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On the Capability of Rhamnolipids for
Oil Spill Control of Surface Water

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in
The Department
of
Building, Civil, and Environmental Engineering

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Abstract

On the Capability of Rhamnolipids for Oil Spill Control of Surface Water

Since the risk of oil spills will never diminish and they continue to be a recurring event, methods to manage them are required to be cost efficient and effective.

Dispersants are one of the practical responses to oil spills at sea to break the slick into fine droplets. To reduce toxicity of dispersants in the marine environment and enhance biodegradation of the dispersed oil, biosurfactants can be used instead of chemical surfactants in the dispersant formulations.

The objective of this research was to evaluate the capability of the biosurfactant rhamnolipid (JBR425) in dispersing oil slicks and ways to improve its efficiency. At 25° C and salinity of 35‰, JBR425 (2%) in saline applied at a dispersant-oil ratio (DOR) of 1:2, could disperse 65% of Brut crude oil into the water without settling, but the percentage drop to 12.5% after 2 min of settling. Different solvents and additives were used to increase its efficiency in terms of percentage dispersion and stabilization of the dispersed oil in water. Starch and cellulose, as natural polymeric additives, were used to increase the stability of the emulsion but they were not effective.

Solvents play the major role in dispersant formulations since they help surfactants miscible with the oil. NaOH, ethanol, and octanol were used at different concentrations, but they did not enhance the effectiveness of the biosurfactant, because NaOH and ethanol increased the tendency of the biosurfactant solution towards water and octanol towards oil phase. The solution of JBR425 (2%) in saline was also applied as foam to

increase the contact time and area between oil and surfactant. Foam-surfactant application did not enhance the efficiency of the biosurfactant. A mixture of ethanol and octanol (JBR425 (8%) + 60% ethanol + 32% octanol) applied at DOR=1:8, showed promising capability in dispersing oil into the water. It greatly enhanced the efficiency of JBR425 to 82% and then to 21% after 2 minutes of settling. For more stable emulsions, at least two surfactants with different solubilities in water are necessary.

Dispersants are very sensitive to salinity and temperature. The formulation was modified for such applications by changing the ethanol-to-octanol ratio; with 70% ethanol at low temperature (10°C) applications and 40% ethanol in fresh water applications. In fresh water, the efficiency of JBR425 increased significantly from 11.5% to 23%, but for low temperature applications did not improve much, from 8% to 13.5%.

The efficiency of Corexit 9500, a commercial dispersant, was also evaluated. At 25°C and salinity of 35‰ it dispersed 84% of the Brut oil without settling and 45% after two minutes of settling. Its efficiency to disperse oil at 10°C and two minutes of settling dropped to 22%, and to 28% in fresh water at 25°C.

Dedication

I would like to dedicate this thesis to my dear husband, for his love and support through out my life and during the preparation of the thesis.

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List of Symbols

CMC	Critical Micelle Concentration
DOR	Dispersant-to-oil Ratio
EOR	Ethanol-Octanol Ratio
GC/FID	Gas Chromatography/ Flame Ionization Detector
HLB	Hydrophilic-lipophilic Balance
IFT	Interfacial Tension
n	number of experiments
O/W	Oil-in-water emulsion
PAH	Polycyclic Aromatic Hydrocarbons
SD	Standard Deviation
SDS	Sodium Dodecyl Sulphate
UV	Ultra Violet spectrophotometry
W/O	Water-in-oil emulsion

CHAPTER ONE

Introduction

1.1 Background

Oil spills, no matter how large or small, have long been of concern to pollution control authorities. While the prevention of oil spills should be of the highest priority, there is always a risk of spill on land and water during its extraction, transport, refinery and use. Due to its destructive nature, once an area has been contaminated by oil, the whole character of the environment is changed.

When crude oil or refined petroleum products are released at sea, they float on top and form a film of oil on the water surface that is called *slick* of less than one to a few millimeters in thickness (Aynechi, 1998). A slick is immediately subjected to natural physical, chemical and biological processes known as weathering processes. Weathering processes cause significant changes in oil properties such as viscosity, density and interfacial tension which make the subsequent cleanup measures difficult or impossible due to increased viscosity. Meanwhile these natural processes are very slow and have dramatic ecological effect on marine environment and coastal habitats. When a slick reaches shorelines, it can cause economic damages to recreational areas, harbors and vessels, commercial fisheries and shellfish grounds, power plants and drinking water suppliers (National Research Council, 1989). Preventive measures and contingency planning should be pre-established for different oil types and situations to rapidly respond to the spills and limit the consequences of the spillage.

Criteria to choose the most effective techniques for cleanup vary from spill to spill and depend on the type and quantity of spilled oil, weather conditions and surrounding environment. In any spill response, the first priority is to stop the source of leakage. The second priority is to contain the slick with booms to prevent it from further expansion, and then collect the oil from the water surface by skimmers. There are usually limitations for using booms and skimmers since they cannot be used where there are high waves, currents, and high-speed winds. Also, these types of equipment require extensive manpower and time to operate and still they can recover a maximum 10% of the volume of the oil spilled (Schramm, 2000). The percentage recovery may even fall to 1.5-2% of the volume of spilt oil in unfavorable sea conditions (NETCEN, 1997).

Dispersants are one of the practical responses to oil spills at sea by breaking the slick into fine droplets. The development of modern dispersants began after the TORREY CANYON spill in 1967 off the coast of England (Ficco and Lewis, 1999). Unfortunately the early aromatic-based dispersants destroyed aquatic life for miles around (Shanley, 1999).

Dispersants basically accelerate the natural dispersion and degradation of the oil slick. They break the slick into tiny droplets, therefore providing more surface area for further break down through biodegradation or photo-oxidation. Dispersants also solubilize oil compounds to facilitate their biodegradation (Shanley, 1999). Breaking the slick would prevent it from coming ashore and reduces the chance of seabird contamination. Dispersants are applied via ships or aurally to the spilled oil in the sea.

Dispersants can treat up to 90% of a spill and for much lower price than mechanical recovery (Shanley, 1999) (Table 1.1). Even after an immediate mechanical collection, dispersants can be used to minimize oil contamination of birds and sea animals (Lang and Wagner, 1993).

Table 1.1 Oil Spill Clean-up Options Expenses

Strategy	Cost per m.t.
Mechanical	\$12,527
Mechanical w/dispersants	\$13,927
Dispersant w/mechanical	\$2,502
Dispersant only	\$2,137

(Dagmar Ektin, Cutter Information Corp.)

The two major issues associated with the use of dispersants are their effectiveness and toxicity of the dispersant itself and the dispersed oil in the marine environment. However, recent chemical dispersants cause less ecological damages than if the spilled oil remains untreated (Schramm, 2000).

An oil dispersant is a mixture of chemicals. However, surfactants are their most important components because they are responsible for the actual oil dispersion. Surfactant molecules are composed of two parts, the hydrophilic portion and the lipophilic portion. Because of this amphiphilic nature (having both hydrophilic and hydrophobic groups), surfactant molecules reside at the oil-water interface and lower the

interfacial tension between water and oil, enabling the oil layer to be broken easily to smaller droplets with little energy from the waves (Ficco and Lewis, 1999). Surfactants actually solubilize the oil through forming small aggregates known as micelles which disperse into the water column.

To reduce the toxicity of dispersants in the marine environment and enhance biodegradation, biosurfactants can be used instead of chemical surfactants in the formulations. Biosurfactants are metabolic by-product of some microorganism species and they can be produced from less expensive and available substrates such as sugars, vegetable oil, and wastes. They have special advantages over the chemical ones such as biodegradability, lower toxicity, and stability against extreme salinity, temperature, and pH (Mulligan and Gibbs, 1993). Biosurfactants are better candidates as opposed to chemical surfactants because they do not contribute more toxicity than that which has already been created by the dispersed oil in the water.

