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Dispersants for Crude Oil Spills: Dispersant Behavior Studies

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Dispersants for Crude Oil Spills: Dispersant Behavior Studies

A Major Qualifying Project Report
submitted to the faculty of Worcester Polytechnic Institute
in partial fulfillment of the requirements for the
degree of Bachelor of Science

Submitted to:

Project Advisor: John Bergendahl, WPI Professor

Project Advisor: Nikolaos Kazantzis, WPI Professor

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Date: 28 April, 2011

Abstract

The purpose of this study was to experimentally investigate the behavior of the dispersant employed in clean-up efforts to the Gulf of Mexico affected by the Deepwater Horizon oil spill, namely COREXIT 9500A®. Laboratory results provided insight into the characteristics of the dispersant and shed light onto some unexpected observations. Analysis of the data and observations formed several conclusions pertaining to the properties of the dispersant itself as well as the methods of application involved in the clean-up efforts.

Acknowledgements

This project would not have been possible without the assistance of our advisors Professor John Bergendahl and Professor Nikolaos Kazantzis as well as the samples of dispersant provided by Marco Kaltofen.

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List of Abbreviations

ASTM	American Society for Testing and Materials
CCC	Critical Coagulation Concentration
CMC	Critical Micelle Concentrations
DLVO	Derjaguin, Landau, Verwey and Overbeek
EVOS	Exxon Valdez Oil Spill

Executive Summary

Background

In April of 2010 the Deepwater Horizon oil rig exploded releasing an estimated 4.9 million barrels of crude oil into the Gulf of Mexico. The main technique employed to minimize the damage inflicted was the use of dispersants, mainly COREXIT 9500A®. Dispersants similar to this product have been used in several other oil spill disasters however little information has been released on the properties and behavior of these chemicals. Even after observing some of the adverse effects of using this product, no significant research appears to have been done in the way of investigating why this may be occurring.

Objectives

Our goals for the project include an initial classification and investigation of the emulsion formed by the dispersant and its apparent properties, specifically focusing on stability. From this point we furthered our study by experimentally investigating what may adversely affect the stability and relate observations from the laboratory to those occurring in the environment.

Methodology

A prolonged period of time was spent designing and executing experiments which would reveal different aspects of the dispersant behavior. Primarily the focus was on creating a consistent and realistic environment which would appropriately model the natural environment to which the dispersant is applied. This included the creation of a sea water solution and diagnosing the appropriate volume of COREXIT necessary to form an emulsion of significant sample size to measure turbidity and absorbance. Following the familiarization the with dispersant and the emulsion formed, we were able to then advance to applying permutations to the system in efforts to obtain information on how the dispersant functions when more variables are introduced which are likely present in the Gulf of Mexico. Measurements to evaluate the extent of the emulsion development were taken using a turbidimeter and a spectrophotometer. These variations include a decrease in salinity, the addition of particulates including sand and humic acid, introducing air bubbles to the system, taking data readings from different temperatures settings and finally the addition of motor oil to the solution. With these influences on the system we were able to acquire valuable data readings in addition to several observations which will be explained qualitatively in the proceeding document.

Results and Analysis

Through the experimentation discussed above we were able to determine that temperature has the most significant impact on the stability of the emulsion. The salinity of the solution appears to have a significant impact on the micellular formation of the emulsion droplets, allowing for increased emulsification with increasing salinity. Humic additives, on the other hand, appear to have a negative effect on the dispersants ability to form an emulsion with sea water; the effect is also magnified when more gas is dissolved in the system.

Conclusion & Recommendations

Conclusions which arose from the various permutations include the negative effects which both temperature increase and decrease have on the stability of the emulsion. These results deviate from the expected behavior of the dispersant and are possibly an explanation to some of the observations made in the oil contaminated waters. This leads to the belief that the dispersant may not have been formulated for appropriate use at sub sea level conditions. The second most significant result is the affects the adjustment of salinity has on the stability of the emulsion phase, this is very telling about the complications which may ensue when the ocean meets the Mississippi River and the salinity decreases. Other results are included on the kinetics of the emulsion formation which were not included in our initial experimental intentions but provided interesting information on how time may affect the properties of the dispersant under various additions to the solution.

Further recommendations pertain to the extent of experimentation which were available to us. Our most important recommendation is to create a more realistic simulation of the oil spill environment, this includes obtaining samples of the waters affected by the oil spill and the addition of crude oil rather than modeling the system with motor oil. Further investigation should be conducted with different and more advanced technologies to explore other aspects of the dispersant such as surface properties and bonding abilities.

Chapter 1: Introduction

1.1 Oil Spills

The Gulf of Mexico was the site of a massive oil leak that occurred on April 20, 2010 called the Deepwater Horizon oil spill for the British Petroleum (BP) platform that exploded. The explosion was the reason for a large fire and released an estimated 780,000m^3 (206 million gallons, or 4.9 million barrels) of oil into the Gulf, (Jackson, J. B. C., et al, 1989).

The area of the spill increased over time to several hundred square kilometers and has since been reported to have decreased in size. The result of the oil spill caused a ban on fishing in 1180,000 km^2 of the Gulf in May 2010 by the US government, (Jackson, J. B. C., et al, 1989 and Kerr et al., 2010). Many researchers have since tried to assess the impact of the spill and its future consequences.

Figure 1.1 General location and extent of 2010 Gulf of Mexico oil spill in June.

(Jackson, J. B. C., et al, 1989)

As of November 2010, the amount of oil still in the Gulf is unknown but from studies conducted by experts in the field an estimated 13%-39% is still present in the Gulf that would hopefully be removed by evaporation or microbial decomposition. The COREXIT dispersants being used could have potentially formed oil plumes at 1 km depths that have high concentrations between 1-2 ppm of oil

(Jackson, J. B. C., et al, 1989 and Kerr, 2010). The discrepancy of how much oil is currently in the Gulf is uncertain due to the oil that has gone underwater.

The actual amount of oil in the Gulf is an issue of immense concern because of the effects that crude product has on the surrounding beaches and marshes. Currently, there are no adequate models to determine the consequent effects on plant and animal life, residing in both land and sea, the effect on the local fishing economies in these areas and the general health and well-being of sea food being consumed by the masses in that area, (Jackson, J. B. C., et al, 1989).

The oil continuously flowed into the Gulf for three months after the initial explosion while remediation efforts to stop the oil spill were considered. In disasters that occurred around the world, such as the Chernobyl Ukraine nuclear reactor explosion in 1986, it has been suggested that more negative effects have resulted from remediation efforts put forth by man-kind, (Davydchuk, 1997 and Cronk et al, 1990) and this may be the case in terms of the Deepwater Horizon oil spill as well. In the case of the affected waters within the Gulf of Mexico, the nutrients found in the Mississippi River coupled with the warm water temperatures in the Gulf could improve conditions for the natural "oil eating microbes" that breakdown oil of low molecular weight, and thus improving the dissipation of oil.

COREXIT dispersants were used to treat the oil in salt water creating complications involving removing the liquid solid waste produced and the unknown effects it causes to aquatic life. When other chemicals are used to treat damaged natural habitats including a variety of plant and animal life, it is usually ineffective (Jackson, J. B. C., et al, 1989).

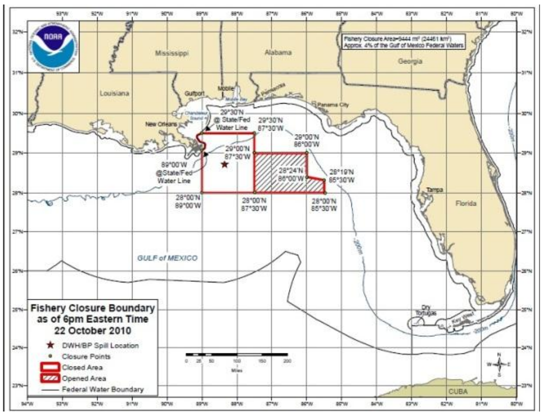

Figure 1.2 The Site of the Gulf Spill: Closed Areas as of October 22, 2010 (Amendola, 2010)

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1.1.1 Effect of Oil Spills

Oil spill occurrences are one of the most environmentally devastating accidents that gain attention around the world. There have been many accidents reported in places such as India, Norway, America, England, Spain and Japan, (Campbell et al., 1993, Lyons et al., 1999, Qiao et al., 2002, Chiau, 2005, Balseiro et al., 2005 and Sultan Ayoub Meo et al, 2008).

One example of an oil spill is when the Tasman Spirit Greek oil tanker in 2003 cracked and an estimated 28,000 tons of crude oil flowed into the sea. When the air pollution was measured after the oil started to appear onshore it was discovered that 11,000 tons of volatile organic compounds had been released into the atmosphere, (Sultan Ayoub Meo et al, 2008).

When oil washes onto shore lines it creates a poisonous atmosphere for the people who live nearby in cities and surrounding areas, (Tasman Spirit oil spill assessment report, 2005). When there is a crude oil spill in sea water, land effects are sometimes unavoidable and cause coughing, sore throat, shortness of breath, asthmatic attacks and runny nose. Wildlife such as marine mammals, fish and seabirds have died as a result of oil spills, (Lyons et al., 1999, Moritam et al., 1999, Carrasco et al., 2006, and Sultan Ayoub Meo et al, 2008)

1.1.2 The Exxon Valdez Spill (EVOS)

Another glaring example of an oil spill occurred on March 24, 1989, when the Exxon Valdez, a super tanker, hit Bligh Reef close to Prince William Sound, Alaska, USA. The accident caused 39,000 metric tons of crude oil to come in contact with 3,500 km of shoreline from Kenai, Southwestern Alaskan peninsulas and Kodiak Island Archipelago's. The spill started very close to Nearshore, a system renowned for its aquatic life, (Bowyer, R. Terry, et al. 2003).

Seven years later research conducted at these shorelines indicated that increased numbers of microbes were still present in areas where the oil remained in sediments, (Braddock et al. 1996). The trapped oil is still dangerous as potential tidal action and storm could cause the oil to be released back into the sea. (Braddock et al. 1996). A general trend showing the decline in oil concentration has been found, (Short et al, 1996). “Numerous marine organism were harmed as a result of (EVOS)”, (Bowyer, R. Terry, et al, 2003).

1.1.3 Effect of Oil Spills on Plants and Habitats

Oil Spills also affect coastal marshes that provide a home for numerous wildlife inhabitants and act as safeguards to the shoreline from intense wave action. Although many experiments have been done, experts still cannot categorize the various effects that can occur in marsh vegetation. Unknowns about the effects on vegetation stem from a lack of understanding when oil interacts at the cellular level, (Webb, 1977).

The discharged oil or oil dispersion mixture may reduce habitat use and cause migration patterns to change, alter the food availability and cause increase deaths among animal populations. The possibility of oiled plants dying is increased and if this happens the roots would die leading to a higher tendency for erosion to take place with the loose soil.

Figure 1.3 Decaying coral in the Gulf of Mexico, 2010, From the National Oceanic and Atmospheric Administration (Deeper Insights, 2010)

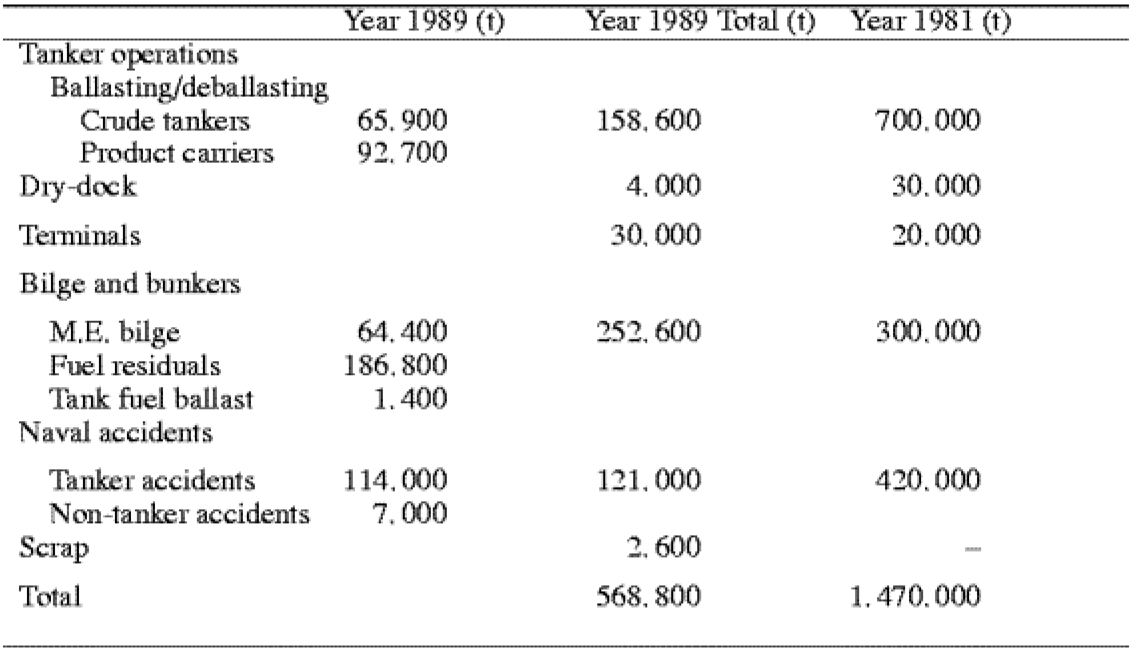
Figure 1.4 Cleanup of a beach that the Gulf of Mexico contaminated (Amazing Images, 2010).

1.1.4 Clean-up Methods for Oil Spills

Cleaning up oil spills is a major issue but terms such as "cleanup" and "countermeasure" are frequently used and have modified meanings when applied to oil spill cases. The cleanup operation usually means cleaning up an area that can be accessed and is visible. Examples usually show that the penetration of oil is much deeper than the corresponding cleanup, as is seen with shore cleanup. Clean up operations should be well thought out and planned because the operations may cause more damage than the oil itself. Many large oil spills are caused by marine transport collision, grounding and shipping operations such as bunkering and loading/unloading. Examples of large cleanups that have taken place can be seen in disasters such as the "grounding of the Amoco Cadiz (1978), the explosion of Irenes Serenade (1980), the grounding of the Exxon Valdez (1989) and the grounding of the Sea Empresss (1996)", (Nikolaos P. Ventikos et al, 2004).

In the last couple of decades, there have been many advancements and this can be seen in the oil pollution cases in 1981 compared to 1989.

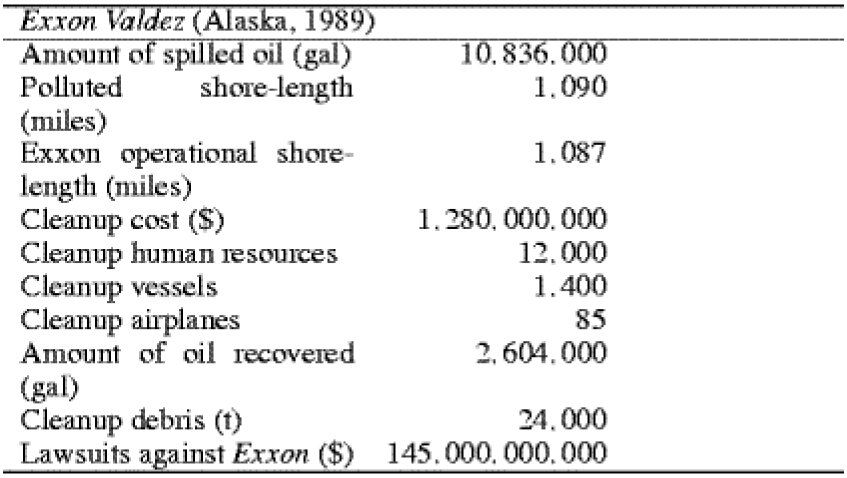
Table 1.1 Oil marine pollution from maritime transport procedures (1981 and 1989), (Nikolaos P. Ventikos et al, 2004).



	Year 1989 (t)	Year 1989 Total (t)	Year 1981 (t)
Tanker operations			
Ballasting/deballasting			
Crude tankers	65.900	158.600	700.000
Product carriers	92.700		
Dry-dock		4.000	30.000
Terminals		30.000	20.000
Bilge and bunkers			
M.E. bilge	64.400	252.600	300.000
Fuel residuals	186.800		
Tank fuel ballast	1.400		
Naval accidents			
Tanker accidents	114.000	121.000	420.000
Non-tanker accidents	7.000		
Scrap		2.600	–
Total		568.800	1.470.000

The response to an oil spill depends mainly on the availability of money which is why proactive initiatives usually produce the best result. The Exxon Valdez incident caused about $145,000,000,000 in damages to the environment, leading to the mobilization of 85 aircrafts and 1400 vessels in clean up efforts. The breakdown of the cost of the Exxon Valdez incident can be seen below, (Nikolaos P. Ventikos et al, 2004).

Table 1.2 Fiscal and operational analysis of the Exxon Valdez spill (1989)



Exxon Valdez (Alaska, 1989)	
Amount of spilled oil (gal)	10.836.000
Polluted shore-length (miles)	1.090
Exxon operational shore-length (miles)	1.087
Cleanup cost ($)	1.280.000.000
Cleanup human resources	12.000
Cleanup vessels	1.400
Cleanup airplanes	85
Amount of oil recovered (gal)	2.604.000
Cleanup debris (t)	24.000
Lawsuits against *Exxon* ($)	145.000.000.000

When an oil spill occurs, containing the pollution at the source is the first step. A combination of recovery, disposal and the containment of oil is performed thereafter. The two main countermeasures used in oil spills are marine and shore operations, (E. A. Tsocalis et al, 1994). Oil spills have dreadful implications for people who use the sea as a livelihood, or animal and plant life in the ecosystems surrounding areas of the spill.

The conventional methods to remove oil from the sea include mechanical clean up, chemical clean up and natural degradation. Mechanical clean up usually involves containment and recovery of oil techniques which are synonymous with high economic investment. Chemical methods are focused on aiding the mechanical process by making the separation easier and natural degradation focuses on observing nature take its course through wave action.

Some common mechanical cleanup methods are barriers, also known as booms (mechanical barrier), skimmers which are devices that recover oil and oil and water mixtures from the sea surface. Heavy oil skimmers are also employed (skimmers that remove high viscosity oils), skimmer vessels (remove oil from surface) and sorbent materials (recover oil through adhesion), (Nikolaos P. Ventikos et al, 2004).

Chemicals are used to change the characteristic features of the oil, (E. Vergetis, 2004). Dispersants are the main chemicals used that reduce the interfacial tension between water and oil so that it breaks down the oil into droplets and quickly disperses into the water. The use of dispersants is a topic of immense concern because of its potential ecological effects and its relatively short use in real aquatic environments.

Other chemicals include a mixture of additives such as emulsion breakers (separates water and oil mixtures), gelling agents, burning agents, neutralizing agents, sinking agents, bioremediation chemicals (accelerate oil's natural degradation), viscoelastic additives and herders.

There are several advanced techniques for the removal of oil in sea water that are still considered experimental. Bioremediation, in-situ burning and cleanmag are examples of these techniques. Bioremediation uses many different additives to increase natural biodegradation. In-situ burning uses controlled ignition of an area of oil spilled. It is recommended for large spills and for pollution in the

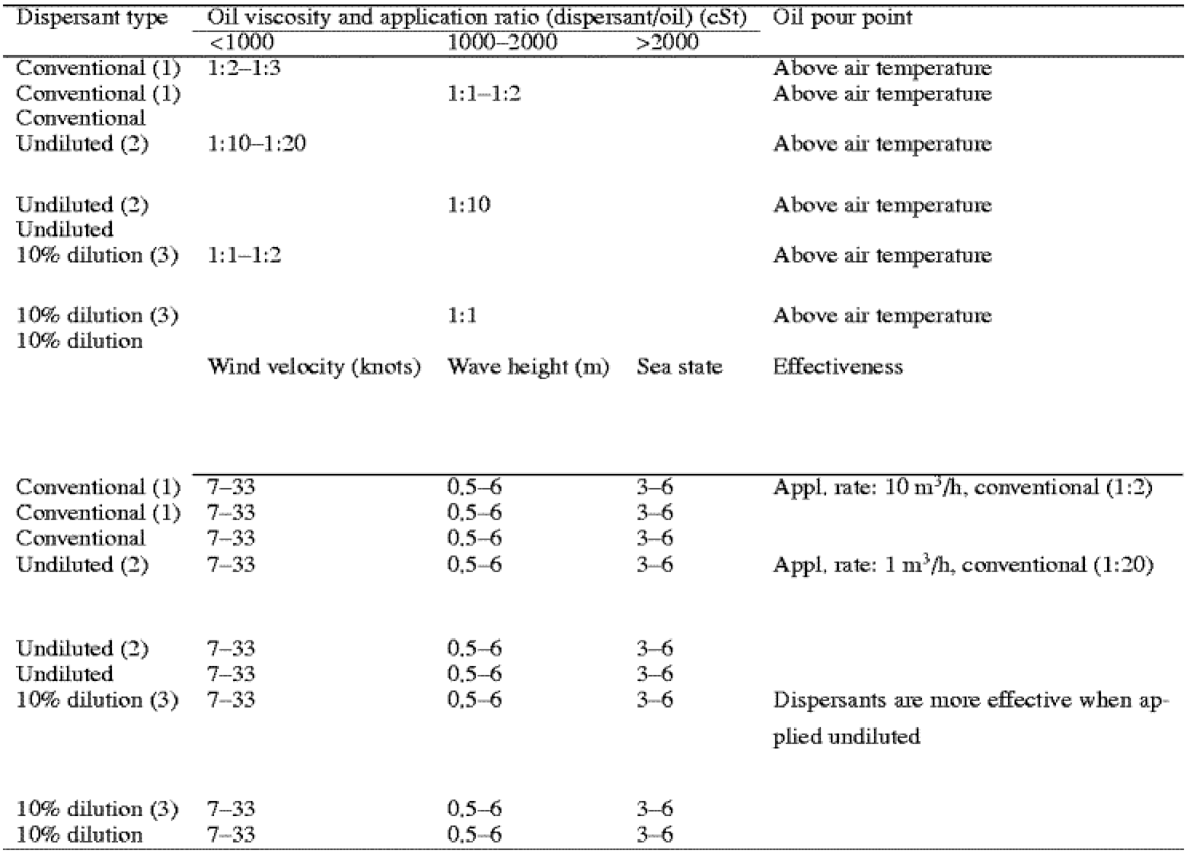
Artic. Cleanmag is a material that has magnetic properties that show a large capacity to absorb oil and prevent it from polluting a larger area.

The usage of equipment to deliver and to be useful to respond to oil spills depends on variables such as:

i. Current velocity
ii. Wave height
iii. Viscosity of spilled oil

So, depending on criteria such as the current velocity, sea state and the type and weathering phase of the oil spilled it changes what method can be applied to the oil spill to be effective or even feasible. The table below shows a preview of what factors are judged for dispersant use to be considered to be used in the event of an oil spill.

Table 1.3 Detailed operational data for dispersants (K. Lee, 1985)



Dispersant type	Oil viscosity and application ratio (dispersant/oil) (cSt)			Oil pour point
	<1000	1000–2000	>2000	
Conventional (1)	1:2–1:3			Above air temperature
Conventional (1)		1:1–1:2		Above air temperature
Conventional				
Undiluted (2)	1:10–1:20			Above air temperature
Undiluted (2)		1:10		Above air temperature
Undiluted				
10% dilution (3)	1:1–1:2			Above air temperature
10% dilution (3)		1:1		Above air temperature
10% dilution				
	Wind velocity (knots)	Wave height (m)	Sea state	Effectiveness
Conventional (1)	7–33	0,5–6	3–6	Appl. rate: 10 m³/h, conventional (1:2)
Conventional (1)	7–33	0,5–6	3–6	
Conventional	7–33	0,5–6	3–6	
Undiluted (2)	7–33	0,5–6	3–6	Appl. rate: 1 m³/h, conventional (1:20)
Undiluted (2)	7–33	0,5–6	3–6	
Undiluted	7–33	0,5–6	3–6	
10% dilution (3)	7–33	0,5–6	3–6	Dispersants are more effective when applied undiluted
10% dilution (3)	7–33	0,5–6	3–6	
10% dilution	7–33	0,5–6	3–6	

Many different combinations of techniques such as mechanical booms and chemical dispersants can be used in conjunction if the parameters for both overlap. Therefore both can be used without concern for one limiting the effectiveness of the other.

Hence, the steps that are followed before choosing a method to apply on an oil spill are as follows:

i. The state of the sea is recorded (wind velocity, wave height, spilled oil viscosity and current velocity.
ii. Check what methods of oil spill removal can be used based on the current state of the sea. Also check what methods can be used in conjunction with each other for greater removal.
iii. Make a decision on the method to be used at the oil spill site. This decisions should consider factors such as availability, the capability of the proposed equipment, the volume of the oil spill, the quality of the available personnel and if there is any constraints such as non-ideal debris in the oil polluted water.

The most frequently used removal method is mechanical if the conditions permit. The success of the method selected varies with the deployment time and the type of equipment used to deliver the chosen method. Some of the methods can damage the coast for example the mechanical use of heavy trucks and intense vacuums; therefore care has to be taken when choosing the best method. The removal of the oil from seawater should be beneficial to the environment and not destroy it in the process, (E. Vergetis, 2004).

Figure 1.5 Containment boom used during the Gulf of Mexico Oil Spill (Nichols, 2010).

Figure 1.6 C-130 Airplane delivering dispersant to the Oil Spill in the Gulf of Mexico, 2010 (Lehmann, 2010).

1.2 Dispersants

Dispersants started being used in the 1960's. In the 1970's and 1980's, many countries were reluctant to use dispersants, most likely, due to the negative effects and media coverage that occurred from the Torrey Canyon spill. Dispersants that were used in the Torrey Canyon spill caused conclusive environmental damage which perpetuated that the use of dispersants were unsafe. Current dispersants are said to be much safer by experts, (Etkin, 1999, p. 77), (R. R. Lessard et al, 2000).

A dispersant is similar to a detergent that is used on clothes, instead of removing dirt from a fabric; it removes oil from sea water surface. It is applied by spraying usually using airplanes onto the site of the oil slick and this causes the oil to immerse into water column at low concentrations. Dispersants were made to lower the impact of oil in the sea water on shorelines and natural habitats and in the case of the Gulf spill reduce the contamination and illness of fish, fisheries and invertebrates, marine mammals like the humpback whale, turtles like the endangered Kemp's ridley, green, leatherback and loggerhead, birds who feed and nest in marshes like the brown pelican, diving ducks and the threatened species the piping plover, (R. R. Lessard et al, 2000).

Figure 1.7 Picture of Kemp's Ridley turtles in the Gulf of Mexico (Witherington, 2010).

"Dispersants are made of surface active agents that are dissolved in one or many solvents", (R. R. Lessard et al, 2000). Dispersants are attracted to both oil (lipophilic) and water (hydrophilic) and dispersants work by decreasing the surface tension between the layers to achieve the alignment of both the lipophilic and hydrophilic end. Dispersants cause the two immiscible liquids to mix. Dispersants have to be mixed and the wave action from sea water is what provides this energy when applied to a body of water. The sea currents cause the oil droplets to disperse into the water column which enables more aquatic life to survive these disasters, (R. R. Lessard et al, 2000).

The two dispersants mostly used in the Gulf included COREXIT 9500 and 9527 which are made of the constituents shown below:

Table 1.4 List of components of the Dispersant used in the Gulf of Mexico (Questions and Answers, 2011)

Chemical Components of COREXIT 9500A and 9527	
CAS Registry Number	**Chemical Name**
57-55-56	1,2-Propanediol
111-76-2	Ethanol, 2-Butoxy-*
577-11-7	Butanedioic acid, 2-sulfo-, 1,4-bis(2-ethylhexyl) ester, sodium salt (1:1)
1338-43-8	Sorbitan, mono-(9Z)-9-octadecenoate
9005-65-6	Sorbitan, mono-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) derivs
9005-70-3	Sorbitan, tri-(9Z)-9-octadecenoate, poly(oxy-1,2-ethanediyl) derive
29911-28-2	2-Propanol, 1-(2-butoxy-1-methylethoxy)-
64742-47-8	Distillates (petroleum), hydrotreated light
**Chemical component Ethanol, 2-Butoxy- is not included in COREXIT 9500A*	

The constituents of the dispersants include two surfactants and an alcohol. The rest of the additives were included to improve stability of the dispersant or increase the function of the dispersant.

1.2.1 The Use of COREXIT 9500A & 9527®

COREXIT 9527 is a newer dispersant but it has the same low to moderate toxicity and general effects of COREXIT 9500A, (A. George-Ares et al, 2000) and (Michael M. Singer et al, 1996).

COREXIT 9527 is made by Exxon Production Research Company and it is marketed as a "self-mixing" concentrate dispersant. It has 3 nonionic and 1 ionic surfactant in a solvent of glycol ether, (K. Lee, et al, 1985). Field studies have shown that COREXIT 9527 can be distributed using an aircraft.

While COREXIT 9527 is considered a newer dispersant, research has shown that COREXIT 9527 has negative effects on the development and fertilization of sea urchin. There is also research to suggest that the dispersant also disrupts the formation of marine photo plankton and other bacterivores, (K. Lee, et al, 1985).

1.2.2 Dispersant Influence on Oil

When a dispersant is added to water it disperses the oil into smaller slicks and eventually sinks into the water column within hours. The reason for the destabilization of oil in water emulsion is caused by thermodynamic instability. The dispersant plays a key role in increasing the rate at which the oil is separated from the water, (Fingas, Merv, 2007)

Processes such as "gravitational forces, surfactant loss to water, and subsequent loss of surfactant to the water column, creaming, coalescence, flocculation, Ostwald ripening, and sedimentation" result in the destabilization and resurfacing of oil in water emulsions, (Fingas, Merv, 2007). The application of a dispersant is pivotal in optimizing its effectiveness to minimize how the oil affects shorelines, mammals and birds on the water surface and to improve the biodegradation of the oil in the water column. Currently, research conducted shows no "concrete" data about how effective dispersants added to huge bodies of water have reduced the shoreline impact, mammal and bird welfare, and improved biodegradation, (Fingas, Merv, 2007).

There is a current debate that exists about the function of some dispersants which cause inhibition of biodegradation rather than the opposite. No clear correlation of dispersant use being effective has been produced in modern studies. There are many factors that define how effective a dispersant can be in the sea and these include the energy of the sea (force of breaking waves), composition of the oil, the type of oil, the amount, type and temperature of dispersant used, the salinity and temperature of the water. Though all the previous factors are important, the most essential attributes in the formation of the emulsions made by the dispersant include the composition of the oil and the sea energy.

In terms of toxicity, recent tests conclude that the dispersed oil is more toxic than the dispersants but it was found that the chemically dispersed oil was more toxic than that of physically dispersed oil. Chemically dispersed oil was found to contain between five to ten times more polycyclic aromatic hydrocarbons (PAHs) when the water column was tested after using a typical dispersant, (Fingas, Merv, 2007).

Other influences on oil in water dispersion include the way in which the dispersed droplets especially chemically dispersed interact with high concentrations of sediment. The formation of some oil with sediment aggregates called oil mineral aggregates (OMAs) have been stable and fallen further into the depths of the water column, (Fingas, Merv, 2007).

1.2.3 Existence of Underwater Plumes

The dispersant mixed with oil underwater poses a problem as seen in the *New York Times* article Gulf of Mexico Oil Spill 2010. The problem occurs because it is unknown, how a large quantity of dispersant that has been ingested by the water column affects aquatic life. The warm waters of the Gulf of Mexico and the sea currents moving away from the shore have helped to quell some of the destruction that could have taken place but as Samantha Joye, a professor of marine sciences from the University of Georgia highlighted that there is a layer, many centimeters thick on the sea floor about 16 miles from the point of the leak at the wellhead. Many other independent researchers have also lamented that a large portion of the oil stays buried on the seafloor. Since these claims have been identified by respected professionals, it has been verified by the National Oceanic and Atmospheric Administration (NOAA) that at least one major and minor oil plume exist. A previous study by Dr. Camilli has shown the main plume to be about 3,600 feet below the water surface and extends for about 20 miles southwest.

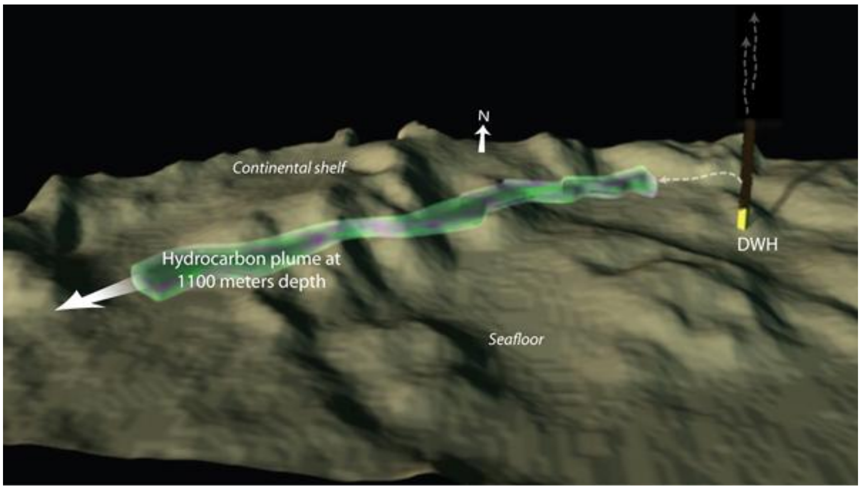


Figure 1.8 Mapping of an oil plume in the Gulf of Mexico (Scientists, 2011)

Chapter 2: Background

There are several topics that were covered in preparation to investigating our project goal. Our background research was divided into several main areas of interest including characterizing micelles and emulsions through surface properties, the influence of surfactants and the influences of various additives to an emulsion surfactant system. This chapter will mostly consist of information which helps to understand how emulsions are formed on a microscopic level, how these emulsions stabilize and what we will be able to do test and influence this stability.

