplets can still form and be difficult to remove. A concern then arises regarding the capability to detect and monitor nano-droplets in water and their concentrations. Not only may they be difficult to detect by current wastewater monitoring systems,^{3,203} but the oils that participate in spontaneous emulsification (e.g., aromatics) are some of the most toxic and environmentally adverse.^{1,204} Therefore, it is crucial to identify systems that promote spontaneous emulsification so that preventative measures can be taken to eliminate these components from entering the environment.

Pure water and oil do not spontaneously emulsify alone;²⁰⁵ a third solute component is needed. This solute can be a surfactant or a small molecule that is miscible in both water and oil (e.g., ethanol).^{95,206} The specific solute chemistry needed for spontaneous emulsification to occur is dependent on the system parameters including oil type,^{104,207} water salinity,⁹⁸ and the desired emulsion type (i.e., oil in water or water in oil^{102,208}). It has also been demonstrated that the order in which these components are combined determines if spontaneous emulsification occurs and the emulsion type that forms.^{102,205,209} In some cases, it has been shown that a third component alone is not enough to cause spontaneous emulsification and a co-surfactant or salt is needed.^{105,210} There have been several systems found to spontaneously emulsify and lists on the composition of these systems have previously been published.^{97,198} **Table 4.1** lists some examples of systems that have been shown to spontaneously emulsify.

Oil	Additive	Salt	Emulsion Type	Reference
Linear Alkyl Oils (C8-C16)	Brij 30 (non-ionic surfactant)	-	Oil in Water	207
Dodecane	AOT (ionic surfactant)	NaCl (75 mM)	Oil in Water	104
Toluene	Ethanol, Propanol, Propanoic Acid	-	Oil in Water and Water in Oil	102

Table 4.1: Examples of systems that have been shown to spontaneously emulsify.

Energy is typically required to disperse one fluid into another immiscible fluid. This process is known as emulsification where the dispersed phase appears as droplets inside of a surrounding continuous phase. The energy required for emulsification is dependent on the interfacial tension between the two fluids: larger interfacial tensions require more energy. This energy requirement arises from the formation of new surface area during droplet formation as described in **Equation 4.1**:

$$\Delta G = \Delta A \gamma - T \Delta S$$

(4.1)

where ΔG is the free energy of the system, ΔA is the change in dispersed phase surface area, γ is the interfacial tension, *T* is the temperature, and ΔS is the change in entropy. Formation of smaller droplets (i.e., large interfacial areas) or high interfacial tensions require more energy input. However, emulsification can occur *spontaneously*, without any energy inputs, when the two immiscible fluids are not initially in thermodynamic equilibrium. This results in the formation of either a microemulsion or a spontaneous emulsion, the latter which can also be referred to as a spontaneous miniemulsion or spontaneous nanoemulsion.

The major difference between microemulsions and spontaneous emulsions is their thermodynamic stability. Microemulsions are thermodynamically stable^{101,211,212} whereas spontaneous emulsions are not^{196,199} but may exhibit long kinetic stability.⁸⁷ In addition to their stability, microemulsion and spontaneous emulsions have other distinguishing characteristics like size, interfacial tension, and surfactant concentration. Despite the naming convention, microemulsions droplets, often referred to as "swollen micelles", are typically between 10 and 100 nm in size^{87,97,196} and rarely exceed this 100 nm limit.^{213–215} Spontaneous emulsions contain larger droplets that are closer in size to typical nanoemulsions which contain droplets between 20 and 500 nm in diameter^{87,196,199,209,213} and often exceed 100 nm diameters.¹⁹⁸ Microemulsions require ultralow interfacial tensions (< 0.1 mN m⁻¹) to form^{97,100,101,206,211,212,214,216,217} compared to spontaneous emulsions which can form at appreciable interfacial tensions(> 1 mN m⁻¹).^{99,101,102,208,213} Although it is not a requirement, microemulsions typically contain large surfactant concentrations (10-30 wt.%)^{101,213} compared to spontaneous emulsions^{209,211}.

Several mechanisms for spontaneous emulsification have been previously described in literature. Of these, three are discussed frequently: negative interfacial tension (ultralow interfacial tension), diffusion (diffusion and stranding and micelle swelling), and interfacial turbulence.⁹⁷ Each of these formation mechanisms has been described previously in **Section 1.4.2**.

In addition to establishing mechanisms for spontaneous emulsification, there has also been some efforts to quantify the spontaneity of these systems. The concept of "spontaneity" is not well defined in literature but is frequently invoked to quantify the rate and extent of emulsification. Spontaneity is typically assessed in industry according to the Collaborative Pesticide Analytical Committee of Europe (CPAC) and the United Nations Food and Agriculture Organization (FAO) where emulsification is visually evaluated as "good", "moderate", or "bad" based on the rate of emulsification.²¹⁸ This technique is highly subjective and has low reproducibility between laboratories.⁹⁷ Spontaneity has also been measured as the time required for a spontaneous emulsion to reach an equilibrium state by measuring droplet size over time via light scattering.²¹⁸ However, this has since been criticized as inadequate for not quantifying the extent of emulsification and a new technique was proposed by measuring the specific interfacial area over time via laser diffraction.²⁰⁷ Furthermore, droplet sizes may not be at an equilibrium immediately after emulsification and would thus depend on the stability of the emulsion rather than the formation. Both techniques also have drawbacks in that they use mixing or flow during the measurement process which artificially increases the rate of emulsification indicated by the relatively short emulsification times and thus, reduces the resolution of the measurement.^{207,218}

The objective of this study is to better understand the mechanisms of spontaneous emulsification in systems that pollute the environment and ultimately create nano-sized emulsions that are difficult to remove from wastewaters. Visual observations were made of spontaneous emulsification, and the long-term stability of these emulsions was characterized by measuring the droplet size over a period of 40 days. The specific mechanisms responsible for spontaneous emulsification were determined by: utilizing dynamic light scattering as a simple, accurate method to quantify spontaneity; visually observing the presence and absence of Marangoni flows; investigating the impact of oil concentration on droplet size; and measuring dynamic interfacial tension of model droplets. Nonylphenol polyethoxylate (NPE) was selected as a model nonionic surfactant due to its use as a general purpose detergent for the US Navy (MIL-D-16791G, Type I) and its abundant use in studies involving wastewater and pollution.^{15,32,44,219} Toluene, xylenes, cyclohexane, and mineral oil were used as model oils to represent components of crude oil, fuels, and degreasing solvents that are known to exist in many industrial wastewater systems such as in the bilge of a ship.^{13,32,66,72,131} Together, these experiments illuminate the mechanisms involved in the spontaneous emulsification of these relevant components and provide insights on the likelihood of nanoemulsion formation and persistence in oily wastewater.

4.2: Materials and Methods

4.2.1: Materials

Toluene (anhydrous, 99.8%), xylenes (reagent grade, $\geq 75\%$ xylene isomers), cyclohexane (ACS reagent $\geq 99\%$), and mineral oil (heavy) were purchased from Sigma-Aldrich. Nonylphenol polyethoxylate (NPE) ((C₂H₄O)_n·(C₁₅H₂₄O), n=10) was provided by Stepan Co. (MAKON-10). Deionized (DI) water (Barnstead Nanopure Infinity, 18 Mohm·cm resistivity) was used for the aqueous phase of the emulsion. Structures for the chemicals used can be found in **Figure 4.1**.

4.2.2: Spontaneous Emulsion Preparation

DI water and NPE were mixed for at least 5 minutes to make a 500-ppm (0.71 mM) (CMC of NPE from literature^{220,221} is 43 to 63 ppm or 0.061 to 0.09 mM) surfactant solution. Oil was pipetted on top of the NPE solution carefully to prevent oil droplet formation. All emulsions contained 5000-ppm oil unless otherwise stated. Due to the small amount of oil added, oil did not cover the entire surface of the aqueous phase. Oil and NPE solutions were left in contact until spontaneous emulsification was complete (approximately 90 minutes). Emulsion stability was then monitored for 40 days by measuring the droplet size.



Figure 4.1: Chemical structures of (A) NPE where n = 10, (B) toluene, (C) o-xylene, and (D) cyclohexane.

4.2.3: Dynamic Light Scattering

Surfactant micelle and emulsion droplet size were measured via DLS using a Malvern Zetasizer Nano ZS at a scattering angle of 173°. Each size distribution was collected using three runs on at least three separate samples and is reported as the average of all the samples tested. Diameters are reported using the Z-average diameter. Bimodal distribution peaks are labeled with their corresponding mean diameter (D_{50}). Diameter values are reported with an error of one standard deviation. All size distributions are averages of at least 3 samples. A polydispersity index (*PDI*) was calculated using the standard deviation of the size distribution (σ) through **Equation 4.2**.

$$PDI = \frac{\sigma^2}{D_{50}^2} \tag{4.2}$$

4.2.4: Spontaneity of Emulsification

NPE micelle size was measured as a function of time in the presence of toluene, xylenes, cyclohexane, and mineral oil separately. Approximately 0.8 mL of 500-ppm NPE solution was placed into a glass DLS measurement cell and the initial micelle size was measured. Approximately 0.2 mL of oil was then added on top of the NPE solution, covering the entire surface of the aqueous phase, and DLS measurements were made approximately every two minutes for a total of 60 minutes. The distance from the oil-water interface to the fixed laser path was 0.225 cm. Each experiment was performed in triplicate and the micelle diameter and time are reported with an error of one standard deviation.

While other techniques have been previously developed to investigate spontaneity^{207,218}, the method demonstrated herein allowed for higher temporal resolution and, thus, a more accurate analysis of spontaneity. This was achieved by eliminating external energy inputs to ensure that the spontaneity was driven solely by the internal energy of the system. Implementation was straightforward, resulting in high reproducibility. Multiple parameters were extracted from these tests including effective diffusion coefficients and swelling rates. Additionally, this method was used

to distinguish between the mechanisms of micelle swelling and diffusion and stranding. For example, diffusion and stranding would result in a bimodal size distribution of micelles and droplets at the moment of homogeneous nucleation while micelle swelling results in a shift of a single monomodal size distribution as micelles fill with oil.

4.2.5: Impact of Oil Concentration on Droplet Size

Different volumes of toluene were placed on top of 500 ppm NPE solutions to create emulsions with predetermined oil concentrations (5000, 1000, 500, 100, 50, and 10 ppm). Once the toluene was placed on top of the aqueous solution, it was left to spontaneously emulsify until the bulk toluene was no longer visible on the surface of the aqueous phase (minimum of 90 minutes). At this time, it was assumed that all the micelles consumed all the oil and reached a maximum size for the given oil concentration. DLS was then performed to measure the droplet size.

4.2.6: Dynamic Interfacial Tension

Dynamic interfacial tension measurements were made using a pendant drop tensiometer (DSA30, KRÜSS Inc.) using the Young-Laplace equation. Aqueous droplets containing 500 ppm NPE were formed in a continuous phase of oil (toluene, xylenes, cyclohexane, or mineral oil). The interfacial tension was recorded every 30 seconds for a minimum of 15 minutes. This was repeated in triplicate for each sample and reported as an average with an error of one standard deviation.

4.3: Results and Discussion

4.3.1: Visual Observations of Spontaneous Emulsification

When toluene was placed in contact with a 500 ppm NPE solution, spontaneous emulsification was observed. **Figure 4.2** shows images of toluene in contact with an NPE solution for 0, 30 and 90 minutes as well as the droplet size distribution after 90 minutes of contact. As time progressed, opaque regions could be seen flowing through the aqueous phase, indicated by the white arrow at 30 minutes. At approximately 90 minutes, the bulk toluene was no longer visible on top of the aqueous phase and flow was no longer observed.



Figure 4.2: Spontaneous emulsification of 5000 ppm toluene in a 500 ppm NPE solution after 0, 30, and 90 minutes of contact. The toluene-water interface is marked by the red dotted line at 0 minutes. The toluene droplet size distribution at 90 minutes is also reported. Note that toluene was used in such a small quantity that it did not completely cover the air-water interface. The two white asterisks labelled on the far-left image indicate optical artifacts (light reflections) and are not to be mistaken for features of emulsification. These reflections appear in each image.