This thesis consists of six chapters as summarized:

- Chapter One gives an introduction to the subject and discusses an overview of research activities.
- In Chapter Two, the sources, fate, effects of the oil spilled, oil chemistry and some oil properties will be discussed. Also the main oil spill response action, together with their advantages and disadvantages will be mentioned.
- In Chapter Three, dispersant formulations and their mechanisms of action will be explained. Also surfactants, as the main component of dispersants, will be discussed.

- Chapter Four presents all experimental materials and methods used in this investigation. A brief explanation of the preliminary experiments, which lead to the final protocol and setup, together with the results will be mentioned.
- Chapter Five summarizes the results obtained in this study. In addition, the results will be discussed.
- Chapter Six forms the conclusions of this thesis, economic study, and some possible future work that can be done in this area to improve the results.

1.2 Objectives

The overall objectives of this research are:

1. To evaluate the effectiveness of JBR425 on crude oil dispersion,
2. To compare the effectiveness of JBR425 with Corexit 9500,
3. To determine the stability of the emulsions through a time study,
4. To evaluate different solvents to increase the efficiency of JBR425,
5. To investigate if foam-surfactant application can improve surfactant efficiency in comparison with surfactants if applied drop-wise,
6. To investigate if polymeric additives can increase the stability of the oil-in-water emulsion,
7. To investigate the effect of salinity on the efficiency of JBR425 and Corexit 9500,
8. To investigate the effect of temperature on the efficiency of JBR425 and Corexit 9500,
9. To investigate the efficiency of JBR425 and Corexit 9500 on two other types of oil.

CHAPTER TWO

Literature Review

Introduction

Unfortunately the risk of oil spills will never diminish and oil spills continues to be a recurring event. Oil spill response is to minimize the damage that could be caused by the spill. Dispersants are one of the limited practical responses that are available to respond to oil spills at sea. Where dispersants are to be considered as part of the response strategy it is necessary that the oil spill contingency plan (local or national) give a clear policy statement on their use, on the procedure in place for prior approval, and on the resources available for a rapid response.

Oil spills are caused by a variety of incidents, from relatively minor events such as overfilling of tanks during crude oil loading, through ship and tanker accidents of varying degrees of severity, up to very large events such as blow-outs at offshore oil exploration and production facilities.

Each spill scenario will have different characteristics, such as the type of oil, the size of spill, the release rate and the location. These factors will influence the choice of the most appropriate method, including dispersants use. With all dispersants, timely application ensures the highest degree of success. For effective treatment with dispersants, they should be applied in correct quantities to reduce dispersant loss and proper droplet size to maximum dispersant-oil contact.

2.1 Sources of Oil Input into the Waters

An accidental spill is only one of the several ways that oil enters the seawater. Spills usually happen due to bad weather (hurricanes, storms, earthquakes), intentional acts of violence (like war, vandalism, or dumping) and human mistakes. In fact, the major spills are associated with transporting and storing oil. About 92% of all oil spills involving tankers happens at terminals during loading and unloading oil (Government Publication of Canada, 1994). Different sources of oil input into the oceans and sea are shown in the Figure (2.1).

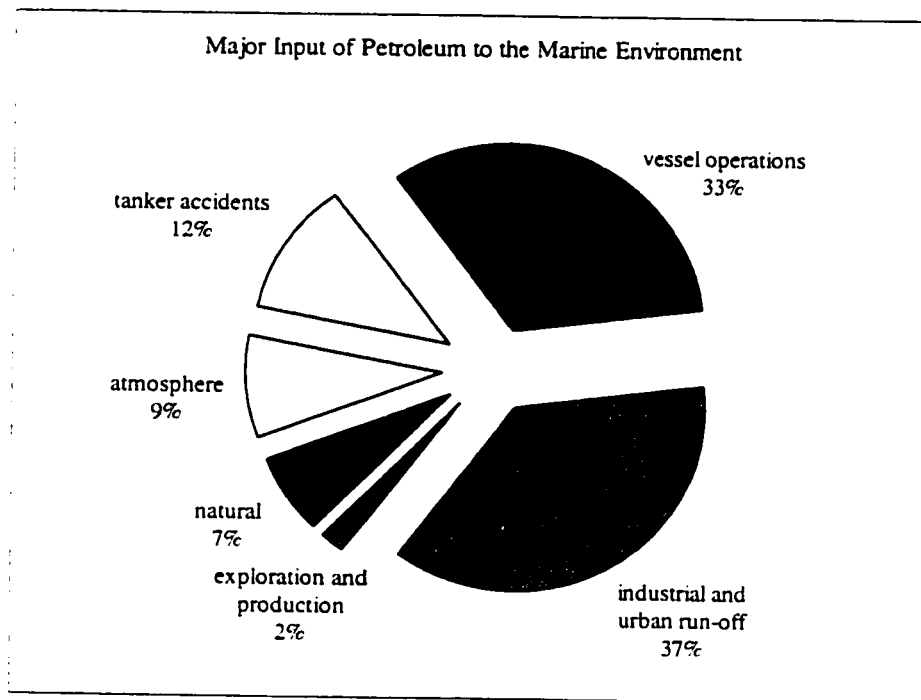


Figure 2.1 Major Input of Petroleum into the Marine Environment (AIP, 2001)

Accidental spills are not only a result of human errors. Cold or hot weather can snap pipes, heavy icing can disable a ship, and offshore blowouts may occur at drilling sites (Government Publication of Canada, 1994). In the open oceans, most surface and

near surface waters contain petroleum hydrocarbons ranging from 1 to 10 ppb. Coastal waters near harbors and industrialized areas may contain up to 100 ppb (Government Publication of Canada, 1994).

2.2 Fate of Spilled Oil

The characteristics of both the oil and the environment determine the behavior and the fate of the spilled oil.

2.2.1 Weathering

When oil is released at sea, it would be exposed to some natural physical, chemical, and biological processes known as weathering that changes the chemical composition and physiochemical properties of the oil. Weathering processes include: "spreading; evaporation and dissolution of selected low molecular weight components; dispersion of whole oil droplets into the water column; coalescence and return to the surface slick of those droplets with entrapment of seawater; photo-, microbial-, and auto-oxidation; and emulsification and tarball formation." (Payne and Phillips, 1985). Waves and local currents, water and air temperature, wind speed, and the type and amount of spilled oil affect the degree of weathering and environmental damage (Maclean, 1993). Water temperature also affects microbial biodegradation. Light compounds ($<C_{10}$) are first attacked by microorganisms, followed by C_{12} - C_{24} (Muller-Hertig et al, 1993). The heavier and complex compounds are resistance to microbial attack.

Weathering processes increase density, viscosity, pour point, and the volume of oil (due to trapping of water) complicate the cleanup measures: skimming, pumping,

sorbents, recovery operations and dispersant function. When dispersants are applied, they also undergo weathering processes.

2.2.2 Chocolate Mousse and Tarball Formation

Weathering processes finally result in the formation of a stable water-in-oil emulsion named "Chocolate mousse". This emulsion has up to 70-80% water and such water content increases mousse viscosity and complicates the cleanup measures (Payne and Philips, 1985). Asphaltenes, waxes, resins, organometalics, and oxygen-, sulphur-, and nitrogen-containing aromatics act as natural emulsifying agents stimulate formation and stabilization of chocolate mousse. These compounds surround water droplets in the mousse and prevent them from coalescing. Photo-oxidation of oil compounds also enhances mousse formation. These photo-oxidation products have polar groups that are soluble in oil and act as surfactants facilitating incorporation of water into the oil phase and forming chocolate mousse (Thingstad and Pengerud, 1983).

High viscosity of the mousse makes it difficult for the dispersants to get into these emulsions. High emulsion stability impedes water droplet coalescence which could help break the mousse. Aged emulsions are more difficult to disperse due to high water content and the effect of natural surfactants in oil that tend to stabilize the mousse (National Research Council, 1989). The more stable the mousse becomes, the less likely it would undergo bacterial degradation (Payne and Philips, 1985).