In regards to this project these properties and characteristics are significant because, with investigation, they may reveal why the dispersant used in the Gulf is not behaving as was expected and what impact the environment may face as a result. One theory previously used for Enhanced Oil Recovery (EOR) involved zeta potential of a water-crude-surfactant system. As can be seen in figure 2.1 below, the maximal oil recovery, as a result of the ability for the oil to float, occurs at the same height of the maximum zeta potential as the concentration of surfactant increases in a bitumen pilot. By observing the trends seen below, the appropriate amount of surfactant can be estimated based on the zeta potential of the oil droplets (Schramm, 1992). As we can see, adding infinitely more surfactant will not necessarily result in more oil recovery and there is no need for excess in the environment, consequences of which have not been fully investigated.

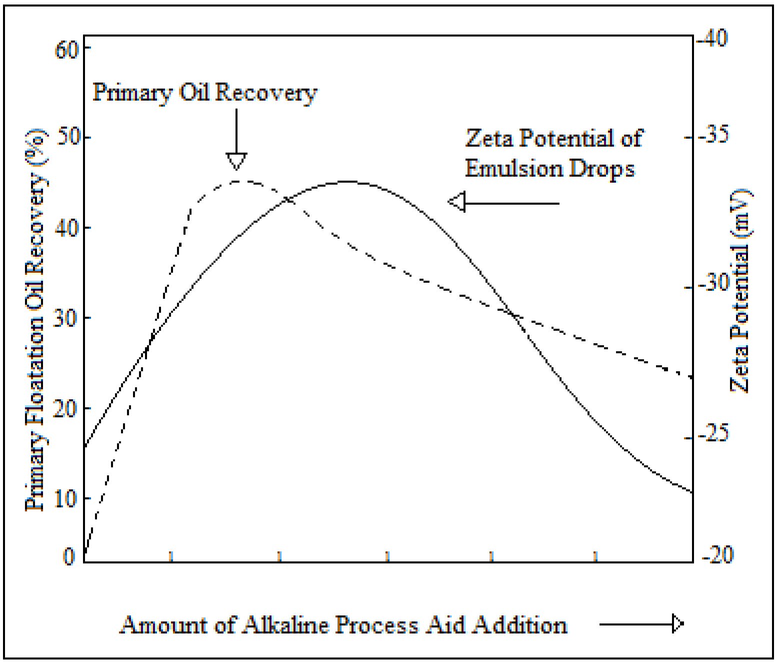


Figure 2.1 Plot of oil recoveries versus process aid addition level from the hot water flotation processing of an oil sand in a continuous pilot plant. Also shown is the correspondence with the zeta potentials, measured on-line, of emulsified bitumen droplets in the extraction solution (Schramm, 1992)

2.1 Surfactants

Surfactants are used in making emulsions and dispersing two phases of immiscible liquids. Surfactants are able to do this by lowering the interfacial tension between the molecules within both two liquid phases individually and also allow the continuous and dispersed phase to interact (Jones, 1995). The dispersed phase in our case is the oil, surfactant and the droplets they form. The continuous phase is the other liquid phase in our emulsion in which the oil and surfactant is dispersed, the ocean water (Schramm, 1992). Surfactant molecules are composed of hydrophilic headgroup with the opposite end being hydrophobic. Surfactants are classified based on the surface charge of the headgroup which could be anionic, cationic, nonionic or zwitterionic (Schramm, 1992). A table 2.1 can be seen below listing the surface charge with its associated CMC.

Table 2.1 A list of surfactant classifications with associated CMC values and structures for low electrolyte concentration at room (Jones, 1995).

Classification	CMC (M)	Structures
Anionic	10^{-3}-10^{-2}	Negative ion tail (Cl^-, Br^-)
Cationic	range	Positive ion tail (Na^+)
Nonionic	10^{-5}-10^{-4}	OH tail neutral
Zwitterionic	10^{-3}-10^{-1}	COO^-, SO_3^-

The best way to explain the process of emulsion formation through surfactant addition is through using an example. In this example we will discuss a system in which there is an oil phase, an aqueous phase and a surfactant. A micelle will form with surfactant addition and the hydrophilic headgroups will be surrounding the hydrophobic ends and an oil droplet. Ions from the surrounding aqueous solution are attracted to the charged surface of the micelle and collect around the surface. An illustration of this process can be seen below in figure 2.2.

There are several factors which can affect the CMC and size of the micelle as a result of the surfactant. These factors are surfactant concentration, organic additions to the continuous phase and microscopic bubbles in the water. As surfactant concentration is increased the surface tension decreases gradually until a minimal surface tension is reached. This is the point where micelles form spontaneously; this point is the critical micelle concentration (Schramm, 1992). This is illustrated graphically in figure 2.2 below.

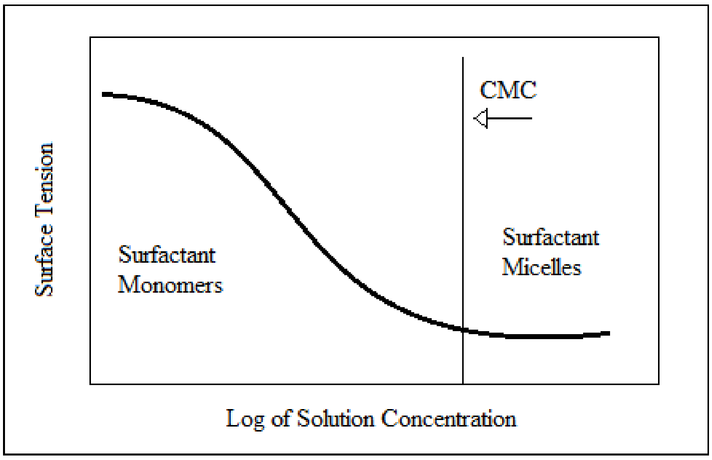


Figure 2.2 A graph showing the surface tension trends and micelle formation from monomers as the dilute surfactant concentration is increased slightly (Scramm, 1992)

2.2 Micelle Characterization

Micelles are aggregates of surfactant molecules in solution with colloidal dimensions. These will spontaneously form at sufficiently high concentrations of surfactant, the concentration at which this occurs is the critical micelle concentration (CMC). Microemulsions are emulsions in which the aggregate has reached the CMC and the droplets are between 10 nm and 100 nm in diameter and the emulsion is thermodynamically stable (Schramm, 1992).

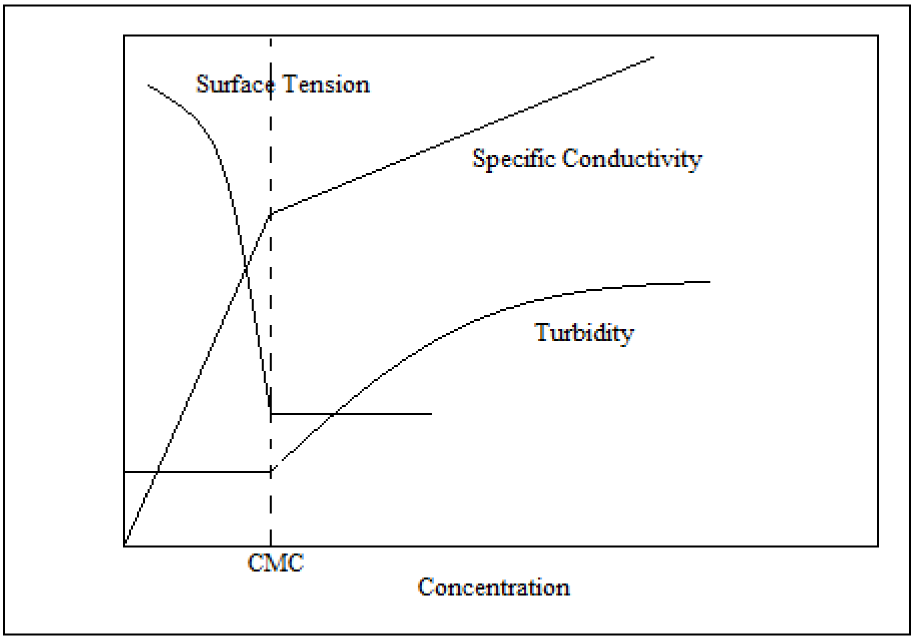


Figure 2.3 Various behavioral properties of emulsion droplets before and after CMC (Scramm, 1992)

2.2.1 Surface Interactions & Electrical Properties

There are several theories and models on the electrical double-layer however for the purpose of this report we will look into only two. The first is whether or not the emulsion formed can be described by the Derjaguin, Landau, Verwey and Overbeek (DLVO) Theory. The other model we will observe as is provides solid data and works in combination with the DLVO Theory is the Ionizable Surface-Group Model. We also did research on the surface interactions between microscopic, for which we look in depth into Van der Waals forces, and macroscopic particles.

2.2.2 DLVO Theory

The DLVO Theory suggests that there is a very small range in ion concentration at which the emulsion droplets will coagulate, which will occur at the Critical Coagulation Concentration (CCC). The theory also states that if the potential energy of interaction (V) is large in comparison to thermal energy [Given range of V>15kT](Schramm, 1992). The DLVO Theory compares the total interaction energy, which is the combination of both the attractive and repulsive forces, and the distance between the particles. Results of experiments performed in research of the DLVO Theory show that the energy of interaction decreases exponentially as distance between particles increases (Schramm, 1992).

2.2.3 Ionizable Surface-Group Model

One of the accepted theories on how interfacial charge is affected is through the ionization of functional groups on the surfaces of the dispersed phase. This model is strongly dependent on pH and electrolyte concentration (Schramm, 1992). This model is used by comparing the behavior of the emulsion, such as CMC and formation time when varying concentrations of a single electrolyte. This model demonstrates some trends along with the DLVO theory such as CMC correlation with electrolyte concentration.

2.2.4 Van der Waals Forces

Van der Waals forces act on all particles and are important in the interaction of micelles and the emulsions. Van der Waals force is a combination of various forces such as induction, orientation and dispersion forces. Dispersion forces are present in all situations meaning they apply directly to our specific emulsion. These forces are effective over a range of distances on both the macroscopic and microscopic scale (Israelachvili, 1992). Dispersion forces may be either repulsive or attractive and is constantly effected and changing due to the surrounding molecules.

Another interesting suggestion made by Israelachvili is that when the two surface layers overlap, if they are at significantly small separation, the resulting density is different from the bulk liquid

(Israelachvili, 1992). Whether or not this change in liquid mean density is significant or not will be investigated further in our experimental section.

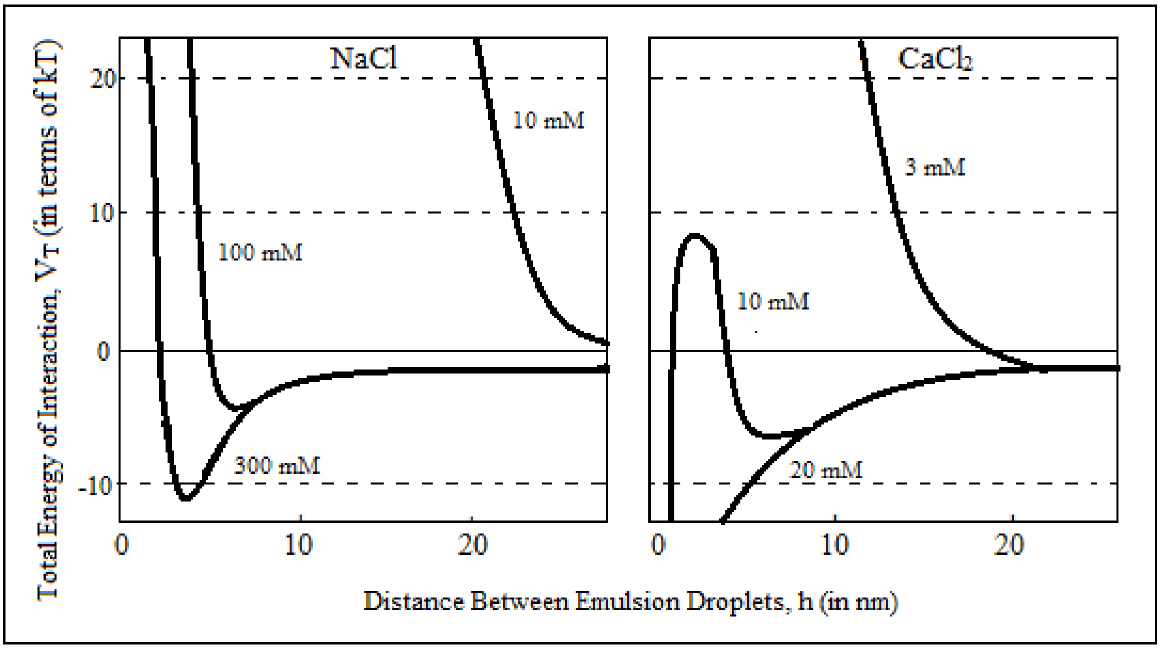


Figure 2.4 Energy diagrams for bitumen-in-water emulsions in the presence of NaCl and $CaCl_2$ (Israelachvili 1992)

2.2.5 Double-Layer

One area of micelles which contributes to emulsion stability of oil-in-water dispersions are the electrical forces surrounding the emulsion droplet (Schramm, 1992). Because these forces can result in repulsive or attractive interactions over significant distances, and thus are the cause for droplets to remain dispersed. One of our predictions is that droplet coalescence is a cause for the sinking phenomena occurring in the Gulf of Mexico.

The Gouy-Chapman Double Layer Model presents a prediction for how a charged surface in a charged solution develops a "double-layer". The thickness of this double-layer relative to the droplet size is important because it influences the repulsion between droplets (Schramm, 1992). The emulsion droplet forms, if oil-in-water, with the hydrophilic headgroups on the water interface. There will be a charge on the surface which we will determine in our research, which attracts oppositely charged ions from the solution, called counterions. This collection of counterions creates a relatively uniform cloud around the emulsion droplet (Elimelech, 1995). An illustration of this phenomenon can be seen below in figure 2.5.

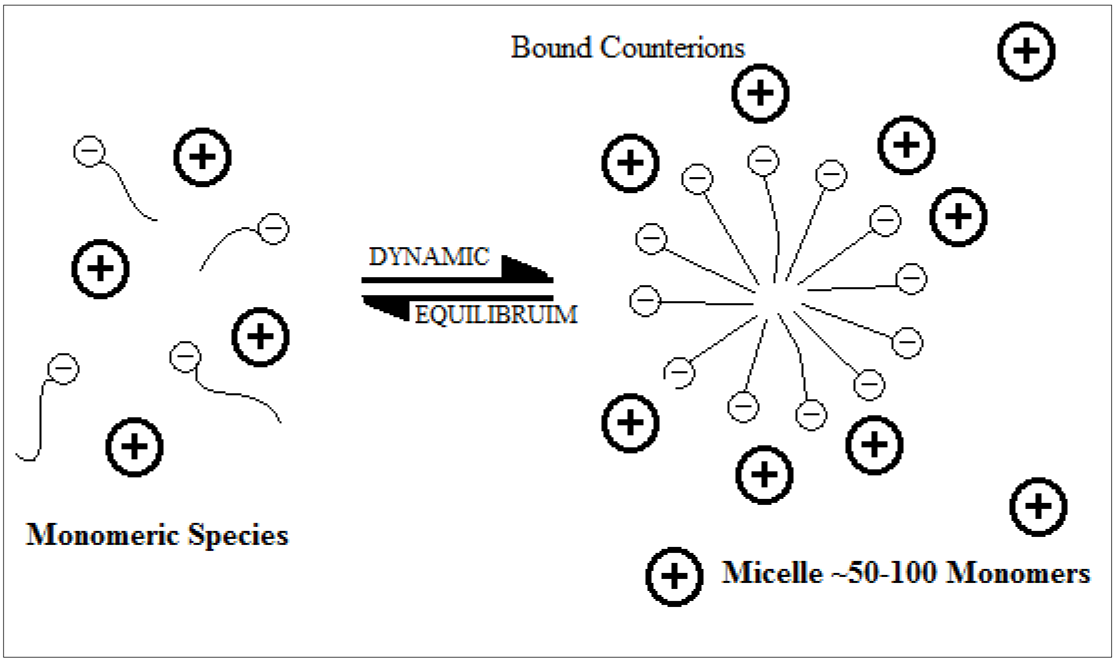


Figure 2.5 An illustration of the dynamics and formation of the electric double layer surrounding a micelle (Jones, 1995).

2.3 Emulsion Characterization

There are several different sizes of emulsions can form, based on droplet size. There is usually a range in sizes of emulsion droplets, this distribution can be observed, plotted and skewed to compensate for changes in stability (Schramm, 1992). In this work, the emulsion had significantly small micelles to be classified as a microemulsion. In an ideal situation involving an oil, water and surfactant system there are several different things which occur simultaneously. There will be individual surfactant molecules, surfactant molecules which have gathered into a micelle and some surfactant molecules will be attached to an oil droplet with the hydrophobic tail.

Stability has been previously touched on in various sections but here we will discuss how to create and maintain the stability of an emulsion. The electric double-layer prevents coalescence, high viscosity of either phase can lead to decreasing the rates of coalescence and creaming. The volume of the dispersed phase is also an important factor on stability; less of the dispersed phase will reduce collisions and maintain stability (Schramm, 1992).

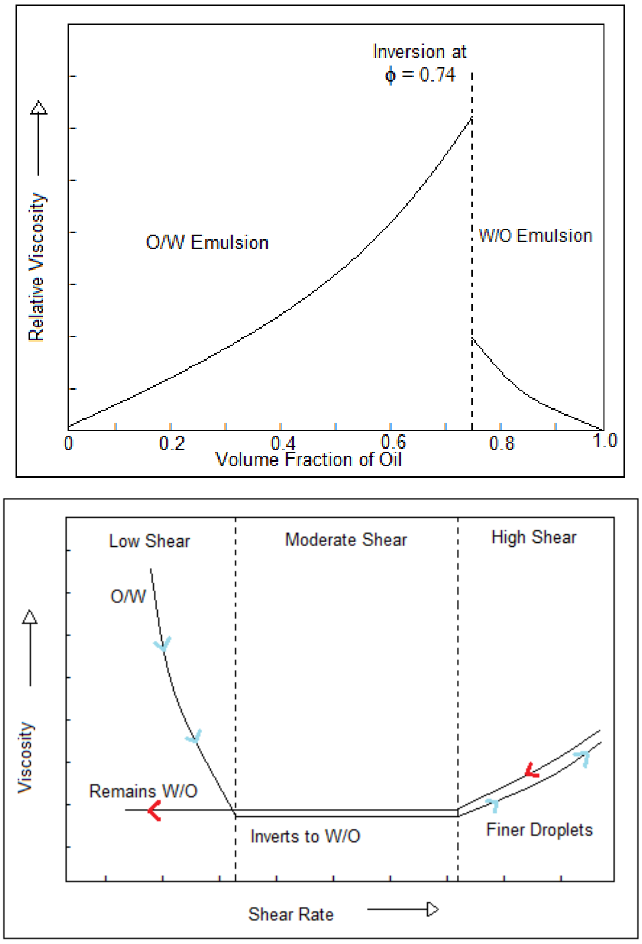


Figure 2.6 Two different graphs showing inversion of emulsions with viscosity as a function of volume fraction of oil or shear rate (Jones, 1995).

Chapter 3: Objectives

The objectives and intentions of experimenting with the COREXIT dispersant are as follows. Each objective will be investigated with the intentions of determining the basic properties of this emulsion and to observe emulsion stability along with how it may be negatively influencing the effectiveness of COREXIT as a dispersant.

1. Characterize the micelles and emulsion as a whole of the COREXIT 9500A emulsion through experiments such as determining the critical micelle concentration (CMC) and surface properties which could negatively affect the stability of the emulsion.

2. Create stability experiments on what could adhere to the emulsion and cause it behave differently than expected. Some of these additions include sand, and other organic particles of various sizes based on what is found in nature, also observing the effects of adding air bubbles as would be common in turbulent ocean conditions.

3. Investigate possible ways which the "sinking" phenomena currently seen in the Gulf could be replicated, based on predictions of what could be occurring based on background knowledge.

Chapter 4: Experimental

4.1 Artificial Sea Water

The samples of sea water were made using our specifications requiring salinity of 35g per kg of seawater and include the salts in table 1 below (D.R Kester et al, 1967). These quantities are specifically for making one liter of salt water solution.

Table 4.1 Table of Salts required to make Artificial Seawater

Gravimetric Analysis			
Salt	Molar Mass	Suggested Measurement	Actual Measurement Used
Sodium Chloride (NaCl)	58.44	23.926	23.91
Sodium Sulfate (Na_2SO_4)	142.04	4.008	3.988
Potassium Chloride (KCl)	74.56	0.667	0.6693
Sodium bicarbonate ($NaHCO_3$)	84.00	0.196	0.1955
Potassium Bromide (KBr)	119.01	0.098	0.0959
Boric Acid (H_3BO_3)	61.83	0.026	0.0276
Sodium Flouride (NaF)	41.99	0.003	0.0034

In order to manufacture synthetic sea water, a one kilogram basis was used to replicate the results produced by the D.R Kester method. Assuming one liter is equal to one kilogram, the constituents in table 1 were added to a one liter volumetric flask. A magnetic stirrer was used to mix the constituents for 20 minutes. The liter volumetric flask was left to settle for 10 minutes.

The density of the solution in the liter flask was measured to ensure the mixture is as similar to a realistic scenario as possible. Density was measure by first massing an empty liter flask using a mass balance to obtain an accurate reading of the synthetic salt solution. Then the liter flask with the salt solution was weighed and since the volume of water was known, the density of the salt solution was found.

The mass of the salt solution was 513.1 grams and the volume measured was 500 mL of solution.

$$\text{Density} = \frac{513.1g}{500cm^3} = 1.026 \text{ g/cm3}$$

This was to ensure that the synthetic sea water was the same or close to actual sea water which density is 1.026 grams per cm^3 .The density of seawater increases with depth to about 1.028 grams per cm^3 and on the surface it is 1.025 grams per cm^3 (D.R Kester et al., 1967).

After the density was confirmed to produce accurate results similar to that of seawater, the mass of salts needed to make 20 Liters of solution was calculated for further experiments. Then calculated how much could be made each time using two liter flasks because those were the largest flasks available.

20 Liters of solution was made to have a sufficient supply of sea water for future testing. To produce 20 Liters, or 5.28 gallons of synthetic sea water, 20 times the amount in grams of salts used in table 1 will be needed because the amount for a liter is what was used to validate the synthetic sea water. Since the solution can only be made in 2000L portions due to a volumetric flask limitation, (the highest volume flasks available were 2000L) the mass of salts used for each volumetric flasks is shown in the table 2 below:

Table 4.2 Mass of Salt required for synthesis of 2000L of sea water

Gravimetric Analysis	
Salt	Grams for 2000L Volumetric flask
Sodium Chloride (NaCl)	47.85
Sodium Sulfate (Na_2SO_4)	8.016
Potassium Chloride (KCl)	2.668
Sodium bicarbonate ($NaHCO_3$)	0.01921
Potassium Bromide (KBr)	0.196
Boric Acid (H_3BO_3)	0.052
Sodium Flouride (NaF)	0.006

Table 4.3 Sample of Making Artificial Seawater in 2000L Portions

	Pure Water	After Seawater Components Added to Pure Water
Mass of beaker (g)	823.2	823.2
Mass of water + beaker (g)	2812.8	2877.4
Volume of Water (mL)	2000	2000
Mass of water (g)	1989.6	2054.2
Water Density (g/mL)	0.9948	1.0271

In order to manufacture 20L, the procedure for the 2L volumetric flask was done ten times. The manufactured seawater was collected in a large 20L Nalgene container.

4.2 Turbidity Testing

To test the turbidity of the dispersant and selected surfactant components, COREXIT 9500A, 2-Butylethanol and sodium bis(2-ethylhexyl) sulfosuccinate in both fresh and simulated sea water. Three 500ml samples of both fresh and sea water were made and each of the three chemicals were added to both the fresh and sea water. The dispersants were added in a ratio of 1to 50 of oil used to dispersant used. The ratio was used because it was suggested as the optimum ratio by NALCO© Energy Services in 2006, the creators of the dispersants. See the calculation below for the amount of dispersant added:

Volume of water for sample = 500ml and since ratio is 1:50 oil to dispersant.

We estimated that a thickness of 10% of the volume of water would be the volume of oil, so in accordance the volume of dispersant was calculated using the following equation

$$\frac{50ml}{50} = 1ml \text{ of dispersant.}$$

To produce a range in values of turbidity, varying concentrations of the dispersant and components were used. Initially four different volumes of 1.0mL, 1.5mL, 2.0mL and 4.0mL of each chemical was used in order to determine the critical micelle concentration (CMC) which causes an emulsion to be formed. For an explanation, see Chapter 2: Background.

Steps using the turbidimeter:

1. 1mL of each dispersant or component was added.
2. Each was mixed using a measuring cylinder with a magnetic stirrer to ensure uniformity.
3. The solution was allowed to settle for 20 minutes.
4. The Turbidimeter was turned on, the reading was taken with nothing in the nephlometer, and the vials were washed with distilled water.
5. Pure water was used to get a baseline reading for the pure water and dispersant mixtures. Artificial seawater was also used to produce a baseline for the artificial seawater and dispersant mixtures.

Additional steps:

In each case the seawater samples were tested first then the pure water samples. To test the seawater and COREXIT 9500A some of the sample from the 500mL measuring cylinder was transferred to the turbidimeter vials using a 10mL pipette from the top layer of the vial. The mixture was added to the turbidimeter vial until the white fill line was reached (see figure 4.2). Opened the turbidimeter lid (see figure 4.1) and placed the turbidimeter vial inside the turbidimeter and closed the lid. Waited three minute s for the readings to stabilize before the results were noted. This was repeated for the middle and bottom layers of the measuring cylinders. The results are shown below in figure 4.1. To ensure validity, identical turbidity tests were re- performed 24 hours after the initial mixing. The same vial was used to maintain consistency between readings. The entire procedure was also repeated using 1.5mL, 2.0mL and 4.0mL.

Figure 4.1 Showing Hach 2100N Turbidimeter

Figure 4.2 Illustrates Empty and fill vials used to test for Turbidity in Hach 2100N Turbidimeter

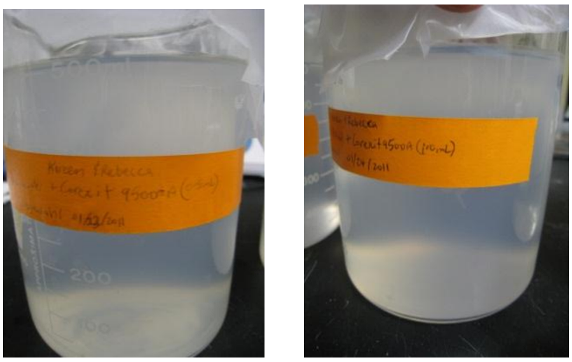


Figure 4.3 Side view of 500mL of seawater mixed with 0.5mL and 1.0mL of COREXIT 9500A

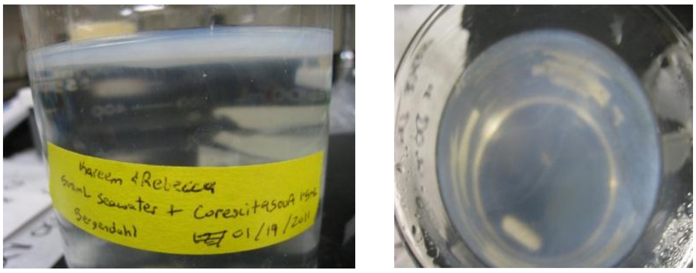


Figure 4.4 Side and top view of 500mL of Seawater mixed with 1.5mL of COREXIT 9500A

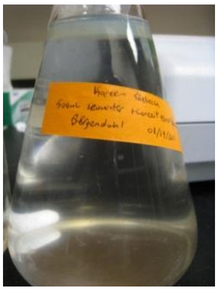


Figure 4.5 Side view of 500mL of seawater mixed with 2.0mL of COREXIT 9500A

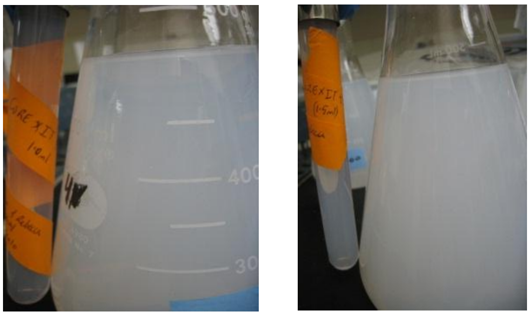


Figure 4.6 Side view of 500mL of pure water mixed with 1.0mL and 1.5mL of COREXIT 9500A

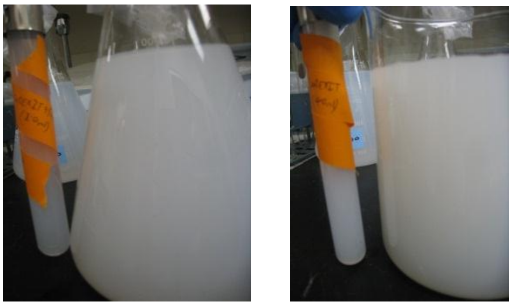


Figure 4.7 Side View of 500mL of seawater mixed with 2.0mL and 4.0mL of COREXIT 9500A

4.3 Light Spectroscopy Testing

Visible light spectroscopy was also another method that was used to help determine the critical micelle concentration of the COREXIT 9500A and the other components used.

Spectroscopy readings were performed at 590nm because this was the wavelength that had the most distinct absorbance peak after performing a spectral analysis with the entire spectrum of light using 2.0mL seawater and COREXIT 9500A sample. An example of the entire spectrum of absorbance is shown in figure 4.8 below. The range of the axes was changed to fit the graphical data represented.

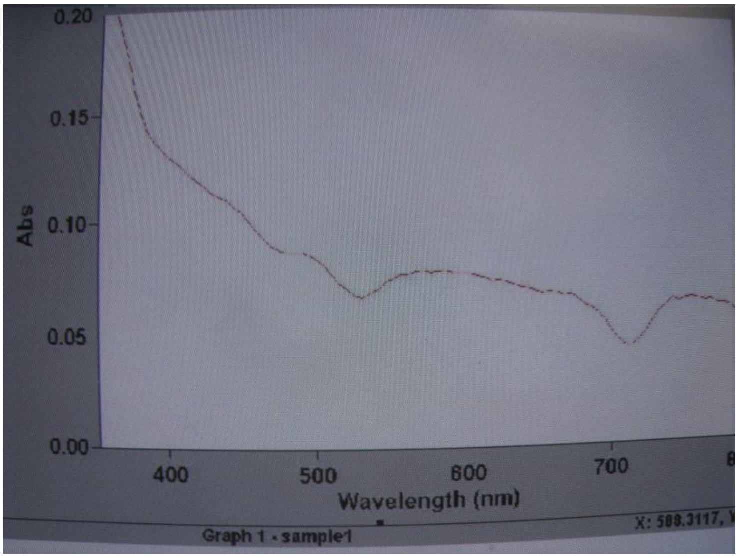


Figure 4.8 Picture of graph used to evaluate wavelength of greatest absorbance

The analysis was done in a similar method to the turbidity where the top, middle and bottom layers of each sample were placed in a cuvette (see figure 4.9) and a spectral analysis of the absorbance was produced. The data was represented graphically as shown in figures 5.1 below.

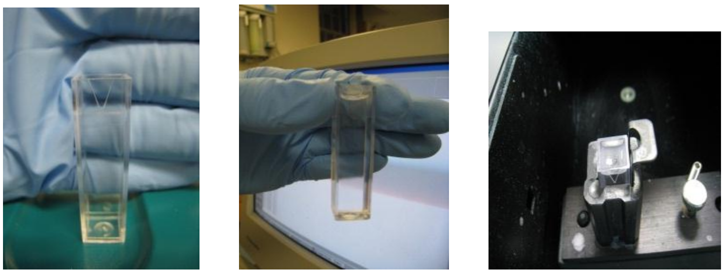


Figure 4.9 The Cuvette used for the light spectroscopy of the bottom reading of 500mL Seawater and COREXIT 9500A (1.0mL)

To perform the experiment a cuvette was taken out of the storage box and held on the opaque edges then a 4mL pipette was used to transfer some distilled water into the cuvette until the water filled it. Then the Varian Cary 50 Scan U.V visible spectrophotometer spectral machine lid (see figure4.10) was opened and the cuvette was placed inside aligning the opaque section with the section that would not be penetrated by light (see figure 4.9). The lid was closed and the spectral machine was zeroed and then the procedure was repeated excluding zeroing the machine with varying concentrations of COREXIT 9500A's top, middle and bottom layers. Instead when the lid was closed the program was started and the simulation that controlled the machine was activated to run. The procedure was repeated with the other dispersants in a similar manner to COREXIT 9500A.

Figure 4.10 (Left) The Varian Cary 50 Scan U.V visible spectrophotometer (Right) An illustration of the printout of readings using the U.V spectrophotometer at 590 nm

4.4 Component Testing

There were two components of interest within the COREXIT 9500A which were investigated initially, the first is 2-Butylethanol and the second, Sodium bis(2-ethylhexyl)Sulfosuccinate. These two components were selected from the list of eight seen in figure 1.4 from the background chapter because they are the main components aiding in the emulsion formation whereas the others are stabilizers or additives to help with the application and mixture of the oil and water phases. It was believed that this investigation will yield data helping us to further characterize the emulsion based on the dispersant building blocks.

4.4.1 2-Butylethanol

The 2-Butylethanol was obtained from Fischer Scientific and came in the form of a liquid. Special caution was taken with this particular chemical in regards to the warnings provided on the container. This chemical was added to 500mL of both sea water and deionized water in similar dosages to the COREXIT as it was assumed that the most likely critical micelle concentration would fall within the 1.0 to 4.0 mL range. Similar protocol was taken with the 2-Butylethanol as with the COREXIT, where the solvent, either simulated sea water or deionized water, was stirred using a stirring plate and the component was then added, allowed to form a miscible solution and was then tested after the distinct phase had formed. Because we were provided such a significant sample of 2-Butylethanol, a 20 to 50mL sample was poured into a beaker from which the designated volume was the extracted using a 0-5mL automatic micropipette.