The observed mixing behavior was caused by convective flows which arise from interfacial tension gradients along the oil-water and air-water interface.^{205,222} Initially, regions of high oil concentration have a high interfacial tension with water and demand surfactant. Surfactant flows horizontally along the air-water interface toward the oil (i.e., high to low surfactant concentration) and is caused by the fact that the oil phase did not cover the entire air-water interface. Simultaneously, oil is transported in the vertical direction from the bulk oil droplet to the aqueous phase while consuming surfactant that was once at the oil-water interface. As a result, the oil-water interface is surfactant starved and this perpetuates the horizontal surface flow. These horizontal and vertical flows create a convective flow called a Marangoni roll cell^{205,223} and were observed during spontaneous emulsification. Images of the observed roll cells can be seen in **Figure 4.3**.



Figure 4.3: Images depicting (A) convective flow due to interfacial tension gradients along the interface forming streams of toluene droplets from a larger, bulk toluene droplet in an aqueous phase which contained 500 ppm NPE and (B) a roll cell (dark regions surrounding the outside of the roll cell arrows) formed during spontaneous emulsification of the same toluene droplet located in image A.

Roll cells can be seen on either side of the bulk toluene droplet creating jets of toluene droplets that progress into the aqueous phase and break apart (**Figure 4.3**). The direction of the roll cell flow was opposite to those previously observed.³⁹ The sinusoidal wave indicated by the white arrow in **Figure 4.2** is a relaxation oscillation of Marangoni roll cell.^{223,224} Xylenes also showed visible signs of spontaneous emulsification and convective flow. Images showing emulsification after 40 minutes of oil-water contact for all three oils can be seen in **Figure 4.4**. Toluene had the most visible mixing and appeared to be more spontaneous than both xylenes and cyclohexane. Cyclohexane did not show any visible signs of spontaneous emulsification.



Figure 4.4: Spontaneous emulsification of 5000-ppm toluene, xylenes, and cyclohexane with a 500-ppm NPE solution after 40 minutes of contact. The scale bar applies to all images.

4.3.2: Emulsion Stability

Although emulsification was spontaneous, this was not the equilibrium state. **Figure 4.5** illustrates the change in emulsion transparency over 30 days for toluene, xylenes, and cyclohexane. After 17 days, toluene emulsions appeared translucent while xylene emulsions were slightly more opaque. After 30 days, all three emulsion compositions were transparent indicating that the emulsions had not yet achieved a thermodynamic equilibrium.



Figure 4.5: Photographs of toluene, xylene, and cyclohexane emulsions aged for 90 min, 17 days, and 30 days. After 30 days, all emulsions were transparent. The scale bar applies to all images.

To identify if any instability mechanisms were active during the ageing process, DLS was used to record droplet size distributions over 40 days and can be seen in Figure 4.6. For toluene, the droplet size after 90 minutes shows a peak at 176 nm. After 15 days, this peak broadens, and the droplets grow to a larger size of 340 nm. A bimodal distribution can be seen at 30 days with a large peak near the NPE micelle size (14.5 nm) and a second, small peak at 310 nm. After 40 days, only one peak remains that is identical to the NPE micelle size distribution. A similar process occurs during the ageing process of xylenes apart from swollen micelles (21 nm) remaining at 40 days. Note that the use of the term "swollen micelle" here does not indicate formation of a microemulsion but rather is used to describe an oil-filled micelle with a size on the same order of magnitude as an NPE micelle (i.e., less than 100 nm in diameter). Otherwise, the dispersed phase will be referred to as "droplets". Cyclohexane shows a bimodal distribution at 90 minutes; one peak at the NPE micelle size (12.0 nm) and another peak at 285 nm. This indicates that not all the micelles are used to form droplets of cyclohexane, and a large portion of NPE micelles remain. After 15 days, a bimodal distribution remains with a slight peak at 457 nm and a large peak at 13.7 nm, indicating that the NPE micelles have swollen. Between 15 and 30 days, all the droplets return to the NPE micelle size. Swollen micelles have been seen in a similar system but without mention of spontaneous emulsification.¹⁵² Reverse micelle swelling has been seen in a kerosene-Span 80water system which resulted in a W/O emulsion.¹⁰¹ Figure 4.7 shows the trend in the Z-average swollen micelle and droplet diameters from 90 minutes to 40 days for each oil.

From visual observations and data in **Figure 4.6** and **Figure 4.7**, three instability mechanisms can be inferred: Ostwald ripening, gravitational separation (creaming), and evaporation. Increases in droplet size between 0 and 15 days are likely due to Ostwald ripening because of the oils' high water solubility and small droplet sizes.^{83,87,114} As the micelles grew larger due to Ostwald ripening, they became increasingly unstable to gravitational separation and creamed to the air-water interface.⁸³ Emulsions containing cyclohexane were the fastest to destabilize and return to the initial micelle size. This is most likely because a relatively small amount of oil was emulsified (indicated by the presence of micelles after emulsification), and droplets likely did not get dispersed far from the air-water interface due to the lack of observed convective flows. This allowed droplets to cream and evaporate at a faster rate.



Figure 4.6: Evolution of swollen micelle and droplet size distributions from 90 minutes to 40 days of ageing for toluene (left), xylenes (middle), and cyclohexane (right). For all 40-day size distributions, the NPE micelle size distribution is overlaid for comparison (dashed line). All peaks are labeled with their corresponding average size (D_{50}) .



Figure 4.7: Z-average swollen NPE micelle and droplet diameters for toluene, xylenes, and cyclohexane between 90 minutes and 40 days. Error bars represent one standard deviation. Dotted line represents the NPE micelle diameter. The y-axis is plotted on a logarithmic scale.

A calculation using the Stokes' velocity and accounting for Brownian motion predicts that a 500 nm diameter oil droplet would take less than 19 days to cream from the bottom of the vial to the air-water interface (3 cm). All calculations and assumptions are available in Appendix B. Size distributions in Figure 4.6 show that droplets larger than 500 nm are present and therefore, are capable of creaming at a faster rate (e.g., a 1000 nm droplet would take 4.5 days to reach the airwater interface). Another consideration is that not all the droplets reside at the bottom of the vial and do not have to travel as far to reach the air-water interface (see the high concentration of droplets at 90 minutes near the air-water interface in **Figure 4.5**). Although creaming was observed before 40 days, a creamed layer did not remain at 40 days. Because of this observation, it is believed that the oils evaporated into the vial headspace after creaming to the air-water interface. This is also suggested by the aroma of each oil present when the samples were opened for size measurements. Before each size measurement, the emulsion was gently mixed by swirling the vial just enough to evenly disperse the concentrated emulsion layer that can be seen at the top of the aqueous phase in Figure 4.2 and Figure 4.5 at 90 minutes. This was only performed for systems that were not already uniformly dispersed to obtain representative and uniform samples. The low energy input of swirling was not expected to have an impact on droplet size.

Since only NPE micelles or slightly swollen NPE micelles remained after 40 days, it can be concluded that the oil was no longer in solution due to evaporation. To confirm this, an emulsion was made with excess toluene on top of the aqueous phase to ensure total coverage of the air-water interface with an oil-water interface. Excess toluene (10 mL of toluene on top of 10 mL of an aqueous phase containing 500 ppm NPE) replaced the entire air-water interface and created an oil-water interface unlike the last experiments in which the oil did not cover the air-water interface. Therefore, once creaming occurs, the toluene will no longer evaporate and leave the system. If the toluene-filled micelles coalesce or undergo disproportionation into the bulk toluene phase, there will be excess toluene in contact with the aqueous phase to replenish any lost toluene. Because of this replenishing, an equilibrium state could be obtained that was not previously observed. **Figure 4.8** shows the Z-Average swollen micelle and droplet diameters from 90 minutes to 40 days and images of the emulsion at 0, 2, 11, and 32 days.

Excess toluene resulted in slower micelle swelling when compared to emulsions with 5000 ppm toluene. After 90 minutes, NPE micelles grew to 17.6 nm in the presence of excess toluene whereas

5000 ppm toluene caused NPE micelles to grow to approximately 112 nm. This occurred due to the lack of convective flows from interfacial tension gradients along the interface when toluene covered the entire interface. Excess toluene also prevented evaporation of toluene in the water phase. Once formed, the droplets did not significantly reduce in size over 40 days as was seen with emulsions containing 5000 ppm toluene (see **Figure 4.7**). Spontaneous emulsification in the absence of any observable Marangoni flows suggests that interfacial turbulence although expedited the process, is not needed for spontaneous emulsification and that another mechanism is active.



Figure 4.8: Z-Average swollen NPE micelle and droplet diameters for an emulsion containing 5000 ppm toluene (solid symbols) and excess toluene (open symbols) between 90 minutes to 40 days. Error bars represent one standard deviation. The y-axis is plotted on a logarithmic scale. To the right of the plot are images of the spontaneous emulsion with excess toluene at 0, 2, 11, and 32 days. Light reflections can be seen in the bottom corners of each vial and should not be mistaken for features of emulsification.

4.3.3: Spontaneity via Micelle Swelling

Previously, emulsion sizes were measured after emulsification occurred. To further investigate the spontaneity and mechanisms of emulsification, DLS was performed during emulsification. To do this, 0.8 mL of a 500 ppm NPE surfactant solution was placed into a DLS measurement cell. After measuring the initial micelle size, 0.2 mL of oil (~ 173,400 ppm) was placed on top of the aqueous

phase. These experiments were attempted at an oil concentration of 5000 ppm but the oil did not cover the entire air-water interface and as a result, Marangoni flows were present. This increased the rate of spontaneous emulsification to the point where micelle swelling could not be captured. Unlike the previous experiments, the oil phase covered the entire surface of the aqueous phase and convective flows were not observed.

Figure 4.9 shows NPE micelle size distributions before and after exposure to toluene. NPE micelles were measured to be 10.6 ± 0.1 nm in diameter. Once toluene was placed on the surface of the surfactant solution, NPE micelles began to swell over time. After 30 and 60 minutes of exposure to toluene, the micelles grew to 17.9 ± 0.6 and 26.6 ± 1.6 nm, respectively. As time increased, the micelle size distribution broadened and the PDI increased; for 0, 30, and 60 minutes, the PDI was 0.12 ± 0.01 , 0.14 ± 0.01 , 0.18 ± 0.02 , respectively. This indicates that not all the micelles were swelling at the same time but instead, it is likely that micelles closer to the oil-water interface began swelling before micelles located farther from the oil-water interface.

Micelle swelling was measured periodically over 60 minutes for toluene, xylenes, and cyclohexane; these results can be found in **Figure 4.10A**. Two distinct regions can be seen for each oil. Here, region one will be referred to as the "diffusion region" where the micelle size is somewhat constant and similar to the initial NPE micelle size (d₀). An inflection in micelle size occurs at t₀ the time at which the micelle size begins to linearly increase. This inflection point marks the onset of region two which is the "swelling region". A third, equilibrium region can be seen for cyclohexane and occurs at approximately 46 minutes. At this point, swelling stops and the micelle size remains constant. This region is not observed for toluene or xylenes because the spontaneous mixing of larger oil droplets (as seen in **Figure 4.2** and **Figure 4.4**) increased the count rate past the range that could be used to reliably collect data using DLS. In other words, larger oil droplets obstructed the DLS laser, preventing accurate measurements of the swelling micelles.



Figure 4.9: Swollen NPE micelle size distribution before (0 min) and after contact with toluene for 30 and 60 minutes. Intensity was normalized to the size distribution at 0 min. Z-average diameters are reported above each size distribution.



Figure 4.10: NPE micelle swelling response in the presence of excess oil for (A) 60 minutes and (B) magnification of data in the early stages of swelling. Plot B illustrates the intersection of each data series with the initial micelle size (d₀ horizontal line) to determine approximate values of t₀ (reported in Table 4.2). Error bars represent one standard deviation in both micelle diameter and time.