As weathering processes goes on, the oil lose more lighter hydrocarbons and increase its density (become heavier than water), become semi-solid and form "tarballs"

that would settle out onto the sediments (Lang and Wagner, 1993) where they are anaerobically degraded to CH₄ and CO₂ by microorganisms (Muller-Hurtig et al., 1993).

2.3 Effects of Oil Spill

2.3.1 Ecological Effects

Oil tends to adsorb to solids whether it is on a beach, a rock, the feathers of a sea bird or body of the surface feeding fish which may end up in their death or sickness due to chronic effects (National Research Council, 1989). Hydrocarbons, especially lower molecular weight ones, evaporate and can be inhaled by animals and human. They easily adsorb through animal skin and threaten their health (Oil.Spill.Web, 2001). The oil slick may impede oxygen and light penetration (OHMSETT, 2001). As the oil moves towards the land, ecological concerns increase. Oil slick threatens the marine life of shallow waters and near shore marine waters, and finally pollutes coastal regions and land animals (Noyan Aynechi, 1998)

Seabirds and some marine mammals can be drastically affected (National Research Council, 1989). Birds are attracted to oil on water and this increases the risk. Their feathers become coated with oil and this results in death from loss of body heat, inability to fly through loss of buoyancy or direct poisoning from oil (Stanley, 1969). Marine mammals may ingest some of the oil while trying to clean their fur. Also, oil destroys their insulating ability or pollutes their eye and nostrils (National Research Council, 1989).

Fish, especially young fish and eggs, are very sensitive to oil in water. Dispersed or dissolved oil may enter their bodies through their gills or eaten and consequently

accumulate in liver, gall bladder and stomach and even if it does not end up with their death it has long-term sublethal effects on feeding and respiration, reduced reproduction and loss of stamina (Government Publication of Canada, 1994). Surface feeding fish may become coated with oil and result in their death or make them unfit for human consumption (Stanley, 1969).

As oil compounds gradually precipitate, animals such as worms, shrimp and oysters, crabs and lobster, living near the shore on or in the bottom sediments are greatly in risk of contamination (Government Publication of Canada, 1994).

Oil spills also affects marine plants. These plants are necessary for the life of other organisms in the water. Plants in the area between high and low tides are more at risk since they are in the area of tides and may become coated (Government Publication of Canada, 1994).

2.3.2 Economic Damage

Oil spills pose great economic damage to coastal regions, tourist beaches and recreational areas, harbors and vessels, commercial shellfish grounds and fishing banks. It may contaminate public water supplies and intake sources for power plants. Clean up of oil-contaminated areas and facilities is time-consuming, difficult, and also very costly not only due to the amount of money needed for the clean up, but also because of the destruction and losses that may last for months or years (National Research Council, 1989).

Spilled oil may contaminate desalination plants that provide drinking water. Oil hydrocarbons naturally disperse and may enter into the intake of a water treatment plant

(National Research Council, 1989). Tainted fish is not suitable for human consumption. After an oil spill, fishing may be suspended for a period of time and commercial fisheries lose income (National Research Council, 1989).

2.4 Oil Chemistry and Properties

Oil chemistry and properties greatly influence the dispersion process and the dispersants' effectiveness. Oil, both crude and refined, is complex mixture of hydrocarbons that are formed naturally below the surface of the earth. Due to different sources and ages of oils, they rarely have the same chemical composition. Crude oil is a mixture of up to 85% hydrocarbons and a small group of compounds that contain trace metals such as nickel, vanadium, iron, aluminum, sodium, calcium and copper (NRC, 1989).

It is very important to know the physical and chemical properties of the spilled oil since it indicates its environmental behavior and effects under local conditions such as the extent of oil evaporation and dissolution and how fast they occur, emulsion and tar ball formation, toxicity to marine life and people working on site from volatile oil compounds.

2.4.1 Crude Oil Classification

Crude oil is a mixture of complex hydrocarbon compounds that range from light gases to heavier tars and waxes (Government Publication of Canada, 1994). Crude oils are classified as light, medium, and heavy crude based on their proportions of hydrocarbon groups, low, medium and high molecular weight hydrocarbons.

2.4.1.1 Hydrocarbon Classification

Low molecular weight hydrocarbons- Hydrocarbons that contain up to 10 carbon atoms are considered as light hydrocarbons (Oil.Spill.Web, 2001). They include small saturates especially aliphatics, and small aromatics (Clayton, Jr. et al., 1993). Their boiling point is less than 200 °C (Lang and Wagner, 1993) and they have simple molecular structures. These two physical properties allow them to dissolve and evaporate rapidly within hours after the spill (Oil.Spill.Web, 2001). Saturates with less than 18 carbon atoms are the most dispersible compounds of the oil. Small aromatics, with one or two benzene rings, evaporate rapidly following the spill but fairly dissolve in water. Larger aromatics neither dissolve nor evaporate (Fingas, 1994).

The liquid state of oil, in normal temperatures, is due to the presence of the lower molecular weight hydrocarbons, which act as solvents for heavier and less soluble oil compounds. Within hours of a spill, when the lower molecular weight hydrocarbons evaporate or dissolve, the viscosity of oil increases. The most volatile compounds, with 15 and less carbon atoms, are the most toxic ones. Evaporation of these compounds reduces the acute toxicity of the remaining surface oil to the marine environment (NETCEN, 1997).

Medium molecular weight compounds- This group of hydrocarbons ranges from C₁₁ to C₂₂ and has a more complex molecular structure compared with lower molecular weight oil hydrocarbons. These medium weight hydrocarbons (such as phenanthrene with three benzene rings) dissolve and evaporate in several days and may leave some residues in water or sediments (Oil.Spill.Web, 2001). They are more toxic than low molecular

weight hydrocarbons (Clark, 1997), but they are less bioavailable (due to lower water solubility), therefore less likely to affect animals (Oil.Spill.Web, 2001).

The less water-soluble compounds are, the least likely to be degraded by microorganisms since microorganisms cannot take them up unless there is a surfactant to facilitate their uptake through microbial cells (Hommel and Ratledge, 1993). Microorganisms produce biosurfactants to facilitate the uptake of the hydrophobic compounds.

High molecular weight hydrocarbons- The hydrocarbons with more than 23 carbons atom are known as heavy-weight compounds. They include asphaltenes, resins, and waxes (Clayton, Jr. et al., 1993). These hydrocarbons have very complex and large molecules and do not evaporate or dissolve in water (Oil.Spill.Web, 2001). They remain and form water-in-oil emulsions following the spill and finally create tar balls that sink or submerge in water (EPA, 2001). These compounds also act as natural surfactants in oil and tend to stabilize water-in-oil emulsions (Bridie et al., 1980; Canevari, 1969). Since they neither degrade, nor dissolve or evaporate, they persist in seawater and sediments and cause chronic effects on aquatic life (Helton, 1996).

Resins and asphaltenes are almost similar. "Both groups are composed of condensed aromatic nuclei which may carry alkyl and alicyclic systems containing atoms such as nitrogen, sulphur, and oxygen." according to Bobra, (1990). Asphaltenes are large resins that also contain metals such as nickel, vanadium, and iron (Fingas, 1994). Asphaltenes are soluble in aromatic solvents but insoluble in alkane solvents (Bobra, 1990). Resins are polar and their molecular weights are generally in the range of 800 to

1500 g/mol (Bobra, 1990). Waxes are higher molecular weight aliphatics with melting points greater than 20°C (Fingas, 1994). They crystallize out when an oil is cooled below its pour point.

2.4.3 Effect of Oil Viscosity on Dispersion and Dispersant Effectiveness

Natural and chemical dispersion of either crude or refined oils is a function of chemical composition and physical properties of an oil. Low temperatures, evaporation and dissolution of low molecular weight hydrocarbons, and formation of water-in-oil emulsions all increase oil viscosity. Higher viscosities inhibit dispersants from being well mixed and penetrate into the oil to reach the oil-water interface, where they can actually start dispersing oil (Clayton, Jr. et al, 1993). Natural dispersion is also retarded since wave energy would be transmitted through the viscous slick rather breaking it (National Research Council, 1989).