Measurements were taken for both turbidity and spectroscopy using the same extraction and testing protocol of the COREXIT addition. The wavelength selected for spectroscopy readings was 590 nm in order to receive comparable results to the COREXIT.

One major difference in this experiment was the disposal of the solution after testing was completed, whereas the COREXIT has been deemed safe to dispose in the sink, the 2-Butethanol is a very strong and concentrated substance on its own. A disposal beaker was labeled and left in the fume hood for proper disposal.

4.4.2 Sodium bis(2-ethylhexyl) Sulfosuccinate

Sodium bis(2-ethylhexyl)Sulfosuccinate was obtained from Fischer Scientific as well however came as a solid. Additional care was taken with this product as it was provided in pure form. This substance is rather bizarre in its common form, it is a similar consistency of fiberglass insulation used in construction. It is bright white and appears to be manufactured in sheets which are then rolled up for packaging convenience. The solid was particularly difficult to separate and mass, initially a metal chemical scoop was employed but did not work well because it could not penetrate the solid. After much trying, the best method was to use our hands, with latex gloves of course. Using a balance we massed out approximate quantities of 1.0, 1.5, 2.0 and 4.0 grams of the Sodium bis(2-ethylhexyl)Sulfosuccinate.

Dissolving this solid in both salt and deionized water provided us with another challenge. After an initial attempt to directly add the sample to the solvent, the solid became hydrated but did not dissolve. The best method determined for dissolving the Sodium bis(2-ethylhexyl)Sulfosuccinate was first to break up the sample by pulling apart the layers. This needs to be done carefully with as little pressure to the sample or the layers will stick to each other. The sheets of Sodium bis(2-ethylhexyl)Sulfosuccinate dissolved fairly easily in the water which was set up on a stirring plate prior to addition, then allowed to mix until the system was miscible or for a minimum of 30 minutes to ensure the mixture was sufficiently combined.

Samples were taken from the top, middle and bottom locations and data was collected for turbidity and spectroscopy.

4.5 Disturbing the System with Natural Permutations

Turbidity and spectroscopy were used to provide a base line in order to find when COREXIT 9500A formed an emulsion under ideal conditions. The aggregation of micelles could then be formed in a controlled environment which would cause the dispersant to act in the manner it was designed. To provide more insight into the properties of COREXIT 9500A tests were done to change the conditions of the water while the formation of an emulsion was occurring. These changes were proposed to be indicative to the varied conditions observed throughout the oceans in the world where COREXIT 9500A would be used. To simulate these changes in the laboratory numerous experiments to disturb the system were planned and conducted. These included:

1. Mixing with Sand Particles
2. Changing the Salt water salinity
3. Adding air bubbles
4. Changing concentration of humic acid
5. Changing concentration of humic acid with bubble addition
6. Changing the temperature of the seawater
7. Adding oil

After these perturbations were used to examine the changes in the base case initially investigated. COREXIT 9500A was tested with Sunoco Ultra-premium motor oil SAE 5W-30 for gasoline engines to simulate how seawater behaves with crude oil. Crude oil was not used due to its lack of availability and motor oil was recommended by Professor John Bergendahl as an adequate simulation.

4.5.1 Testing with Sand Particles

In the natural system that is being replicated in the sea's and oceans sand is present and in particular since the oil spill in the Gulf of Mexico happened sub sea level there is a high probability that sand particles could have influenced the formation of emulsion. In order to observe how sand affects the formation four main sizes of sand were used. The sizes differ by factors of ten and include 0.0029 inches, 0.0117 inches, 0.0394 inches and 0.187 inches in increasing order. The sand was collected using a collection of standard testing sieve ASTM- II USA specification to filter the aforementioned sizes that were stacked from the larger to the smaller decreasing downwards. When sieving was done the varying sizes were gathered in respective labeled containers. The magnitude of the sand used was determined to incorporate the large variety of sizes that could be encountered by COREXIT 9500A.

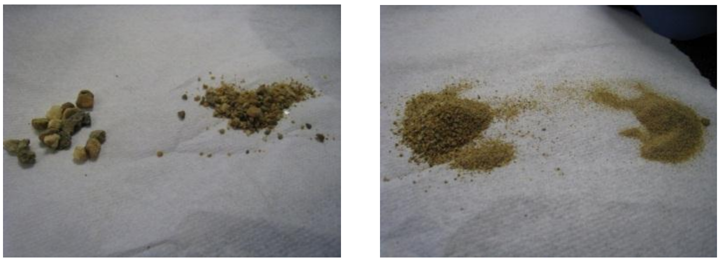


Figure 4.11 Sand used in experiments ordered in decreasing size from left to right and include 0.187 inches, 0.0394, 0.0117 inches, inches and 0.0029 inches.

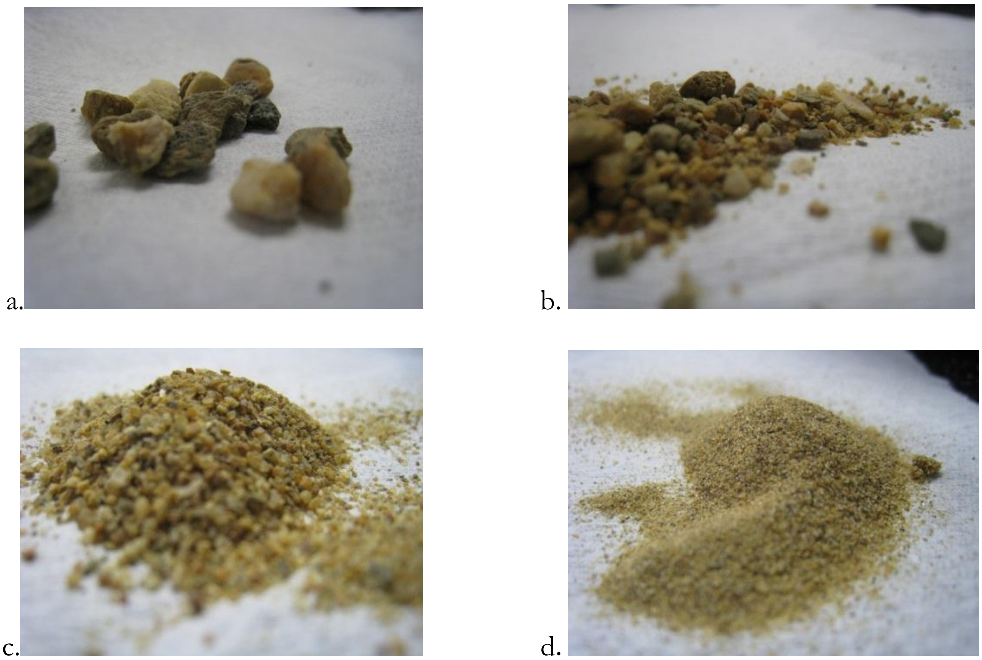


Figure 4.12 Magnified view of sand particles used in experiments ordered in decreasing size and includes a. 0.187 inches ,b. 0.0394 inches, c. 0.0117 inches, d. 0.0029 inches

Two methods were carried out when making the seawater, sand and COREXIT 9500A mixtures. The first method, denoted as emulsion first, involved placing 500ml of simulated seawater into a 500mL beaker then 1.1mL of COREXIT was added. 25g of 0.0029 inch sand was weighed in a petri dish and was added to the beaker. Paraffin was cut with scissors and placed over the top of the beaker and the beaker was inverted 10 times then allowed to rest. The sand mixed with the emulsion did not form clearly enough to make easy observations so the procedure was repeated with 1.5mL, 2.0mL and 2.5mL of COREXIT for the 0.0029 inch sand. Spectroscopy readings were done after allowing the mixture to settle for two days. In the second method, denoted as sand first, the main difference is that the sand was added first to the seawater and then the COREXIT 9500A is added afterwards. The second method follows all the same steps as the first after the COREXIT 9500A is added and for 0.0029 inches of sand this method was performed. The procedures for both methods were repeated for 0.0117 inches, 0.0394 inches and 0.187 inches of sand. Turbidity readings were not done because the layer produced for the emulsion layers were not enough to attain accurate turbidity readings since the volume needed for the corresponding vials is 30mL.

4.5.2 Testing with Salinity

In natural systems such as the sea and ocean, many lower salinity bodies of water coexist, in particular estuaries and rivers that are habitats for many different plants and organisms. To replicate how COREXIT 9500A behaves with these lower salinity conditions, a mixture of pure water and simulated seawater was combined in varying proportions that included 100% seawater, 75% seawater, 50% seawater and 0% seawater. Covering this range gives a proper representation of all the bodies of water that have salinity between these two extremes.

Table 4.4 Table representing the volume of seawater ratios to volume of pure water ratios for the change in salinity experiments

Ratio	Volume of Salt Water in 500mL Beaker	Volume of Pure water in 500mL Beaker
100% seawater, 0% pure water	500 * 1 = 500mL	500*0 = 0mL
75% seawater, 25% pure water	500 * 0.75 = 375mL	500 * 0.25 = 125mL
50% seawater, 50% pure water	500 * 0.50 = 250mL	500 * 0.50 = 250mL
25% seawater, 75% pure water	500 * 0.25 = 125mL	500 * 0.75 = 375mL
0% seawater, 100% pure water	500 * 0 = 0mL	500 * 1 = 500mL

Four 500mL beakers were labeled A through D. 375mL of simulated seawater was collected four times in four separate 500mL beakers then 125mL of pure water was added to the beakers for the 75% seawater ratio experiments. The 500mL beakers were put on magnetic stirrers and a magnetic stirrer bar was added to each beaker. A 10mL measuring cylinder was used to measure 0.9mL of COREXIT. The stirrer was turned on a low speed to uniformly mix the constituents for 10 minutes before 0.9mL of COREXIT was added to the beaker labeled A. 1.1mL, 1.3mL and 1.5mL of COREXIT were added to the remaining beakers labeled B through D. The COREXIT was added to the center of the beakers slowly to ensure proper homogenous mixing. The mixtures continued to mix for 30 minutes before stopping the stirrer. The mixtures were left to stand for 2 days before spectroscopy readings were taken. The procedure was repeated for 100%, 50% and 0% seawater readings. For the 100% seawater and 0% seawater readings, no mixing of the constituents was necessary since they were the extremes of both seawater and pure water. Only simulated seawater was collected for 100% seawater and only pure water was collected for 0% seawater readings.

0.9mL to 1.5mL spans the range when the COREXIT at normal conditions would form an emulsion since a lower salinity than the original simulated seawater was being used in each of the beakers more COREXIT would be required. The previous experiments done for pure water readings indicated that the emulsion is much harder to form so when decreasing the salinity a higher COREXIT volume was expected to produce the same result. Using this observation a COREXIT value higher than 1.1mL was preferentially determined. 0.9mL COREXIT was used as the starting point in order to accommodate variances in expected results while a 0.4mL range from 1.1mL to 1.5mL COREXIT was expected to give the same trend as the pure seawater and pure distilled water results taken initially. Investigation into how the change of salinity affected the emulsion produced was necessary to achieve a better understanding of how COREXIT forms in a wide variety of conditions.

4.5.3 Addition of Air Bubbles

The addition of air bubbles was selected as a permutation to observe the effect which they may have on the emulsion. This was chosen in regards to the sinking effect of the oil within the water table from where the COREXIT was injected at the base of the rig. The main objective was to see if the bubbles would attach to the emulsion and to observe what effect they have, whether it be a benefit to the stability or disturb the phases more than expected. It is know that there is generally less oxygen dissolved in the water as depth increases, if the COREXIT acts properly at the surface of the water but is not below, one significant discrepancy between the two locations is the air concentration.

Air was added using a bubbling stone with a tubular attachment which could be connected at the air spouts provided in the lab. An image of the bubbling stone and set up within a 500 mL beaker can be seen below in figure 4.13.

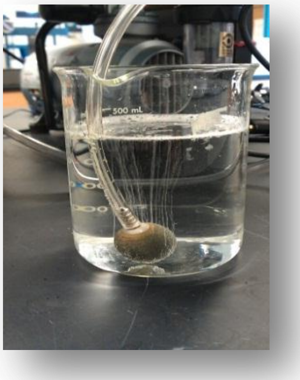


Figure 4.13 Bubbling set up

The procedure involved for bubble addition was similar to that of the previous experiments where a 500mL solution of salt water or deionized water was selected and then a concentration of COREXIT was added. For this experiment 1.2mL of COREXIT was used for salt water, deionized water and then in addition to humic acid which will be discussed in section 4.4.4 below. Stirring in this set of experiments was omitted, as the bubbles provided enough turbulence to provide adequate mixing. The sample was allowed to remain bubbling for a two hour period after which they layers were allowed to settle (this required about one hour). After the phases had developed, readings were taken at the initial time, 1 hour after, and then again at three and nine hours after the initial reading. Readings were taken using both the turbidimeter and the spectrophotometer using the same protocol previously used where each phase was measured and recorded.

4.5.4 Testing with Humic Acid

Humic acid is a material composed of various organic substances which are naturally present in the environment. The majority of the composition is soil and surface water organics such as plant and animal matter which has been decomposed by microbes (Vidali 2009). This was selected to include in our experiments because it is most certainly present in the actual system, also these humic substances contain a range of functional groups which we predict will cause different behavior on how the COREXIT emulsifies within the water. In many cases, the humic acid itself behaves as an aggregate in solution, perhaps to an extent to which it will improve, or adversely affect, the dispersion abilities of the COREXIT. It was also another step to more adequately model the Gulf system for the sake of our investigations.

The concentration of humic acid to use was researched, a range of 20 to 200 mg per Liter of solvent, in our case sea water was chosen according to a previously published study. The source suggested these values because the 20 to 100 mg per Liter range provides an appropriate model for the environment, even though actual concentrations present are typically quite a bit larger. The graph below, figure 4.14, was a result from a case study on the proton binding abilities of humic acid addition, notice that the results are generally consistent with one another as concentration increases, a different trend emerges upon reaching the 200mg per Liter humic acid concentration. Although this study was performed using a different base solution, we chose to investigate the elevated concentration to determine if the same effects could be seen in our sea water and COREXIT sample.

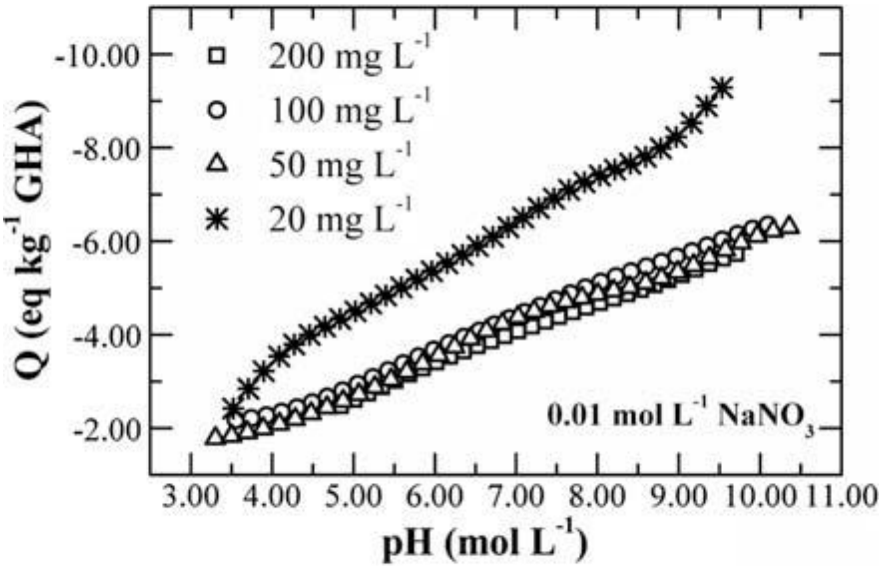


Figure 4.14 Example of humic acid influence on proton binding in 0.01M of sodium nitrate

The amount of humic acid to add to a 500mL solution of sea water was calculated according to the following equation to obtain humic concentrations of 20, 50, 100 and 200 mg per Liter.

$$\boldsymbol{Desired\ Concentration\ \left(\frac{mg}{Liter}\right) \times 0.50Liters\ Sea\ Water = x\ mg\ for\ 500mL}$$

With these calculations it was determined that the above concentrations could be obtained if we added

10, 25, 50 and 100 mg of humic acid, respectively. The humic acid was added to 500 mL of sea water and mixed using a stir bar and plate, the flakes of humic acid (an image of which can be seen below in figure 4.15) took approximately one hour to fully dissolve within the sea water.

Figure 4.15 Humic Acid

Figure 4.16 Humic acid at in decreasing concentrations from left to right

At the point when the solution was homogeneous, 1.2mL of COREXIT was added to the four different beakers containing various concentrations of humic acid. Stirring continued until the mixture was miscible then allowed to settle until phases were formed. Another image above, figure 4.16, shows the four beakers at various concentrations of acid in addition to COREXIT. Samples were taken from all three phases areas of each of the four beakers and tested using turbidity and spectroscopy.

4.5.4.1 Humic Acid with Bubble Addition

This experiment was performed after observing the results of the bubbles with the standard sea water and deionized water. The resulting readings were very similar to the initial values but further investigation was taken to rule out whether or not bubbles indeed did or did not have an effect on the mixture.

The same solutions formed for the humic acid initial experiment were used for this second set. Using the same procedure as was used for the system without humic acid, where the bubbles themselves provided significant mixture, the solution was allowed to bubble for 2 hours after which it rested for approximately 1 hour until the phases formed. Samples were taken from each level of the solution and tested using the turbidimeter and spectrophotometer.

4.5.5 Temperature Adjustment

The change in temperature of the body of water that a dispersant is applied to is of vital importance. To characterize how the change in temperature affects the emulsion formed when COREXIT 9500A in added to seawater was investigated. In April, in the Gulf of Mexico when the Deepwater Horizon oil spill took place the temperature was between the ranges of 15°C to 30°C. Since the conditions in the Gulf of Mexico changes over time examining how COREXIT 9500A changes with these conditions will be important for future use of this dispersant to inform the user of features that they may be unaware of.

The experiment created tested how COREXIT 9500A formed an emulsion with the simulated seawater at three temperatures that was indicative of three of the broadest ranges. A refrigerated temperature of 10 °C, room temperature at 26 °C and an increased temperature at 36 °C were used as a template to illustrate the three main changes that are possible in the Gulf of Mexico. The temperatures provide a standard room temperature that increased and decreased from its original temperature so that the effect of both of those changes could be quantified and analyzed. These temperature ranges were chosen to give a qualitative outlook on how the change in temperature affects emulsion formation.

Using three temperatures that were easily attainable in the laboratory was of significant importance. It was important to ensure that multiple experiments could be done at the same temperatures and there was uniformity between the conditions used. Room temperature was used as the median between the two other temperatures because it was the easiest to perform because no heating or cooling source was necessary. Due to the lack of isolated cooling units a preset refrigerator temperature had to be used for the lower temperature range. Since heating units were easily found in the lab, the temperature of 36 degrees was chosen for several reasons. A 10 degree increase was used for the increased temperature because increasing the temperature by 10 degrees should double the reaction rate as denoted by reaction kinetics principles. It was also easy to maintain the heating unit at that elevated temperature for a prolonged period of time without straining the unit or wasting excessive energy.

The procedure for temperature readings – room temp

Four beakers were labeled A, B C and D. (A) represented refrigerated temperature, (B) denoted room temperature, (C) represented increased temperature and (D) denoted increased temperature with increased COREXIT volume. Four portions of 500mL of simulated seawater were added to four 500mL beakers. A stirrer bar was added to each beaker and then the beakers were placed on stirrers. The stirrers were turned on to a low setting to create a uniform mixture. A 10mL measuring cylinder was used to measure 1.5mL of COREXIT 9500A three times and 2.0mL of COREXIT 9500A. The three 1.5mL of COREXIT was poured gently into the center of the beakers labeled A, B and C while the 2.0mL of COREXIT was poured gently into the center of the beaker labeled D. The mixture were allowed to mix for 30 minutes before the stirrer was turned off and covered with paraffin. The time was noted and the beakers were left to sit at room temperature for 4 hours before spectroscopy readings were done and then spectroscopy readings were subsequently repeated for kinetic data at the 8, 24 and the 48 hour mark. The procedure was repeated for the refrigerated and heated temperatures.

For the mixtures that were used for the refrigerated temperatures after the stirrer was stopped the mixtures were transferred to closed cap bottles with the same labels. They were put immediately in the refrigerator and after 4 hours they were taken out for spectroscopy readings. The readings at the time intervals mentioned above were also carried out. After the 96 hour spectroscopy readings were done the bottles were transferred to room temperature and left to settle for 2 days in order to see if the emulsion formed was affected by a change in temperature. After the mixture was settled spectroscopy readings were taken and noted. For the heated mixtures instead of being placed in the refrigerator they were placed in an oven at 36°C but they followed the same procedure as the mixtures in the refrigerator.

1.5mL of COREXIT was used because it was higher than the critical micelle concentration (CMC) volume of 1.1mL. To ensure that a large, observable emulsion layer was formed 1.5mL of COREXIT was used as opposed to 1.2mL which would have just been over the estimated value observed from previous experiments.

4.5.6 Oil Addition

To this point the actual system in the Gulf of Mexico was not being represented accurately instead the COREXIT 9500A was being characterized for its properties independently from the COREXIT and oil mixture. The emulsion was being formed in a mixture solely consisting of COREXIT and simulated seawater. Experimenting how COREXIT emulsion formed with a seawater system only will help to characterize what should happen if the same condition changes were to occur in an oil and seawater system. Therefore examining the COREXIT, seawater and oil system provided valuable insight into what changes could possibly occur with variances in the mixing ratio of the three components.

Two sets of experiments were undertaken; the first involved using a fixed volume of oil and increasing the volume of COREXIT. On the other hand, the second experiments involved using a fixed volume of COREXIT and increasing the volume of oil in the system. The first experiment covered the span of what happens as the COREXIT 9500A is increased in volume and the oil to seawater ratio stays the same. This is indicative to what happens when more COREXIT is added to the system past the volume necessary for an emulsion to form. The COREXIT 9500A range was chosen to test how the dispersant functioned when the volume was clearly below the critical micelle concentration at 0.6mL to how the dispersant functioned when the volume was distinctly above the critical micelle concentration at 4.0mL.

Since initial estimates for the use of COREXIT was based on oil to COREXIT 9500A ratio of 50:1 when performing experiments with a fixed volume of oil, 50mL were used. The overall volume of the system stayed the same at 500mL with the seawater component being 450mL and the oil component being 50mL. The second experiment introduced what would happen if less COREXIT 9500A was added to a site with a larger volume of oil. In the second case the volume of oil increases to half the volume of the seawater and oil system which probably will never occur but in experimenting with the system changing the initial system conditions drastically may lead to important discoveries about the properties of the dispersant. The oil range was chosen to span miniscule amounts of oil in seawater phase for example when the volume of oil used was 5mL to even oil in seawater phase when the volume of oil was 250mL.

Ideally crude oil should have been used in the seawater and oil system with COREXIT 9500A but since the availability of crude oil was limited, Sunoco Ultra-premium motor oil SAE 5W-30 was recommended as a substitute by Professor John Bergendahl as can be seen in the figure 4.17 below.

Figure 4.17 (Left) – The COREXIT 9500A in a 50mL beaker (Right) - Sunoco Ultra-premium motor oil SAE 5W-30

For the first experiment five 500mL beakers were labeled A, B, C, D and E. 450mL of simulated sea water and 50mL of motor oil was added to each beaker. A magnetic stirrer bar was added to each beaker and the beakers were place on magnetic stirrers. The stirrers were turned on to a low setting and a 10mL measuring cylinder was used to measure 0.6mL, 1.0mL, 1.5mL, 2.0mL and 4.0mL of COREXIT 9500A. The different volumes of COREXIT 9500A were poured into beakers A, B, C, D and E respectively. The mixtures were stirred for 30 minutes and then the stirrers were turned off. The beakers were covered with paraffin and allowed to stand for 2 days. After the mixture settled and the emulsion had formed spectroscopy readings were taken. Two different sets of spectroscopy results were obtained because the system had two distinct phases, the oil phase and the seawater phase. As can be seen in graphs 5.26 and 5.27, the top, middle and bottom sections of the oil phase were measured using spectroscopy and turbidity as well as the top, middle and bottom phases of the seawater phase. The values obtained were noted and graphs constructed. The top and bottom layers were determined from a qualitative view of both layers. The middle layer was determined quantitatively from averaging the highest and lowest volumes of a particular phase from the measuring cylinder.

The COREXIT 9500A range was chosen to test how the dispersant functioned when the volume was clearly below the critical micelle concentration at 0.6mL to how the dispersant functioned when the volume was distinctly above the critical micelle concentration at 4.0mL.

For the second experiment four 500mL beakers were labeled A, B, C and D. 5mL, 25mL, 100mL and 250mL of motor oil were placed in beakers A, B, C and D respectively. Beakers A,B,C and D were filled with simulated seawater up until the 500mL mark. A magnetic stirrer bar was added to each beaker and the beakers were place on magnetic stirrers. The stirrers were turned on to a low setting and a 10mL measuring cylinder was used to measure 2.0mL of COREXIT 9500A four times. 2.0mL of COREXIT 9500A was poured into beakers A, B, C and D respectively. The mixtures were stirred for 30 minutes and then the stirrers were turned off. The beakers were covered with paraffin and allowed to stand for 2 days. After the mixture settled and the emulsion had formed spectroscopy readings were taken.

Chapter 5: Results and Analysis

5.1 Initial Determinations

On a more observational basis which is supported by the graphs is that sea water and deionized water act much differently when they encounter any concentration of COREXIT. The sea water quickly separated into a distinct emulsified phase whereas the emulsion within the deionized water tests remained suspended throughout for much longer.

Experimental results from these initial familiarization investigations with sea water in particular, provided adequate information to narrow the appropriate COREXIT dosage from a range of 1.0mL to 4.0mL per 500mL of water to a range of 1.1mL to 1.3mL. This range in concentration for our sample size is where the CMC lies, more specifically, from turbidity results seen below in figure 5.1, we determined that for the solution without any variations micelles form at 1.1mL of COREXIT.

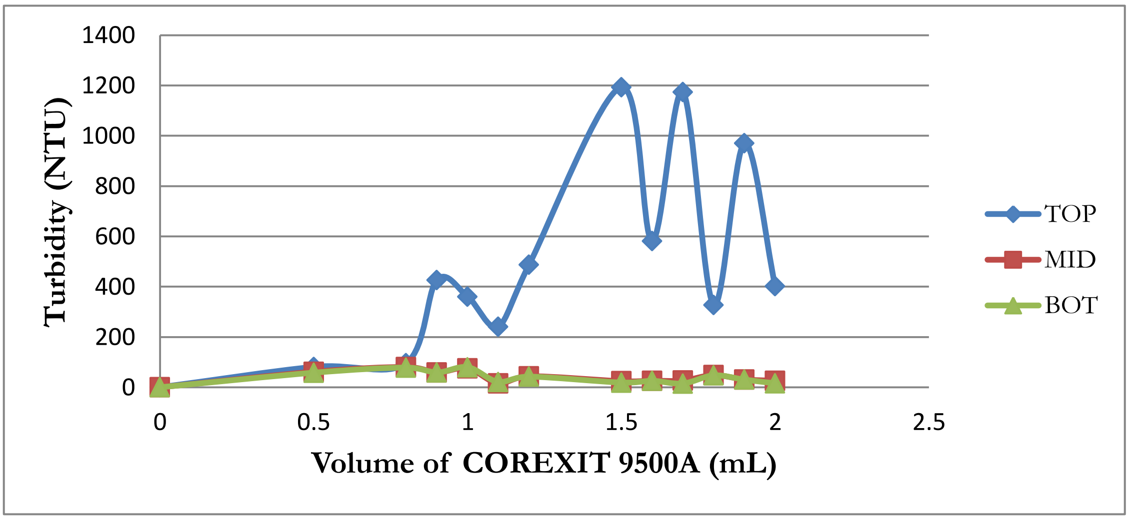


Figure 5.1 Increasing volumes of COREXIT 9500A in 500mL of sea water showing CMC

This observation is supported by our background research on turbidity trends before, at and after the CMC is reached, these diagnostics tell us that turbidity should have similar values of absorbance as dispersant concentration increases until CMC is reached at which point the slope should significantly increase. We can see above that, in fact the turbidity experiences a significant increase in value at around 1.1mL of COREXIT for the 500mL sample of sea water.

5.1.1 COREXIT 9500A Concentration

Our first goal was to pin point a range where the CMC lies which we determined was between 1.1 and 1.5mL then later deduced that the exact location was between 1.1 and 1.2 mL of COREXIT per 500mL of sea water. Graphical representation of these results can be seen above in figure 5.1. We were able to deduce this conclusion due to the spike in the turbidity graph at the location at which point micelle concentration should be most dense and therefor yield the highest reading in NTU. All further experiments with a range of variables were tested with concentrations of COREXIT around this point to observe an optimal reading where the emulsion should be most stable.

5.1.2 Component Analysis

5.1.2.1 2-Butylethanol Addition

This section will explain the results found for turbidity when 2-Butylethanol is added to 500mL of salt water and deionized water. The first results to be discussed are the turbidity readings resulting from the increase in 2-Butylethanol concentration. The figure below (figure 5.2) shows the readings obtained from the addition to deionized water.

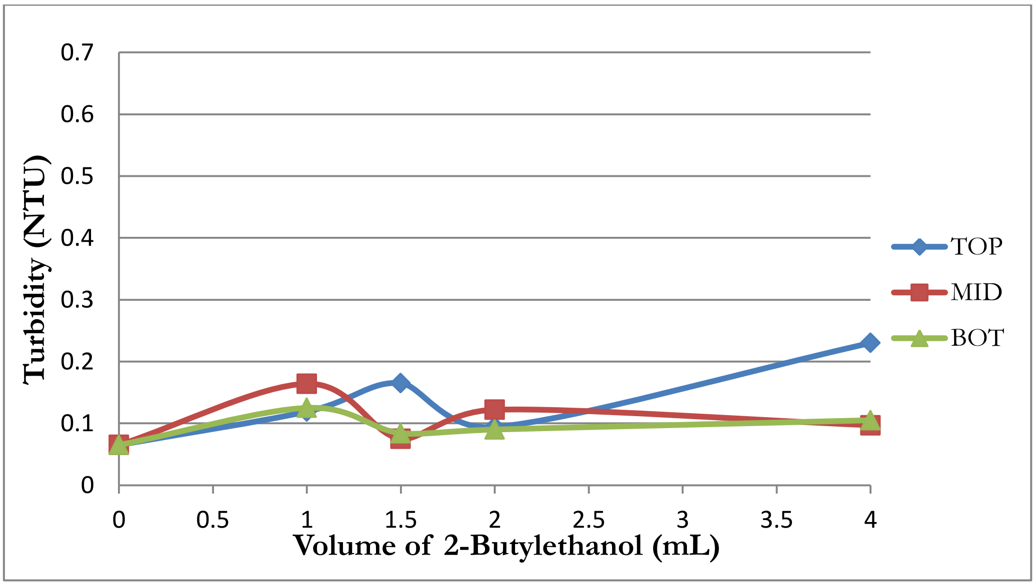


Figure 5.2 Turbidity results for addition and increase of 2-Butylethanol to 500mL of deionized water

These graphical results show that 2-Butylethanol addition results in relatively uniform turbidity values for the three phases formed in the solution. The bottom and middle layers follow similar trends with increasing concentration, and the most stable top emulsion layer formed occurs at 1.5mL where the greatest concentration difference occurs. Some interesting observations pertaining to this representation of data include the points where the middle phase is higher than the top phase, at 1mL and 2mL of 2-Butylethanol. Another comment on the 1mL addition is that the middle layer has a higher reading than the 1.5mL reading for the top layer. This suggests that the emulsion is most dense at the middle layer for this particular concentration which is an interesting finding in relation to the observations of the actual system in the Gulf of Mexico. This alone, however is not enough to conclude anything definitive about the effects of 2-Butylethanol or the properties of COREXIT as the single component should not at any point separate from the overall composition.

A more appropriate representation of the system was created using our simulated sea water rather than deionized water as it will most certainly influence the formation of the emulsion with the charged particles. The results for turbidity of 500mL of salt water with increasing volumes of 2-Butylethanol can be seen in figure 5.3 below.

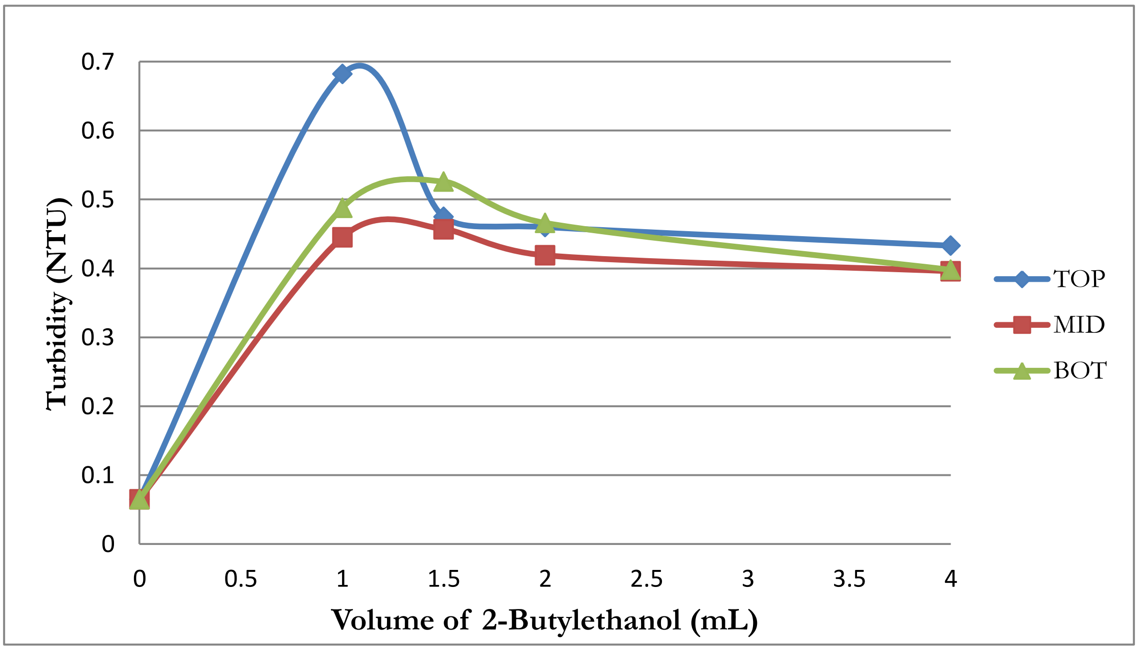


Figure 5.3 Turbidity results for addition and increase of 2-Butylethanol to 500mL of sea water

The results from the plotted turbidity measurements display a consistent shape trend in turbidity as the volume of 2-Butylethanol increases. All three phases display a large slope from the basis reading where no 2-Butylethanol was added, to the 1mL addition of the top layer and 1.5mL addition for the middle and bottom samples. For increasing concentrations past this point the turbidity measurements decrease gradually and level after 2mL of 2-Butylethanol.