Figure 4.10B shows the transition between the diffusion and swelling regions in more detail. Toluene and xylenes show a slight increase in diameter (less than 1 nm) followed by an immediate decrease back towards the initial micelle size before time t_0 . This is likely due to experimental error during the placement of oil on top of the aqueous solution causing some initial micelle swelling to occur. Each oil displayed a different t_0 , calculated from the intersection between the initial micelle size (solid black line) and the linear swelling region (dotted lines) in **Figure 4.10B**. Values for t_0 are reported in **Table 4.2**. A delay in swelling response can be attributed to the time it takes for the oil molecules to diffuse from the oil-water interface, through the water, and into the micelles at the point where the measurement is being taken (see **Figure 4.13**). Because of this, the absolute value of t_0 is arbitrary as it can change by altering the distance from the oil-water interface to the measurement location. However, the same distance of 0.225 cm was used for each experiment, giving the relative values of t_0 significance for comparing the spontaneity of different oils.

From the calculated t_0 values, it appears that toluene reached the NPE micelles first, followed by xylenes, and cyclohexane. This implies that toluene is the "most spontaneous" of the three oils tested. Micelle growth rates (k_m), calculated as the slope of the swelling region from t_0 to 60 minutes (t_{60} ; 46 minutes for cyclohexane), also suggest that toluene is the most spontaneous of the three oils and are reported in **Table 4.2**.

Similar to values of t_0 , only the relative values of k_m are meaningful due to the experimental setup. Toluene resulted in the fastest growth of NPE micelles at almost twice the rate of xylenes and 5.5 times the rate of cyclohexane. This demonstrates that toluene is capable of emulsifying with NPE faster than xylenes and cyclohexane and thus, is more spontaneous. As a result of this spontaneity, toluene-filled micelles grew to the largest size after 60 minutes of swelling (d₆₀).

A positive correlation was found between an oil's spontaneity and its solubility in water; that is, oils with a larger solubility (e.g., toluene, see **Table 4.2**) were more spontaneous. To further demonstrate this, mineral oil was used to represent an insoluble oil ($S_0 \sim 0$ ppm). After 24 hours, there were no visible signs of spontaneous emulsification and the NPE micelles did not swell when in contact with mineral oil (from 10.7 to 10.2 nm after 24 hours). If mineral oil did contain water-soluble components, they were not at a significant concentration to cause micelle swelling. And

even if the oil molecules are water soluble, the surfactant micelles must also have the capability of solubilizing those molecules.

Table 4.2: Initial micelle diameter (d₀), swelling start time (t₀), micelle growth rate (k_m), micelle diameter at 60 minutes (d₆₀), and solubility in water at 25 °C (S₀) for toluene, xylenes, cyclohexane, and mineral oil. Errors represent one standard deviation.

Oil	d ₀ (nm)	t ₀ (min)	k _m (nm/min)	d60 (nm)	S ₀ (ppm)	
Toluene	10.7 ± 0.2	6.18 ± 0.67	0.315 ± 0.03	26.6 ± 1.6	515 ⁷⁶	
Xylenes	10.7 ± 0.2	7.49 ± 1.2	0.176 ± 0.01	20.0 ± 0.7	177 ^{a 79,203}	
Cyclohexane	10.7 ± 0.2	10.1 ± 3.6	0.057 ± 0.01	12.7 ± 0.2	55 ⁷⁶	
Mineral Oil	10.7 ± 0.2	×	0	10.3 ± 0.03	0 ^{b 203}	
^a Average solubility of o-xylene, m-xylene, and p-xylene.						
^b Solubility of decane (C ₁₀ H ₂₂) in water. Mineral oil contains a mixture of alkanes greater than decane.						

Values of t_0 can be normalized by the distance over which the molecules traveled to reach the measurement location (0.225 cm), giving a diffusion coefficient for each oil in the NPE solution (D_{oil-NPE}). **Equation 4.3** shows how the diffusion coefficients were calculated where $\langle x^2 \rangle$ is the mean square displacement.

$$D_{oil-NPE} = \frac{\langle x^2 \rangle}{2t_0} \tag{4.3}$$

Table 4.3 reports the calculated values of $D_{oil-NPE}$ as well as the diffusion coefficient from literature for each oil in water ($D_{oil-water}$). It is important to note that $D_{oil-NPE}$ does not represent diffusion strictly due to Brownian motion but is a combination of Brownian, molecular, and turbulent diffusion as well as micelle solubilization.

Oil	Doil-NPE (*10 ⁻⁶ cm ² /s)	Doil-water (*10 ⁻⁶ cm ² /s)	Doil-NPE / Doil-water
Toluene	68 ± 7	8.5 ²²⁵	8.0
Xylenes	56 ± 9	8.5 ²²⁶	6.6
Cyclohexane	42 ± 10	8.4 ²²⁵	5.0

Table 4.3: Calculated diffusion coefficient for each oil in a 500 ppm NPE solution ($D_{oil-NPE}$), diffusion coefficient for each oil in water ($D_{oil-water}$), and the ratio of $D_{oil-NPE}$ to $D_{oil-water}$.

Diffusion coefficients of all oils in water increase when NPE is added to the aqueous phase. An increase in the diffusion coefficient could be due to Marangoni flow. However, this flow was less prominent when the oil covered the entire surface of the water as it did in micelle swelling experiments. When the oil resided as a small droplet on the surface, as in **Figure 4.3**, a larger interfacial tension gradient at the air-water-oil interface existed and resulted in stronger convective flows. In micelle swelling experiments, the oil covered the entire surface of the water which resulted in a more uniform interfacial tension across the interface and thus, dampened or inhibited the flow. Diffusion coefficients may have increased simply due to the presence of NPE micelles and the non-zero solubility of oil inside the micelles. To investigate this, micelle sizes were measured as a function of oil concentration and compared with predicted micelle sizes.

4.3.4: Impact of Oil Concentration on Micelle Size

Figure 4.11 shows the measured and predicted equilibrium swollen micelle size at different concentrations of toluene. Equilibrium was obtained after at least 90 minutes or when all the oil was consumed by the micelle solution and was no longer visible on the surface. Predicted micelle diameters were calculated under the following assumptions: The NPE micelle aggregation number (*n*) was 172 (average from 3 literature values^{221,227,228}). The aggregation number and number of micelles in solution (*N_m*) were constant during swelling. The total number of surfactant molecules (*N_s*) at a concentration of 500 ppm was calculated using an average molecular weight of 702 g/mol.²²¹ All toluene added was distributed equally into each micelle and none was left dispersed in the water. The swollen micelle diameter (*d_s*) was taken as the initial micelle diameter (*d₀*) plus the diameter of a sphere of toluene (*d_t*) containing the same volume as the number of toluene molecules in each micelle (*N_t*). The number of toluene molecules per micelle was taken as the

total amount of toluene molecules at a given concentration (n_t) divided by N_m . A molar volume of 1.06×10^{-4} m³/mol was used for toluene (V_{mol}) .⁷⁶ Predicted swollen micelle diameters were calculated using **Equation 4.4**, **4.5**, and **4.6**, where N_A is Avogadro's number.

$$d_s = d_0 + d_t \tag{4.4}$$

$$d_t = 2\left(\frac{3N_t * V_{mol}}{4\pi N_A}\right)^{\frac{1}{3}} = 2\left(\frac{3n_t * V_{mol} * n}{4\pi N_s * N_A}\right)^{\frac{1}{3}}$$
(4.5)

$$N_m = \frac{N_s}{n} \tag{4.6}$$



Figure 4.11: Measured (red squares) and predicted (open circles) equilibrium NPE micelle diameter for different concentrations of toluene. Error bars represent one standard deviation.

Predicted micelle diameters agree well with the measurements but overestimate the diameters at low concentrations (< 500 ppm). At concentrations of 500 and 1000 ppm, the predicted value is within one standard deviation from the measured value. When the concentration of toluene was 5000 ppm, the predicted diameter was 92 nm smaller than the measured diameter.

An overestimation of the swollen micelle diameters could be caused by underestimating the number of micelles in solution (e.g., if there are more micelles then the magnitude of swelling would decrease) or the assumption that all the oil was distributed into the micelles and none was dissolved in water. Since these predictions are accurate within one standard deviation at concentrations of 500 and 1000 ppm, it is more likely that the former is true; the number of micelles at low concentrations were underestimated. At concentrations near the solubility of toluene in water (515 ppm), the assumption that all the toluene was distributed equally into each micelle and none was left dispersed in water appears to match the data. This suggests that toluene prefers to be inside the NPE micelles and is only in the water as it transports from the oil phase to the micelles. The preference for toluene to be inside NPE micelles instead of water supports the claim that diffusion coefficients increased in the presence of NPE micelles due to the oil's increased solubility inside micelles compared to pure water.

An underestimation of the micelle size at 5000 ppm is most likely due to the false assumption that the aggregation number and number of micelles are constant. Instead, as the oil emulsifies, larger micelles grow, forming droplets and consuming surfactant from smaller micelles. This means that the number of micelles decreased, and the aggregation number increased.

4.3.5: Dynamic Interfacial Tension

Dynamic interfacial tension measurements for toluene, xylenes, cyclohexane, and mineral oil in contact with an aqueous solution containing 500 ppm NPE can be found in **Figure 4.12**. Equilibrium interfacial tension measurements were not accessible due to spontaneous emulsification of the oil into the aqueous phase and the transfer of surfactant from the aqueous phase to the oil phase. Spontaneous emulsification was observed inside of the water droplet and as a result, the density of the aqueous phase decreased to unknown values over time which caused an increase in the interfacial tension (see **Figure B1** and **Figure B2** in **Appendix B**). Transport of

surfactant from the interface into the bulk oil was also likely as NPE is miscible with xylene.¹⁸³ Additionally, systems that did not display significant or any spontaneous emulsification (cyclohexane and mineral oil) also exhibited an increase in interfacial tension over time. This suggests that initially, surfactant adsorbed to the interface followed by desorption into the oil phase which reduced the amount of surfactant at the interface (i.e., increased the interfacial tension). Since the equilibrium interfacial tension could not be obtained, the initial interfacial tension was used as a comparison between oils.²¹⁶

These relatively high interfacial tensions suggest that the mechanism of ultralow or negative interfacial tension was not responsible for the observed spontaneous emulsification and is in agreement with other work.^{99,101,102,208,213} Systems that were more spontaneous also had larger interfacial tensions (toluene and xylenes) in comparison to systems that showed little to no spontaneous emulsification (cyclohexane and mineral oil). Indeed, the correlation between interfacial tension and spontaneity was opposite of what one would expect if interfacial tension had a significant role in the spontaneous emulsification of these systems.



Figure 4.12: Dynamic interfacial tension of toluene, xylenes, cyclohexane, and mineral oil with an aqueous solution containing 500 ppm NPE. In these experiments, the pendant drop contained the aqueous phase and was surrounded by a continuous phase of oil.

4.3.6: Mechanism of Spontaneous Emulsification

The previous results give insight into how spontaneous emulsification occurred for these systems. Convective flow caused by the Marangoni effect visibly contributed to emulsification when oil did not cover the entire surface of the aqueous phase (**Figure 4.2**, **Figure 4.3**, and **Figure 4.4**). However, when oil covered the surface of the aqueous phase, Marangoni flows were not observed but spontaneous emulsification still occurred (**Figure 4.8**). This suggests that diffusion was the dominating mechanism and Marangoni flows can contribute to but are not primarily responsible for spontaneous emulsification of these systems. Additionally, these convective flows were driven in part by the diffusion of oil into the aqueous phase as Marangoni flows were not observed for oils with little to no solubility (cyclohexane and mineral oil).

Figure 4.13 shows a diagram of the proposed governing mechanism for spontaneous emulsification during DLS experiments. At some time less than t_0 , oil molecules begin to diffuse through the water. At t_0 , the oil molecules reach the fixed measurement location, enter surfactant

micelles in that vicinity, and swelling is detected. Between time t_0 and 60 minutes (t_{60}), the micelles at the measurement location grow linearly with time (see **Figure 4.10**).

The proposed mechanism of spontaneous emulsification requires the oil to be soluble in water and the surfactant micelles, if only slightly (see S_0 in **Table 4.2**). Insoluble oils (mineral oil) could not diffuse through the water and into micelles while toluene, xylenes, and cyclohexane were shown to be soluble in both water and the NPE micelles. This mechanism also requires the presence of surfactant micelles (i.e., the surfactant concentration must be above the CMC) which has been seen previously.¹⁰¹ To confirm this, toluene was placed on top of an NPE solution below the CMC (10 ppm) and spontaneous emulsification was not observed (see **Figure B3** in **Appendix B**).