Oils content greatly affects its properties and dispersibility in water. Oils that contain mostly resins, asphaltenes, and larger aromatics and waxes would barely disperse. Oils with mostly saturate, such as diesel fuel, enhance chemical dispersion and even disperse naturally without dispersant application, only with the mixing energy of waves and winds (Schramm, 2000). Waxes and especially asphaltenes are important in formation and stabilization of water-in-oil emulsions (chocolate mousse), which make cleanup measures difficult or impossible (Bridie et al., 1980; Canevari, 1969).

Dispersants cannot perform well on oils with absolute viscosity less than about 100 cpoise (cP) because they need a minimum retention time in the slick to influence interfacial properties (Mackay and Wells, 1983). Generally dispersants are more effective

for oil viscosities less than 2000 cStokes and almost no dispersion occurs at viscosities over 10,000 cSt (Cormack et al., 1986/87).

Dispersants' effectiveness greatly depends on oil viscosity, Dispersants should be applied within 24 hours of a spill, before the lighter hydrocarbons are lost to the air and water (Agnes Shanley, 1999).

2.5 Oil Spill Cleanup Measures

2.5.1 Mechanical Recovery

Mechanical methods include booms, skimmers, and sorbents. They all help to pool the oil and stop it from spreading out (OHMSETT, 2001).

2.5.1.1 Booms

Booms are floating devices to contain and concentrate oil for later recovery by skimmers or to preserve the sensitive areas or facilities. It is necessary to contain and concentrate the slick prior to skim the oil because the skimmers cannot collect thin slick. Booms can be used to divert the oil into a collection device or any other desired destination (Oil.Spill.Web, 2001).

2.5.1.2 Skimmers

Skimmers are often used in conjunction with booms. A skimmer collects oil from the surface of the water. There are many commercial skimmers at the market but they mostly suitable for sheltered and quiet water and only a few types can be used in response to actions at sea (OHMSETT, 2001). Yet there are many types of skimmers for different kinds of oil and weather conditions. Weir skimmers are the most widely distributed skimmers for open sea and near shore skimming (Oil.Spill.Web, 2001). They work like a dam. Oil flows over a wall and collects on the other side (OHMSETT, 2001).

Oleophilic (oil attracting) skimmers attract oil with belts, disks, or mop chains and then the oil is recovered by squeezing the belts. Its viscosity range is 100-1000 cSt and is useful for relatively calm waters. Suction skimmers work like a household vacuum

cleaner. They store the oil in a tank but emptying these tanks is very difficult (Oil.Spill.Web, 2001).

2.5.1.3 Sorbents

Sorbents are materials that soak up oil from the water. Good sorbents have hydrophobic properties, i.e. attract the oil and repel the water. Therefore the sorption capacity of the commercial sorbent materials decreases as water content increases (Twardus, 1980). Sorbents usually work well unless they fill up with water and then they sink and create a bigger problem. Sorbents can be either natural organic, natural inorganic, or synthetic. Natural organic sorbents include peat moss, sawdust, feathers, and anything else natural that contains carbon. Natural inorganic sorbents include materials like clay, sand or even volcanic ash. Synthetic sorbents are man-made, and include substances like polyethylene and nylon (OHMSETT, 2001).

2.5.2 Chemical Treatment

Dispersants are chemicals that are applied to the oil slick to break it up into tiny droplets. Dispersants basically accelerate the natural dispersion and biodegradation of the oil (Ficco and Lewis, 1999). Breaking the oil slick prevents it from coming ashore and reduces the chance of contamination of seabirds and surface feeding fish. Tiny droplets also provide more surface area to undergo biodegradation or photo-oxidation. Dispersants help solubilize the heavier oil hydrocarbons, therefore facilitating their natural biodegradation (Gerson, 1993). Dispersants can treat up to 90% of a spill and the cleanup cost is much less than mechanical cleanup (Agnes Shanley, 1999).

After dispersant application, the energy of waves, winds, and currents would rapidly disperse the chemically dispersed oil into the upper ten meters of the water column. If the formed droplets are less than 0.07 mm in diameter, they would remain dispersed in the water and would not come to the surface to reform the slick (Lunel, 1996). Chemically dispersed oil droplets do not stick to suspended particles and will not settle onto the sediments (NRC, 1989). Also even if surfactant application does not totally disperse the oil slick, at least it lowers its absorbency to sand and solid surfaces if the slick reaches ashore (Schramm, 2000).

Dispersant effectiveness is the amount of oil that the dispersant puts into the water column versus that which remains on the surface. There are many factors that affect dispersant effectiveness: sea energy, oil composition, state of oil weathering, rate of dispersant application, dispersant type, temperature, salinity of the water, etc. The most important factors for dispersant effectiveness are the composition of the oil, sea energy and amount of dispersant applied (Schramm, 2000).

Dispersants should be applied within hours of the spill before weathering processes increase the viscosity of the oil too much for the dispersing agent to act effectively (Agnes Shanley, 1999). That is why emergency measures and approval for dispersant use should can be pre-established so that in case of accidents, appropriate measures be taken as soon as possible.

2.5.2.1 Dispersant-oil ratio (DOR)

For effective treatment with dispersants, they should be applied in correct quantities to reduce dispersant loss. If the amount of spilled oil is not known, it is very

difficult to determine the quantities of oil to be treated because the thickness of the slick vary considerably from a few microns to millimeters. The Dispersant-Oil Ratio (DOR) for a modern dispersant is about 7.5 to 38 liters per 4,050 square meter (2-10 US gallon per acre), or a dispersant to oil ratio of 1:50 to 1:10. This value may vary depending on the type of oil, type of dispersant, degree of weathering, temperature, and thickness of the slick (EPA, 2001).

2.5.2.2 Droplet Size

The size of the dispersant droplets is of great importance. Proper droplet size maximizes dispersant-oil contact. Drops of dispersant which are too large pass through the oil slick and are lost into the water and drops which are too fine are deflected by the wind and the oil. Drops with an average diameter of 400 to 700 μm are usually recommended (Bonn Agreement, 1999).

2.5.2.3 Method of Dispersant Application

Dispersant may be sprayed either by airplanes or ship. Aircraft provide the most rapid method of applying dispersants but have uneven application rates and up to 50% dispersant loss (Bonn Agreement, 1999). The altitude of the aircraft should be as low as possible and the wind direction should be identical to the flight path (EPA, 2001). In aerial treatment, dispersants are applied undiluted (Bonn Agreement, 1999). Since 1985, small twin-engined planes have been used for dispersant spraying, since they have the flexibility of use of the single-engined planes with increased capacities (Bonn Agreement, 1999).

To apply dispersants with ships or boats, dispersants are sometimes prediluted (10%) with seawater although they become less effective especially on oil with viscosities greater than 500 cSt (Bonn Agreement, 1999). The most effective method of application from a workboat is to use a low-volume, low-pressure pump so the chemical can be applied undiluted. In treatment by ship, to avoid the disadvantage of the bow wave which pushes the pollutant far away from the ship and the spraying devices, the spray equipment should be placed ahead of the bow wake or as far forward as possible from vessel so the dispersant be applied to the oil before the bow wave passes. Natural wave or boat wake action usually provides adequate mixing energy to disperse the oil (EPA, 2001).

2.5.3 In-situ Burning

In-situ burning is burning the oil where it was spilled. The spill is usually contained by fire-resistant booms at the spill site, and then set on fire. This method is more appropriate for light oils, since the light oil fractions are more susceptible to burn (OHMSETT, 2001). This method, in case of approval, should be used not long after the spill before the light oil fraction is lost to the air. The chances for in situ burning would become less and less for aged emulsion due to increased water content and decreased light oil fraction due to evaporation. Light oil compounds are more responsive for burning.