A significant deviation from the predictions on the phase formation behavior is that the bottom phase has consistently higher readings than the middle layer; this suggests that there is a larger emulsion concentration on the lowest sampling point within the system. The greatest difference between the top reading and the middle and bottom layers occurs at around 1.1mL of 2-Butylethanol which agrees with the determination that the CMC lies at relatively the same volume of COREXIT.

A major comparison between the use of deionized water and sea water is that the readings of the latter are much larger in comparison. Similarly, the range in values for the sea water is greater than the deionized water with values ranging within 0.1 NTU of each other. More distinct phase formations occur in the salt water experiments, meaning more stable emulsion formation.

5.1.2.2 Sodium bis(2-ethylhexyl) Sulfosuccinate Addition

The proceeding section will present and discuss the results found for the addition of sodium bis(2-ethylhexyl)sulfosuccinate to deionized and sea water solutions. Turbidity and spectroscopy collections were executed for this component addition. First turbidity results will be discussed and compared followed by an evaluation of the spectroscopy experiments. Figures 5.4 through 5.7 below graphically display the experimental findings, beginning with sodium bis(2-ethylhexyl)sulfosuccinate addition to deionized water.

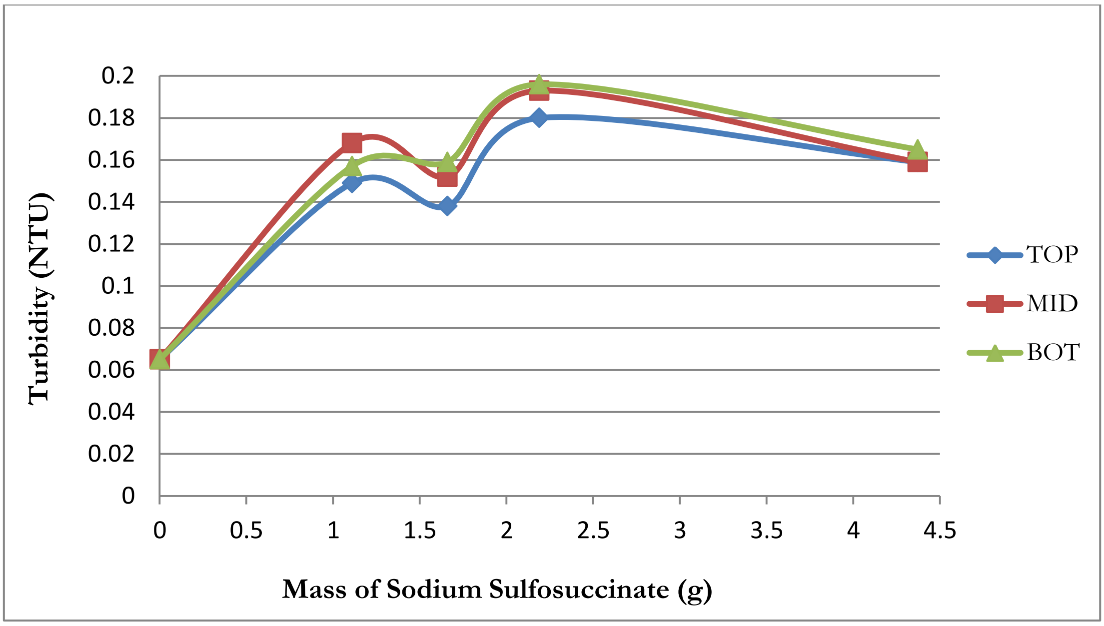


Figure 5.4 Turbidity results for addition and increase of Sodium bis(2-ethylhexyl) sulfosuccinate to 500mL of deionized water

Figure 5.4 above shows that the addition of this component to deionized water results in the same trend throughout each of the three layers. It appears that there is little difference between the turbidity readings at each of the three sampling locations for increasing amounts of sodium bis(2-ethylhexyl)sulfosuccinate, meaning the emulsion is fairly uniform and does not produce the desired phase formation. The top layer has the lowest turbidity readings and the bottom layer generally has the highest which deviates from the behavior of the COREXIT and signifies that the majority of the component, although by a small margin, lies at the bottom of the sample and decreases with distance from the bottom of the beaker.

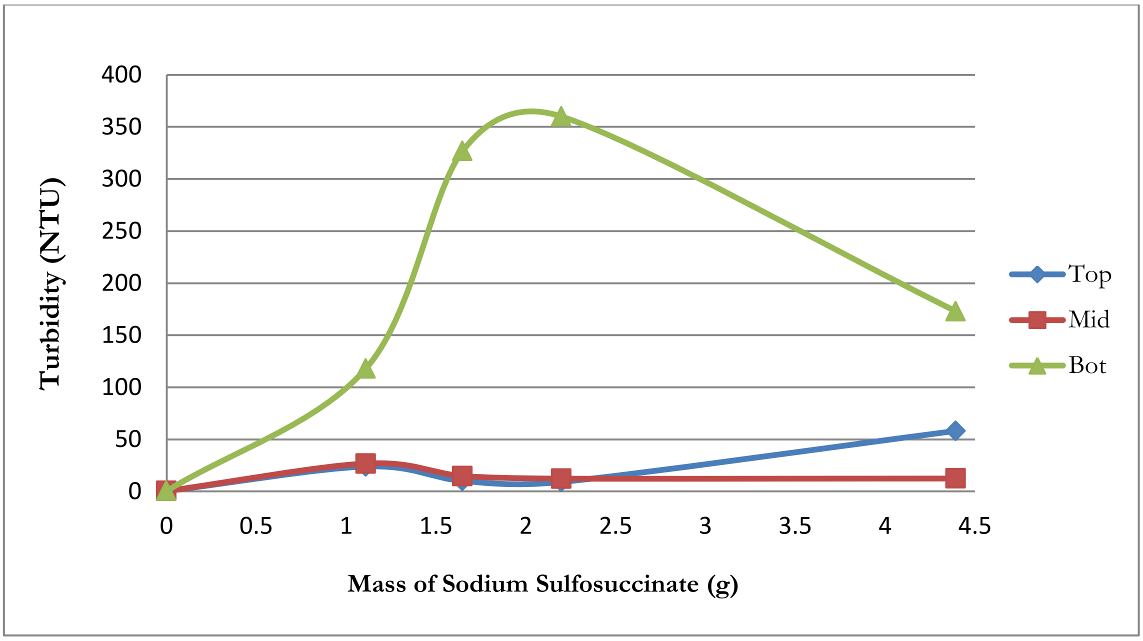


Figure 5.5 Turbidity results for addition and increase of Sodium bis(2-ethylhexyl) sulfosuccinate to 500mL of sea water

The graphical representation above, in figure 5.5 exhibits some interesting behavior of the sodium bis(2-ethylhexyl)sulfosuccinate in addition to sea water. The bottom sample results in the highest turbidity readings with a peak around 2 grams, the top layer is elevated at the highest mass addition and the middle layer remains relatively constant around 20 NTU. Overall, the turbidity values of the sea water experiment is significantly higher than those involving deionized water, more specifically, the readings for the bottom layer of the sea water solution suggests a significantly more dense population of stable suspension of particles. This is an interesting finding because no other experiment displayed such difference between top and bottom layers where the bottom resulted in such elevated turbidity readings. This means the greatest emulsion concentration lies within the depths of the beaker rather than at the surface, this could possibly relate to the observations of oil and COREXIT within the depths of the water table.

Next, the effects of the addition of sodium bis(2-ethylhexyl)sulfosuccinate was evaluated using spectroscopy at 590nm for deionized and sea water. Figures 5.6a and 5.6b shown below display the results for deionized water.

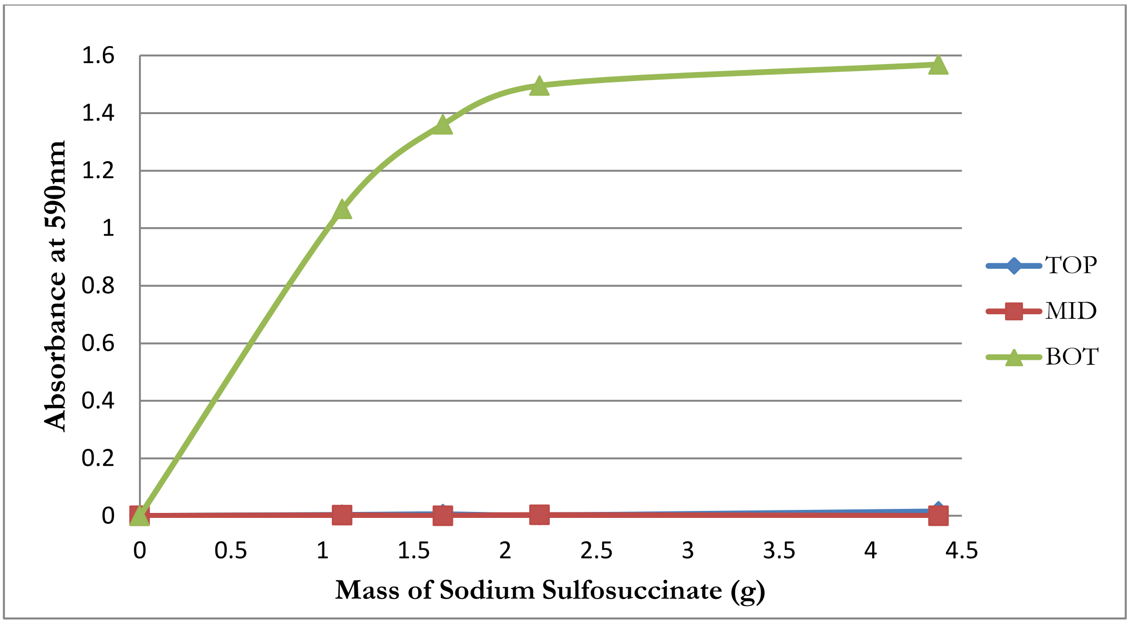


Figure 5.6a Spectroscopy results for addition and increase of Sodium bis(2-ethylhexyl) sulfosuccinate to 500mL of deionized water

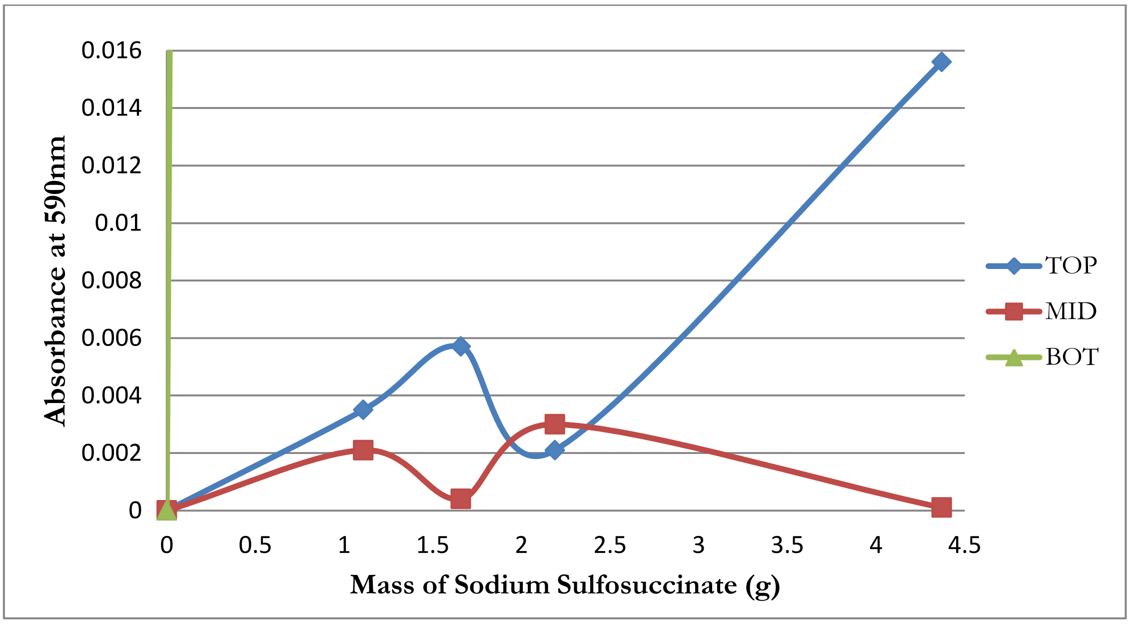


Figure 5.6b Magnified view of top and middle layers from figure 5.6a

The above figures 5.6a and 5.6b are plots of the same experiment however, must be shown on two different plots because the trends for the top and middle samples are very close to zero and the bottom readings are significantly larger. With bottom layer readings so significantly larger, it can be deduced that the majority of the emulsion is formed at the bottom of the solution and there is minimal suspension towards the top of the experimental volume.

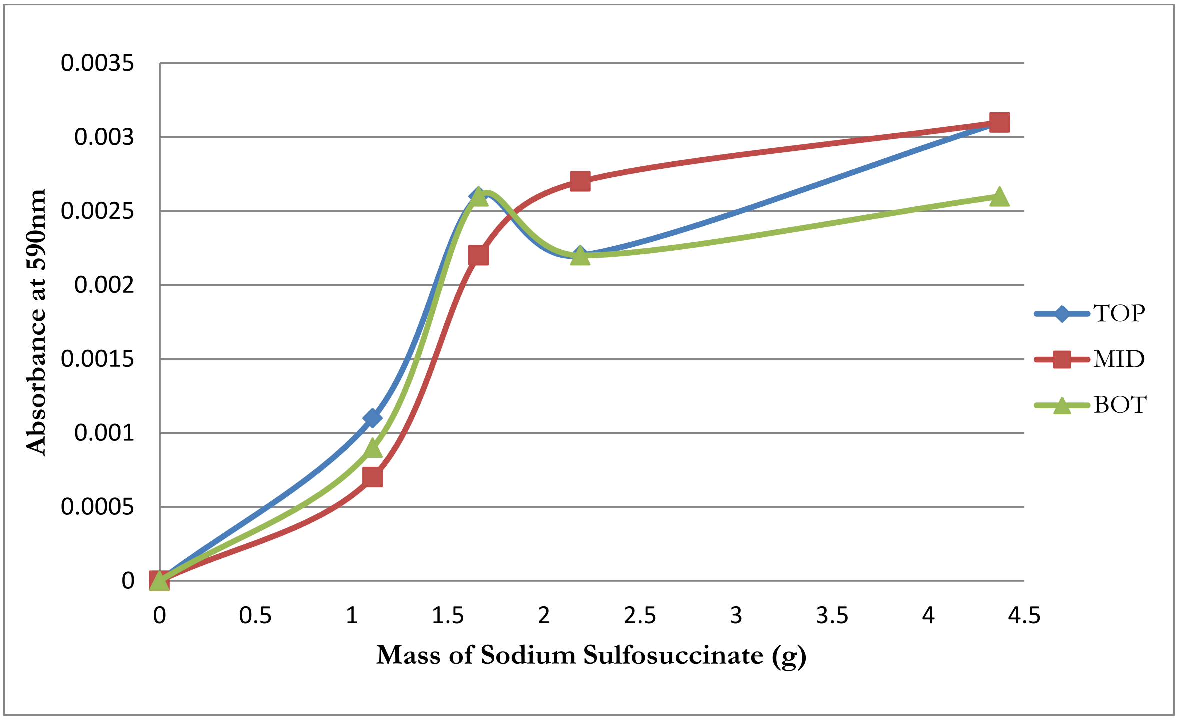


Figure 5.7: Spectroscopy results for addition and increase of Sodium bis(2-ethylhexyl) sulfosuccinate to 500mL of sea water

The graph of absorbance for sodium bis(2-ethylhexyl)sulfosuccinate addition to sea water seen above in figure 5.7 suggest uniform emulsion formation between the three testing sites. In this case, the top and bottom phases show similar trends as the sodium sulfosuccinate concentration increases. One observation that is different for this experiment is that the middle layer has a higher absorbance after 2grams of the constituent was added.

An interesting result yielded from the above graphs of absorbance is that the sea water solution produced a more uniform emulsion throughout the beaker and the deionized water produced a much greater distinction between the highest readings of the bottom layer from the other two sampling locations. All previous experiments to this point produced the opposite result. This suggests that the sodium bis(2-ethylhexyl)sulfosuccinate and 2-Butylethanol act in a contradicting manner where the latter forms better emulsification in salt water and the sodium sulfosuccinate creates a better emulsion in deionized water.

5.2 Salinity Variation Results

Salinity experiments were performed in efforts to observe the effects of ion concentration on the behavior of the dispersant at various concentrations of COREXIT, also to model the effects of what may happen when the COREXIT within the water table of the ocean encounters an estuary where salinity over a relatively small distance.

5.2.1 Fifty Percent Sea Water by Volume

The first set of salinity experiments to be commented on is the highest dilution of the simulated sea water. Absorbance for varying volumes of COREXIT is plotted below in figure 5.8 where each layer of the sample was measured using the spectrophotometer.

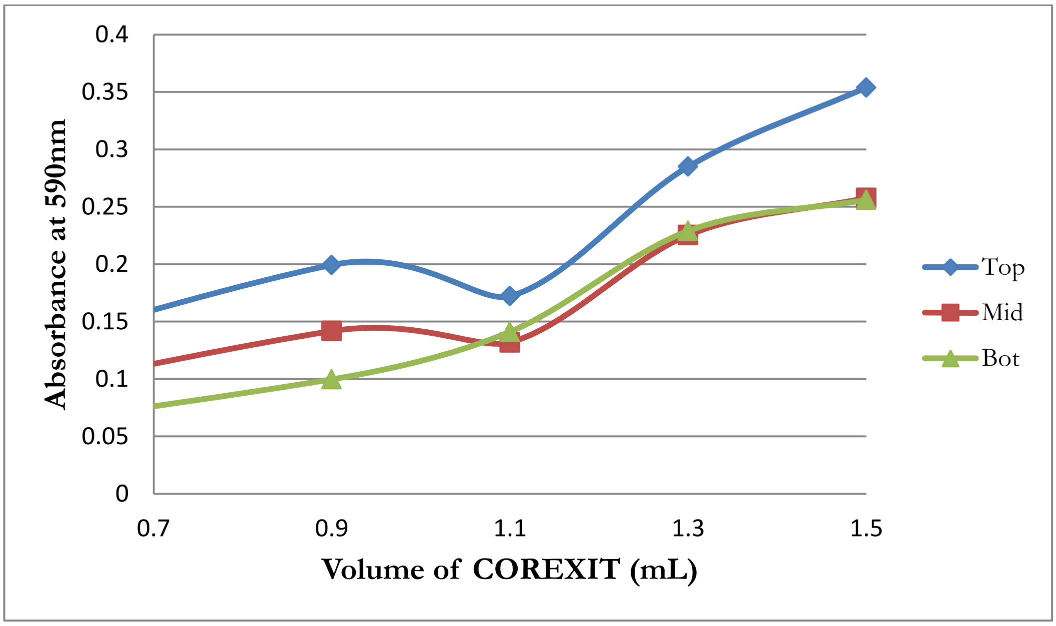


Figure 5.8 Diagram of absorbance at 590nm of a 50% seawater and 50% pure water mixture as the volume of COREXIT increases.

The graph of the data collection suggests that the top layer has the highest concentration of emulsified droplets, and also that the CMC is reached between 1.1 and 1.2mL of COREXIT addition. This agrees with the previously determined CMC of COREXIT in pure salt water which lies at 1.1mL. One deviation from the usual results is that the absorbance at the bottom sampling site is almost equal to the absorbance at the middle of the solution.

Another observation which should be made in regards to these results is that the top middle and bottom layers follow the same absorbance trend as the volume of COREXIT is increased from 0.7 to 1.5mL. This qualitative analysis, quantitatively describes than the emulsion is generally uniform throughout the entire solution. Another brief note is that the absorbance for this concentration of salinity are relatively low, signifying that there is only a small amount, comparatively, of emulsion droplets suspended throughout.

5.2.2 Seventy-Five Percent Sea Water by Volume

The next experiment on salinity was to observe the effects of an increase in salt water concentration that was still less that the full ion concentration. Absorbance for varying volumes of COREXIT is plotted below in figure 5.9 using data obtained from the spectrophotometer.

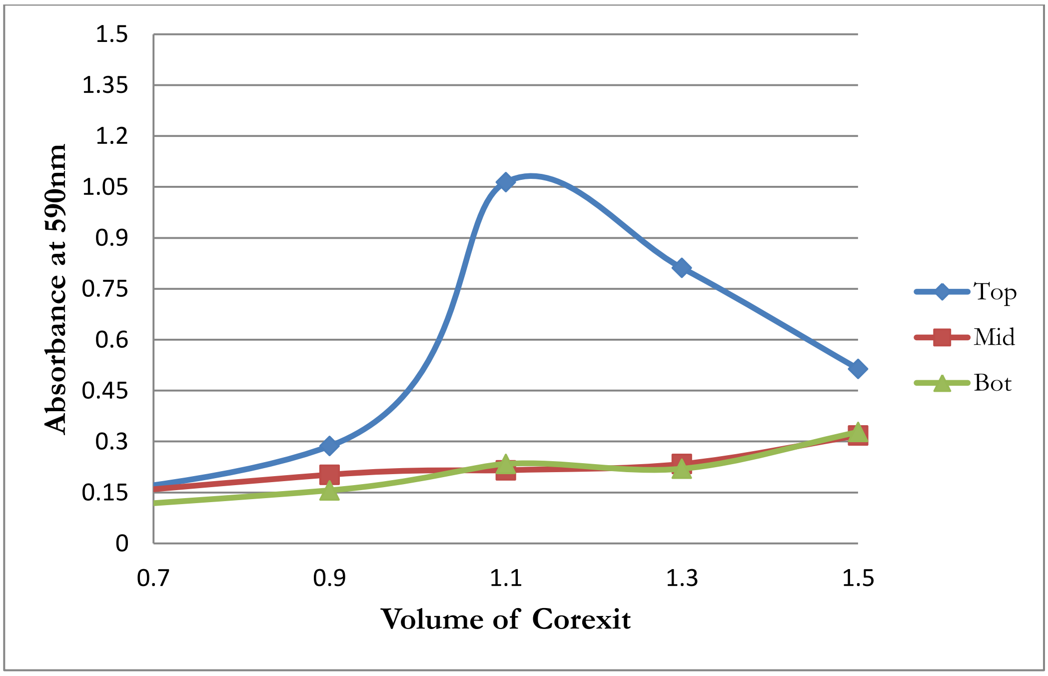


Figure 5.9 Diagram of absorbance at 590nm of a 75% seawater and 25% pure water mixture as the volume of COREXIT increases.

First, note that the y-axis of this plot is set to a 1.5 maximum value in efforts to compare with the following results of section 5.2.3 where collection was used from a pure salt water sample. In figure 5.9, the top layer produces a much higher absorbance reading than those of the middle and bottom layers, this is an expected and desired observation, as has been explained before, describes a more stable emulsion layer. There is a sharp increase from 1.0 to 1.1mL of COREXIT addition, suggesting that the CMC lies within this concentration. As the concentration of COREXIT increases, after the 1.1mL addition, the top values of absorbance begin to decrease and the bottom in middle, which follow a similar trend as dispersant addition increases, show an increase in absorbance. This observation suggests that the emulsion reaches the most stable point with the greatest micellization and then decreases once this COREXIT volume is surpassed. Likewise, the bottom and middle samples increase in absorbance after the CMC is exceeded, leading to more uniform absorbance at each of the sample sites, an undesirable affect when the stability of the top layer is in question.

5.2.3 One Hundred Percent Sea Water by Volume

As one of our initial tests on the behavior of the dispersant within the pure simulated sea water solution, the following graph is plotted below for reference in comparing to the results of the 50 percent and 75 percent of salt water by volume. Similar data collection and plotting methods were used to formulate an image with would allow seamless comparison between the three dilutions.

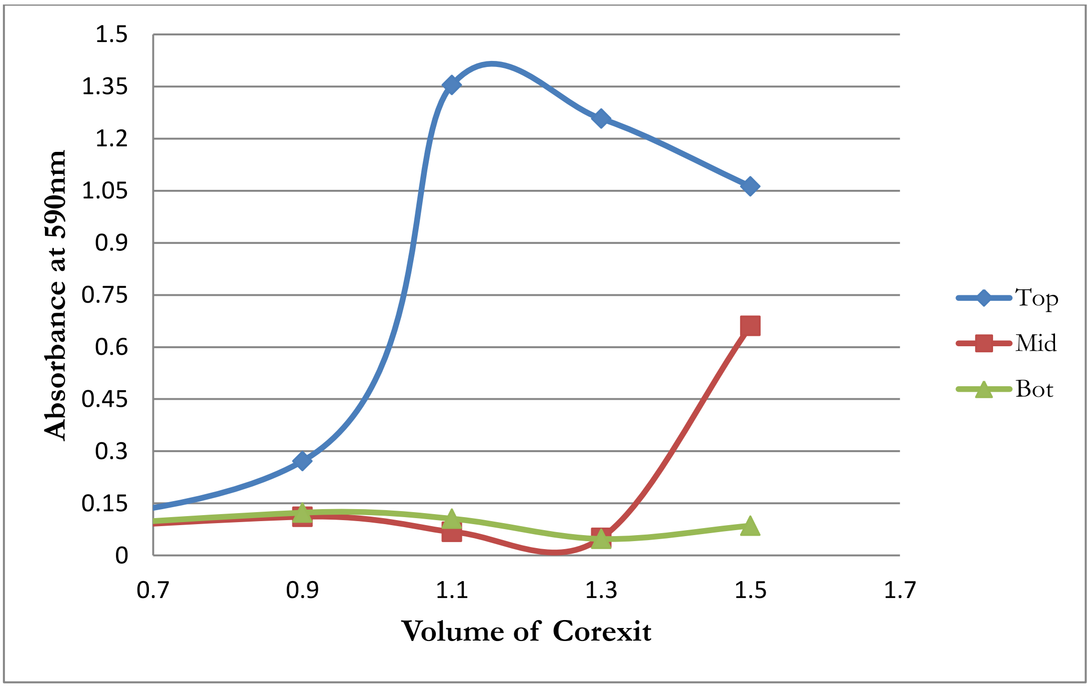


Figure 5.10 Diagram of absorbance at 590nm of a 100% Seawater as the volume of COREXIT increases.

Figure 5.10 above is most comparable to figure 5.9 showing the results for 75 percent salt water by volume. The most prominent observation is that the CMC occurs at nearly the exact same position for both 75 percent and pure salt water however, the absorbance values of the top layer for the pure salt water are greater for the 1.1, 1.3 and 1.5mL additions. The second most pictorially obvious observation is that the middle layer in the pure sea water solution increases significantly between 1.3 and 1.5mL, denoting that the emulsion becomes less stable, although within a smaller distance from the surface than in the 75 percent experiments in which the bottom and middle layer absorbance approach much closer values to those of the top sample. In relation to this observation, although the stability within the top layer of the emulsion of pure salt water decreases, it is a less abrupt change as concentration of COREXIT increases.

5.3 Sand Addition Results

The following section will discuss the findings associated with influencing the dispersant system with the addition of sand particles of various sizes. These results will later lead to conclusions associated with the dispersant behavior, beginning with the variations in data associated with a different method of adding the sand to the system.

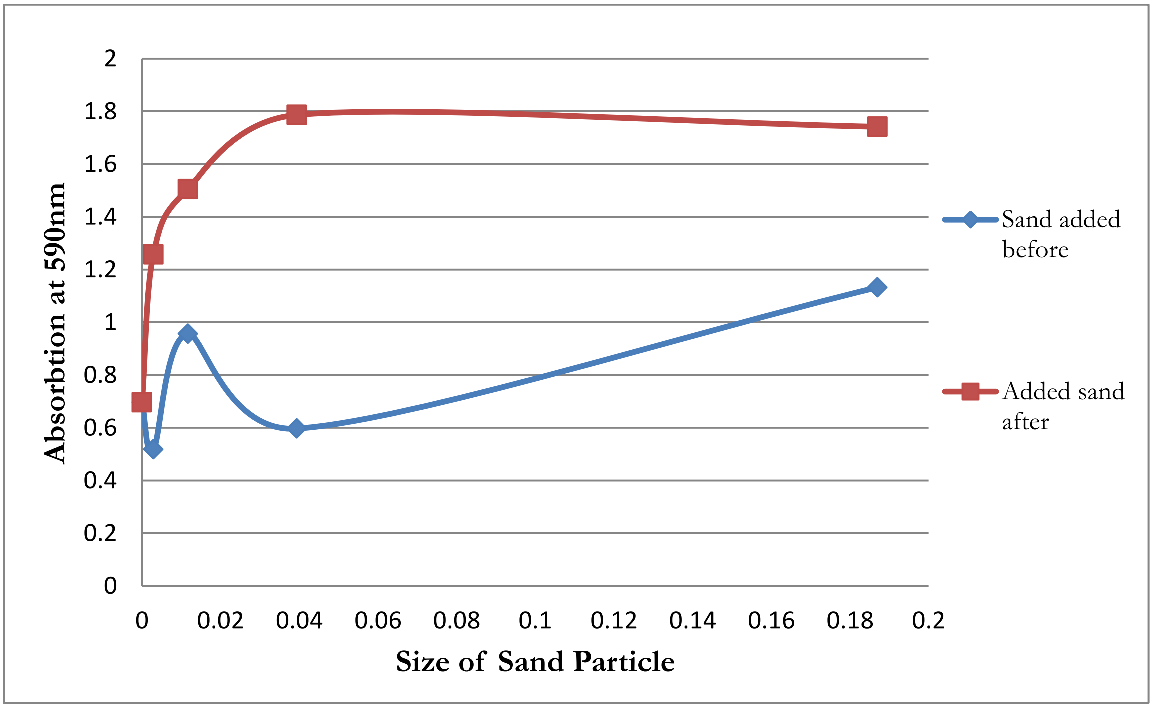


Figure 5.11 Graph of spectroscopy comparing the formation of emulsion when sand added before and after emulsion formed for top layer.

These two conditions exhibit how sand below and above the COREXIT emulsion layer impacts and vary its effectiveness. The size of the sand particle was also varied to show trends that may be significant. The top layer of the emulsion formed follows an increasing trend then levels off at around the 1.7abs when the sand is added after the COREXIT 9500A. When COREXIT 9500A is added before the trend is significantly lower and follows no particular trend this could be because when the sand is added before it does not come in close enough contact with the COREXIT 9500A. Only minimal contact is experienced through mixing with a magnetic stirrer when the sand is already at the bottom of the beaker. Therefore a max absorbance of 1.1abs was recorded. When the sand was added after the COREXIT 9500A the sand was in contact because it had to pass through the COREXIT layer.

The top layer of the emulsion would contain more of the sand particles because as seen from the ideal conditions, it produces the largest absorbance hence more of the emulsion is being formed at the top. The top layer does exhibit more retention of the sand particles consistently for the sand added after COREXIT while the sand added before follows a slightly similar trend except for the 0.0394inches of sand. This could have been caused by non-uniform mixing or a change in the mixing intensity that may have caused more of the sand to not have been retained by the top layer.

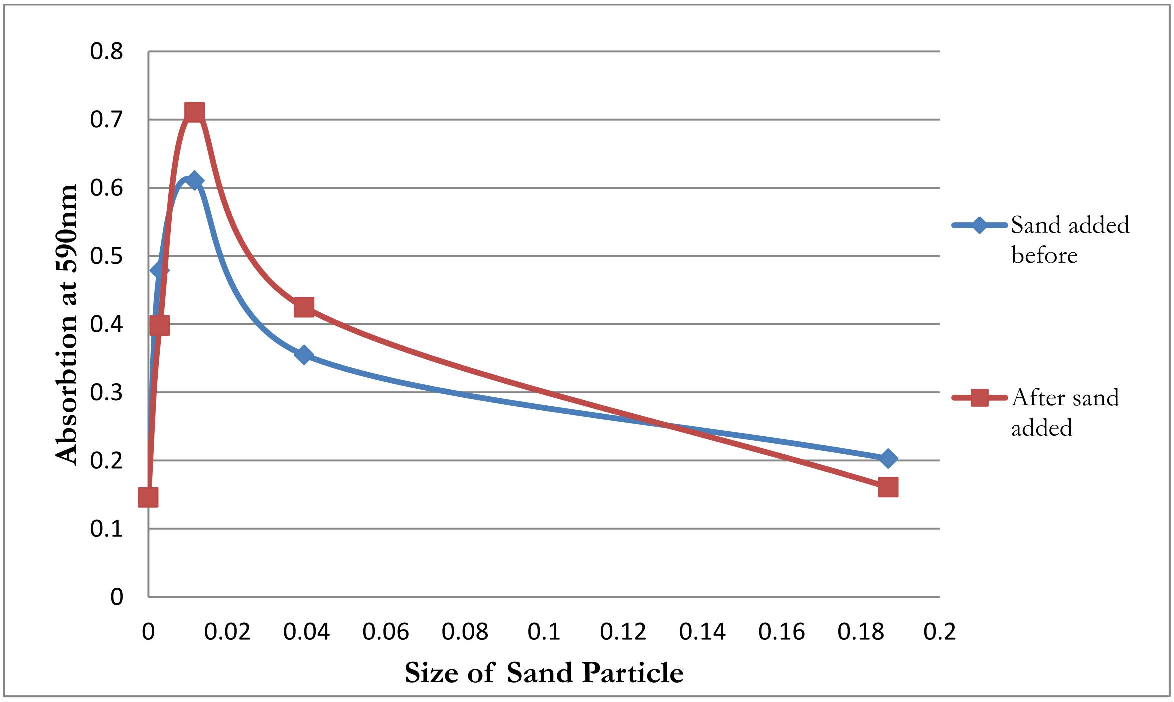


Figure 5.12 Graph of spectroscopy comparing the formation of emulsion when sand added before and after emulsion formed for middle layer.