Experiments with varying oil concentration confirm that oil molecules favor being inside micelles as opposed to dispersed in water (**Figure 4.11**). At some critical concentration of oil, micelles grow rapidly and consume surfactant from the smaller, surrounding micelles. After approximately 90 minutes, the oil was spontaneously emulsified and reached an equilibrium for these timescales (hours). However, this is a metastable state because the emulsions are not stable at larger timescales (several weeks, see **Figure 4.5**, **Figure 4.6**, and **Figure 4.7**).



Figure 4.13: Diagram displaying the governing mechanism for spontaneous emulsification of toluene, xylenes, and cyclohexane in an NPE surfactant solution during DLS experiments. The initial micelle size (d_0) is smaller than the micelle size after swelling with oil (d). Image not to scale. Times *t* correspond to relevant times in micelle swelling experiments (Figure 4.10 and Table 4.2).

4.4: Conclusions

Spontaneous emulsification was observed when toluene, xylenes, and cyclohexane were individually placed in contact with an aqueous solution containing a nonionic surfactant. The main findings were as follows:

- The dominant mechanism for spontaneous emulsification was diffusion-driven micelle swelling, resulting in the formation of surfactant-stabilized oil droplets between 100 and 500 nm in size within 90 minutes.
- To accurately assess spontaneity, micelle swelling rates were directly measured by a novel method based on dynamic light scattering. Spontaneity was correlated with the oil's solubility in water.
- When present, Marangoni flows increased the rate of spontaneous emulsification.

- Interfacial tension values for all systems were appreciable (4-16 mN m⁻¹) and inversely correlated with spontaneity, indicating that spontaneous emulsification was not driven by ultralow interfacial tension.
- Though formed spontaneously, oil droplets destabilized over the course of 40 days due to Ostwald ripening, creaming, and eventual evaporation.

This work provides a fundamental understanding of the mechanisms governing spontaneous emulsification, knowledge of which is valuable for optimizing nanoemulsion fabrication as well as controlling or preventing spontaneously formed emulsions in oily wastewater. The components studied here are found in many wastewater systems and could lead to the formation of nanoemulsions that may be difficult to detect and remove during water treatment operations. And although the emulsions displayed limited stability under static laboratory conditions, it is rarely the case that wastewater is stationary for extended amounts of time. Thus, spontaneously formed oil droplets could be dispersed indefinitely in wastewater depending on environmental and processing conditions (e.g., mixing, presence of salts, additional surfactants).

CHAPTER 5: PREDICTING SPONTANEOUS EMULSIFICATION IN SALTWATER ENVIRONMENTS USING THE HLD MODEL

The following chapter contains text, figures, and tables with permission from²²⁹ **Cole R. Davis**, C. J. Martinez, J. A. Howarter, and K. A. Erk, "Predicting Spontaneous Emulsification in Saltwater Environments Using the HLD Model," *Langmuir*, (2021).

5.1: Introduction

As discussed in previous chapters, spontaneous emulsification is the mixing and emulsification of oil and water without any external energy input often resulting in sub-micron droplets.^{88,95} Spontaneous emulsion formation can be beneficial for many applications,^{199,230,231} but it can also be problematic when the mixture of oil and water is undesirable. For example, spontaneous emulsions can form with components in bilge water,^{88,158} crude oil,²⁰⁸ and wastewater systems.²³¹ The removal of emulsified oil from water is not trivial and requires expensive filtration systems.^{131,232,233} Therefore, it is beneficial to understand how and under what conditions these systems spontaneously emulsify to better mitigate this phenomenon and reduce energy and expenses associated with wastewater treatment.

There are three primary mechanisms by which spontaneous emulsification can occur: ultralow interfacial tension,^{99,104} interfacial turbulence,^{88,97,222} and diffusion.^{88,97} The primary mechanism of emulsification for many spontaneous systems is diffusion.^{91,102,104} A spontaneous emulsion formed by diffusion can occur via diffusion and stranding^{95,98} or micelle swelling.^{88,97,106} Diffusion and stranding occurs when oil diffuses into the aqueous solution creating a region of supersaturation. Once this supersaturated region reaches a critical concentration, oil droplets spontaneously nucleate and grow. Micelle swelling also relies on diffusion of oil into the aqueous phase but instead of creating a region of supersaturation, the oil enters and resides in the surfactant micelles. Over time, the micelles increase in size as they uptake the oil.

To this point, the selection of chemicals used to form spontaneous emulsions have been mostly trial and error and, as a result, the fundamentals of spontaneous emulsification are not well understood.⁹⁸ However, the hydrophilic lipophilic difference (HLD) model can be an aid in selecting the chemicals needed to produce a spontaneous emulsion. HLD can predict the phase

formation of an emulsion (e.g., oil-in-water versus water-in-oil) and is often used for microemulsion systems.^{234–236} Microemulsions also form spontaneously but differ in many ways from spontaneous emulsions like their thermodynamic stability and droplet size.⁸⁸ Unlike the HLB value which only describes the surfactant(s), the HLD model describes the entire system and can account for salinity, oil type, temperature, and surfactant type.²³⁷ The HLD model is described fully in the methods section of this chapter. A calculated HLD value greater than zero predicts a water-in-oil emulsion while an HLD value less than zero predicts an oil-in-water emulsion.^{235,237} As the value of HLD approaches zero, the interfacial tension and interfacial curvature are minimized while the oil solubility is maximized,^{235,237} creating conditions favorable for a spontaneous emulsification even though studies have shown trends with salinity that agree with HLD calculations.^{91,104,210,213,238}

Very little research has been done to explore the impact of salt on spontaneous emulsification. For oil-in-water emulsions, anionic surfactants (e.g., sodium lauryl sulfate) only formed spontaneous emulsions when salt was present, specifically near the system's optimal salinity or an HLD near zero.^{91,104,213} Increasing the salinity or the oil carbon number (EACN) resulted in a water-in-oil emulsion meaning that the HLD changed from negative to positive.^{104,210} For an oil soluble surfactant (water-in-oil emulsion), increased salt decreased spontaneity (i.e., the rate and extent of emulsification) and eventually inhibited spontaneous emulsification at approximately 1 M KCl.¹⁰⁶ As salt concentration increased for the water-in-oil system, the HLD increased further from zero. For a nonionic surfactant (Triton X-114), addition of salt decreased the oil droplet size of the spontaneous oil-in-water emulsion.²³⁸ Of the studies previously performed, all outcomes were consistent with HLD calculations although none used HLD to predict or explain spontaneous emulsification.

In this study, a model is suggested to aid in predicting spontaneous emulsification. To do this, HLD calculations were made and correlated with spontaneous emulsification measurements (e.g., visual observations, spontaneity measurements, and turbidity measurements). To change the HLD of the system, three different surfactant systems (nonylphenol polyethoxylate, sodium dodecyl benzene sulfonate, and a mixture of those two surfactants) were used at various concentrations of NaCl (0 to 0.42 M). Both surfactants were selected due to their relevance in wastewater systems
and use in previous wastewater studies.^{15,16,21,32,44,219,239} The addition of salt further increases the relevance to wastewater as many systems contain salts (e.g., bilge water on board marine vessels). These experiments and the resulting model will inform the selection of surfactants and salt concentrations to promote or prevent spontaneous emulsification.

5.2: Materials and Methods

5.2.1: Materials

Toluene (anhydrous, 99.8%), sodium dodecylbenzene sulfonate (SDBS, technical grade, $M_w = 348.5 \text{ g/mol}$) (CH₃(CH₂)₁₁C₆H₄SO₃Na), and sodium chloride (anhydrous, $\geq 99\%$) were purchased from Sigma-Aldrich. Nonylphenol polyethoxylate (NPE, (C₂H₄O)_n·(C₁₅H₂₄O), n=10, $M_w = 660.9 \text{ g/mol}$) was provided by Stepan Co. (MAKON-10). Aqueous solutions were made using deionized (DI) water (Barnstead Nanopure Infinity, ≥ 18 Mohm·cm resistivity). All chemical structures can be found in **Figure 5.1**.



Figure 5.1: Chemical structures of (A) toluene, (B) NPE where n = 10, and (C) SDBS.

5.2.2: Surfactant and Micelle Characterization

Equilibrium surface tensions were measured via pendant drop tensiometry (DSA30, KRÜSS Inc.) using the Young-Laplace equation. Air was used as the bubble phase surrounded by an aqueous continuous phase. These measurements were used to create interfacial tension isotherms for NPE, SDBS, and an equal molar NPE-SDBS solution at salt concentrations from 0 to 0.42 M NaCl. Critical micelle concentrations (CMCs) were calculated using the intersection between two fitted curves of the equilibrium surface tensions above the CMC and below the CMC. The surface excess concentration was calculated from the slope of the adsorption isotherm $\left(\frac{d\gamma}{dlnc}\right)$ before the CMC along with **Equation 5.1**, Gibbs adsorption isotherm:

$$\Gamma = -\frac{1}{mRT} \left(\frac{d\gamma}{dlnC} \right) \tag{5.1}$$

where *m* is the number of adsorbed species at the interface (m = 1 for nonionic surfactants or ionic surfactant in salt solutions and m = 2 for ionic surfactants without added salt), *R* is the universal gas constant, *T* is the absolute temperature, γ is the equilibrium surface tension, and *C* is the bulk surfactant concentration.^{156,220,240} From the surface excess concentration, the surfactant head group area (A_0) was calculated using **Equation 5.2**:

$$A_0 = \frac{10^{20}}{\Gamma N_A}$$
(5.2)

where N_A is Avogadro's number.^{241,242} Using A_0 , the surfactant packing parameter (*P*) was calculated to determine the expected micelle structure at concentrations above the CMC using **Equations 5.3**, **5.4**, and **5.5**:

$$P = \frac{V}{A_0 l_c} \tag{5.3}$$

$$V = (27.4 + 26.9n) * 10^{-3} + V_{benzene}$$
(5.4)

$$l_c = (0.154 + 0.1265n) + l_{benzene}$$
(5.5)

where V is the volume of the surfactant's hydrophobic tail in nm³, l_c is the critical length of the surfactant's hydrophobic tail in nm, and n is the number of carbon atoms in the linear portion of the surfactant tail (n = 9 for NPE and n = 12 for SDBS).^{112,243} Both surfactants contain a benzene ring connecting the hydrophobic tail to the hydrophilic head group. For these calculations, the benzene ring was included as part of the hydrophobic tail and therefore, the volume and diameter of a benzene molecule was used for $V_{benzene}$ (0.1481 nm³) and $l_{benzene}$ (0.28 nm), respectively. The volume and length of benzene were calculated using the density (.876 g/cm³), molecular weight (78.11 g/mol), and bond length (0.139 nm) of benzene.

For the mixed surfactant system containing equal molar NPE and SDBS, the nonideal mixed micelle model was used to calculate the mole fraction of surfactant at the interface, surface, or in the micelle (*x*). **Equation 5.6** was solved iteratively for *x* using the bulk mole fraction (at equal molar, $\alpha_1 = \alpha_2 = 0.5$), the CMCs of each pure surfactant (C_1 and C_2), and the CMC of the mixed surfactant system (C_{12}^*).^{244,245} Subscripts 1 and 2 denote surfactant one and surfactant two of the mixed system, respectively.

$$x_1^2 ln \left[\frac{\alpha_1 C_{12}^*}{x_1 C_1} \right] = (1 - x_1)^2 ln \left[\frac{\alpha_2 C_{12}^*}{(1 - x_1) C_2} \right]$$
(5.6)

5.2.3: Spontaneous Emulsion Preparation

Aqueous solutions were prepared by adding the appropriate amount of a 1 M NaCl solution to DI water followed by a 10 wt.% surfactant solution to achieve the desired surfactant concentration. The aqueous solutions were mixed for a minimum of 10 minutes using a vortex mixer to ensure proper homogeneity. To begin spontaneous emulsification, toluene was pipetted carefully onto the surface of the aqueous solution to eliminate mixing and droplet formation. Toluene was added at 10 vol.% to ensure complete coverage of the air-water interface. This was performed to eliminate Marangoni flows that increase the rate of emulsification.⁸⁸

5.2.4: Dynamic Light Scattering

Micelle and emulsion size distributions were measured via dynamic light scattering (DLS) using a Malvern Zetasizer Nano ZS with a scattering angle of 173° . Diameters are reported as Z-average diameters and peaks are labelled using their corresponding mean diameter (D₅₀). Sizes are reported as an average of at least three measurements with an error of one standard deviation.