2.6 Evaluation of oil Response Methods

The role of response to the spill is to provide a net environmental benefit. However, there are some advantages and disadvantages to each method. Still the best we

can do is to prevent spills from happening. Among all the advantages and disadvantages of the different spill cleanup measures, their application highly depends on different sea conditions, oil type, state of the weathering of the spilt oil, sensitivity of the marine life of the area, depth of the water column, accessibility to the area of the spill, and other parameters. Sometimes mechanical and chemical methods can be used in conjunction with each other to increase the efficiency or reduce the costs. For example, a chemical treatment can follow a mechanical recovery to disperse the remaining oil.

2.6.1 Mechanical Recovery

Advantages

- The oil is removed from water so marine environments is less exposed to the toxic oil elements.
- Some of the oil may be recovered.

Disadvantages:

- The equipment requires extensive manpower and time to operate (Schramm, 2000).
- They can recover a maximum of 10% of the spilt oil (Schramm, 2000), and even as low as 1.5-2% recovery in unfavorable conditions. (Schramm, 2000, NETCEN, 1997).
- Oil should be recovered before it emulsifies.

- They cannot be used in strong currents and sea conditions, where currents exceed one knot (1.85 km/hour) (Oil.Spill.Web, 1998).
- The other problem with mechanical recovery is the ability of pump to drain the skimmer. All pump types very quickly get filled with oil which then become virtually solid (Oil.Spill.Web, 1998).

2.6.2 Chemical Treatment

Advantages (Bonn Agreement, 1999):

- Generally dispersants can be used in stronger currents and greater sea conditions,
- It is the quickest response method,
- Breaking the oil slick prevents the oil from coming ashore,
- Reduces the possibility of contamination of sea birds and mammals,
- Inhibits formation of water-oil emulsions (chocolate mousse),
- Biodegradation is enhanced.

Disadvantages (Bonn Agreement, 1999):

- Dispersing the oil may adversely affect some marine organisms,
- Dispersant itself may be harmful to some marine organisms,
- If dispersion of oil is not achieved, effectiveness of other response methods on oil treated by dispersants may decrease,

- They may not be effective on every type of oil or weathered oil,
- A minimum mixing energy of waves is needed,
- It is not recommended to be used in shallow waters,
- Limited time window when dispersants can be used efficiently.

2.6.3 In-situ Burning

Advantages

- It is fast and easy,
- It is less expensive.

Disadvantages:

- Produces air pollution,
- Limited time window before light hydrocarbons are lost to air and before the oil emulsifies,
- Not suitable for heavier types of oil,
- Cannot be used near harbors and coastal areas.

CHAPTER THREE

Dispersants and Mechanism of Action

Introduction

A typical oil spill dispersant is a mixture of surfactants, solvents and additives (Ficco and Lewis, 1999; Clayton et al., 1993). The composition of dispersants defines its toxicity and effectiveness. Some chemical surfactants or some type of solvents, like aromatic hydrocarbon-based solvents, are very toxic (Shanley, 1999).

Biosurfactants have advantages over chemical surfactants. They are less toxic and have great ability to lower oil-water interfacial tension at very low concentrations. They can be produced from less expensive and renewable materials. Biodispersants may be better candidates as opposed to chemical dispersants since we do not want to expose marine environments to more toxicity than has already been created by the dispersed oil.

Surfactants are the main components of an oil dispersant since they are responsible for the actual oil dispersion (Fiocco and Lewis, 1999). The effectiveness of any dispersant depends on its solvent (Al-Sabagh and Ata, 1999). Additives are used to increase dispersant effectiveness especially in terms of stability of the dispersed oil droplets since unstable dispersed oil would resurface and form the slick again.

3.1 Dispersants

A typical oil spill dispersant is a mixture of surfactants, solvents and additives (Ficco and Lewis, 1999; Clayton, et al., 1993).

3.1.1 Surfactants

Surfactants are the main components of an oil dispersant (Fiocco and Lewis, 1999). Although a dispersant may contain one or more surfactants, blends are more effective (Sabagh and Ata, 1999). The commercial surfactants that are used in modern oil dispersants are a blend of nonionic and anionic types with different solubilities in oil and water, i.e. different HLB values (Fiocco and Lewis, 1999). Generally, at a certain HLB, blends of surfactants are more effective than a single surfactant (Al-Sabagh and Ata, 1999). Because some mixed surfactants form a complex at the interface, lowering interfacial tension and producing a strong interfacial film, this complex may not be easily ruptured and a stable emulsion is formed (Schramm, 2000). For the most stable oil dispersion, the optimum HLB value of 9-11 is recommended. This value can be derived from a mixture of surfactants with HLBs of approximately 5 and 15 (Brochu et al., 1986/87).

3.1.2 Solvent

The effectiveness of any dispersant primarily depends on its solvent (Al-Sabagh and Ata, 1999). Since surfactants that tend to make oil-in-water emulsions are moderately hydrophilic, solvents help them to be miscible with the oil. They solubilize blends of surfactants and additives. Solvents also reduce dispersant viscosity to reach a

suitable level for different application methods (Fiocco and Lewis, 1999). Generally, there are three types of solvents that can be used in dispersants: water solvents, water-miscible solvents, and hydrocarbon solvents (Clayton et al., 1993).

3.1.2.1 Water Solvents

Sometimes water and alcohols are used as cosolvents to increase the solubility of surfactants and decrease dispersant viscosity for different application systems. They may also be applied as cosurfactants (Fiocco and Lewis, 1999).

3.1.2.2 Water-Miscible Solvents

Water miscible solvents are hydroxy compounds that enhance the blending of surfactants into a water stream. Surfactants with low HLB values (i.e. more lipophilic) are less soluble in water. Therefore they should be mixed with water-miscible solvents before application (Clayton et al., 1993). Hydroxy solvents are less toxic than petroleum-based solvents (Al-Sabagh and Atta, 1999). Examples of water-miscible solvents in modern dispersants include oxygenated compounds, such as glycol and glycol ethers (Fiocco and Lewis, 1999; Clayton et al., 1993).

3.1.2.3 Hydrocarbon Solvents

Hydrocarbon solvents are basically petroleum-based solvents. These solvents, such as kerosene, contain aromatics that are very toxic (Clayton et al., 1993). To reduce hydrocarbon solvents' toxicity, de-aromatized kerosene and isoparaffinic solvents can be used (Fiocco and Lewis, 1999). This type of solvents is effective for highly viscous oils

since they promote surfactant mixing and penetration into the oil (Clayton et al., 1993). These solvents should be used for spills of originally viscous oils, spills in low temperatures, or weathered oils that have increased viscosity. These solvents can be used either undiluted or diluted with water, if necessary (Oil.Spill.Web, 2001).

3.1.3 Additives

To increase dispersant effectiveness, some chemicals or materials can be added to the dispersant mixture. Additives may contribute to the stability of the dispersed oil or provide nutrients (nitrogen and phosphorous) for the indigenous microorganisms, therefore enhancing oil biodegradation (Clayton et al., 1993, Muller-Hurtig et al., 1993).

Polymeric materials are believed to have the capability to stabilize emulsions. Natural materials such as proteins, starches, gums, cellulose, and their modifications, as well as some of the synthetic compounds, such as polyvinyl alcohols, have the capability to adsorb strongly at interfaces and form a barrier between drops and even lower the interfacial tension. Polymers can form a substantial barrier of high strength and rigidity at the interface that can retard the approach and reunion of emulsion droplets. Adsorption of polymeric molecules at the interfaces increases interfacial viscosity that would not easily be ruptured. Polymeric molecules also form bridges among surfactant micelles (Figure 3.1). This would keep the dispersed oil stable in the water and do not resurface (Myers, 1991).