The trend of both graphs follows an increase in absorbance until the addition of 0.0117inches of sand then a gradual decrease occurs which is probably because the larger particles are falling to the bottom of the beaker while the particles of a magnitude similar to 0.0117inches are suspended in the liquid. The middle layer was not affected by the addition of the sand before or after the COREXIT was added and this was most likely due to the fact that the same median amount of COREXIT emulsion formed remains in the middle layer regardless. Another factor that would affect the similarity is that the middle layer contains less COREXIT than both the top layer at 1.7abs and the bottom layer at 1.1abs at their respective highest absorbance's.

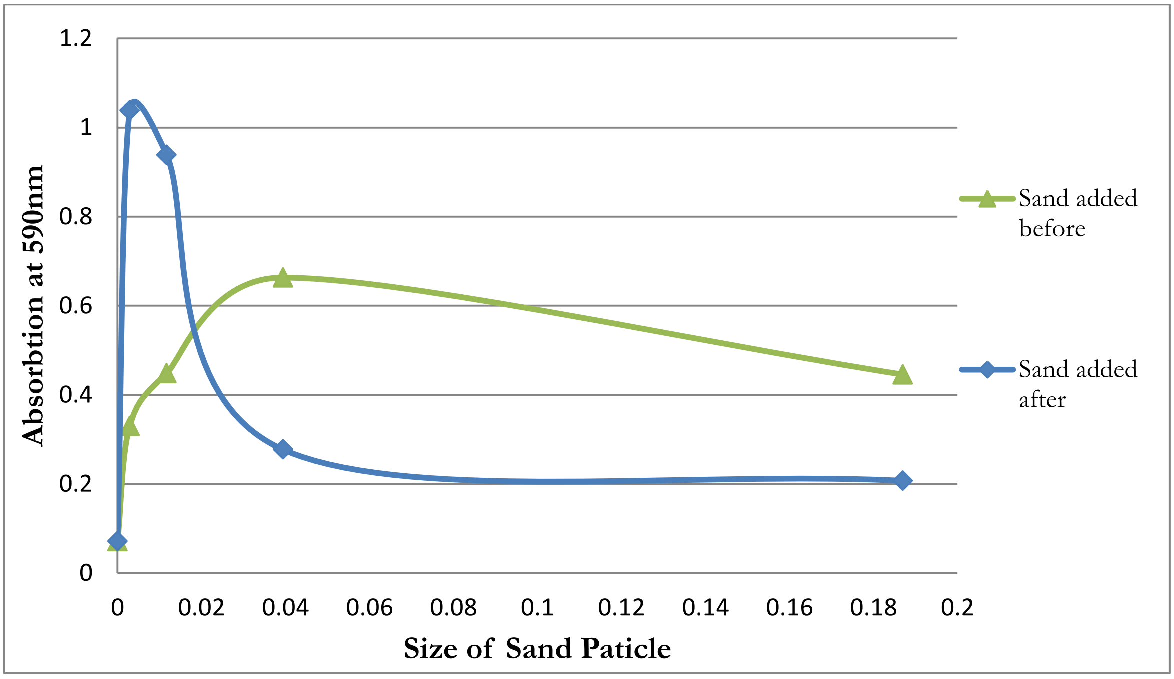


Figure 5.13Graph of spectroscopy comparing the formation of emulsion when sand added before and after emulsion formed for bottom layer.

The bottom layer shows two opposite trends where the sand added before increases and levels off at around 0.42abs and the sand added after layer decreases from around 1.05abs to 0.2abs. The figure 5.13 above shows that the bottom layer is directly affected by the position of the sand layer. When the sand is added before the COREXIT emulsion layer gradually increases and levels off but the overall absorption is relatively low at around 0.65abs. When the 0.0394 inches of sand is introduced the bottom layer still retains an increasing absorption layer. The largest sand particle introduced at 0.187 inches did not adhere to the COREXIT emulsion in an increasing manner and hence the absorption started to decrease. This shows that COREXIT has a limit to how much sand particulate it can suspend at any one point in time.

The sand added after trend shows a gradual decrease as the particle size increases and this is because the particle comes in direct contact with the sand. The lighter, smaller particles are suspended by the COREXIT emulsion and causes the absorbance as the particle size increases to be reduced because less is trapped in that layer. The method of application does impact the amount of sand trapped beneath the sea surface and this data also gives insight into actual circumstances that could be encountered in the Gulf of Mexico due to the random and chaotic nature of the mixing that occurs in the sea.

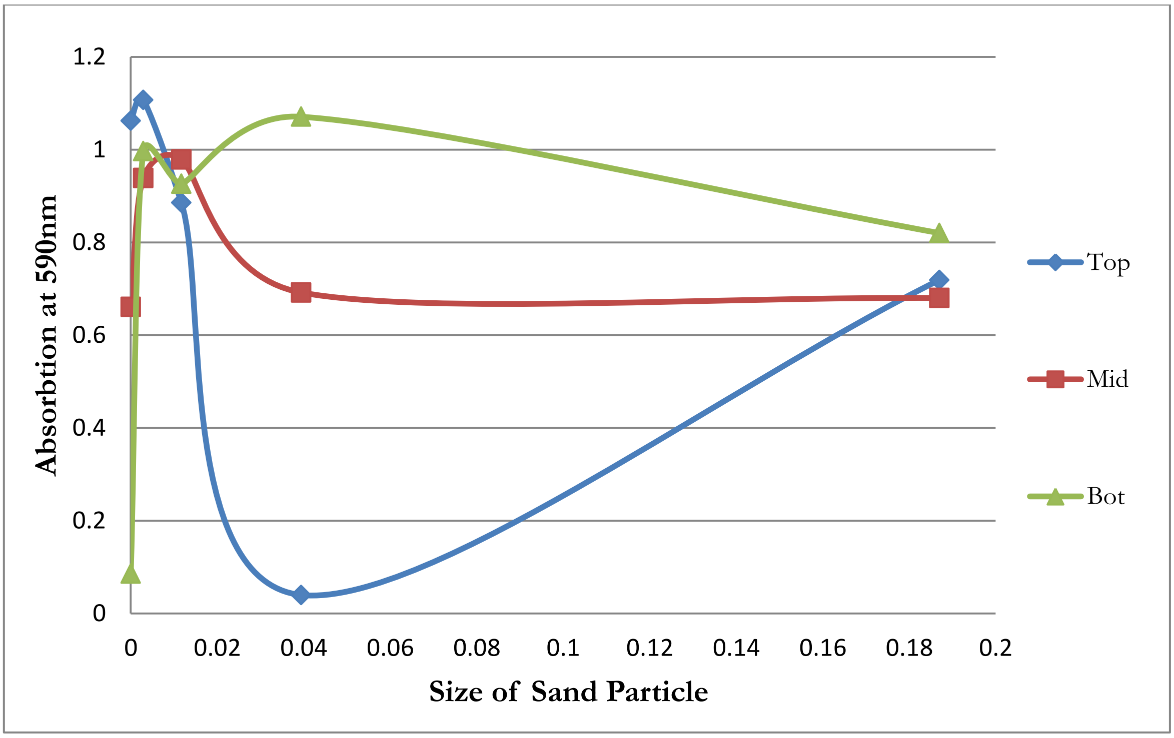


Figure 5.14 Graph of spectroscopy readings varying the size of sand particles for 1.5mL COREXIT

When sand was added after 1.5mL of COREXIT the figure 5.14 above was generated. The top layer is initially on top as expected but when 0.0117 and 0.0394 inches of sand was added the top layer decreased and caused an increase in the bottom layer while the middle layer slightly decreased but was much higher than 0.05abs for the 0.0394 inches of sand in the top layer. The emulsion was stable but in a manner that was not expected as the bottom layer contained the highest absorbance for the heavier particles 0.0394 inches and 0.187inches and the top layer exhibited the highest absorbance for the lightest sand particle and the middle layer for the 0.0117 inches. This shows that as the particle size increases the ability for the emulsion to sustain sand particles in the top layer decreases even though the highest absorbance ideally occurs in this layer.

The overall stability is greatest when 0.0394 inches of sand is present but for the other sizes of sand particles the overall stability is very low. The absorbance for all the sand sizes besides 0.0394 inches are really close to each other and this indicates a homogenous mixture which decreases the effectiveness of the COREXIT. The COREXIT emulsion trapped for prolonged periods of time in other layers may cause complications that have long term implications.

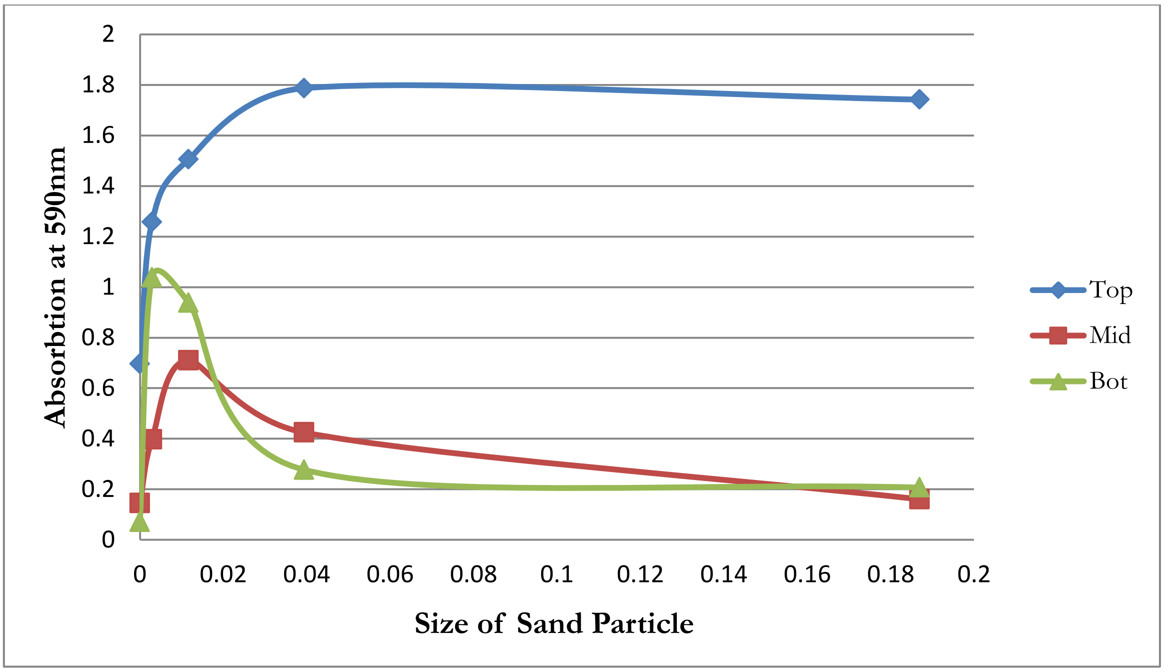


Figure 5.15 Graph of spectroscopy readings varying the size of sand particles for 2.0mL COREXIT.

When sand was added after 2.0mL of COREXIT the figure 5.15 above was plotted. The graph shows a trend of stability as the top layer is consistently higher than the middle and bottom layers. As the size of the sand particle increases the difference in absorbance between the bottom and top layers also increase. Increasing the size of sand past 0.0394 inches the absorbance slightly decreases for the top layer when 0.187 inches was added. The bottom layer has a higher absorbance than the middle layer continuously throughout the range of sizes of sand except the 0.394 inches. The highest absorbance in the bottom layer is about 1.0abs and its lowest is 0.025abs and this supports the notion that the COREXIT 9500A is being trapped within the bottom layer.

The overall absorbance of the layers was more distinct and this was probably due to the increased volume of COREXIT forming the emulsion. Therefore an increase in the maximum absorbance recorded can be seen in the 2.0mL reading which was about 1.8abs in comparison to the 1.5mL reading which was about 1.1abs. This difference is significant and exhibits signs that with the addition of sand more COREXIT might be needed to adequately form a stable emulsion layer where as previously in ideal conditions all of the COREXIT went to form the emulsion layer.

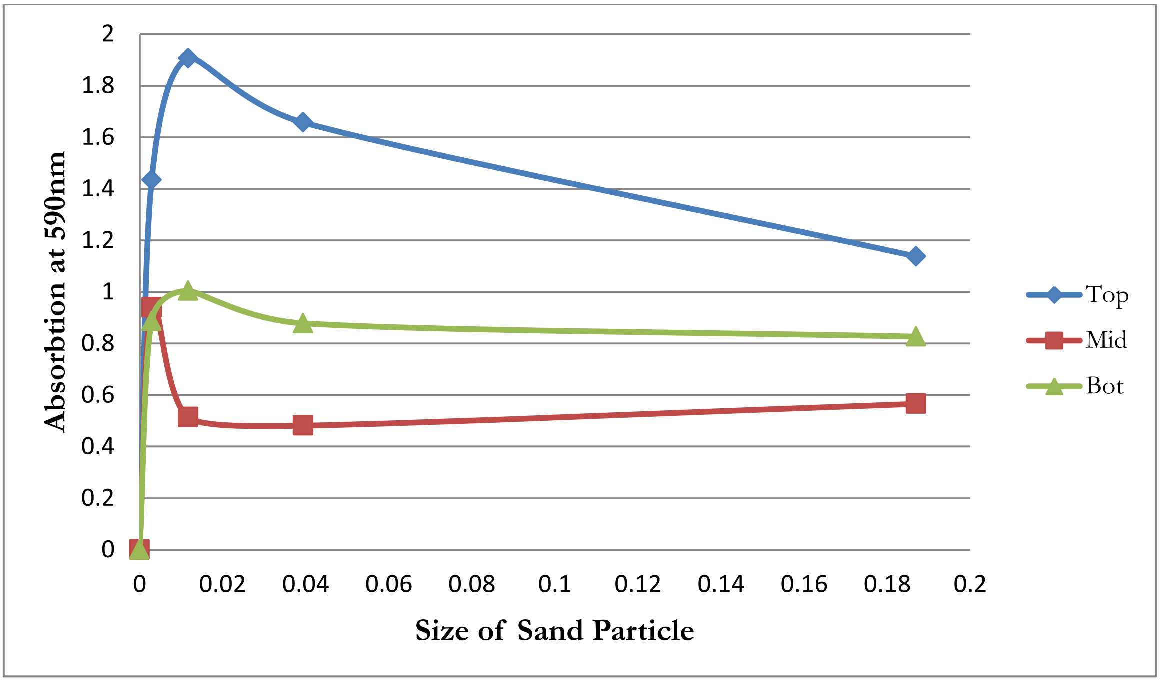


Figure 5.16 Graph of spectroscopy readings varying the size of sand particles for 2.5mL COREXIT.

When sand was added after 2.5mL of COREXIT the figure 5.16 above was generated. The top, middle and bottom absorbance layers were distinct except for the largest particle of 0.187 inches where the trend decreased significantly. The separation of the top and bottom layers was greater than the separation of the top and middle layers. The greatest difference between the top and middle layers for 2.0mL and 2.5mL is about the same at around 1.2abs. The greatest difference for the 2.0mL of COREXIT occurred when 0.0394 inches of sand was added while for 2.5mL of COREXIT the greatest difference transpired when 0.0117inches of sand was added. This shows that the 2.0mL of COREXIT emulsion retained and suspended larger sand particles. The 2.5mL COREXIT emulsion just slightly decreases in absorbance among the 0.0394 inches of sand for the top and middle layers while the bottom layer more or less stays the same. It was expected that once the COREXIT reached a volume where stability could be achieved with sand particles the same trend would be followed and it does besides the 0.0394 inches of sand which may have not had the same mixing intensity as the other sand particles at 2.5mL of COREXIT. The difference in mixing may have skewed the results but due to the high readings of absorbance were recorded for the top and bottom the decrease was more pronounced where as in the middle layer case it was definitely less obvious of a change in absorbance.

The bottom layer was clearly greater than the middle layer for the 2.5mL COREXIT graph while the 2.0mL bottom layer was less distinct. This shows that as the COREXIT is being increasingly trapped when the volume of COREXIT increases. The absorbance of the 2.5mL of COREXIT is very similar to the 1.5mL of COREXIT readings at around 1.0abs. However, since the bottom, middle and top layers were inverted for the two larger sizes of sand for the 1.5mL COREXIT readings the emulsion may not have been stable but when 2.0mL of COREXIT was added the stability of the predicted layers were formed. Hence from this initial stability the increase in COREXIT volume to 2.5mL is representative of an addition to the stable layer which causes more COREXIT to be trapped underneath the middle layer. For the top layer of both the 2.0mL and 2.5mL volume of COREXIT graphs absorbance decreased when the larger 0.187 inch sand was added.

5.4 Addition of Air Bubbles

5.4.1 Salt Water & Deionized Water

After several rounds of experiments of influencing both salt and pure water systems with air bubbles at a range of COREXIT concentrations from 1.1mL to 1.3mL, it was determined that the perturbation for these samples were minimally affected by the higher dissolved oxygen content. In both spectroscopy and turbidity measurements the emulsion at the three respective phases remained about the same, the largest discrepancy found was 7.78% from the base readings of the designated solutions. The most sensitive to the air bubbles occurred at 1.2mL of COREXIT added to 500mL of water, results for these readings can be seen in the table below where initial readings are compared to those perturbed by bubble addition.

Table 5.1 Comparison of bubbled solutions to initial readings with stirring for 1.2mL of COREXIT

		Deionized Water			**Sea Water**		
		Initial	**Bubbles**	**% Difference**	**Initial**	**Bubbles**	**% Difference**
Turbidity (NTU)	Top	9.51	9.32	2.00	488	458.5	6.05
	Middle	9.97	9.80	1.71	44.3	47.5	6.74
	Bottom	9.77	9.71	0.61	42.7	46.3	7.78

An analysis was used to ensure that the values of the phases which interacted with the bubbles were close enough to the initial values so the effects could be concluded as null. Because all discrepancy is less than 10% and each of the layers appears to follow the same trends, the data suggests that bubbles do not have a significant effect on the emulsion formation of COREXIT 9500A in neither deionized water, nor sea water.

5.4.2 Salt Water & Humic Acid

Two situations were studied for the solution of salt water and humic acid with the addition of 1.2mL of COREXIT. As was discussed in the methodology section 4.5.4, humic acid was added, readings were taken using two different types of mixing including the standard of stirring and then using the bubbling stone. This was pursued in attempt to observe if bubbles have an effect on a system with an additional variation after the results from section 5.4.1 above showed little influence.

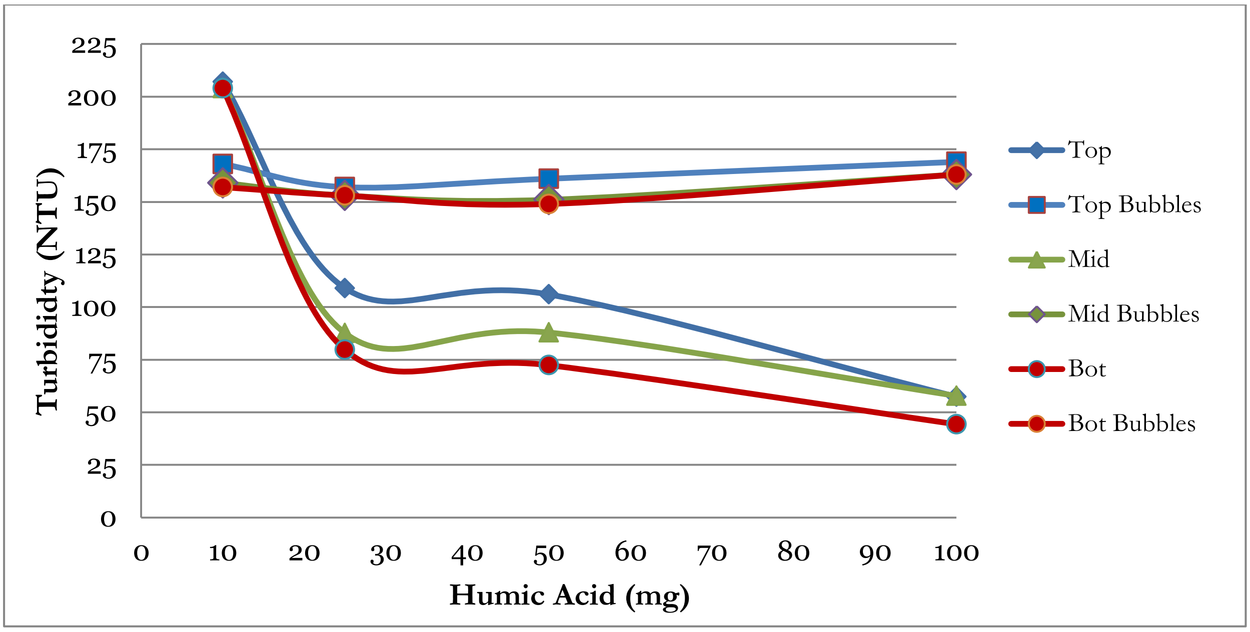


Figure 5.17 1.2mL COREXIT in sea water with increasing concentration of humic acid (bubbles & stirring)

There appears to be a much more significant influence from the bubbles on the formation of the emulsion when humic acid is present. Graphical representation of these results can be seen above in figure 5.17. It is clear that the resulting values for a humic acid variation on sea water and 1.2mL of COREXIT follow a distinct trend under stirring and bubbling conditions where each of the testing locations vary similarly as humic acid concentration increases. It appears that the top layer contains the highest droplet concentration, however there is not much distinction between the top, middle and bottom layers, contradicting the results of the system including only COREXIT and sea water where the CMC is obvious and there is a large difference between the readings of the top layer and those of the middle and bottom.

The readings for turbidity where bubbles were included in the system were distinctly higher than those from stirring the solution, also there is very little variation in turbidity as the humic acid concentration increases throughout the sampling sites. Stirring, on the other hand, has the highest value when 10mg of humic acid was added, greatly decreasing until 25mg was added then once again decreasing more gradually as addition mass increases past 50mg.

In comparison to the results from the standard, humic acid inhibits the formation of a stable emulsion layer which would emerge over time to the surface of the sample. These results could possibly provide insight into the sinking phenomena the oil and COREXIT emulsion that the Gulf is experiencing. On another note, the comparison between stirring and bubbling the mixture suggests that oxygen concentration nullifies the effects of humic acid concentration present, so the effects of humic acid may have more of an impact at deeper locations within the water table where less oxygen is present.

5.5 Temperature Variation

5.5.1 Room Temperature

The room temperature results in this section should mimic the preliminary cases that were also done at room temperature. At the 48 hour interval the top layer was significantly higher than the middle layer by about 1.0abs. This shows that the emulsion layer is distinctly stable but it was found that the bottom layer was higher than the middle layer which means that more COREXIT is being trapped beneath the middle layer even if by a small difference of 0.1abs. This indication gives insight into if the temperature is increased the COREXIT may have an affinity to become stable above and below the sea surface.

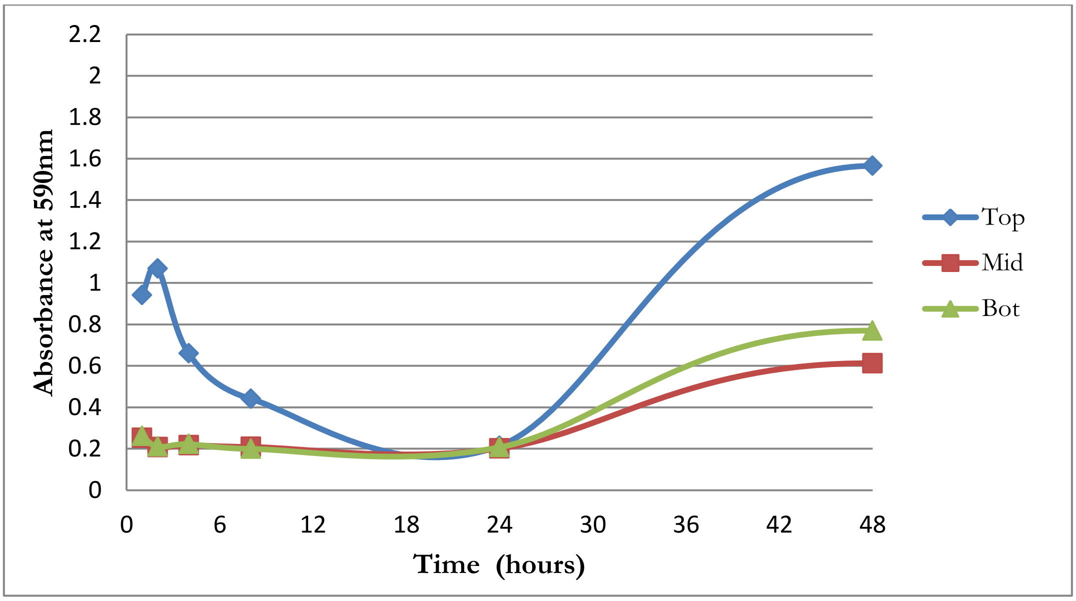


Figure 5.18 Graph of Spectroscopy readings for 1.5mL COREXIT 9500A in 500mL of Seawater at room temperature

For room temperature the highest point was also at the two hour point where the top layer shows a peak of 1.1abs and the middle and bottom layer a peak of around 0.2abs.

5.5.2 Temperature Decrease

Since the emulsion was formed between one and two days the temperature readings at the 48 hour time interval is the most significant. Another important reading is the initial data which shows a peak since this may be an indication of the strength of the emulsion when the COREXIT is just added to another fluid. For the refrigerated temperature the stability of the emulsion is very low as can be seen at the 48 hour point on the graph above for all layers which is around 0.2abs. These data points are displayed graphically in figure 5.19 below. The closer the absorbance readings the more homogenous the mixture is which means that the emulsion is not aggregating out of solution. So at the refrigerated temperature the emulsion is not as effective as seen in previous room temperature related results.

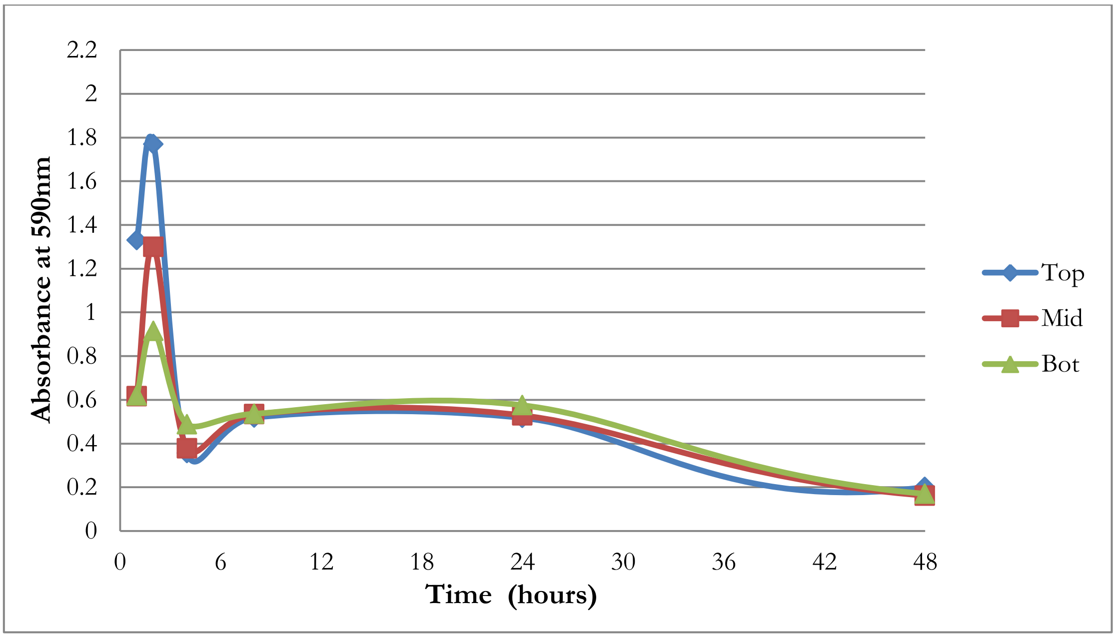


Figure 5.19 Graph of Spectroscopy readings for 1.5mL COREXIT 9500A in 500mL of Seawater at refrigerated temperature

For the refrigerated temperature the second point at around two hours shows a high increase from the standard absorbance exhibited by 1.5mL at room temperature. The top, middle and bottom layer decrease in absorbance from 1.8abs, 1.3abs and 0.9abs respectively.

5.5.3 Temperature Increase

For the increased temperature at 1.5mL of COREXIT at the 48 hour interval the top layer exhibits an extremely stable emulsion with the difference between the top and middle layers being about 1.1abs. This illustrates that the emulsion gets more stable as the temperature of the seawater increases. The trend of the bottom layer having a higher absorbance than the middle layer was not seen here but it may not be a linear trend that as the temperature increases the bottom layer absorbance increases. The increase of COREXIT in the bottom layer may be up until a certain temperature that would have to be investigated more precisely to find. Another scenario that could be plausible is that the COREXIT may increase in the bottom layers at certain temperatures and may not at others giving rise to a sinusoidal growth of COREXIT.

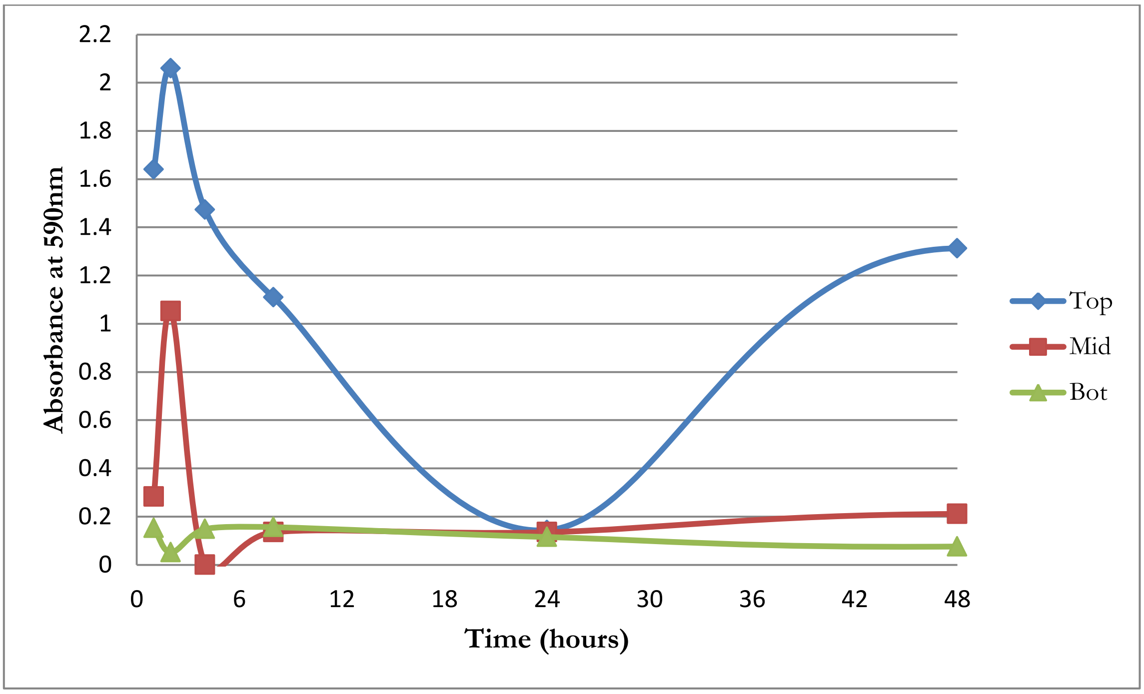


Figure 5.20 Graph of Spectroscopy readings for 1.5mL COREXIT 9500A in 500mL of Seawater at increased temperature (36 degrees Celsius)

For increased temperature the highest point was also found at the two hour point where the top layer absorbance was 2.1abs, the middle 1.1abs and the bottom layer 0.1abs

For increased temperature at 2.0mL of COREXIT at the 48 hour interval the top layer illustrates an immensely stable emulsion with the difference between the top and middle layers being about 1.2abs.

The increase in COREXIT at increased temperature increased the stability of the emulsion but this cannot be assumed to be true as only one increase was done at increased temperature by a difference of 0.5mL of COREXIT. However the results do validate that the bottom layer does not have a higher absorbance than the middle layer because the difference between the two layers is increased from 0.1abs at 1.5mL at increased temperature to 0.3abs at 2.0mL at increased temperature.