Spontaneity of emulsification was measured via DLS and has been described in detail previously.⁸⁸ Each test was performed in triplicate and error bars represent one standard deviation from the mean.

5.2.5: HLD Calculations

The hydrophilic-lipophilic difference (HLD) was calculated for several oil-water-surfactant-salt systems. **Equation 5.7** was used to calculate the HLD using different salinities (*S*), the oil type or effective alkane carbon number (EACN), and different surfactant types or characteristic curvatures (C_c) .^{236,237}

$$HLD = F(S) - k \cdot EACN - \alpha(T - 25) + C_c$$
(5.7)

F(S) is dependent on surfactant type and is equal to $0.13 \cdot S$ for non-ionic surfactants and equal to ln(S + SurfSal) for ionic surfactants where SurfSal is the salinity added to solution by the ionic surfactant. Calculating SurfSal was performed using the concentration of surfactant in solution multiplied by the degree of ionization (approximately 0.66).²⁴⁶ A value of 0.17 was used for k and a value of one was used for the *EACN* of toluene.²³⁷ Since the temperature was constant at 25 °C, the temperature-dependent term in Equation 7 can be ignored. C_c values of -1.91 and -0.90 were used for NPE²³⁵ and SDBS²⁴⁷, respectively. To calculate the HLD of a mixed surfactant system, **Equation 5.8** was used:

$$HLD_{mix} = x_1 HLD_1 + x_2 HLD_2 \tag{5.8}$$

where x_1 and x_2 are the interfacial or micellar mole fractions of the mixed surfactant system calculated using **Equation 5.6**; *HLD*₁ and *HLD*₂ are the *HLD* values from **Equation 5.7** for each of the pure surfactant systems.²⁴⁸

5.2.6: Turbidity

Turbidity measurements were made on spontaneous emulsions using a Molecular Dynamics SpectraMax PLUS UV-Vis spectrometer. Emulsions equilibrated for two days before being measured. An absorbance at 400 nm was selected to compare samples because NPE, SDBS, and toluene did not have any absorbance at this wavelength, and, therefore, the measured absorbance was due solely to the scattering of light by the droplets. Measuring absorbance to determine turbidity of an emulsion has been performed previously.^{249–251} Turbidity increases with droplet concentration and is also sensitive to changes in droplet size.^{250–252} Due to the spontaneous nature of the systems studied here, droplet size was not controllable even when sonication was performed after spontaneous emulsification. However, the changes in droplet size between samples was not expected to impact the turbidity significantly. Additionally, the quantitative results from turbidity measurements were verified visually.

5.3: Results and Discussion

5.3.1: Surfactant and Micelle Characterization

Interfacial tension isotherms were measured to understand the surface adsorption and micellar properties of NPE, SDBS, and NPE-SDBS mixed surfactant systems and how salt impacts these properties. **Figure 5.2** shows the interfacial tension isotherms for all three surfactant systems in NaCl solutions ranging from 0 to 0.42 M. SDBS solutions began salting out (phase separating) at concentrations between 0.27 and 0.31 M NaCl and therefore were not tested above 0.21 M NaCl. From these adsorption isotherms, surfactant and micellar properties were calculated using **Equation 5.1** through **5.6** and are reported in **Table 5.1**.



Figure 5.2: Interfacial tension isotherms for (A) NPE, (B) SDBS, and (C) an equal molar NPE-SDBS mixture at different concentrations of NaCl. Dotted and solid lines represent a best curve fit before and after the CMC, respectively. Error bars represent one standard deviation from the mean of three equilibrium surface tension measurements.

Table 5.1: Surface excess concentration (Γ), surfactant head group area (A_0), critical micelle concentration (CMC), packing parameter (P), and the mole fraction of surfactant in the mixed micelle (x) for NPE, SDBS, and an equal molar NPE-SDBS mixture at different salt concentrations. Errors represent the propagated standard error of the fitted curve(s) from which the calculation originated.

Surfactant	N	PE	SDBS				NPE-SDBS	
[NaCl]	0	0.42	0	0.08	0.10	0.21	0	0.21
(M)								
Γ / 10-6	2.88 ±	2.47 ±	2.07 ±	3.68 ±	3.47 ±	3.38 ±	-	-
(mol/m ²)	0.32	0.46	0.052	0.32	0.74	0.48		
Ao	57.6 ±	67.3 ±	80.1 ±	45.2 ±	47.8 ±	49.1 ±	-	-
(Å ²)	6.4	13	2.0	3.9	10	7.0		
СМС	39.9 ±	30.4 ±	573 ±	57.9 ±	45.2 ±	33.8 ±	35.7 ±	15.2 ±
(ppm)	9.0	11	150	13	21	9.4	9.8	3.3
СМС	$0.060 \pm$	0.046 ±	1.64 ±	0.166 ±	0.129 ±	0.097 ±	0.071 ±	0.030 ±
(mM)	0.014	0.017	0.43	0.037	0.060	0.027	0.019	0.0065
Р	0.46	0.39	0.32	0.57	0.53	0.52	-	-
x	-	-	-	-	-	-	0.76 for	0.55 for
							NPE	NPE

Nonionic surfactants like NPE are relatively insensitive to changes in salt concentration^{242,253} as seen here. As the NaCl concentration increased from 0 to 0.42 M, the head group area increased by approximately 10 Å². However, this increase is within the propagated standard error of the measurement and a t-test concluded that the difference between the two values was not statistically significant (p-value = 0.53, all t-tests are conducted using a two-tailed hypothesis unless otherwise stated). The same holds true for the slight decrease observed in the CMC.

Contrarily, anionic surfactants like SDBS are sensitive to salt. For example, an increase in NaCl from 0 to 0.08 M resulted in a decrease in head group area by approximately 35 $Å^2$ and a decrease in the CMC by an order of magnitude; both decreases were statistically significant with p-values of 0.0005 and 0.006, respectively. A reduction in the head group area was due to the shielding of the anionic SDBS head group by the sodium cations which compressed the Debye length. The

approximated Debye length for the salt-free system was 9.9 nm (i.e., 0.95 mM of Na⁺ ions using an ionization of 66% for SDBS)²⁴⁶ and decreased to 1.1, 0.96, and 0.66 nm when 0.08, 0.10, and 0.21 M NaCl was added, respectively.¹¹² This shielding effect along with the reduced solvent quality contributed to the reduction in the CMC.

For the equal molar NPE-SDBS mixed surfactant system, the CMC at 0 M NaCl was like that of pure NPE. However, due to the presence of SDBS, this mixed system was also sensitive to salt indicated by the reduction of the CMC by approximately 20 ppm to 15.2 ppm from the addition of 0.21 M NaCl and was found to be statistically significant with 95% confidence (p-value was 0.035, using one-tailed hypothesis). This CMC was the lowest value measured across all systems which suggests that the NPE and SDBS interact synergistically. This synergistic effect has been observed previously between Triton X-100 (similar in chemistry to NPE) and SDBS.²⁵³

From the calculated head group area, the packing parameter (P) was also calculated to determine the micelle structure under different salt concentrations. From these calculations, NPE is predicted to form oblong-spherical to cylindrical micelles independent of salt concentration.²²⁰ SDBS is predicted to form spherical micelles in salt-free (i.e., no additional salt added) environments and cylindrical micelles at salt concentrations between 0.08 and 0.21 M NaCl.^{246,254,255}

For equal molar NPE-SDBS mixed surfactant systems, the concentration of adsorbed surfactant at the interface or aggregated in the micelle may not be equal to the bulk surfactant concentration. Therefore, the nonideal mixed micelle model was used to calculate the mole fraction of each surfactant at an interface or in a mixed micelle (x) using Equation 6. At 0 M NaCl, x for NPE was 0.76 (0.24 for SDBS), meaning 76% of the molecules at the interface or in the mixed micelle were NPE and 24% were SDBS. NPE and SDBS have different surface coverage areas (i.e., head group areas), making it important to also consider their respective area fractions at the interface. For NPE, the area fraction of the total surfactant coverage was reduced to 0.69 (0.31 for SDBS) due to the larger head group area of SDBS. In saltwater (0.21 M NaCl), the molar adsorption is more balanced with 55% of the molecules being NPE and 45% being SDBS. However, the area fraction still favors NPE at 0.61 due to the reduction in SDBS head group area with salt. It should be noted that x at 0.21 M NaCl was calculated using the average CMC of NPE at 0 and 0.42 M NaCl and is justified by the statistically insignificant change in CMC over that salt concentration.

5.3.2: Spontaneous Emulsification in NPE-Saltwater Environments

It has been demonstrated previously that NPE can spontaneously emulsify with oils, including toluene, in salt-free systems.⁸⁸ However, the impact of salt on spontaneous emulsification with NPE has not been investigated. **Figure 5.3** shows images of toluene on the surface of an aqueous solution of NPE after four hours of contact in salt-free (top row) and 0.42 M NaCl (bottom row) environments. It should be noted that the entire aqueous surface was covered by toluene, eliminating interfacial turbulence and thus, reducing the rate of emulsification.⁸⁸ A minimum surfactant concentration above the CMC was needed for spontaneous emulsification to occur⁸⁸ and is shown here to be between 50 and 100 ppm of NPE. As salt increased from 0 to 0.42 M NaCl, there was a small increase in emulsification observed at 100 and 500 ppm of NPE indicated by the cloudy, translucent regions. Samples containing 50 ppm NPE did not show visible spontaneous emulsification.



Figure 5.3: Images of spontaneous emulsification for toluene with NPE aqueous solutions containing (top row) 0 M NaCl and (bottom row) 0.42 M NaCl using 10, 50, 100, and 500 ppm of NPE. The top layer of the vial is toluene, and the bottom layer is the aqueous solution. Each image was taken four hours after toluene was pipetted onto the surface of the aqueous solution. The scale bar is 5 mm and applies to all images.

To quantify the impact that salt had on the spontaneity of emulsification in NPE solutions, micelle swelling experiments were performed at 0, 0.21, and 0.42 M NaCl and are presented in Figure 5.4. Time zero represents the initial micelle size of each solution and this increased with salt concentration. At some time after toluene contacted the surface of the aqueous solution, the micelle size increased (i.e., swelling began) linearly over time. Before linear swelling, there was an initial increase and subsequent decrease in micelle size within the first ten minutes. This increase is explained by the placement of oil onto the surface that created interfacial turbulence and mixing resulting in the rapid swelling of few micelles. As these swollen micelles were dispersed into solution, the average size decreased back towards the original micelle size. This phenomena was observed previously for micelle swelling experiments.⁸⁸ The slopes of the micelle swelling curves indicated by the solid lines in Figure 5.4 give the micelle swelling rate (nm/min) and can be compared between samples to quantify their spontaneity. **Table 5.2** shows the micelle swelling rate for each salt concentration. There was no statistical evidence that concluded a significant difference between the 0 M and 0.21 M micelle swelling rates (p-value = 0.29). However, there was a statistically significant difference in the micelle swelling rates when comparing 0 M to 0.42 M (p-value <0.00001) and 0.21 M to 0.42 M (p-value = 0.00002). This result and statistical analysis show quantitatively that salt increased the spontaneity of NPE-toluene systems.



Figure 5.4: Spontaneity measurements via dynamic light scattering over time for 500 ppm NPE solutions containing 0, 0.21, and 0.42 M NaCl. Solid lines represent the fitted curves for the swelling region of each system. Error bars represent one standard deviation from the mean of three measurements.

Table 5.2: NPE micelle swelling rates at 0, 0.21, and 0.42 M NaCl calculated from the slope of the micelle size over time. Error represents the standard error from the corresponding fitted curve.