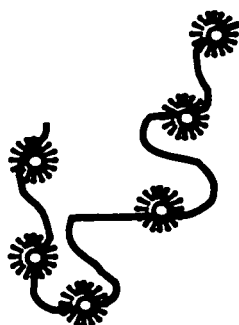


Figure 3.1 Mechanism of Emulsion Stabilization by Polymers (Myers, 1999)

3.2 Surfactants

Surface active agents (abbreviated as surfactants) are compounds that are able to lower the surface tension of a solvent and form aggregates called micelles in a aqueous media. Surfactants molecules consist of two parts, one part with little attraction for the solvent and the other part with a strong attraction for that solvent (Figure 3.2). In aqueous systems, the two parts are called the hydrophilic and the hydrophobic groups. The hydrophilic group (or *head*) is an ionic or highly polar group that makes this part water-soluble. The hydrophobic group (or the *tail*) is a long-chain hydrocarbon radical that is non-polar and has little attraction for water (Myers, 1999), (Figure 3.2).

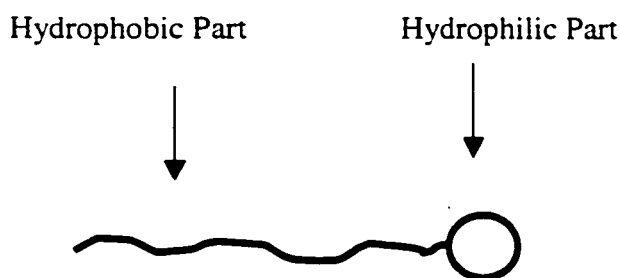


Figure 3.2 Surfactant Structure

Surfactants adsorb at interfaces due to their amphiphilic structure. Surfactant molecules concentrate at the interfaces and reduce the interfacial tension thereby increase the solubility (Myers, 1992). The effectiveness of a surfactant depends on its ability to lower the surface tension (Rosen, 1978). A good surfactant can lower the air-water surface tension to 35 mN/m and the oil-water interfacial tension to 1 mN/m (Mulligan and Gibbs, 1993).

Each surfactant is characterized by an HLB (hydrophilic-lipophilic balance) value. The HLB (hydrophilic-lipophilic balance) value indicates the tendency of a surfactant to dissolve preferentially in oil or water (Mulligan and Gibbs, 1993). Surfactants with high HLB values are hydrophilic and tend to make oil-in-water emulsions while those with low HLB values are more lipophilic and tend to make water-in-oil emulsions. The HLB value varies from 1, the most lipophilic, to 20, the most hydrophilic (Clayton, Jr. et al, 1993). Surfactants may be considered as emulsifiers or demulsifiers, depending on whether it stabilizes or destabilizes an emulsion (Mulligan and Gibbs, 1993).

Surface tension- In the surface region of a liquid the net density of the molecules is less than the bulk phase because the net force at the vapor liquid is towards the bulk phase. As a result, there is more space between surface molecules and this creates a tension along the surface molecules to keep the molecules together (Myers, 1999). Surfactant molecules adsorb at the vapor liquid interface, due to their amphiphilic structure, so reduce this tension. The “surface activity” of a solute can thus be defined as the ability to

lower the tension of a solution by transferring solute molecules to the surface (Thomas et al, 1977).

3.2.1 Types of Surfactants

Surfactants are classified according to their hydrophilic groups, that is their head. The four general groups of surfactants are anionic, cationic, amphoteric, and nonionic which contain negative, positive, positive and negative, and neutral charges as their hydrophobic group, respectively (Figure 3.3). In nonionic surfactants, the hydrophilic group has no charge but has a water solubility due to their highly polar groups that can establish hydrogen bonding with water. Amphoteric surfactants can be either cationic or anionic depending on the pH of solution, and also are those that have both the negative and positive charges (Myers, 1992).

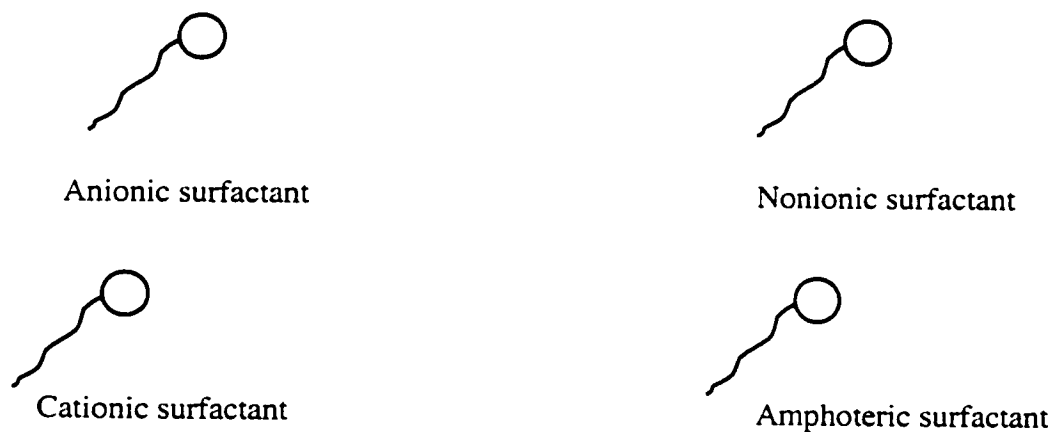


Figure 3.3 Types of Surfactants.

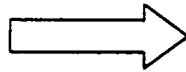
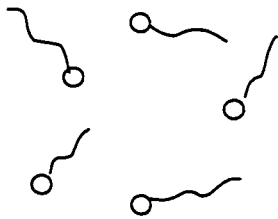
Anionic surfactants are mainly used as detergents (Tsujii, 1998). Anionic surfactants are the best type of surfactants for soil remediation because they sorb very

little to soils that are mostly negatively charged (Mulligan, 1998). Cationic surfactants are particularly used in fabric softeners (Tsuji, 1998) and hair conditioners but they are toxic to some microorganisms (Mulligan, 1998). Amphoteric surfactants are usually used as boosters to enhance detergency. Nonionic surfactants are the most popular, are used as emulsifiers, and also show strong detergency for oily dirt (Tsuji, 1998).

3.2.2 Critical Micelle Concentration (CMC)

Micelles are small surfactant aggregates composed of a number of surfactant molecules (Figure 3.4). Micelles are formed above a critical concentration of surfactant monomers known as critical micelle concentration (CMC) (Hommel and Ratledge, 1993). Efficient surfactants have a very low CMC (Mulligan and Gibbs, 1993).

Below CMC (monomers)



Above CMC (spherical micelles)

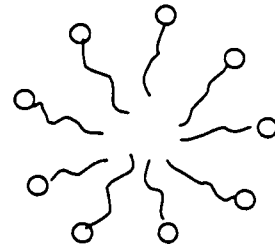


Figure 3.4 Surfactant Micellization

Single molecules of surfactants have limited solubility but micelles are very soluble. When the CMC is reached, higher surfactant concentrations do not decrease surface tension further, but surfactants must be present at concentrations higher than the CMC to form significant concentrations of micelles to have the greatest effect (Schramm, 2000). The CMC is different for every surfactant. The CMC is a function of the surfactant's structure, the temperature of the solution, electrolytes content, pH, and the concentration of the solutes. The average number of surfactants in a micelle is called the aggregation number (Harwell, 1992).

The CMC value is very important since a surfactant should be at levels at least slightly higher than the CMC to be able to lower the interfacial tension and form micelles. For oil-water systems, CMC is defined by plotting interfacial tension vs. surfactant concentration. At the critical micelle concentration, abrupt changes occurs in physical properties of the solution and the general way of obtaining the CMC value is to plot some physiochemical properties versus the surfactant concentration. The break in the plot would define the CMC value (Figure 3.5).