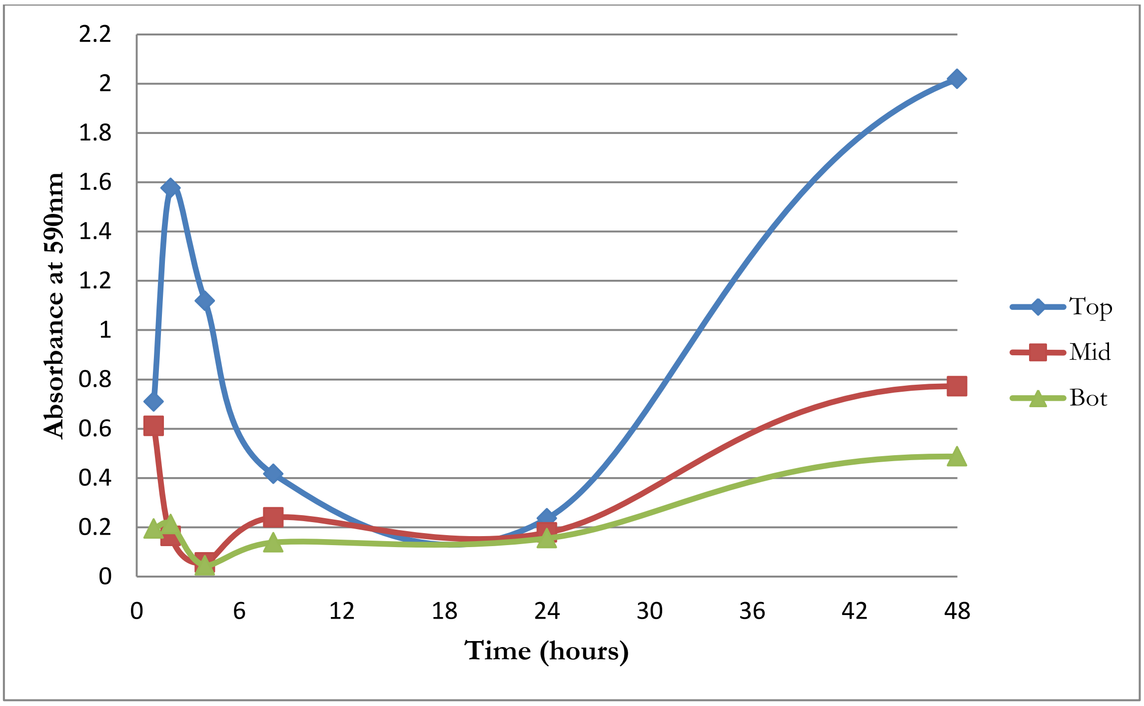


Figure 5.21 Graph of Spectroscopy readings for 2.0mL COREXIT 9500A in 500mL of Seawater at increased temperature (36 degrees Celsius)

For increased temperature at 2.0mL of COREXIT the highest point is shown by the 48 hour point but for the initial readings the two hour point was once again the highest with the top layer absorbance being 1.6abs and the middle and bottom layer being 0.2abs.

If the max absorbance does indicate the strength of emulsion when it is initially added to another fluid then the increased temperature environment may be the best atmosphere to apply the COREXIT to generate the best outcome. Since it does have the highest initial absorbance level recorded it may cause the fluid's surface tension to lessen faster causing easier dispersion.

5.5.4 Temperature & COREXIT Volume Comparison

The top layer of the seawater was where the majority of the COREXIT emulsion was formed and the figures below compare how the change in temperature affects the absorbance of the top layers. As previously stated the reading at the 48 hour mark will be discussed. The points at the 48 hour mark show that as the temperature is increased to room temperature a much higher absorbance is seen, about an 800 percent increase, and this must be where the optimum temperature for the formation of COREXIT lies. Also increasing the temperature to 10 degrees past the room temperature decreases the absorbance up to 18 percent. The 2.0mL mark cannot be compared because of the different COREXIT concentration level however it should be noted that the increase in COREXIT by 0.5mL causes a 25 percent increase in absorbance in the top layer.

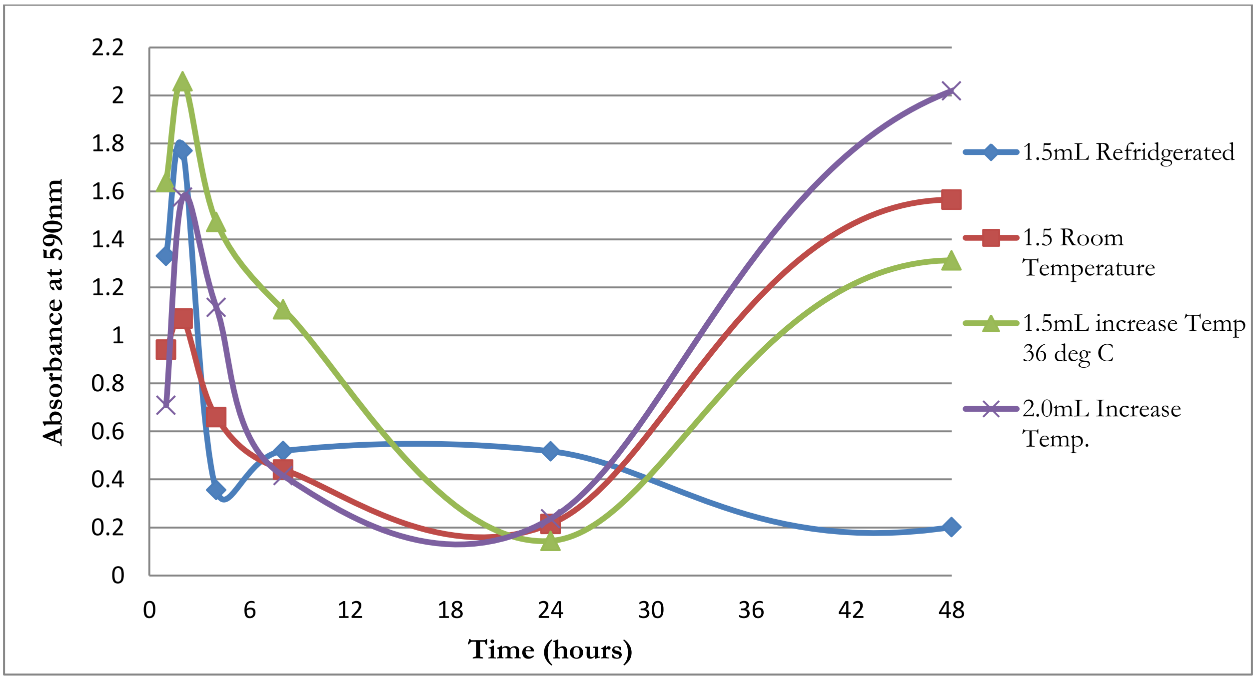


Figure 5.22 Graph of spectroscopy readings comparing the top layer of emulsions at various temperatures over time

The middle layer of the seawater did not provide any significant data but it was the layer that both the top and bottom layers where compared to. The figure 5.23 below compares how the change in temperature affects the absorbance of the middle layers.

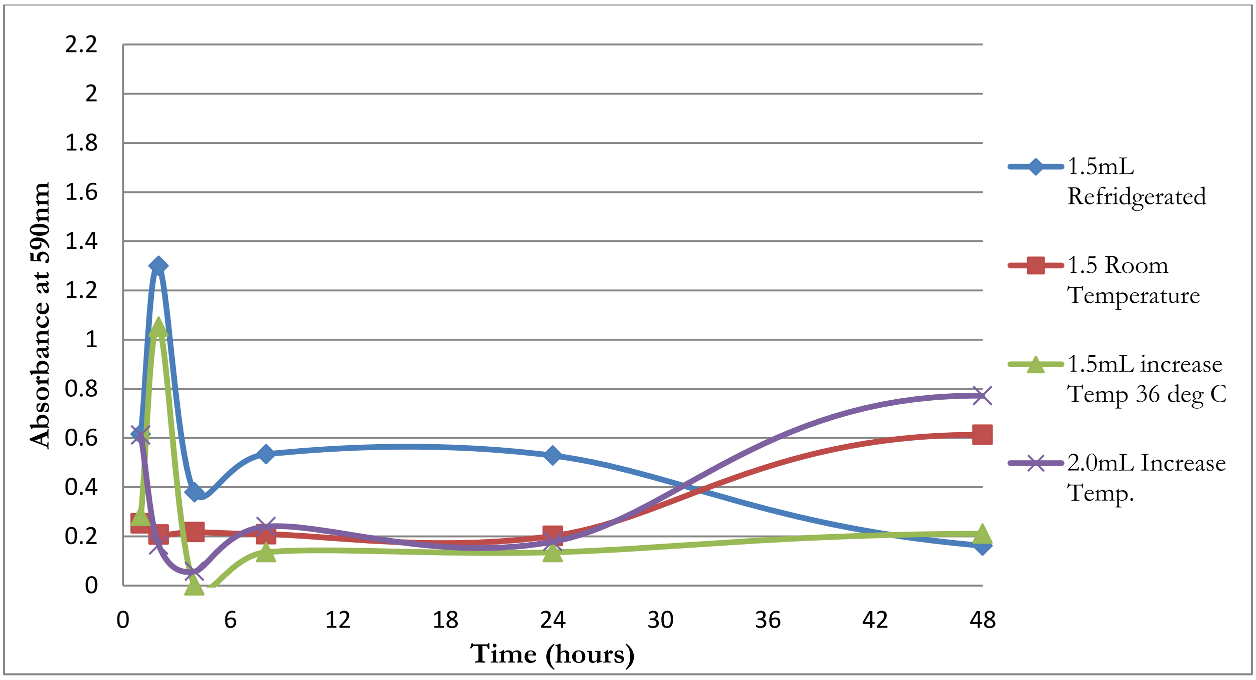


Figure 5.23 Graph of spectroscopy readings comparing the middle layer of emulsions at various temperatures over time

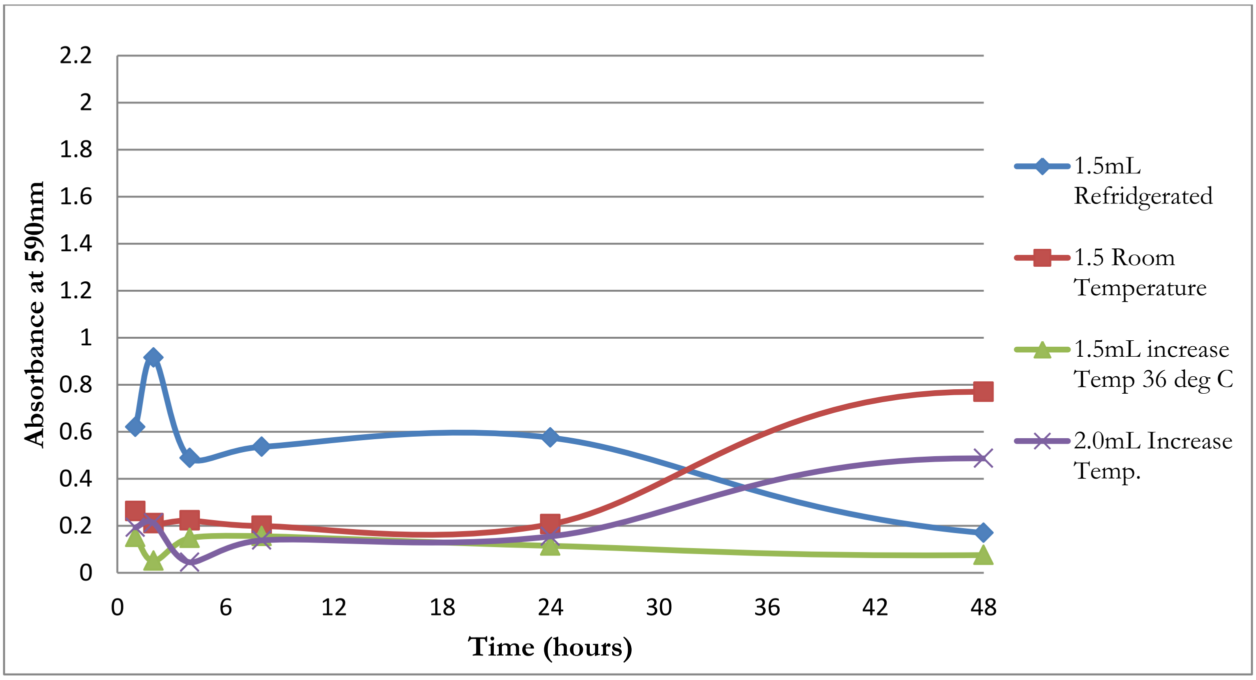


Figure 5.24 Graph of spectroscopy readings comparing the bottom layer of emulsions at various temperatures over time

The bottom layer of the seawater is important because this is the layer where the second highest COREXIT emulsion absorbances are being found in some cases. The figure 5.24 above compares how the change in temperature affects the absorbance of the bottom layers. The highest absorbance value at the 48 hour point is the room temperature so while this may provide the greatest absorbance among the three temperatures for the top reading it also provides the highest for the bottom reading. However, this does not mean that the greater the absorbance of the top layer the greater the absorbance in the bottom layer as can be seen by the increase in temperature at 2.0mL and refrigerated temperature readings that follow a different trend.

5.6 Oil Addition

5.6.1 Variation of COREXIT Volume

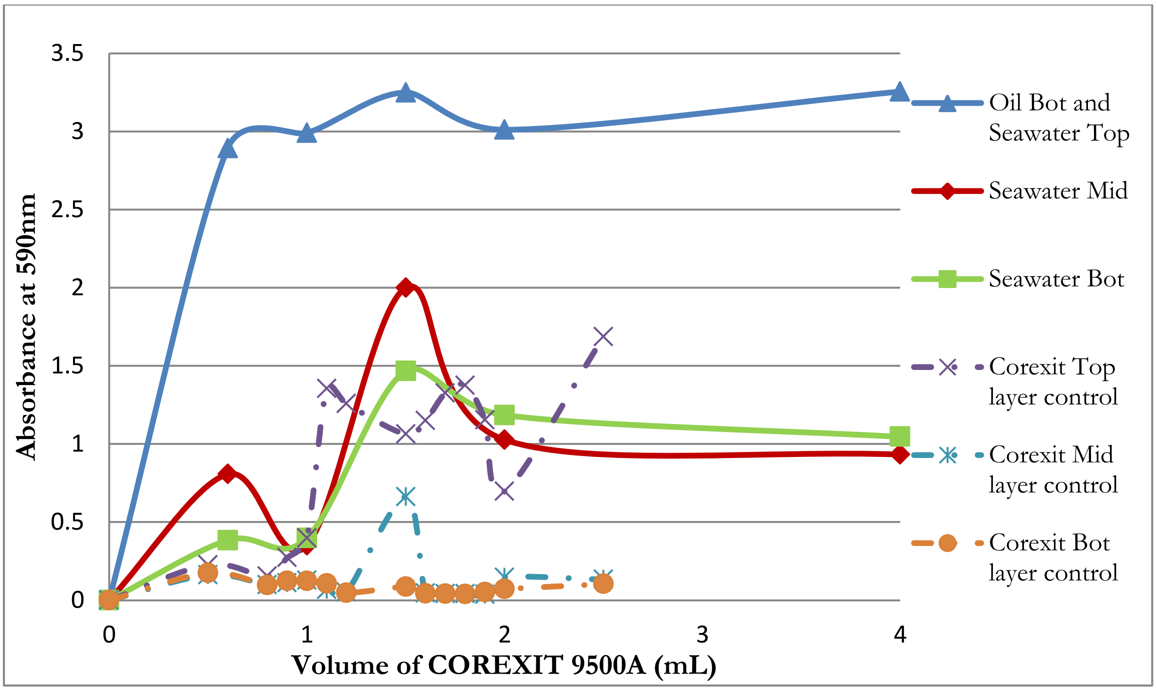


Figure 5.25: Diagram of absorbance in Seawater layer when increasing volumes of COREXIT 9500A is added to 50mL oil and 450mL Seawater

The absorbance of the seawater layers were measured in the oil, seawater and COREXIT mixture. The solid lines indicate the data that was obtained from the oil, seawater and COREXIT mixture while the broken lines indicate the seawater and COREXIT base line. The seawater and COREXIT baseline stops at 2.5mL because the extreme case of using 4.0mL of COREXIT was not needed to find theCMC which was found to be around 1.1mL of COREXIT.

The main points to be discussed will include how applicable the seawater and COREXIT values and trends are to the oil, seawater and COREXIT trends because if they are similar it will be more likely that the experiments conducted for the seawater and COREXIT will be applicable to the same system with the addition of oil. For the seawater and oil system the CMC was found at 1.1mL of COREXIT which can be seen by the steep increase of the line and the stability at the CMC is extremely high as the middle layer is clearly below the 0.25abs and the top layer was above 1.2abs. The oil and seawater system has an increase in the top layer much earlier than the base line system but the greatest stability still occurs at around 1.1mL of COREXIT as can be seen by the steep decline in the middle layer causing the greatest difference between the top and middle layers at this point.

After the 1.8mL point the increase in the amount of COREXIT causes the bottom layer to have a higher absorbance than the middle layer by about 0.2abs. Since the middle layer is less than the bottom layer the stability of the emulsion is increasing as the bottom layer start to retain more COREXIT. This observation indicates that the increase in the amount of COREXIT will cause the bottom layer to be more saturated than the middle and while the COREXIT emulsion formed at the top does increase and may cause the effectiveness of the dispersant to increase it also has detrimental effects by trapping more COREXIT beneath the middle layer into the bottom layer. This may be why the COREXIT is sinking to the bottom of the ocean because an excess amount of COREXIT may have been added to counteract the presumed oil released.

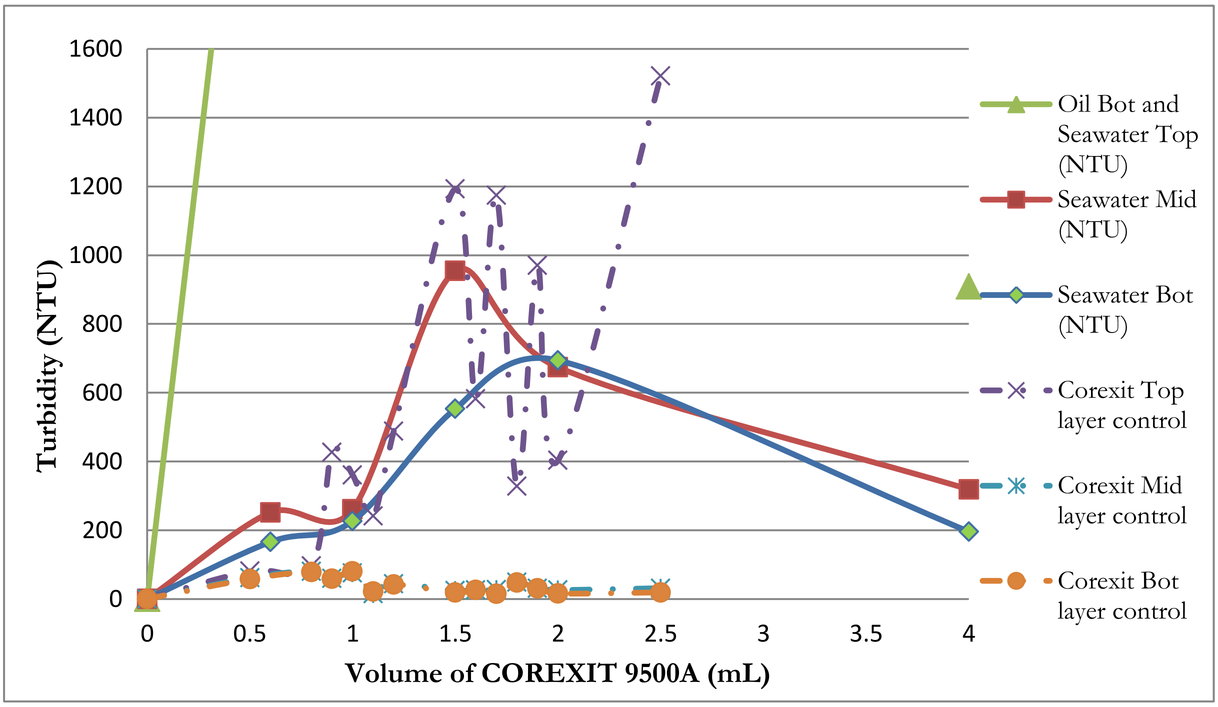


Figure 5.26 Diagram of turbidity in seawater layer when increasing volumes of COREXIT 9500A is added to 500mL oil and 450mL Seawater

Since about 30mL of sample was needed for the turbidimeter it was not deemed to be very accurate especially for the top layer because the emulsion made was sometimes not enough to fill the vial to be read properly. The same results obtained for the absorbance was obtained for the turbidity providing more evidence that excess COREXIT has negative effects on the system.

5.6.2 Variation in Oil Volume

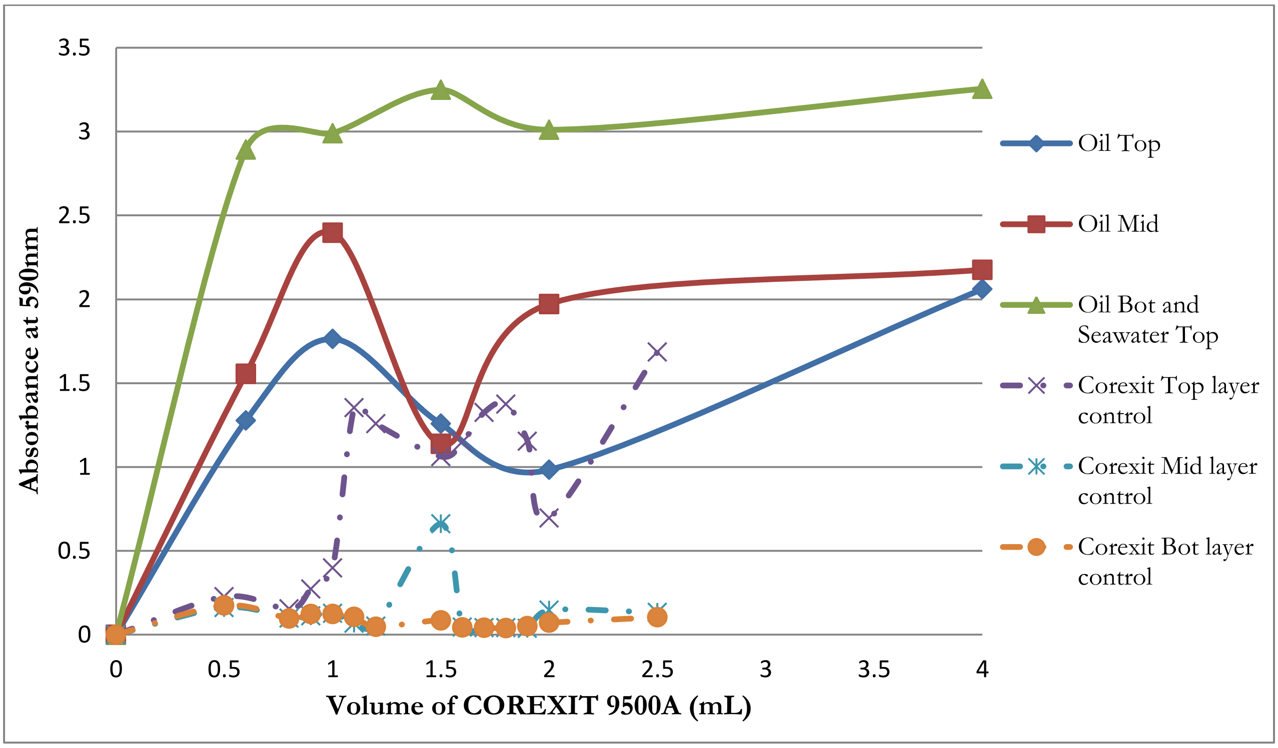


Figure 5.27 Diagram of absorbance in oil layer when increasing volumes of COREXIT 9500A is added to 50mL oil and 450mL Seawater

In the oil layer the top layer acts like the bottom layer of the seawater. Since the emulsion is formed at the intersection between the seawater and oil the regions are inverses of each other. The volume at which CMC takes place occurs between 1.0 and 1.5mL of COREXIT in the oil for the bottom layer while the middle and top of the oil layer act like the middle and bottom of the seawater layer. The top and middle layer is higher than the corresponding bottom and middle layer even though they should be equivalent and this may be due to the viscous nature of oil and the observation that once the

COREXIT interacts with oil it forms a more solid like structure that was read as a higher value by the spectrophotometer.

Since the top layer of the oil acts like the bottom layer of the seawater comparing the seawater layer to the oil layer the top layer would be expected to be higher than the middle layer which was not seen except for the point at around 1.5mL. The base case for the seawater and COREXIT system is not similar to the oil, seawater and COREXIT system when observing the oil layer. This was expected as the properties of seawater and oil are extremely different. No turbidity graph was illustrated for the oil layer because the values were too high and good readings were not able to be taken.

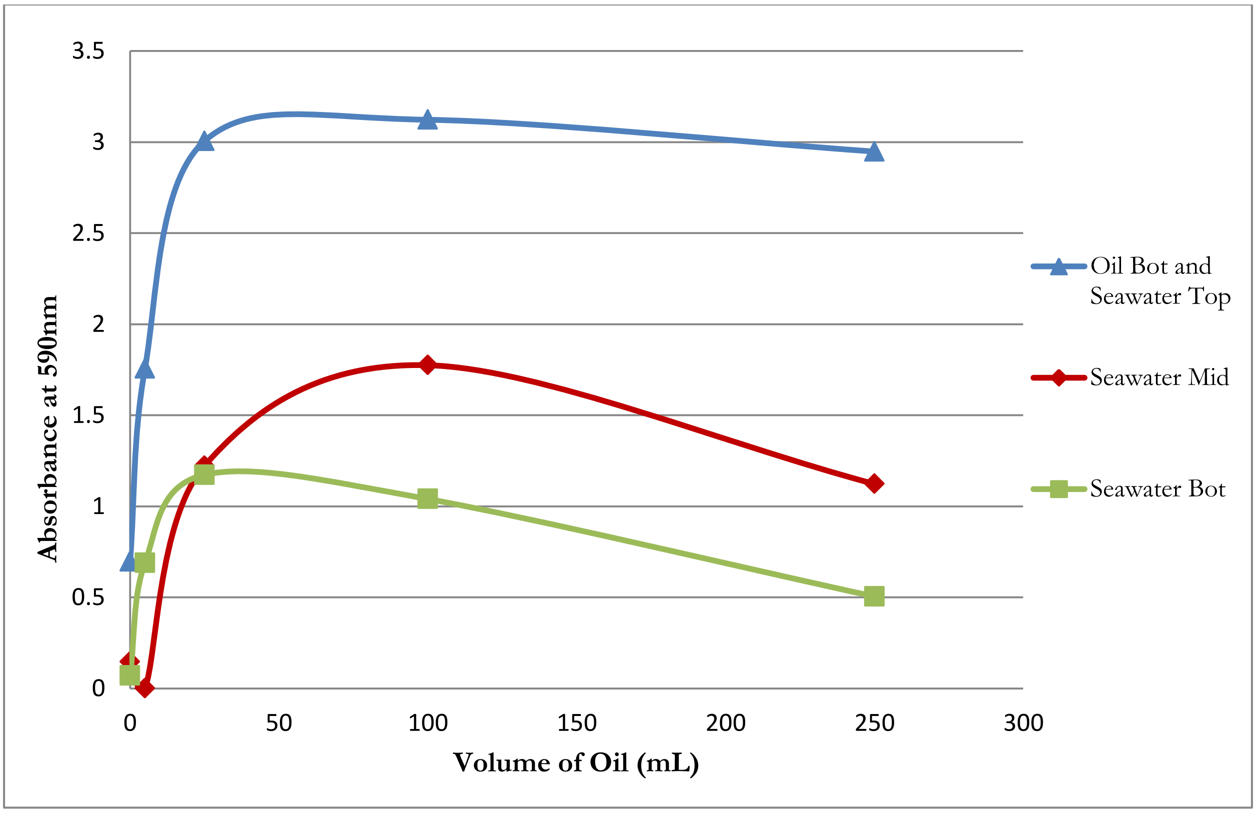


Figure 5.28 Diagram of absorbance in seawater layer when increasing volumes of oil is added to 2.0mL COREXIT 9500A and decreasing volumes of Seawater

This graph simply illustrates how the increase in oil affects the seawater readings. As the volume of oil is increased past a value the absorbance starts to gradually decrease, in the case of 2.0mL of COREXIT the value as illustrated on the graph lies between 25-60mL of oil. The absorbance decreases for the readings because even though the volume of COREXIT stays the same the volume of the oil which is denser than the emulsion increases and this causes the volume of the COREXIT layer within the oil to be stretched throughout a larger volume of oil decreasing the amount at the interface which decreases the absorbance that can read in the seawater layer.

Chapter 6: Conclusions

Micellization occurs at the CMC at the same concentration of COREXIT 9500A when salt water is more than 50 percent by volume. As salinity increases the extent of micelle formation increases which is supported by the findings in section 5.2 above where absorbance increases as salt water concentration increases. This determination proves that the emulsion formed at higher salinity is more stable than that where the solution is diluted by deionized water.

As the concentration of the COREXIT is increased the ability for the COREXIT to form a stable emulsion also increases. As the volume of COREXIT increases the absorbance of COREXIT in the bottom layer also increases. This means that more of the COREXIT emulsion is being trapped in the bottom layer which may be one of the main reasons why COREXIT is descending in the Gulf of Mexico instead of dispersing the oil and performing ideally.

Sand added before and after the COREXIT was added simulates sand above and below the emulsion layer and showed that for the emulsion at the top layer adding the sand after the COREXIT yielded higher absorbance. For the bottom layer higher absorbance were recorded for adding the sand before the COREXIT.

Results from the humic acid experiments suggest that organic matter limits the formation of an emulsion, particularly as the concentration of these particulates increases. The addition of humic material produced results of a more uniform emulsion throughout the beaker which leads to the conclusion that the extent of micelle formation is limited.

The addition of air bubbles in the samples of deionized and sea water with COREXIT proved insignificant, producing similar reading to the control. Alternatively, the bubbles produced more of an effect on a salt water solution containing humic acid and COREXIT. The air within the humic acid solution appears to further inhibit the separation of the emulsion phase resulting in a uniform mixture and minimal, if any, micelle formation.

The increase in temperature increases the stability of the emulsion due to the increasing difference between the middle and top layers. This shows that increasing the temperature causes the COREXIT to perform more effectively. Therefore depending on what the temperature was in the Gulf of Mexico when the COREXIT was added determines how well it acted as a surfactant. Since the application of COREXIT was done at sea level and sub-sea level, varying degree of effectiveness can be expected especially since the deeper the COREXIT was applied the colder the mixing conditions.

At lower temperatures micellization does not seem to occur and this could have increased the COREXIT concentration being found throughout the depths of the sea. If the conditions were cold upon application of COREXIT the emulsion would not form and the COREXIT would be dispersed homogenously as seen at the refrigerated temperature results. Room Temperature also produced the most significant increase in top layer absorbance and therefore could potentially be the optimum temperature at which COREXIT was meant to be applied.

The addition of oil to the seawater and COREXIT system produces similar trends for the CMC as the seawater and COREXIT alone in the seawater layer. In the oil layer of the oil, seawater and COREXIT mixture the inverse trend is observed for the CMC. The bottom layer of the seawater in the oil, seawater and COREXIT mixture is greater than the middle layer at COREXIT values past 1.8mL which means that adding excessive volumes of COREXIT actually causes more COREXIT to be trapped within the bottom layer of the seawater. This means that applying a large quantity of COREXIT to disperse an unknown large quantity of oil may have led to the sinking of COREXIT to the bottom of the Gulf of Mexico.

Overall many factors affected how the COREXIT emulsion was formed and the overall stability of the COREXIT emulsion is directly dependent on some of the factors tested in this experiment. The factors that strongly affect the formation of the COREXIT emulsion include if oil or another viscous fluid is added and the volume of that viscous fluid added, temperature, salinity, humic acid, the addition of smaller sand particles. Other minor factors include the amount of air bubbles that comes in contact with the COREXIT emulsion layer and the addition of large sand particles.

Chapter 7: Recommendations

Our first recommendation relates to the use of COREXIT 9500A in the Gulf of Mexico in regards to proper use of the material, which includes methods to introduce the COREXIT to an area contaminated by an oil spill as well as validating that the dispersant is the proper material for optimal results. Throughout our research it has become apparent that the underwater injection of the COREXIT at the base of the Deepwater Horizon oil rig resulted in unexpected emulsion behavior due to several factors including temperature and dissolved particles. Surface application truly appears to be the best option as the conditions at this point are optimal for droplet breakup.

Further experimentation is suggested to explore different properties of the COREXIT with similar permutations as to the ones we chose for the project. Specifically, more surface chemistry of the emulsion formed should be investigated in relation to electrical potential and possible functional groups which are expelled with chemicals during an oil spill. More advanced technology would be necessary for these experiments but would provide valuable insight on the microscopic workings of the emulsion which is formed by the COREXIT. On another note, other dispersants could also be investigated and compared to COREXIT in regards to how they may behave similarly or contrary when our selected variables are present in the system. This could provide interesting findings on whether one dispersant is more appropriate than another and why.

In regards to our specific experiments, more investigation into the kinetics of the formation and decomposition of the microemusion resulting from the addition of COREXIT would be valuable to the study of the stability of the sample. Similarly, replications should be performed to validate the results we have explained above, although we were able to replicate some initial experiments, time did not permit replication of each.

Finally, experimentation on a more appropriate model of the Gulf conditions should be pursued. This would consist of working with actual samples of sea water from the Gulf of Mexico, and with the proper technology, temperature could be held constant to more appropriately simulate the conditions of the water affected by the Deepwater Horizon oil spill. Another potentially interesting group of experiments could be performed to simulate the surface of the ocean waters where there is constant, turbid movement and other factors come into play such as weather and mechanical disturbances. In addition, a larger scale model would be more helpful in simulating the actual occurrences within an ocean system, and also provide a larger testing sample which could inevitably simplify removing the samples from the various locations within the solution.