[NaCl]	Micelle Swelling Rate				
(M)	(nm/min)				
0	0.377 ± 0.010				
0.21	0.393 ± 0.011				
0.42	0.493 ± 0.014				

5.3.3: Spontaneous Emulsification in SDBS-Saltwater Environments

Solutions containing 5000 ppm SDBS were tested in different salt concentrations to see if spontaneous emulsification with toluene would occur; images of this can be seen in **Figure 5.5**. Unlike NPE, SDBS did not spontaneously emulsify with toluene in salt-free systems, and this was

confirmed using DLS. Salt concentrations above 0.06 M were needed to see emulsification after four hours of contact with toluene. As the salt concentration increased, the solutions became cloudier indicating an increase in emulsification. Increases in spontaneity and emulsification with increasing salt were more apparent for SDBS than NPE.



Figure 5.5: Images of spontaneous emulsification for toluene with 5000 ppm SDBS aqueous solutions containing 0, 0.06, 0.07, 0.10, and 0.21 M NaCl. The top layer of the vial is toluene, and the bottom layer is the aqueous solution. The dotted white line in the 0.07 M NaCl image represents the oil-water interface and the solid blue line represents the top of the emulsified oil layer in the aqueous phase. Each image was taken four hours after toluene was pipetted onto the surface of the aqueous solution. The scale bar is 5 mm and applies to all images.

Figure 5.6 shows how salt impacted the minimum concentration of SDBS that was needed for spontaneous emulsification to occur. As the concentration of salt increased, the surfactant concentration needed for spontaneous emulsification decreased. For example, at 300 ppm SDBS, emulsification was not observed at 0.08 M NaCl but was observed at 0.10 and 0.21 M NaCl. This is likely due to the reduction in the CMC and surface tension of SDBS as the salt concentration increased. To quantify the spontaneity of this system with salt, dynamic light scattering measurements were made over time.



Figure 5.6: Images of spontaneous emulsification for toluene with SDBS aqueous solutions containing (first row) 0.08 M NaCl, (second row) 0.10 M NaCl, and (third row) 0.21 M NaCl using 50, 100, 300, 1000, and 5000 ppm of SDBS. The top layer of the vial is toluene, and the bottom layer is the aqueous solution. Each image was taken four hours after toluene was pipetted onto the surface of the aqueous solution. The scale bar is 5 mm and applies to all images.

Figure 5.7 shows spontaneity measurements for a 5000 ppm SDBS system with 0.10, 0.15, and 0.21 M NaCl at various times after toluene was placed on the surface of the aqueous solution. As the droplet size distributions change from light to dark, the time after contact with toluene increases. The light grey curves in each plot are similar in value to the initial micelle size distributions. This means that after 63, 40, and 17 minutes of contact with toluene, the micelle size did not change for 0.10, 0.15, and 0.21 M NaCl, respectively. In the very next measurement (two to three minutes was the time resolution for these experiments), the intensity of the micelle size distribution decreased and droplets approximately an order of magnitude larger than the micelles (140 to 280 nm) appeared. Over time, the micelle size distributions were diminished, and droplets continued to grow. At approximately 80 minutes, droplets with an average diameter between 630 and 780 nm were formed and the droplet size decreased with increasing salinity.²³⁸



Figure 5.7: Spontaneity measurements via dynamic light scattering for aqueous solutions containing 5000 ppm SDBS with (A) 0.10, (B) 0.15, and (C) 0.21 M NaCl. The time label for each curve represents the elapsed time after toluene was pipetted onto the surface of the aqueous solution. The first curve (light grey) in each plot is similar to the initial micelle size. The next two curves (medium grey and black) represent the first detection of droplets and droplet growth, respectively. Labels for each peak represent the mean droplet diameter of that peak.

The evolution of the size distributions in **Figure 5.7** were not gradual and continuous like those observed for NPE systems which displayed micelle swelling.⁸⁸ Instead, the initial micelle sizes were measured until a near-instantaneous appearance of droplets was measured, creating a bimodal distribution of surfactant micelles and droplets within the two-to-three-minute time resolution of the measurement. A bimodal distribution was also present at later times likely due to non-uniform droplet growth. This indicated that a different mechanism was responsible for spontaneous emulsification other than micelle swelling. This mechanism was likely diffusion and stranding²⁵⁶ due to the sudden appearance of droplets which is expected after nucleation and growth.^{88,91,95,98} Images in **Figure 5.5** and **Figure 5.6** also support this mechanism because a gap can be observed between the oil-water interface and the layer of emulsified oil. This gap has been seen previously⁹⁷ and represents the diffusion region below which supersaturation occurred, promoting nucleation and growth.

Although micelle swelling rates could not be calculated to quantify the spontaneity between these systems, the time until nucleation was used instead. As salt concentration increased from 0.10 to 0.15 and 0.21 M NaCl, the time until nucleation occurred was an average of 58 ± 6 , 39 ± 4 , and 22 ± 6 minutes, respectively. This shows that salt increased the spontaneity of these systems.

5.3.4: Spontaneous Emulsification in Mixed NPE-SDBS Systems

Equal molar NPE-SDBS solutions containing 5000 ppm of total surfactant were tested to identify the salt concentration needed for spontaneous emulsification to occur. **Figure 5.8** shows images after four hours of toluene on the surface of an aqueous NPE-SDBS solution at salt concentrations between 0 and 0.21 M NaCl. After 4 hours, spontaneous emulsification was only seen at salt concentrations above 0.01 M NaCl. This was less salt needed than for pure SDBS systems which required more than 0.06 M NaCl. Like pure SDBS systems, as the salt concentration increased, more emulsification was observed.



Figure 5.8: Images of spontaneous emulsification for toluene with a 5000 ppm, equal molar NPE-SDBS solution containing 0, 0.01, 0.02, 0.10, and 0.21 M NaCl. The top layer of the vial is toluene, and the bottom layer is the aqueous solution. Each image was taken four hours after toluene was pipetted onto the surface of the aqueous solution. The scale bar is 5 mm and applies to all images.

It is important to note that the 0 and 0.01 M NaCl systems did show signs of emulsification after six days of contact with toluene (see **Figure 5.9**). However, this was not considered to be a spontaneous system. First, the droplets in these samples were significantly larger than the spontaneous emulsions with some reaching between 100 and 500 μ m in diameter. Because of their relatively large size, the droplets creamed to the surface quickly after being disturbed and were not dispersed throughout the aqueous phase like the spontaneous systems seen in **Figure 5.8**. These droplets likely formed due to the transportation of samples between laboratories which supplied an external energy input. This would be considered a self-emulsifying system and not a truly spontaneous system because small amounts of energy were needed to form droplets.^{97,98}



Figure 5.9: Images of toluene on top of a 5000 ppm, equal molar NPE-SDBS solution containing 0 and 0.01 M NaCl. These images were taken six days after toluene was pipetted onto the surface of the aqueous solution. Red circles locate larger droplets that can be seen at the surface of the aqueous solution. The scale bar represents 5 mm and applies to both images.

DLS experiments were conducted to quantify the spontaneity of the 5000 ppm, equal molar NPE-SDBS mixed surfactant system. **Figure 5.10** shows the micelle swelling curve for 0.10 M NaCl. Time zero represents the initial micelle size which was 19.5 ± 0.1 nm. After toluene was placed on the surface, the micelle size increased slightly followed by a subsequent decrease as seen previously for pure NPE systems. At approximately 10 minutes, the micelles began swelling linearly with time. The slope of the fitted curve in the swelling region (solid black line) resulted in a micelle swelling rate of 0.296 ± 0.0042 nm/min. This swelling rate was smaller than the rate calculated for all pure NPE systems and was found to be statistically significant (p-value < 0.00001 when compared to salt-free NPE). Like pure NPE, the NPE-SDBS system at 0.10 M NaCl spontaneously emulsified via micelle swelling. However, the addition of SDBS reduced the rate of swelling.



Figure 5.10: Spontaneity measurements via dynamic light scattering over time for 5000 ppm, equal molar NPE-SDBS solutions containing 0.10 M NaCl. The solid line represents the fitted curve for the swelling region. Error bars represent one standard deviation from the mean of three measurements. The micelle swelling rate (i.e., the slope of the fitted curve) was 0.296 ± 0.004 nm/min.

At higher concentrations of NaCl, micelle swelling was initially observed followed by a rapid droplet growth that resembled nucleation and growth (i.e., diffusion and stranding). **Figure 5.11** shows the micelle and droplet size distributions over time for systems containing (A) 0.15 and (B) 0.21 M NaCl. Initial micelle size distributions (0 minutes) are represented by the dashed light grey lines. Micelles began swelling until the size distribution suddenly split into a bimodal distribution (dark grey dotted line) that represented droplets and micelles. Over time, the droplets grew (between 250 and 350 nm) while surfactant micelles remained in solution indicated by the three peaks at 36 minutes for 0.21 M NaCl. As salt increased from 0.15 to 0.21 M NaCl, the time to see rapid droplet growth decreased from approximately 37 to 17 minutes indicating that salt increased spontaneity.



Figure 5.11: Spontaneity measurements via DLS for aqueous solutions containing 5000 ppm, equal molar NPE-SDBS with (A) 0.15 and (B) 0.21 M NaCl. The time label for each curve represents the elapsed time after toluene was pipetted onto the surface of the aqueous solution. Labels for each major peak represent the mean droplet diameter of that peak.

5.3.5: HLD Analysis of Spontaneous Emulsification

To better understand the results for spontaneous emulsification, HLD calculations were made for each system as well as for systems studied previously by Davis, *et al.*⁸⁸ **Figure 5.12** shows the calculated HLD values as a function of salt concentration for different surfactant-oil systems. Green symbols represent samples that spontaneously emulsified while red symbols represent samples that did not spontaneously emulsify. All samples above the green reference line at an HLD of -2.05 were spontaneous and all samples below the red reference line at an HLD of -2.4 were not spontaneous. In the region between an HLD of -2.4 and -2.05, samples transitioned from non-spontaneous to spontaneous.



Figure 5.12: Calculated HLD values as a function of salt (NaCl) concentration for different surfactant-oil systems. Green symbols represent samples that showed spontaneous emulsification while red symbols represent samples that were not spontaneous. The symbol for cyclohexane is yellow because there was very little emulsification that could only be detected via DLS. Xylenes, cyclohexane, and mineral oil systems were observed in a previous study.⁸⁸

Figure 5.12 demonstrates the relationship between HLD and spontaneous emulsification: as the HLD of a system approaches zero, it is more likely to spontaneously emulsify. However, this relationship only shows whether emulsification occurred and does provide information on spontaneity or the extent of emulsification. Therefore, turbidity measurements were made to quantify the relative spontaneity between systems that emulsified.

Figure 5.13 shows the turbidity of spontaneous emulsions after two days of contact with toluene as a function of the calculated HLD value. As the HLD value approached zero (salt concentration increased), turbidity (the amount of emulsified toluene) also increased. Turbidity measurements confirmed the visual observations shown previously but were used here to quantify spontaneity. HLD not only models when spontaneous emulsification will occur but also the relative spontaneity within a given system. This model can then be used to better prevent or promote spontaneous emulsion systems. For example, if a system contains SDBS, toluene, and NaCl, **Figure 5.12** and

Figure 5.13 can aid in determining the amount of salt need to promote emulsification or the amount of dilution needed to prevent emulsification.



Figure 5.13: Calculated HLD values for samples with different turbidities (i.e., total emulsified toluene). Turbidity was taken as the absorbance at 400 nm and was measured after two days of contact with toluene. Error bars represent one standard deviation from the mean of three measurements.

HLD calculations were also made for a spontaneous emulsion system observed by others. Noushine Shahidzadeh et al.¹⁰⁴ observed spontaneous emulsification for systems containing sodium bis (2-ethylhexyl) sulfosuccinate (AOT, $C_c = 2.5$)²⁴⁷ and 0.075 M NaCl. When octane (EACN = 8) was used as the oil, a water-in-oil emulsion formed spontaneously and the HLD value was calculated to be 0.32. When dodecane (EACN = 12) was used as the oil, an oil-in-water emulsion formed spontaneously and the HLD value was calculated to be -0.36. These calculations show that HLD is not only capable of predicting when spontaneous emulsification will occur, but it can also predict the phase behavior of a spontaneous emulsion. Other studies on spontaneous emulsion systems are difficult to calculate HLD values for. This is due to the unknown C_c of the

surfactant, the mixture of surfactants, or the use of short chain alcohols which are not easily accounted for using HLD.