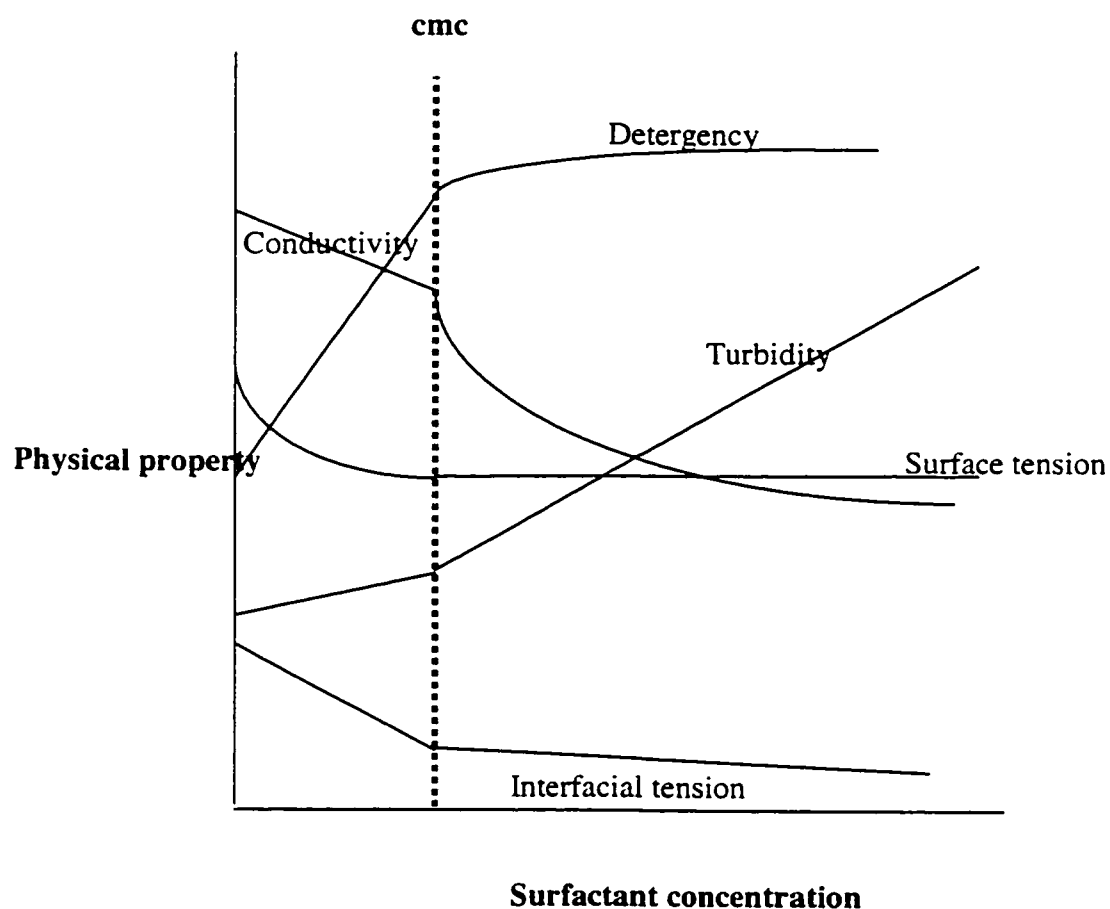


Figure 3.5 Some important manifestation of micelle formation. Abrupt changes in the physical properties of the solution indicates micelle formation (Preston 1948, Myers, 1992)

3.2.3 Areas of Applications

Surfactants are used as adhesives, flocculating, wetting, and foaming agents, demulsifies, detergency power, dispersants and penetrants in many industries and consumer products. No surfactant has all of the above mentioned abilities together.

Surfactants are useful in all the industries and products dealing with multiphase systems (Mulligan and Gibbs, 1993). They have a variety of applications in many industries such as petroleum, pharmaceutical, food, textiles, paper, leather, ore processing, also many consumer products such as: adhesives, cosmetics, paints, soaps, shampoos, creams, and so much more (Myers, 1992) (Table 3.1). A new application of surfactants is in bioremediation of contaminated soils (Samson et al., 1990, Oberbremer et al., 1990). To further stimulate the biodegradation, nitrogen and phosphorus-rich nutrients can be applied to shorelines and soil to stimulate the growth of naturally occurring oil-degrading microorganisms.

Charge type, physiochemical properties (i.e. surface tension, critical micelle concentration, and HLB value); solubility, stability of the emulsion formed, and adsorption behavior are some of the selection criteria for different applications (Mulligan and Gibbs, 1993; Deasi and Desai, 1993). In oil spill dispersants, reduced toxicity is also a major consideration since we don't want to expose to marine environment to more toxicity rather than that of the dispersed oil so far. For application in arctic waters or waters with high salinities, surfactants that are resistance to low temperatures or extreme salinities should be used.

Table 3.1 Typical Characteristics for Surfactants for Various Applications.

Application	Characteristics
Detergency	Low CMC, good salt and pH stability, biodegradability, good foaming properties
Emulsification	Proper HLB, environmental and biological (safety) aspects for application
Foods	Biocompatibility, functionality, sensory perception
Lubrication	Chemical stability, absorption at surfaces
Mineral flotation	Proper adsorption characteristics on the ore(s) of interest, low costs
Petroleum recovery	Proper wetting of oil-bearing formations, microemulsification formation and solubilization properties, ease of emulsion breaking after recovery
Pharmaceutical	Biocompatibility, toxicity

(Myers, 1999)

3.3 Mechanism of Oil Dispersion by Surfactants

Dispersants are applied directly onto the oil slick. Solvents in dispersants help surfactants to mix with the oil and reach the oil-water interface where they can initiate dispersion. Surfactants molecules concentrate at the oil-water interface with their non-

polar (hydrophobic) portion in oil phase and the polar (hydrophilic) portion in water. Residing on the interface, surfactants would lower the interfacial tension therefore dispersing oil into water (Hommel and Ratledge, 1993) (Figure 3.6).