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Appendix A: Experimental Images

A.1 Salinity

<u>100% Pure water</u>

Figure 1 Side view of 500mL of pure water mixed with 1.5mL of COREXIT 9500A

<u>50% Seawater 50% Pure water mixture</u>

Figure: 2 Diagram of 50% Seawater and 50% Pure water with 0.9mL COREXIT 9500A

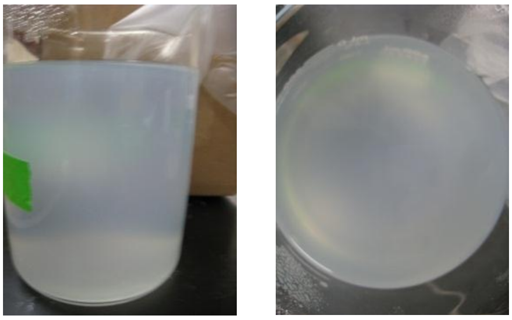

Figure: 3 Diagram of 50% Seawater and 50% Pure water with 1.1mL COREXIT 9500A

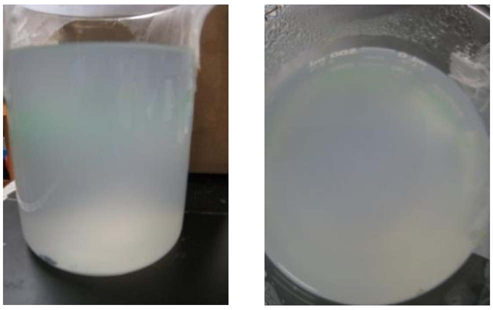

Figure: 4 Diagram of 50% Seawater and 50% Pure water with 1.3mL COREXIT 9500A

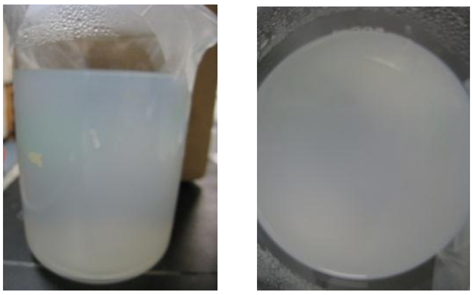

Figure: 5 Diagram of 50% Seawater and 50% Pure water with 1.5mL COREXIT 9500A

75% Seawater 25% Pure water mixture

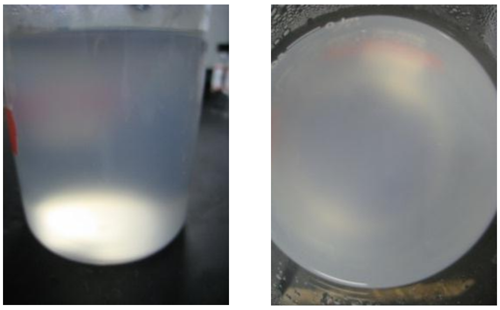

Figure: 6 Diagram of 50% Seawater and 50% Pure water with 0.9mL COREXIT 9500A

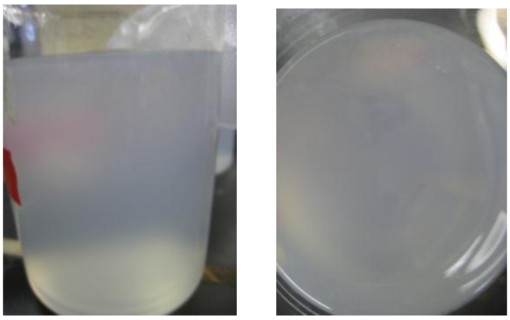

Figure: 7 Diagram of 50% Seawater and 50% Pure water with 1.1mL COREXIT 9500A

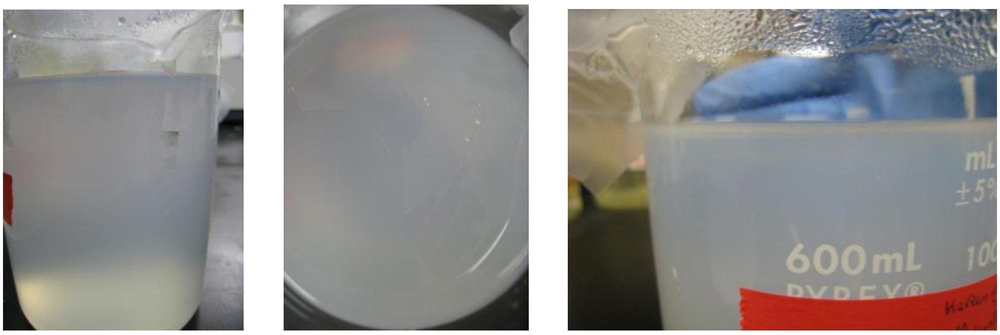

Figure: 8 Diagram of 50% Seawater and 50% Pure water with 1.3mL COREXIT 9500A

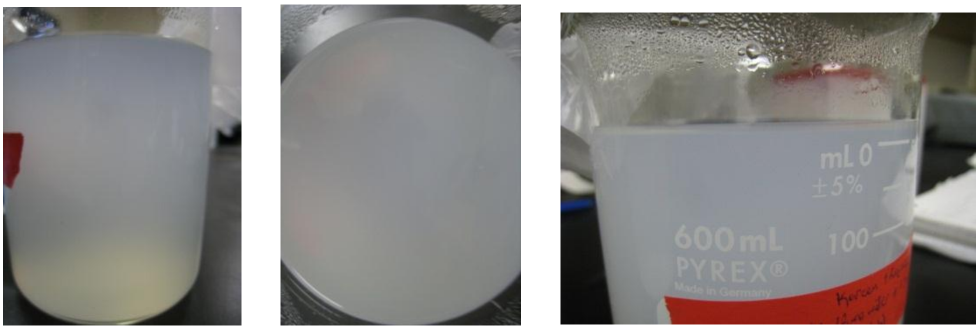

Figure: 9 Diagram of 50% Seawater and 50% Pure water with 1.5mL COREXIT 9500A

<u>100% Seawater</u>

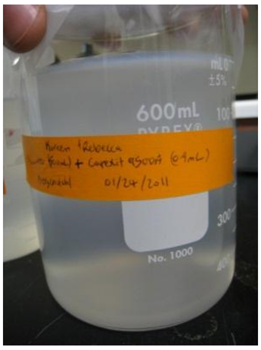

Figure: 10 Diagram of 100% Seawater with 0.9mL COREXIT 9500A

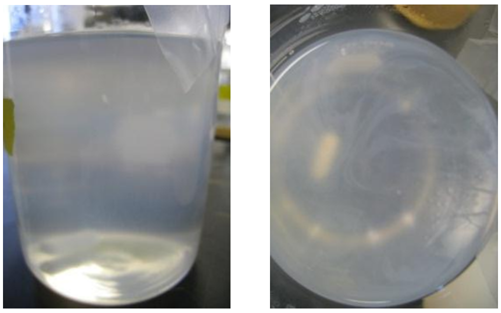

Figure: 11 Diagram of 100% Seawater with 1.1mL COREXIT 9500A

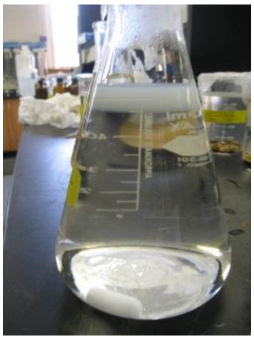

Figure: 12 Diagram of 100% Seawater with 1.3mL COREXIT 9500A

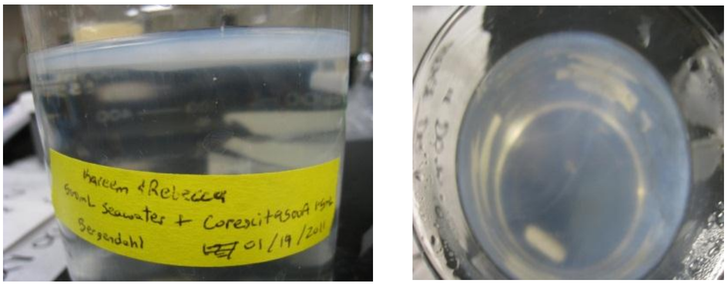

Figure: 13 Diagram of 100% Seawater with 1.5mL COREXIT 9500A

A.2.1 Sand Addition

Below is 1.5mL COREXIT

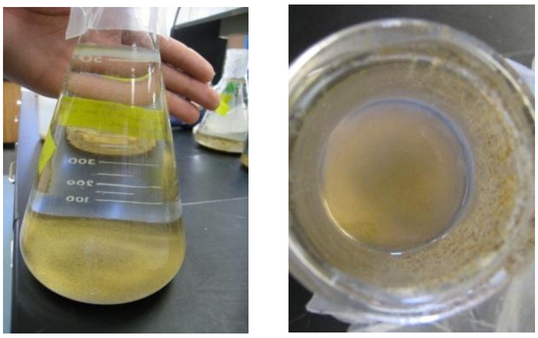

Figure: 14 Emulsion first 500mL seawater + 1.5mL of COREXIT + 0.0029 inch sand

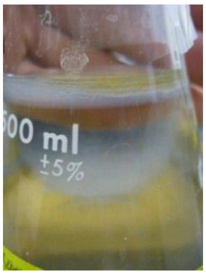

Figure: 15 Emulsion formed first with 500mL seawater and 1.5mL of COREXIT followed by the addition of 0.0029 inch sand

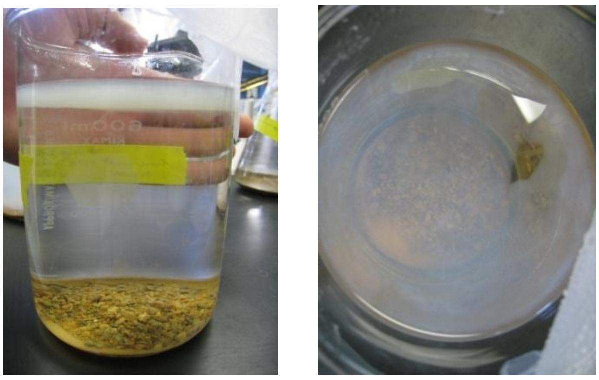

Figure: 16 Emulsion formed first with 500mL seawater and 1.5mL of COREXIT followed by the addition of 0.0394

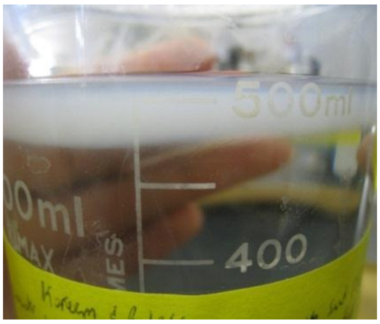

Figure: 17 Emulsion formed first with 500mL seawater and 1.5mL of COREXIT followed by the addition of 0.0394 inch sand

<u>Below is 2.0 mL of COREXIT</u>

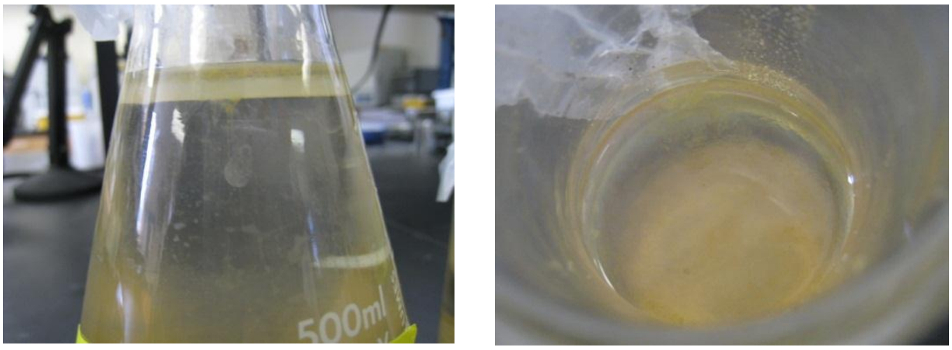

Figure: 18 Emulsion formed first with 500mL seawater and 2.0mL of COREXIT followed by the addition of 0.0029 inch sand

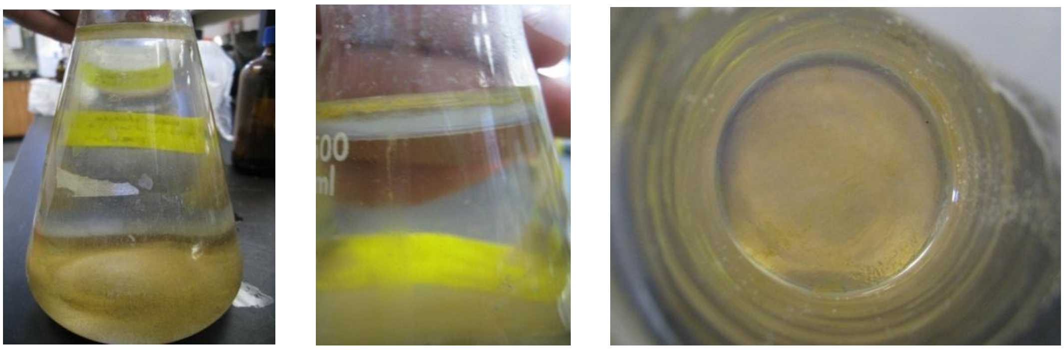

Figure: 19 Emulsion formed first with 500mL seawater and 2.0mL of COREXIT followed by the addition of 0.0029 inch sand

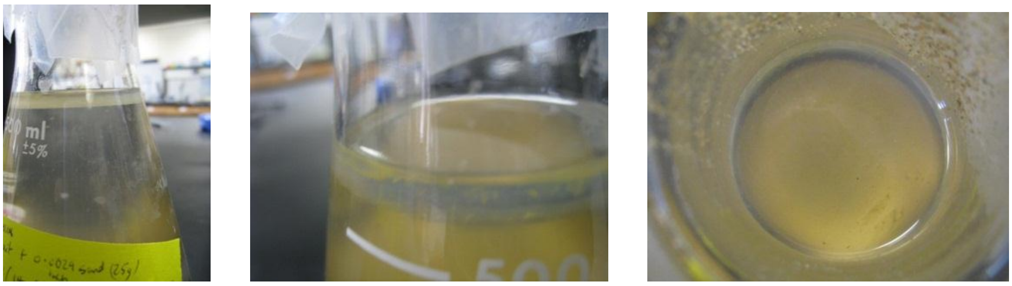

Figure: 20 Emulsion formed first with 500mL seawater and 2.0mL of COREXIT followed by the addition of 0.0029 inch sand

Figure: 21 Emulsion formed first with 500mL seawater and 2.0mL of COREXIT followed by the addition of 0.0117 inch sand

Figure: 22 Emulsion formed first with 500mL seawater and 2.0mL of COREXIT followed by the addition of 0.0117 inch sand

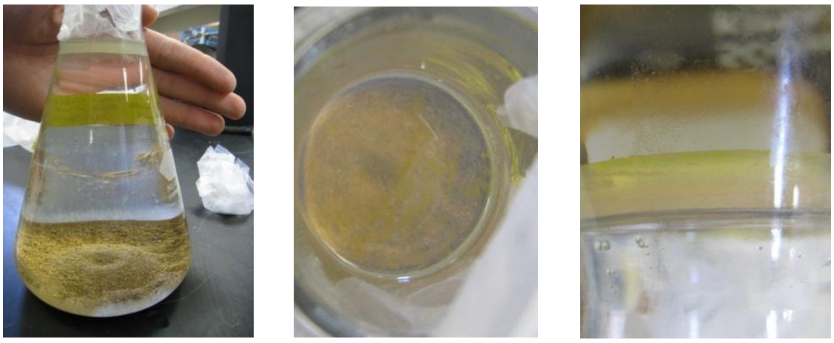

Figure: 23 Emulsion formed first with 500mL seawater and 2.0mL of COREXIT followed by the addition of 0.0117 inch sand

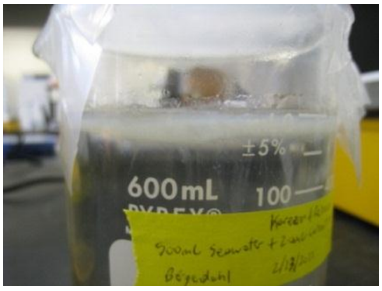

Figure: 24 Emulsion formed first with 500mL seawater and 2.0mL of COREXIT followed by the addition of 0.0394 inch sand

Below is 2.5mL

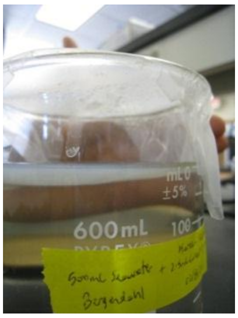

Figure: 25 Emulsion formed first with 500mL seawater and 2.5mL of COREXIT followed by the addition of 0.0029 inch sand

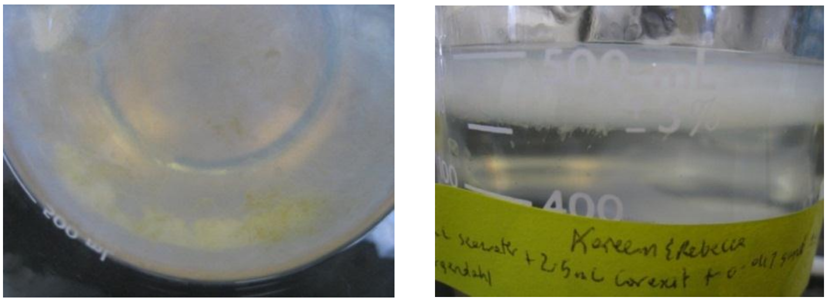

Figure: 26 Emulsion formed first with 500mL seawater and 2.5mL of COREXIT followed by the addition of 0.0117 inch sand

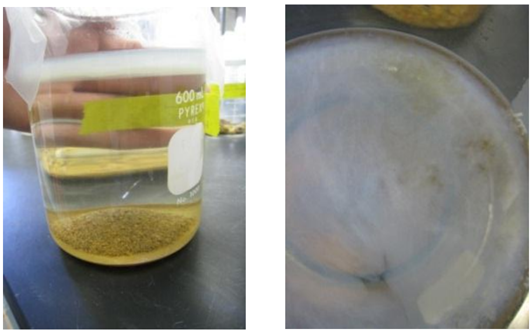

Figure: 27 Emulsion formed first with 500mL seawater and 2.5mL of COREXIT followed by the addition of 0.0394 inch sand

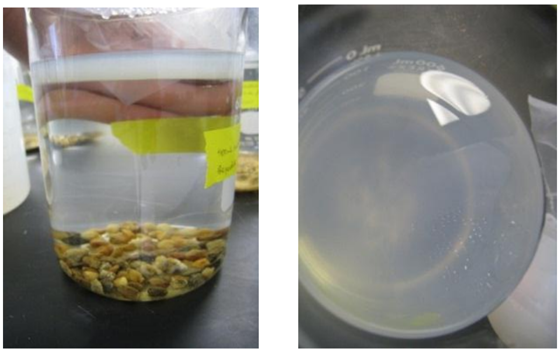

Figure: 28 Emulsion formed first with 500mL seawater and 2.5mL of COREXIT followed by the addition of 0.187 inch sand

<u>Sand Added First at 2.0mL COREXIT</u>

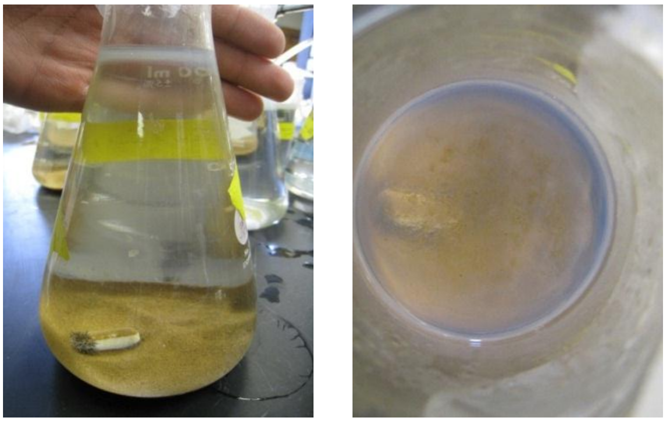

Figure: 29 Sand first with 500mL seawater and 2.0mL of COREXIT followed by the addition of 0.0029 inch Sand

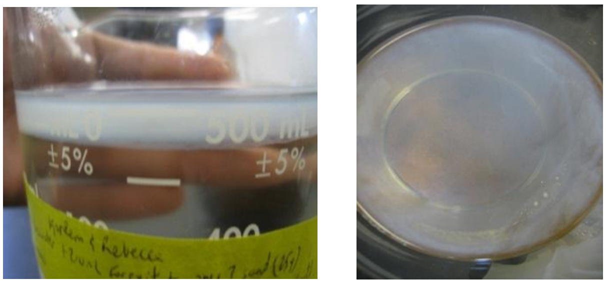

Figure: 30 Sand added first with 500mL seawater and 2.0mL of COREXIT followed by the addition of 0.0117 inch sand

Figure: 31 Sand first with 500mL seawater and 2.0mL of COREXIT followed by the addition of 0.0394 inch sand

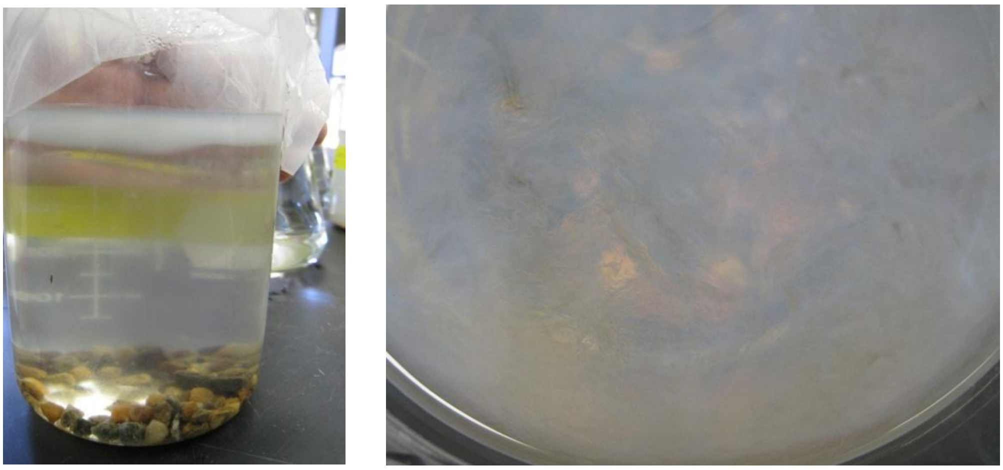

Figure: 32 Sand first with 500mL seawater and 2.0mL of COREXIT followed by the addition of 0.187 inch sand

A.3 Temperature Variation

Refrigerated Temperature

After 4 hours

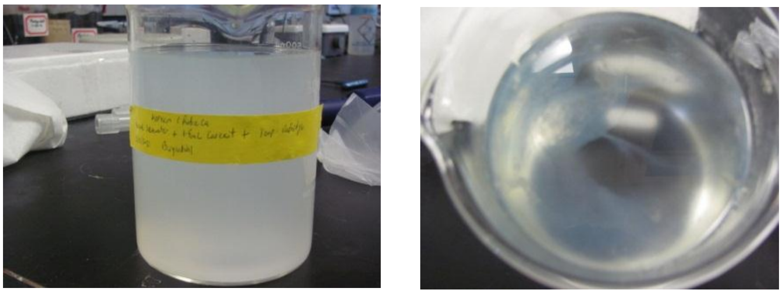

Figure: 33 Diagram of 500mL Seawater mixed with 1.5mL COREXIT 9500A at refrigerated temperature

After 8 hours

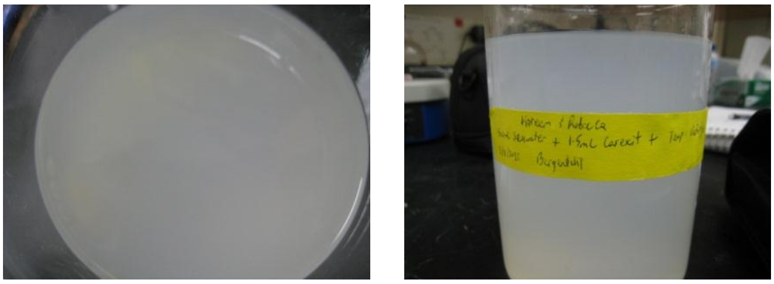

Figure: 34 Diagram of 500mL Seawater mixed with 1.5mL COREXIT 9500A at refrigerated temperature

After 24 hours

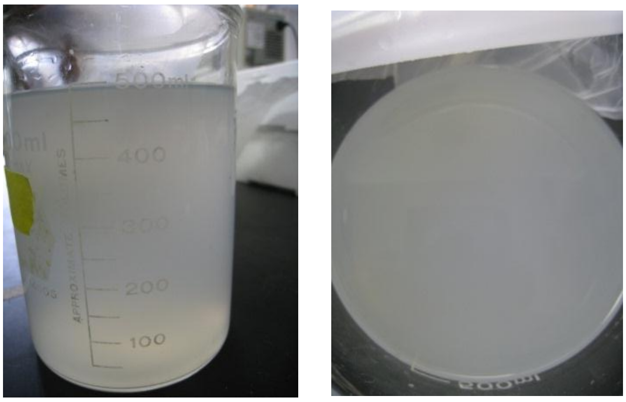

Figure: 35 Diagram of 500mL Seawater mixed with 1.5mL COREXIT 9500A at refrigerated temperature

After 2 days

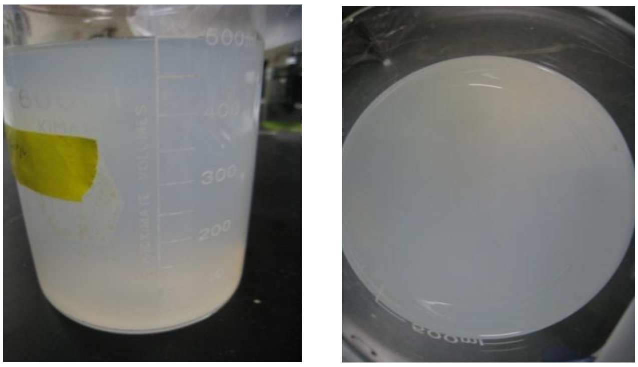

Figure: 36 Diagram of 500mL Seawater mixed with 1.5mL COREXIT 9500A at refrigerated temperature

After taken out of different temperature environment

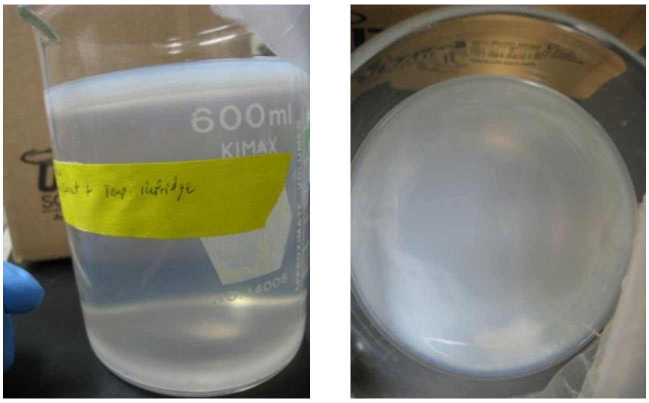

Figure: 37 Diagram of 500mL Seawater mixed with 1.5mL COREXIT 9500A at refrigerated temperature

Room Temperature

After 4 hours

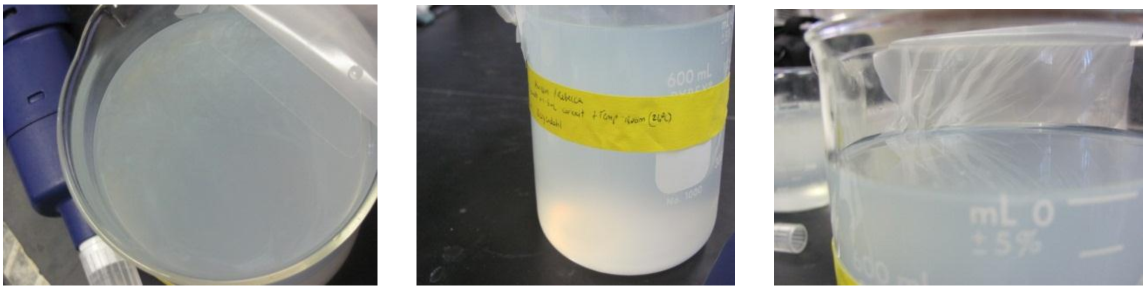

Figure: 38 Diagram of 500mL Seawater mixed with 1.5mL COREXIT 9500A at room temperature

After 8 hours

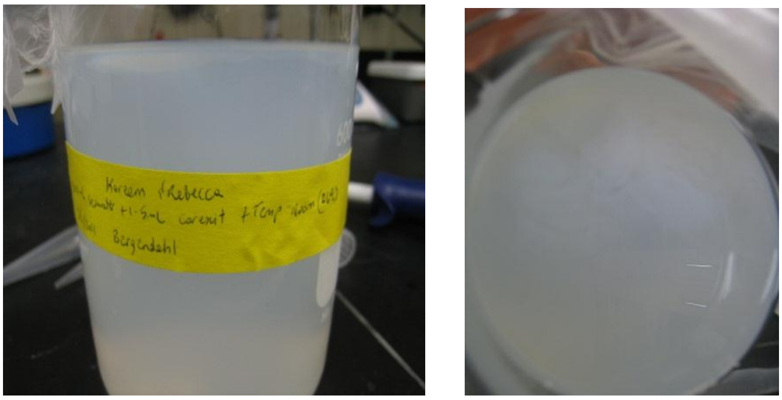

Figure: 39 Diagram of 500mL Seawater mixed with 1.5mL COREXIT 9500A at room temperature

After 24 hours

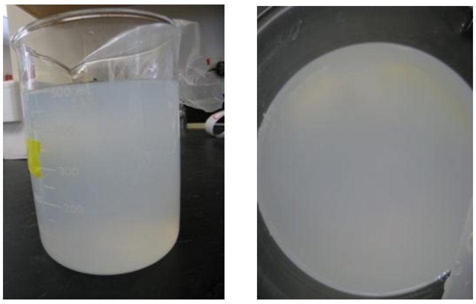

Figure: 40 Diagram of 500mL Seawater mixed with 1.5mL COREXIT 9500A at room temperature

After 2 days

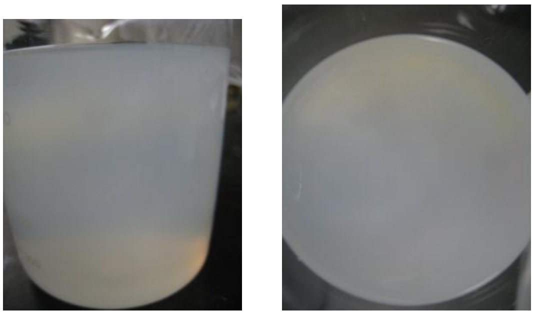

Figure: 41 Diagram of 500mL Seawater mixed with 1.5mL COREXIT 9500A at room temperature

After removed from different temperature environment

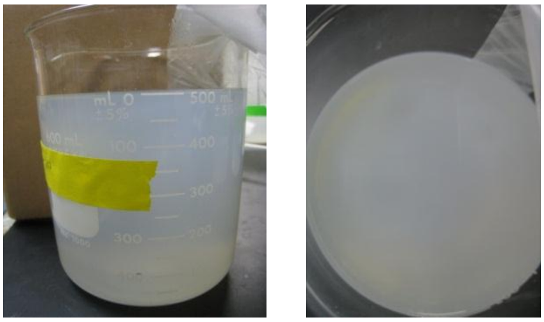

Figure: 42 Diagram of 500mL Seawater mixed with 1.5mL COREXIT 9500A at room temperature

Increased Temperature

After 4 hours

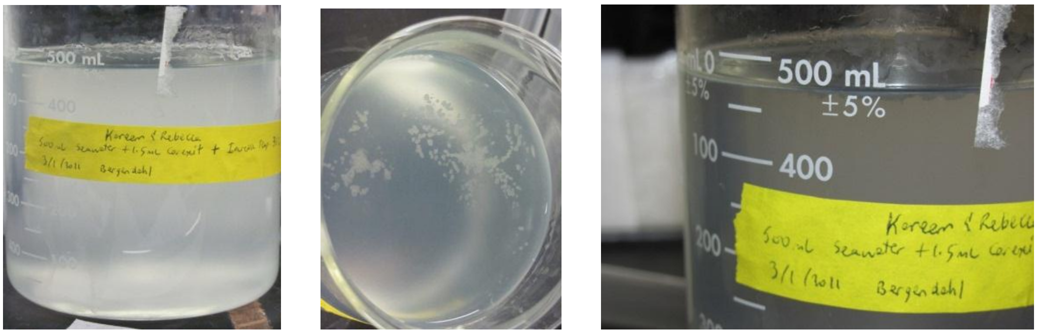

Figure: 43 Diagram of 500mL Seawater mixed with 1.5mL COREXIT 9500A at increased temperature (36 degrees Celsius)

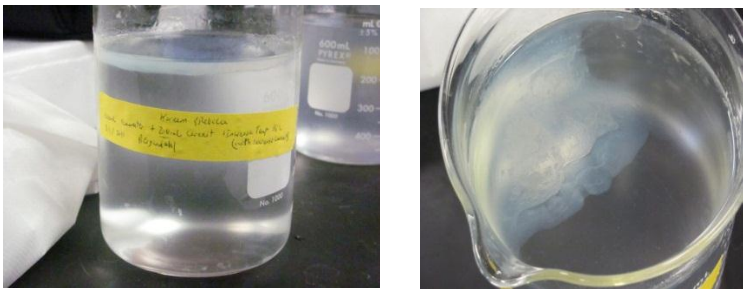

Figure: 44 Diagram of 500mL Seawater mixed with 2.0mL COREXIT 9500A at increased temperature (36 degrees Celsius)

After 8 hours

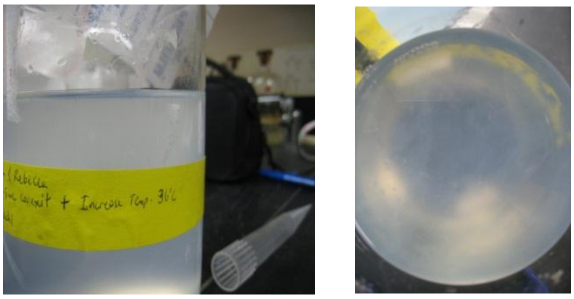

Figure: 45 Diagram of 500mL Seawater mixed with 1.5mL COREXIT 9500A at increased temperature (36 degrees Celsius)