Although the HLD model can be useful for understanding spontaneous emulsion systems, it is not without limitations and these limitations are important to consider when modeling spontaneous emulsions. As seen previously⁸⁸ and in Figure 5.3 and Figure 5.6, spontaneous emulsification is dependent on surfactant concentration which is not accounted for in the current HLD model. This model assumes enough surfactant is present to spontaneously emulsify. The current model also does not account for the phase separation or "salting out" of surfactant which occurred at approximately 0.29 M NaCl for SDBS. Co-surfactants like alcohols are not easily modeled using HLD²³⁷ and are often used to promote spontaneous emulsification.⁹⁷ Mixed surfactant systems can be modeled using HLD, as shown here, but not without additional measurements to obtain the CMC and C_c values. The HLD model is not well defined for mixed oil systems which can also spontaneously emulsify (see Appendix C). Additionally, the HLD model is only predictive within a given system and not across systems. For example, if one surfactant system spontaneously emulsifies at an HLD of -2, that does not mean a different surfactant chemistry will also spontaneously emulsify at that same HLD value. This model is empirical and has not been proven to predict the emulsification of samples that have not been tested. However, the testing of more surfactant and oil chemistries could provide a more predictive model. The goal of this research is not to predict emulsification for all systems but to show the correlation between HLD and spontaneous emulsification that, to the authors' knowledge, has not been adequately discussed.

5.4: Conclusions

Toluene spontaneously emulsified with NPE, SDBS and an equal molar NPE-SDBS mixture in saltwater systems. The main findings were:

 Toluene spontaneously emulsified with nonionic NPE at salt concentrations from 0 to 0.42 M NaCl. As salt concentration increased, there was a slight increase in the spontaneity. The mechanism for emulsification was oil diffusion and micelle swelling.

- Toluene spontaneously emulsified with anionic SDBS but only at salt concentrations between 0.07 and 0.27 M NaCl. As salt concentration increased, spontaneity increased significantly compared to the NPE system. Spontaneous emulsification for this system occurred via diffusion and stranding.
- Toluene spontaneously emulsified with an equal molar NPE-SDBS mixture but only at salt concentrations above 0.02 M NaCl. Similar to pure SDBS, as salt increased, spontaneity increased. Both micelle swelling and diffusion and stranding were observed in this system.
- HLD analysis showed that the occurrence of spontaneous emulsification can be modeled. As the HLD of a system approached zero, spontaneous emulsification was more likely to occur. A transition region in HLD between -2.4 and -2.05 existed where emulsification changed from non-spontaneous to spontaneous. Turbidity measurements showed that HLD can also model the spontaneity of a system.

This work provides a foundation for the relatively unexplored area of spontaneous emulsification in saltwater environments. The HLD model is proposed as a tool to predict spontaneous emulsification and an empirical model was built. This model can be used to help promote spontaneous emulsification and increase spontaneity or to prevent it depending on the application. The addition of salt into this model is a more practical approach because many systems contain salts, including bilge water. To better predict spontaneous emulsification using the HLD model, more empirical data must be collected including different surfactant, oil, and salt chemistries.

CHAPTER 6: SUMMARY AND FUTURE DIRECTIONS

6.1: Summary and Implications of Results

Emulsion stability to coalescence improved for an anionic surfactant (SLES) as the concentration of salt increased from 0 to 1.25 M NaCl (see **Figure 2.2**). This improvement in stability to coalescence was due to an increased surfactant adsorption at the interface (**Figure 2.4**), improved surfactant adsorption kinetics (**Figure 2.5**), the presence of hydration forces at small (~1 to 4 nm) separations (**Figure 2.7**), and the conditions favorable for the formation of a Newton black film. These findings show that salts present in an emulsion system like bilge water could increase the stability of the emulsified oils and create difficult conditions for oil-water separation techniques.

Dynamic and static ageing experiments showed that the ageing conditions significantly impacted the emulsion droplet size distribution over time. Dynamic ageing led to an increase in coalescence at low surfactant concentrations (< 100 ppm, see **Figure 3.1**) and emulsification at larger surfactant concentrations (> 100 ppm, see **Figure 3.4**). This study showed the importance of movement during the ageing of emulsions and is relevant to systems like bilge water as shipboard movement would create similar conditions to the dynamic ageing in this study.

Emulsified oil in wastewater systems is typically concerned with minimizing external energy inputs to prevent emulsification. However, components likely present in bilge water were found to spontaneously emulsify without an external energy input (see **Figure 4.2**). Emulsification occurred via diffusion and micelle swelling and resulted in nanometer-sized droplets that would be difficult to separate from water (see **Figure 4.9** and **Figure 4.10**). This is a major concern for wastewater systems like bilge water because even when care is taken not to emulsify oil in water through external energy inputs, emulsification can occur due to contact of the oil to the surfactant solution. Furthermore, the oils that show spontaneous emulsification (aromatics) are among the most environmentally adverse. Spontaneous emulsions can also show an improved stability compared to conventional emulsions depending on the droplet size, chemical properties like oil solubility, and concentration of components in the system. For example, nano-sized emulsions are less susceptible to creaming than conventional, micron-sized emulsions. However, oils with a

relatively large solubility in water (i.e., oils likely to form spontaneous oil-in-water emulsions) are more susceptible to Ostwald ripening.

Spontaneous emulsification of a nonionic surfactant (NPE) was studied in the presence of NaCl which had little impact on the spontaneity (see **Figure 5.3**). However, the addition of NaCl promoted the spontaneous emulsification of an anionic surfactant (SDBS) that was otherwise non-spontaneous in a salt-free system (see **Figure 5.6**). As the concentration of NaCl increased, emulsification increased. This is concerning for wastewater systems as some amount of salt is likely present (e.g., seawater in bilge water systems). HLD calculations were used to model spontaneous emulsification as a function of salt concentration (see **Figure 5.12**). Using this model, a better understanding of the conditions that favor spontaneous emulsification are understood and from this, preventative measures can be taken.

6.2: Future Directions

Results showing an improved stability to coalescence in the presence of salt would benefit from further investigation including other ionic surfactant chemistries. The improved stability in salt has been demonstrated with anionic SLES surfactant but has not been tested for other surfactant chemistries of surfactant mixtures. Similar results including increased surfactant adsorption and adsorption kinetics should hold true for other anionic surfactants, but the impact on emulsion stability has yet to be measured. Direct measurement and observation of the Newton black film formation with increasing salt would be beneficial to confirm the mechanisms responsible for preventing coalescence.

As dynamic ageing can create smaller oil droplets via emulsification, methods of mitigating the energy input during dynamic ageing should be investigated. This could include, but is not limited to, adding a cap to the surface of the emulsion to prevent breaking waves from forming and increasing the viscosity of the emulsion system to mitigate movement of the emulsion system. Both suggestions could reduce the energy input to the emulsion system during movement and could prevent conditions where further emulsification occurs.

Spontaneous emulsification is a relatively unexplored area of colloid and surface science. As a result, many more oil-surfactant-salt compositions and concentrations must be studied to understand and predict spontaneous emulsification. An increase in empirical data would further improve the HLD model and its prediction of spontaneous emulsification. More specifically, a better understanding of the following would significantly improve the HLD model: the impact of mixed oils, dependence of surfactant concentration, surfactant solubility with salt concentration, and the impact of short chain alcohols on the HLD value and spontaneous emulsification.

Regardless of improvements to the HLD model, it can be used in its current state to make informed decisions when selecting surfactant chemistry, oil chemistry, and salinity to promote or prevent spontaneous emulsification. For example, surfactants with a C_c near zero or ionic surfactants in saline environments are more likely to create the conditions favorable for spontaneous emulsification. Additionally, surfactant mixtures can be used to control the effective C_c of the system. Selecting oils that have an *EACN* near zero can be selected to promote oil-in-water spontaneous emulsification. Conversely oils that have a relatively large *EACN* (e.g., 10 to 18) can be selected to promote water-in-oil spontaneous emulsification. Knowing how each component in the surfactant-oil-salt system influences spontaneous emulsification is beneficial when exploring new spontaneous emulsion formulations.

APPENDIX A: SUPPORTING INFORMATION FOR CHAPTER 2, "IMPACT OF SALTWATER ENVIRONMENTS ON THE COALESCENCE OF OIL-IN-WATER EMULSIONS STABILIZED BY ANIONIC SURFACTANT"

Influence of Drop Size on Dynamic Interfacial Tension

Dynamic interfacial tension measurements between mineral oil and aqueous solutions containing 500 ppm SLES and NaCl can be seen in **Figure A1**. For each salt concentration (0.84 and 0.60 M NaCl) two different drop volumes are used to show the dependence of drop volume on surfactant adsorption kinetics. There was no observable difference between the 3.5 and 1.5 μ L drops at 0.60 M NaCl. A slight increase in adsorption kinetics (i.e., decrease in the interfacial tension) was observed when increasing the droplet size from 3.5 to 6.0 μ L. However, the difference in interfacial tension is likely due to experimental error as it is within the accuracy of the tensiometer (0.3 mN/m). If droplet size were to play a role, the slight increase in surfactant adsorption with increasing droplet size is in opposition to what is displayed in **Figure 2.5**, where smaller drops were used for systems that showed faster adsorption kinetics.



Figure A1: Dynamic interfacial tension for 0.84 and 0.60 M NaCl solutions containing 500 ppm SLES against mineral oil at different drop sizes.

Droplet Size Distributions

Average droplet size distributions for emulsions containing 0, 0.05, 0.21, 0.42, and 1.25 M NaCl and 0.42 M MgCl₂ are shown in **Figure A2**. For each salt concentration, size distributions were measured at 0 (90 minutes), 5, 10, 20, and 56 days of ageing and are overlapped for comparison. Emulsions without salt appear to have decreased in diameter over time, indicated by the significant decrease in droplets between 10 and 100 μ m. This apparent decrease, however, is not an accurate representation of the entire system but is rather a limitation of the measurement technique. Emulsions containing 0.05 M NaCl increased in droplet size over time. After 20 days of aging, droplets greater than 100 μ m in diameter appear as a third peak in the distribution. As the concentration of NaCl increased to 0.21 and 0.42 M, droplet sizes increased over time and was less pronounced as salt concentration increased. For 1.25 M NaCl, droplet size distributions showed negligible change over time apart from small peaks appearing between 100 and 300 μ m starting at 5 days of ageing. In the presence of a divalent salt (0.42 M MgCl₂), the emulsion droplet

size distribution showed little change over time and were similar to the 1.25 M NaCl emulsions which had an equivalent ionic strength.



Figure A2: Emulsion droplet size distributions for 0, 0.05, 0.21, 0.42, and 1.25 M NaCl and 0.42 M MgCl₂. For each salt concentration, emulsions were aged and measured at 0 (90 minutes), 5, 10, 20, and 56 days. Each size distribution is an average of five measurements from three separately prepared emulsions for a total of 15 measurements.

Optical Microscopy

Optical micrographs were taken for each emulsion composition at 0 and 20 days of aging. **Figure A3** shows micrographs for emulsions with low salt concentrations (0 to 0.21 M NaCl) while **Figure A4** shows emulsions at higher salt concentrations (0.42 to 1.25 M NaCl and 0.42 M MgCl₂). For emulsions without salt, the larger droplets seen at 0 days are not present in micrographs after 20 days of aging. For emulsions containing 0.05, 0.21, 0.42 NaCl and 0.42 MgCl₂, optical microscopy did not identify any observable changes in droplets between 0 and 20 days of aging

and highlights the importance of using laser diffraction to identify slight changes in droplet size that would otherwise go undetected. Emulsions containing 1.25 M NaCl show an increase in aggregation number and size (~100 to 200 μ m) but no significant change in the individual droplet size.



Figure A3: Optical micrographs for emulsions containing 0, 0.05, and 0.21 M NaCl at 0 (90 minutes) and 20 days after emulsification.



Figure A4: Optical micrographs for emulsions containing 0.42 and 1.25 M NaCl and 0.42 M MgCl₂ at 0 (90 minutes) and 20 days after emulsification.

Long-Term Emulsion Ageing

Droplet sizes were measured at approximately 455 days for 0.05, 0.21, and 1.25 M NaCl samples and 700 days for 0 M NaCl samples as long-term stability measurements. **Figure A5** shows the volume mean diameter for droplets between 0 and 700 days of ageing. Salt-free samples showed little change over this period indicating that while these emulsions show significant coalescence within the first 20 days, the remaining emulsion is stable to coalescence for up to 700 days. Emulsions containing 0.05 and 0.21 M NaCl showed an increase in droplet diameter between 56 and 455 days. However, the droplet diameters at 455 days were still within one standard deviation from the droplet diameters at 56 days. Emulsions containing 1.25 M NaCl showed no significant change in droplet size from 56 to 455 days. **Figure A6** shows the full emulsion droplet size distributions after long-term ageing.



Figure A5: Volume mean droplet diameters for long-term stability measurements between 0 and 700 days. Note that the x-axis has two breaks in time at 60 days and 462 days. Error bars represent one standard deviation from the mean.



Figure A6: Emulsion droplet size distributions containing 0, 0.05, 0.21, and 1.25 M NaCl between 0 and 700 days of ageing.

Interfacial Rheometry

Table A1 shows the elastic, viscous, and dilatational moduli for different oscillation frequencies and salt concentrations.

Table A1: Elastic, viscous, and dilatational moduli for salt concentrations of 0 M, 0.42 M NaCl, and 0.42 M MgCl₂ at oscillation frequencies of 0.01, 0.05, and 0.10 s⁻¹. Error represents one standard deviation from the mean.

Oscillation Frequency (s ⁻¹)		0.01			0.05			0.10	
Salt (M)	0	0.42	0.42	0	0.42	0.42	0	0.42	0.42
		NaCl	MgCl ₂		NaCl	MgCl ₂		NaCl	MgCl ₂
Elastic	$1.35 \pm$	0.18 ±	0.29 ±	3.35 ±	$0.85 \pm$	$0.80 \pm$	5.17	1.60	1.36 ±
Modulus	0.28	0.08	0.03	0.27	0.07	0.06	\pm	±	0.11
(mN/m)							0.19	0.12	
Viscous	1.63 ±	$0.53 \pm$	$0.47 \pm$	$4.58 \pm$	1.75 ±	1.46 ±	6.68	2.72	$2.34 \pm$
Modulus	0.01	0.01	0.04	0.17	0.05	0.05	±	±	0.05
(mN/m)							0.22	0.05	
Dilatational	2.13 ±	$0.55 \pm$	$0.56 \pm$	$5.80 \pm$	1.95 ±	1.71 ±	8.69	3.16	$2.77 \pm$
Modulus	0.19	0.03	0.04	0.21	0.05	0.06	<u>±</u>	±	0.07
(mN/m)							0.21	0.07	

APPENDIX B: SUPPORTING INFORMATION FOR CHAPTER 4, "DIFFUSION-CONTROLLED SPONTANEOUS EMULSIFICATION OF WATER-SOLUBLE OILS VIA MICELLE SWELLING"

Creaming Velocity Calculation

The creaming velocity was calculated using the Stokes' velocity (v) in **Equation B1**, where ρ_d is the density of the dispersed phase (toluene, 867 kg/m³), ρ_c is the density of the continuous phase (water, 997 kg/m³), g is the acceleration due to gravity, R is the radius of the droplet (250 and 500 nm), and η is the viscosity of the continuous phase (water, 8.9 x 10⁻⁴ Pa·s).

$$v = \frac{2(\rho_d - \rho_c)gR^2}{9\eta} \tag{B1}$$

To account for Brownian motion, **Equations B2** and **B3** were used to calculate the diffusion coefficient for a dilute system (*D*) and the mean squared displacement (*x*), respectively, where *k* is the Boltzmann constant, *T* is temperature, and *t* is time.

$$D = \frac{kT}{6\pi\eta R} \tag{B2}$$

$$x = \sqrt{2Dt} \tag{B3}$$

To calculate the position of a droplet at a given time, t, the Stokes' velocity, v, was multiplied by t to find the displacement in the vertical direction of the vial. This upward movement was assigned a positive value. For Brownian motion, the mean squared displacement was used and was assumed to only act in the negative, downward direction. Although Brownian motion will act randomly, this conservative assumption will act to overestimate the time needed for creaming. To find the

total displacement of the droplet, the positive and negative displacements were summed. Using these equations and assumptions, the time for a droplet of a given size to be displaced 0.03 m in the positive, upward direction was calculated.

Dynamic Interfacial Tension Measurements

Figure B1 shows the average dynamic interfacial tension values for toluene and mineral oil continuous phases in contact with 500 ppm NPE drops. An equilibrium interfacial tension was not observed for the time scales investigated herein as both oils showed a slight increase in the interfacial tension over time. An increase in interfacial tension for toluene (Figure B1A) was attributed to the spontaneous emulsification of toluene inside of the aqueous drop. As emulsification proceeds, the aqueous phase density decreased in time to unknown values and resulted in an increase in interfacial tension. Spontaneous emulsification within the drop was verified by the observed decrease in light transmitted through the drop (see Figure B2). Since mineral oil does not spontaneously emulsify with NPE solutions, the increase in interfacial tension shown in Figure B1B was most likely due to the solubilization of NPE into the oil continuous phase. This dilutes the surfactant concentration resulting in an increased interfacial tension. Equilibrium, steady-state behavior may be possible to observe from longer duration experiments, but the interfacial tension values calculated from droplet profiles would be inaccurate due to the evolving densities of the drop and continuous phase from both emulsification (for toluene system) and NPE partitioning (for mineral oil system). Therefore, because of these measurement limitations, initial interfacial tension values were reported in the manuscript and used to make comparisons between samples.



Figure B1: Average dynamic interfacial tension of (A) toluene and (B) mineral oil (continuous phase) with 500 ppm NPE solutions (drop). Error bars represent one standard deviation of repeated measurements.



Figure B2: Images of a drop containing 500 ppm NPE surrounded by toluene. The left image was taken just after drop formation and the right image was taken after 25 minutes, showing the formation of a spontaneous emulsion within the volume of the drop.
Spontaneous Emulsification Below and Near the CMC (40 to 60 ppm)

Aqueous solutions of NPE were created at concentrations of 10 ppm (< CMC) and 50 ppm (\approx CMC). Toluene was then placed on top of the solutions similar to previous experiments. For the 10 ppm solutions, no signatures of NPE micelles were detected by DLS measurements, and there were no visual or measurable features of spontaneous emulsification (see left image of Figure S3). For the 50 ppm solutions, signatures of swollen NPE micelles were identified from DLS measurements although the scattering signal was very low with high values of uncertainty, most likely due to the very low concentration of micelles. Spontaneous emulsification was also observed, as shown in the right image of **Figure B3**. Thus, solutions with surfactant concentration below the CMC did not exhibit spontaneous emulsification due to the absence of micelles while spontaneous emulsification was observed for solutions with surfactant concentration near the CMC due to the presence of micelles.



Figure B3: Images of aqueous solutions containing (left) 10 ppm NPE and (right) 50 ppm NPE with 5000 ppm of toluene on the surface. Both images were taken two hours after toluene was in contact with the aqueous solution.

APPENDIX C: SUPPORTING INFORMATION FOR CHAPTER 5, "PREDICTING SPONTANEOUS EMULSIFICATION IN SALTWATER ENVIRONMENTS USING THE HLD MODEL"

Ageing of SDBS Spontaneous Emulsions

Figure C1 shows the ageing of a spontaneous emulsion containing 0.08 M NaCl, 5000 ppm SDBS, and toluene from four hours to four days. As the toluene spontaneously emulsifies, a gap is seen between the oil-water interface and the emulsion layer. As the system ages, the gap between the initial spontaneous emulsion layer and the oil-water interface increases and the emulsified layer sediments. At four days, the primary emulsified oil sedimented to the bottom of the aqueous solution creating an opaque bottom layer and a transparent top layer above. A secondary emulsion also formed over this ageing period and remained at the oil-water interface.



Figure C1: Images of a spontaneous emulsion between toluene and an aqueous solution containing 0.08 M NaCl and 5000 ppm SDBS. The spontaneous emulsions are shown for (left) four hours of contact with toluene and (right) four days after contact with toluene.

Toluene droplets have a lower density than the surfactant-salt solution and are expected to cream to the oil-water interface rather than sediment. However, this was not observed. To further investigate this phenomenon, samples were carefully extracted from the transparent, top layer and the opaque, bottom layer and measured using DLS. Figure C2 shows the size distributions for the top and bottom layer of the spontaneous emulsion in Figure C1 after six days of ageing. The transparent, top layer contained SDBS micelles approximately 10 nm in diameter. The opaque, bottom layer also contained SDBS micelles, however, larger droplets between 200 nm and 6 μ m were also measured. This confirms that some droplets did sediment over time. Since the salt and surfactant are the only components in the system denser than water, we can assume that one or both components partitioned within the aqueous solution and became more concentrated around the oil droplets over time. Increases in both salt and surfactant create favorable conditions for spontaneous emulsification and is likely the cause for the observed sedimentation.



Figure C2: Dynamic light scattering (DLS) results for the top and bottom aqueous layer of a spontaneous emulsion containing 0.08 M NaCl, 5000 ppm SDBS, and toluene. These measurements were made after six days of ageing.

Spontaneous Emulsification of Mixed Oil Systems

Figure C3 shows the spontaneous emulsification of different toluene-heavy mineral oil mixtures with a 500 ppm NPE solution. Toluene and mineral oil were premixed before placing them on the surface of the surfactant solution. Once the oil mixture was placed on the surfactant solution, the samples were rested for 40 minutes before they were photographed. As the oil mixture increased in mineral oil content and decreased in toluene content, spontaneous emulsification was reduced. For an oil containing 75 wt.% toluene and 25 wt.% mineral oil, toluene was able to diffuse out of the mineral oil and spontaneously emulsify with the NPE solution. Toluene likely separated from the mineral oil as mineral oil has little to no solubility in water and does not spontaneously emulsify. Additionally, after spontaneous emulsification occurred, large residual oil droplets remained on the surface and were likely mineral oil. As the mineral oil content increased to 75 wt.%, spontaneous emulsification was significantly reduced.



Figure C3: Spontaneous emulsification of toluene-heavy mineral oil mixtures in a solution containing 500 ppm NPE. The toluene-heavy mineral oil mixtures were (left) 75 wt.% toluene and 25 wt.% mineral oil, (center) 50 wt.% toluene and 50 wt.% mineral oil, and (right) 25 wt.% toluene and 75 wt.% mineral oil. A total oil concentration of 5000 ppm was used. This image was taken 40 minutes after the oil mixture was placed in contact with the surfactant solution.

Figure C4 shows optical micrographs of two spontaneous emulsions after 48 hours. Samples with 75 wt.% toluene contained smaller droplets (< 100 μ m in diameter) than samples with 50 wt.% toluene ($\leq 200 \ \mu$ m in diameter). However, both samples appeared to contain larger droplets than 100 wt% toluene samples (100 to 500 nm). This suggests that the presence of mineral oil reduced the spontaneity of emulsification. This agrees with the HLD model in that the addition of mineral (increase in the average EACN) will result in a more negative HLD value indicating conditions that are less favorable for spontaneous emulsification. While these results agree with the general trends of HLD, there is currently no method to quantitatively model this using HLD.



Figure C4: Optical micrographs of spontaneous emulsions with a toluene-heavy mineral oil mixture in 500 ppm NPE. The oil compositions were (left) 75 wt.% toluene and 25 wt.% mineral oil and (right) 50 wt.% toluene and 50 wt.% mineral oil. Both micrographs were taken after 48 hours after the oil mixture was placed in contact with the surfactant solution. The scale bars represent 200 µm.

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VITA

Twenty-seven years prior to the writing of this dissertation, Cole R. Davis was born in Fort Wayne, IN. Raised in Columbia City, IN, he attended Purdue University-Fort Wayne for two years before transferring to Purdue University-Main Campus in West Lafayette, IN. Undergraduate studies led Cole to receive his Bachelor of Science in Materials Engineering with distinction in May of 2018. Most of Cole's undergraduate research was performed studying superabsorbent polymers as internal curing agent for high-performance concrete under Professor Kendra Erk. Post-undergrad, Cole began his PhD in the School of Materials Engineering at Purdue University where he studied the formation and stability of model emulsion systems under Professor Kendra Erk and Professor Carlos Martinez.