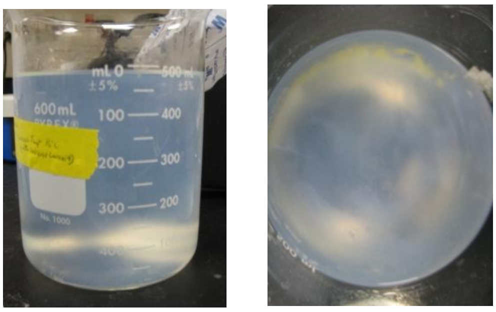

Figure: 46 Diagram of 500mL Seawater mixed with 2.0mL COREXIT 9500A at increased temperature (36 degrees Celsius)

After 24 hours

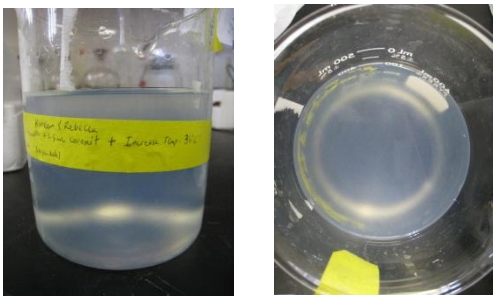

Figure: 47 Diagram of 500mL Seawater mixed with 1.5mL COREXIT 9500A at refrigerated temperature (36 degrees Celsius)

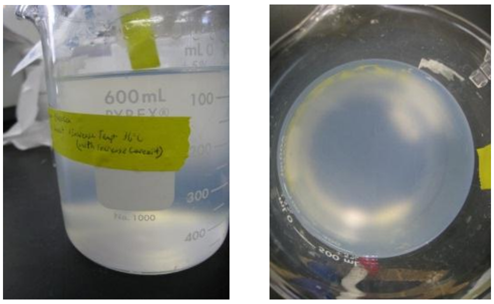

Figure: 48 Diagram of 500mL Seawater mixed with 2.0mL COREXIT 9500A at increased temperature (36 degrees Celsius)

After 2 days

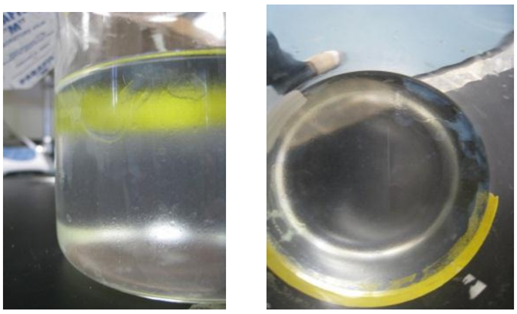

Figure: 49 Diagram of 500mL Seawater mixed with 1.5mL COREXIT 9500A at increased temperature (36 degrees Celsius)

Figure: 50 Diagram of 500mL Seawater mixed with 2.0mL COREXIT 9500A at increased temperature (36 degrees Celsius)

After taken out of different temperature environment

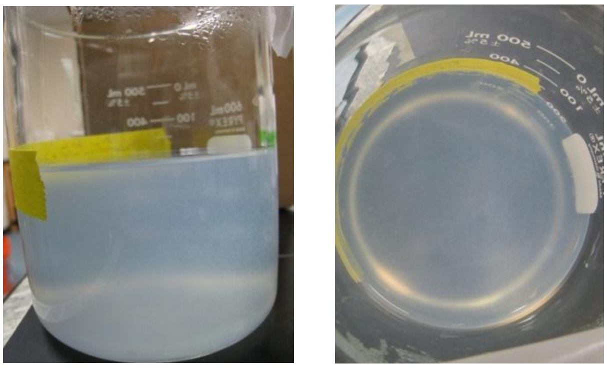

Figure: 51 Diagram of 500mL Seawater mixed with 1.5mL COREXIT 9500A at increased temperature (36 degrees Celsius)

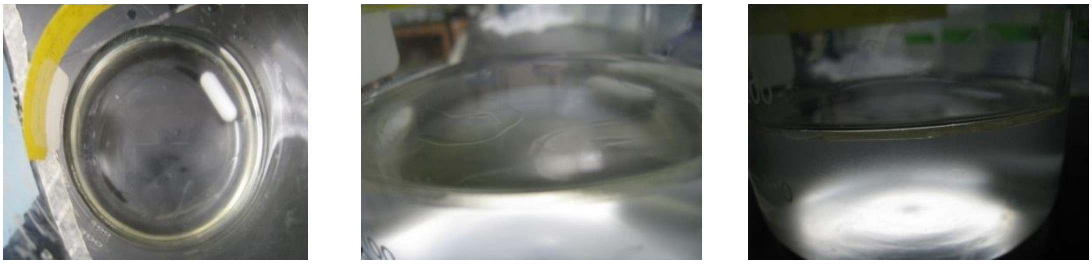

Figure: 52 Diagram of 500mL Seawater mixed with 2.0mL COREXIT 9500A at increased temperature (36 degrees Celsius)

A.4 Oil Addition

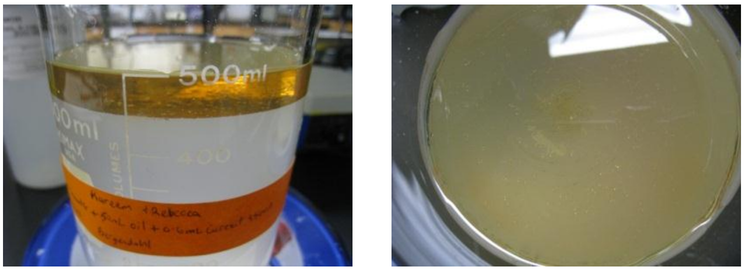

Figure: 53 Diagram of 500mL Seawater mixed with 50mL oil and 0.6mL COREXIT 9500A

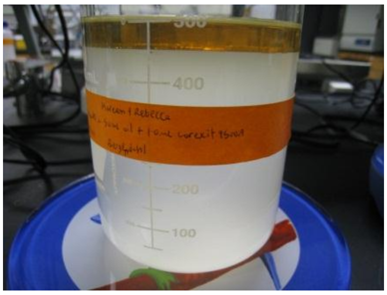

Figure: 54 Diagram of 500mL Seawater mixed with 50mL oil and 1.0mL COREXIT 9500A

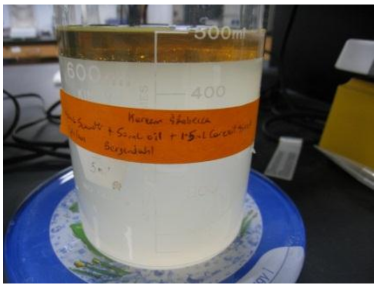

Figure: 55 Diagram of 500mL Seawater mixed with 50mL oil and 1.5mL COREXIT 9500A

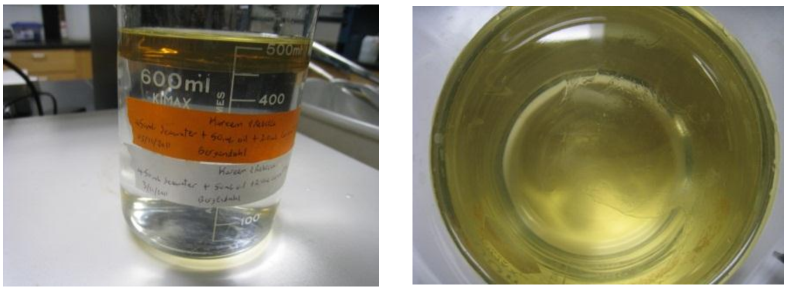

Figure: 56 Diagram of 500mL Seawater mixed with 50mL oil and 2.0mL COREXIT 9500A

After Mixing

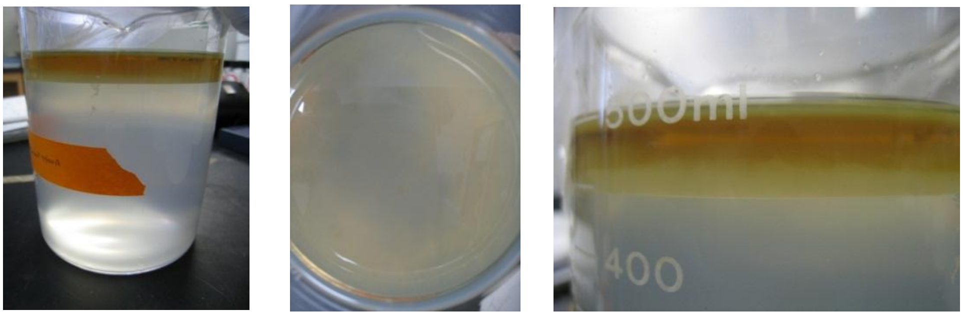

Figure: 57 Diagram of 500mL Seawater mixed with 50mL oil and 0.6mL COREXIT 9500A

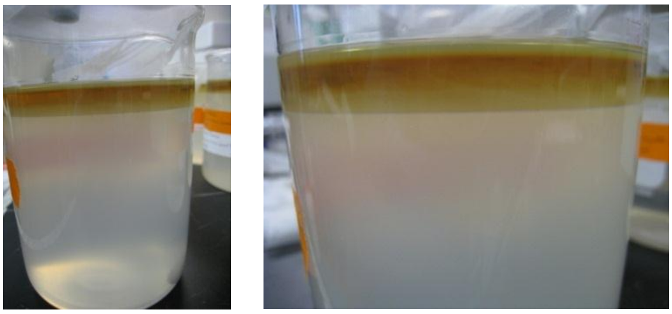

Figure: 58 Diagram of 500mL Seawater mixed with 50mL oil and 1.0mL COREXIT 9500A

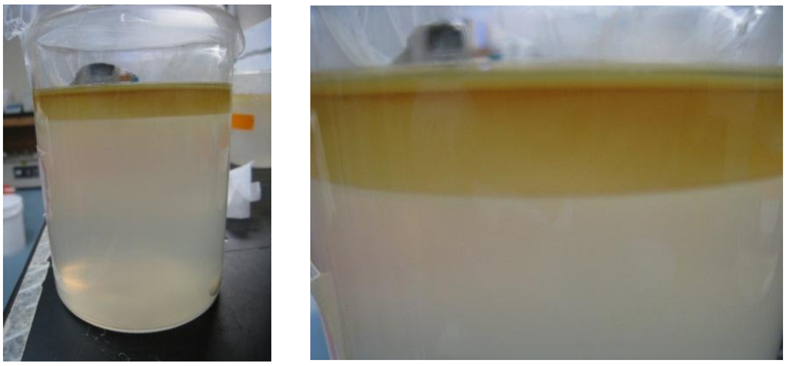

Figure: 59 Diagram of 500mL Seawater mixed with 50mL oil and 1.5mL COREXIT 9500A

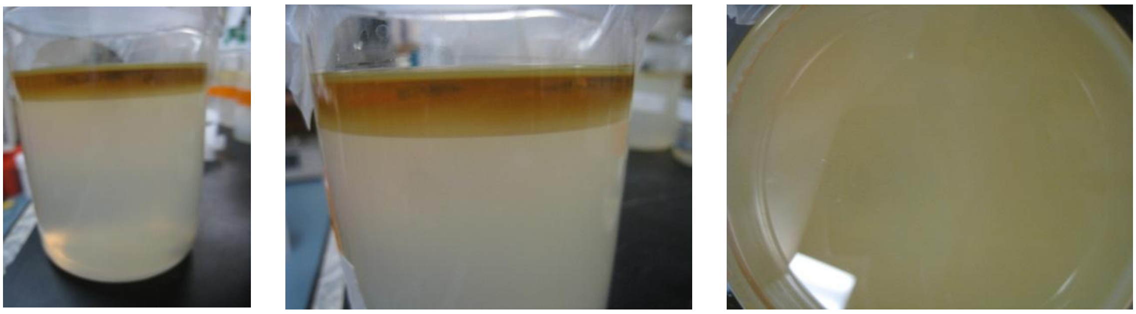

Figure: 60 Diagram of 500mL Seawater mixed with 50mL oil and 2.0mL COREXIT 9500A

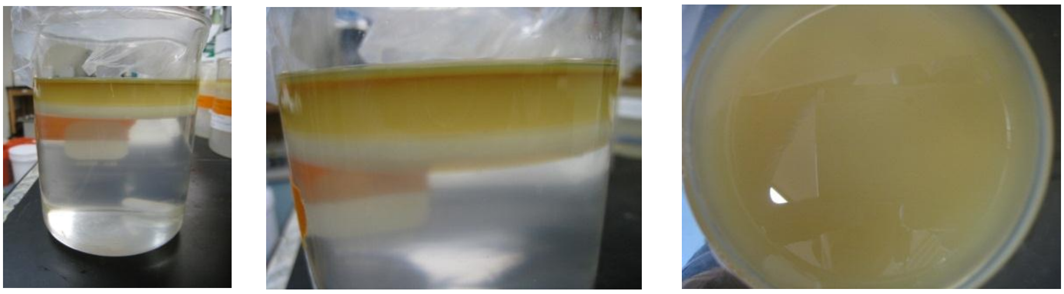

Figure: 61 Diagram of 500mL Seawater mixed with 50mL oil and 4.0mL COREXIT 9500A

Change in Oil Readings

Initial

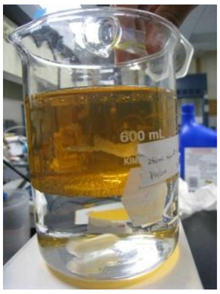

Figure: 62 Diagram of 500mL Seawater mixed with 250mL oil and 2.0mL COREXIT 9500A

After Mixing

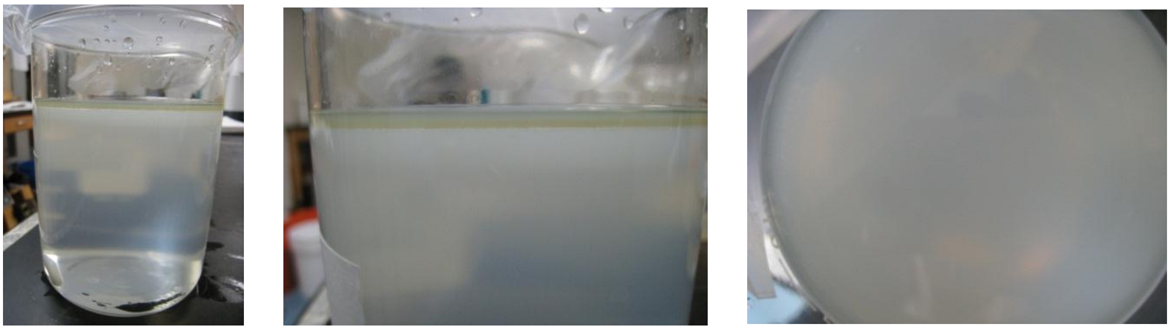

Figure: 63 Diagram of 500mL Seawater mixed with 5mL oil and 2.0mL COREXIT 9500A

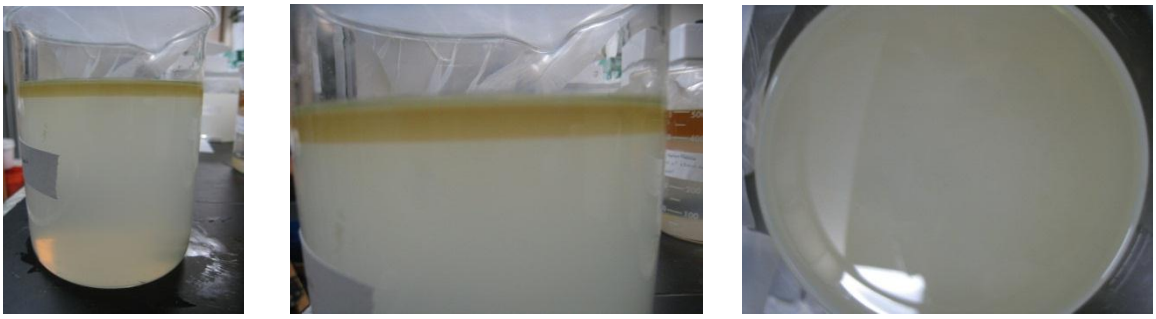

Figure: 64 Diagram of 500mL Seawater mixed with 25mL oil and 2.0mL COREXIT 9500A

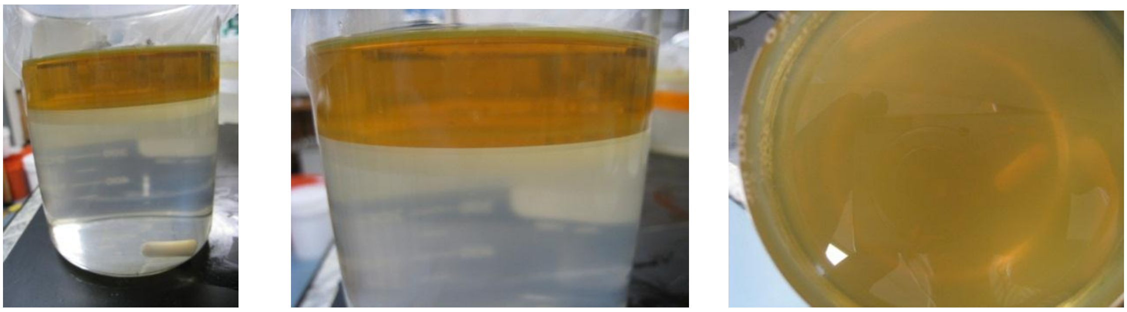

Figure: 65 Diagram of 500mL Seawater mixed with 100mL oil and 2.0mL COREXIT 9500A

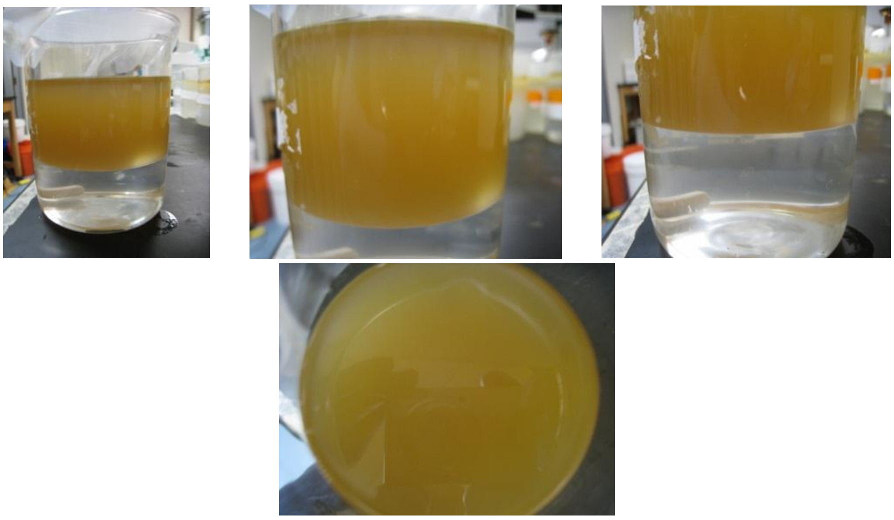

Figure: 66 Diagram of 500mL Seawater mixed with 250mL oil and 2.0mL COREXIT 9500A

Appendix B: Data Collection

Raw Data

Table 1 Component data collection for spectroscopy and turbidity

2-Butylethanol Addition to 500mL of DI Water			
Volume (mL)	Top (abs)	Middle (abs)	Bottom (abs)
0	0.065	0.065	0.065
1	0.119	0.164	0.125
1.5	0.165	0.075	0.084
2	0.094	0.122	0.09
4	0.23	0.097	0.105
2-ButylEthanol Addition to 500mL of Simulated Sea Water			
Volume (mL)	TOP (NTU)	Middle (NTU)	Bottom (NTU)
0	0.065	0.065	0.065
1	0.682	0.445	0.488
1.5	0.475	0.457	0.526
2	0.46	0.419	0.466
4	0.433	0.396	0.398
Sodium Succinate Addition to 500mL of DI Water			
Mass (g)	Top (abs)	Middle (abs)	Bottom (abs)
0	0.065	0.065	0.065
1.109	0.149	0.168	0.157
1.6599	0.138	0.152	0.159
2.1893	0.18	0.193	0.196
4.3721	0.159	0.159	0.165
Sodium Succinate Addition to 500mL of Simulated Sea Water			
Mass (g)	TOP (NTU)	Middle (NTU)	Bottom (NTU)
0	0.42	0.42	0.42
1.1092	23.9	26.8	118
1.648	10.1	14.8	327
2.1976	9.08	12.3	360
4.3927	58.1	12.4	173

Table 2 CMC determination data collection

Turbidity			
COREXIT Volume (mL)	Top (NTU)	Middle (NTU)	Bottom (NTU)
0	0.42	0.42	0.42
0.5	81.5	62.1	58.4
0.8	96.2	80.8	78.6
0.9	427	59.5	59
1	361	76	80.2
1.1	241	15.6	21.3
1.2	488	44.3	42.7
1.5	1193	24.4	19.1
1.6	582	26.2	26
1.7	1174	27	15.4
1.8	328	48.6	47.6
1.9	970	31.5	30.7
2	403	26.3	16.1

Spectroscopy			
COREXIT Volume (mL)	Top (abs)	Middle (abs)	Bottom (abs)
0	0	0	0
0.5	0.2262	0.1619	0.1739
0.8	0.153	0.0989	0.0968
0.9	0.2717	0.1117	0.1234
1	0.3983	0.1278	0.1228
1.1	1.3537	0.0684	0.106
1.2	1.2572	0.0504	0.0478
1.5	1.0623	0.661	0.0858
1.6	1.1502	0.0456	0.0437
1.7	1.3254	0.0407	0.0409
1.8	1.3751	0.0403	0.0385
1.9	1.153	0.0368	0.0507
2	0.6964	0.146	0.0709

Table 3: Spectrophotometer readings for sand particles

500ml of Seawater + COREXIT 9500A at 2.0mL COREXIT			
Size of Sand Particle	Top (590nm)	Middle (590nm)	Bottom (590nm)
0	0.6964	0.146	0.0709
0.0029	0.5174	0.4786	0.3296
0.0117	0.9557	0.6106	0.4481
0.0394	0.5966	0.3548	0.6632
0.187	1.1324	0.2028	0.4456
500ml of Seawater + COREXIT 9500A at 2.0 mL COREXIT			
Size of Sand Particle	Top (590nm)	Middle (590nm)	Bottom (590nm)
0	0.6964	0.146	0.0709
0.0029	1.2569	0.3979	1.0384
0.0117	1.5047	0.7106	0.9385
0.0394	1.7866	0.4247	0.2773
0.187	1.7416	0.1608	0.2071
500ml of Seawater + COREXIT 9500A at 2.5mL of COREXIT			
Size of Sand Particle	Top (590nm)	Middle (590nm)	Bottom (590nm)
0	0	0	0
0.0029	1.4336	0.9394	0.8871
0.0117	1.9058	0.5138	1.004
0.0394	1.6572	0.4813	0.8783
0.187	1.1377	0.5658	0.8267
500ml of Seawater + COREXIT 9500A at 1.5mL of COREXIT			
Size of Sand Particle	Top (590nm)	Middle (590nm)	Bottom (590nm)
0	1.0623	0.661	0.0858
0.0029	1.1071	0.9387	0.9965
0.0117	0.8856	0.9788	0.92626
0.0394	0.0396	0.6918	1.0708
0.187	0.7189	0.6799	0.8199

TABLE 4: Spectrophotometer readings for change in salinity and COREXIT

For Pure water (0% Salinity)			
500ml of Seawater + COREXIT 9500A			
	Spectrophotometer		
COREXIT Volume (ml)	Top (590nm)	Middle (590nm)	Bottom (590nm)
0	0	0	0
0.9	0.2867	0.2024	0.1563
1.1	1.0638	0.2155	0.2343
1.3	0.8112	0.2338	0.22
1.5	0.5142	0.3178	0.328
For 50/50 Mixture (50% relative to regular sea water)			
500ml of Seawater + COREXIT 9500A			
COREXIT Volume (ml)	Top (590nm)	Middle (590nm)	Bot tom (590nm)
0	0	0	0
0.9	0.1993	0.1417	0.0997
1.1	0.1721	0.1319	0.1411
1.3	0.2849	0.2253	0.2289
1.5	0.3539	0.2576	0.256
For 75/25 Mixture (75% relative to regular sea water)			
500ml of Seawater + COREXIT 9500A			
COREXIT Volume (ml)	Top (590nm)	Middle (590nm)	Bottom (590nm)
0	0	0	0
0.9	0.2867	0.2024	0.1563
1.1	1.0638	0.2155	0.2343
1.3	0.8112	0.2338	0.22
1.5	0.5142	0.3178	0.328
For 100% Salinity			
500ml of Seawater + COREXIT 9500A			
COREXIT Volume (ml)	Top (590nm)	Middle (590nm)	Bottom (590nm)
0	0	0	0
0.9	0.2717	0.1117	0.1234
1.1	1.3537	0.0684	0.106
1.3	1.2572	0.0504	0.0478
1.5	1.0623	0.661	0.0858

Table 5: Spectrophotometer Readings for Temperature change

	Top (590nm)	**Middle (590nm)**	**Bottom (590nm)**	**Time (hours)**
1.5mL Refrigerated	1.3312	0.6159	0.6197	1
	1.7703	1.2993	0.9155	2
	0.356	0.3787	0.4881	4
	0.5186	0.534	0.5362	8
	0.5173	0.5285	0.575	24
	0.2012	0.1619	0.1699	48
1.5mL Room Temperature	0.9406	0.2526	0.2619	1
	1.0699	0.2072	0.2101	2
	0.6598	0.2172	0.2227	4
	0.4409	0.2086	0.1993	8
	0.2145	0.2012	0.2071	24
	1.5654	0.6129	0.7697	48
1.5mL Increase temp at 36 degrees C	1.6397	0.2829	0.1527	1
	2.0588	1.0521	0.0516	2
	1.4732	0..3130	0.1481	4
	1.1089	0.1353	0.1562	8
	0.1437	0.1352	0.1152	24
	1.3128	0.2111	0.0759	48
2.0mL at increased temperature, 36 degrees C	0.7086	0.6111	0.1936	1
	1.576	0.1642	0.2125	2
	1.1173	0.0568	0.0454	4
	0.4154	0.2397	0.1385	8
	0.236	0.1782	0.1553	24
	2.0184	0.7719	0.487	48

TABLE 6: Spectrophotometer and Turbidity results for the addition of oil results

Spectroscopy						
450ml of Seawater + 50mL of oil + COREXIT 9500A						
COREXIT Volume (ml)	Top (590nm)	Middle (590nm)	Bottom oil and top seawater (590nm)	Middle seawater	Bottom Seawater	
0	0	0	0	0	0	
0.6	1.2768	1.5548	2.8932	0.8069	0.3841	
1	1.7631	2.3959	2.9903	0.3513	0.3973	
1.5	1.2577	1.137	3.2493	1.999	1.4676	
2	0.9831	1.9721	3.0109	1.027	1.1848	
4	2.0604	2.1761	3.2555	0.9324	1.0458	
Turbidity						
450ml of Seawater + 50mL of oil + COREXIT 9500A						
For Seawater Layer						
COREXIT Volume (ml)	Top (590nm)	Middle (590nm)	Bottom (590nm)			
0	0	0	0			
0.6	3077	252	166			
1		261	227			
1.5		954	553			
2		674	694			
4	909	319	475			
Change in oil layer						
Seawater + 2mL COREXIT 9500A + oil						
For Oil Layer						
Oil Volume (ml)	Top (590nm)	Middle (590nm)	Bottom oil and top seawater (590nm)	Middle seawater	Bottom Seawater	
0			0.6964	0.146	0.0709	
5	3.0315	2.9432	1.7563	1..0504	0.6891	
25	2.2856	3.175	3.0061	1.2229	1.1734	
100	0.1064	0.1283	3.1229	1.7752	1.0406	
250	1.8296	2.0213	2.9485	1.1229	0.505	

Turbidity						
Seawater + 2mL COREXIT 9500A + oil						
Seawater Layer						
Oil Volume (ml)	Top (590nm)	Middle (590nm)	Bottom (590nm)			
0	403	26.3	16.1			
5	459	257	172			
25	2720	1037	906			
100	3465	475	158			
250	477	199	212			

Sources of Error

Errors were encountered throughout the experiment and they ranged from instrumental error to human parallax error to random error.

Instrumental errors associated with the instruments were found from the respective company websites. The turbidity readings from 0 to 1000NTU's were found to have a two percent error while readings from 1000 to 4000NTU were found to have a five percent error. For the spectrophotometer all readings that you were used over the wavelength of 541.94nm which would be represented by all of our results contains an accuracy of seven percent.

An example of how the results are affected for the associated instrumental error for absorbance and turbidity is illustrated below.

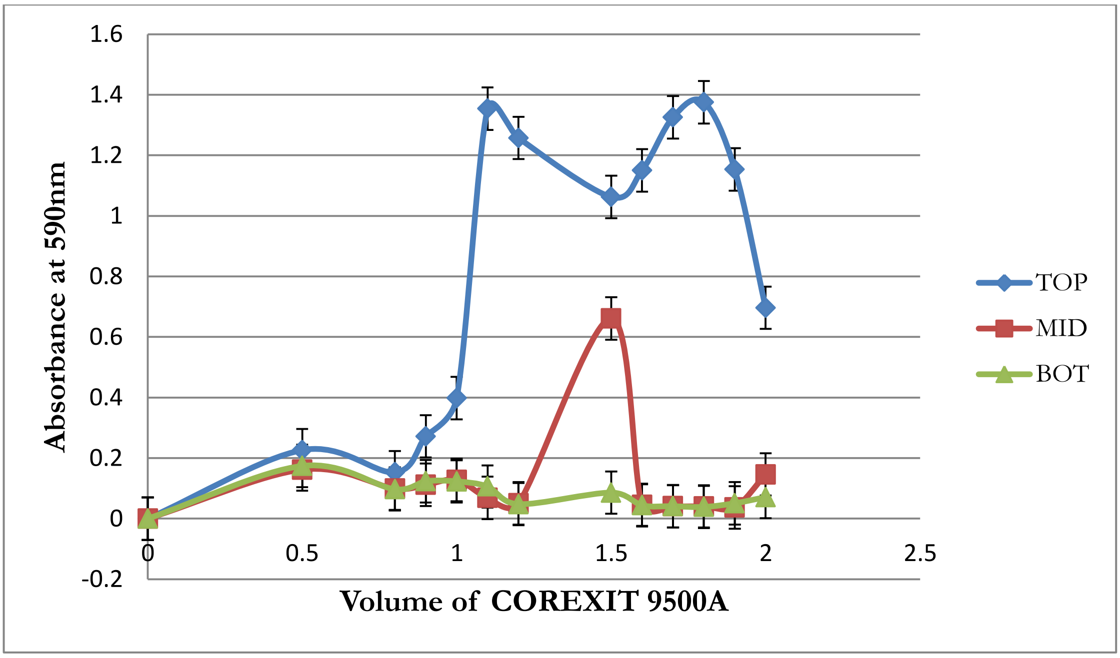

Figure 67 Showing error bars for the absorbance readings

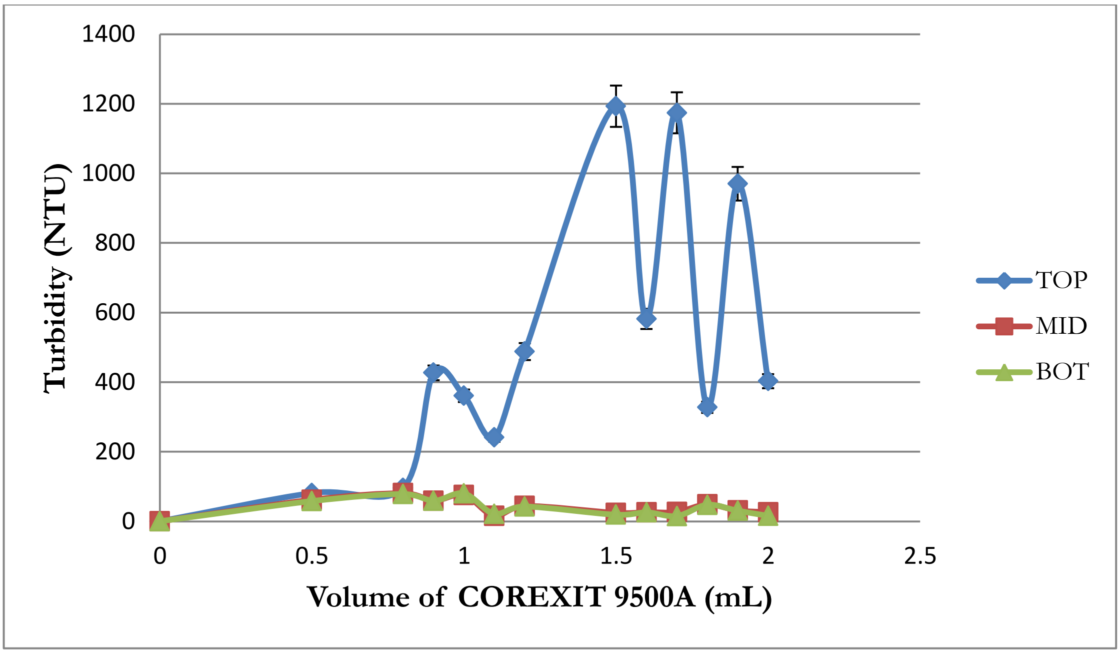

Figure 68 Showing error bars for the turbidity readings

Due to time constraints reproducibility to reduce random error could not be achieved for readings recorded after the base readings when the perturbations were done. So random error may be found within some of our perturbation results where the ideal system is being changed by an external factor. Human error associated with the reading of beakers and pipettes were also observed but this was minimal as corrections to rectify this between group members was done within the initial weeks of experimentation.