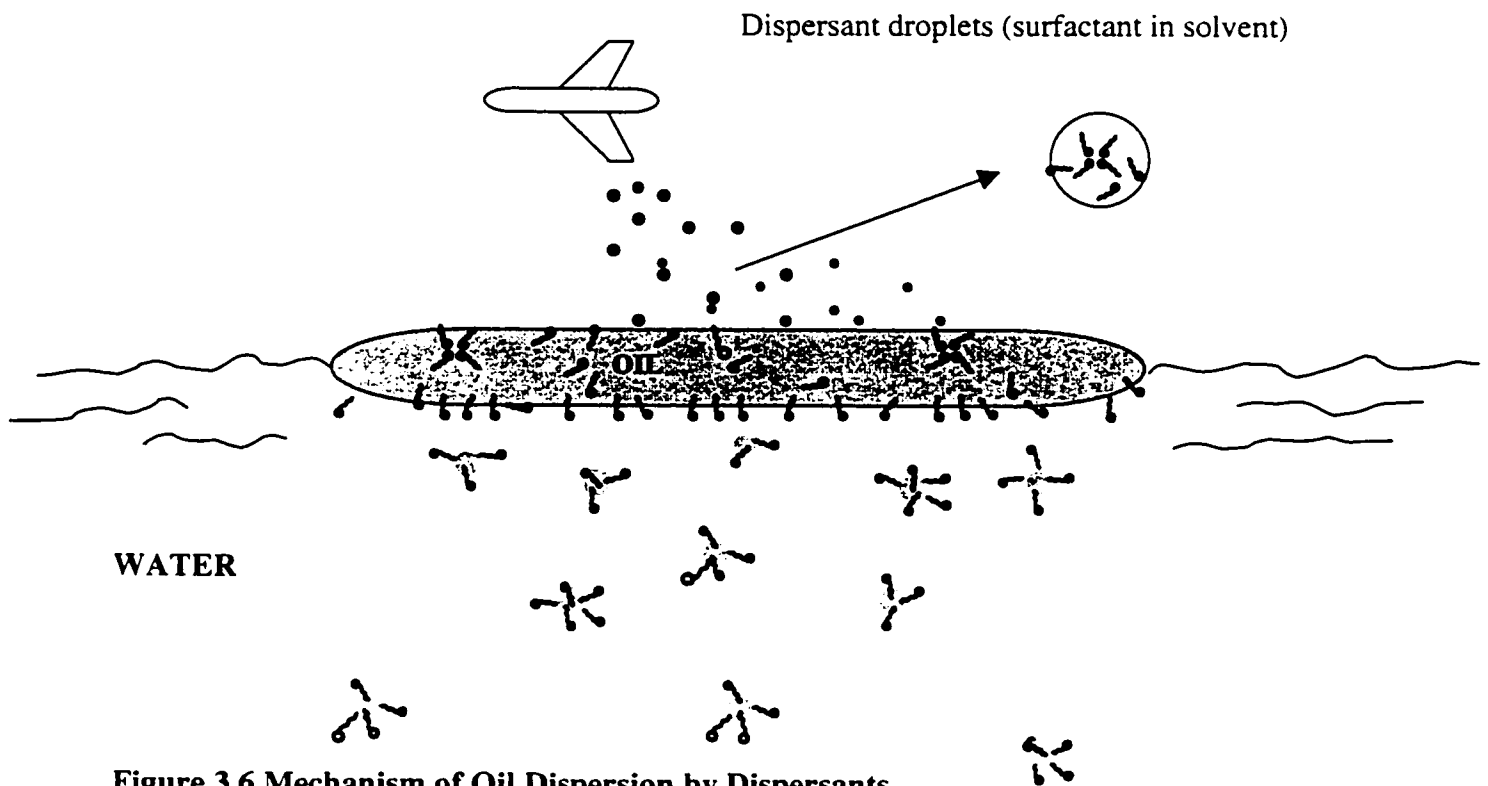


Figure 3.6 Mechanism of Oil Dispersion by Dispersants

Surfactants solubilize oil when they accommodate oil into their micelles (Hommel and Ratledge, 1993). Micelles form oriented monolayers at oil-water interfaces with their hydrophilic portion toward the water (Myers, 1992) (Figure 3.7). Surfactants actually pseudosolubilize the oil (Hommel and Ratledge, 1993)

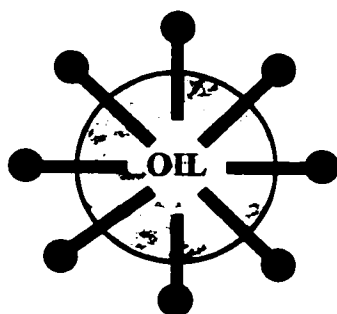


Figure 3.7 Illustration of how surfactants solubilize oil; accommodation of oil droplet into the surfactant micelle.

Dispersants also prevent formation of water-in-oil emulsion, known as chocolate mousse. The water content in the mousse makes it more viscous, and more difficult to break. A chocolate mousse is a stable emulsion which needs to be demulsified prior to oil dispersion. Asphaltenes, resins, waxes and paraffins act as natural emulsifiers that form and stabilize water-in-oil emulsions. Surfactants act as demulsifier and neutralize their effect. Surfactants would make the film around the oil droplet less viscous so facilitating their rupture and resulting in water droplet coalescence. Mechanical energy, providing by waves, can increase the collision rate of droplets (Schramm, 2000). Aged emulsions are more difficult to break because they become more and more stable, so less possible to break. Therefore, the sooner the dispersants are applied, the better they can perform.

3.4 Mechanism of Emulsion Stabilization by Surfactants

Surfactant molecules make a protective film layer around the oil droplet, which increases the surface viscosity of the droplet. Surface viscosity reduces the rate of rupture of the surface and prevents oil-oil droplets from union (Schramm, 2000).

Ionic surfactant molecules in micelles have an orientation with the ionic heads towards the aqueous phase. When two charged surfaces approach each other, their electric double layers overlap and increase the electrostatic repulsive forces. The created repulsive forces would stabilize the dispersed droplets (Schramm, 2000) (Figure 3.8).

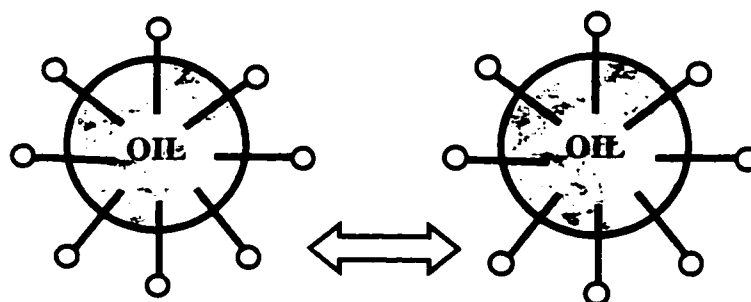


Figure 3.8 Mechanism of Emulsion Stabilization by Anionic Surfactant Molecules

In mixed surfactant mixtures of different HLB values, the stability of the emulsion is greatly enhanced. The presence of two surfactant species produces very low interfacial tensions and increases the effective adsorption of the combination. Adsorption of mixed surfactants on the oil-water interface form a complex at the interface and produce a strong interfacial film, which may not be easily ruptured and this stabilizes the emulsion better than either material alone (Myers, 1999) (Figure 3.9).

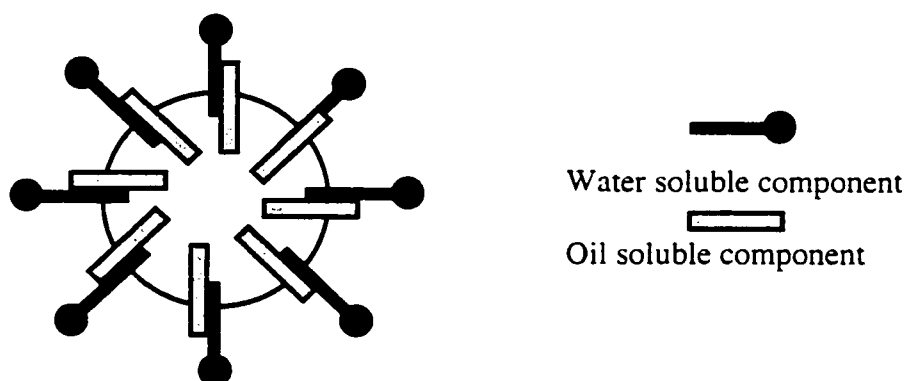


Figure 3.9 Mechanism of Emulsion Stabilization by Two Surfactants of different Solubilities in water (Reference: Myers, 1999)

3.5 Biosurfactants

Biosurfactants have the typical amphiphilic structure of a chemical surfactant. They are biologically produced by bacteria, yeast, and fungi (Desai and Desai, 1993). Biosurfactants are produced either extracellularly to emulsify the substrate, or as a part of the cell wall to facilitate the passage of the substrate (Mulligan and Gibbs, 1993). They have different structures but they all have the ability to emulsify oil-water mixtures (Hommel and Ratledge, 1993). They are mostly anionic or neutral and only a few are cationic (those containing amine functional groups) (Mulligan and Gibbs, 1993). Biosurfactants can be produced easily from readily available, renewable, and less expensive substrates such as sugars and vegetable oil, and waste (Mulligan and Gibbs, 1993).

The hydrophobic part of the biosurfactant molecule is either a long-chain fatty acid, hydroxy fatty acid, or α -alkyl- β -hydroxy fatty acid and the hydrophilic part can be a carbohydrate, phosphate, amino acid, cyclic peptide, carboxylic acid, alcohol, etc. (Mulligan and Gibbs, 1993). Major groups of biosurfactants are glycolipids, phospholipids, lipopeptides, fatty acids and neutral lipids (Biermann et al., 1987).

Biosurfactants have special advantages over the chemical surfactants such as biodegradability and biocompatibility, lower toxicity, effectiveness at high temperatures, pH, and salinity, low interfacial tension and critical micelle concentrations, and a broad range of structures for specific applications (Cooper, 1986). Their CMCs generally are between 1 to 200 mg/L (Lang, 1987).

Biosurfactants have detergency power, wetting ability, and foaming capacity but none of them has all together (Mulligan and Gibbs, 1993). They have many applications in different industries and products such as: food and beverages, cosmetics, building and construction, paint and protective coating, textiles, ink, pharmaceuticals, fire containment, leather processing, industrial cleaning, elastomers and plastics, water treatment, environmental remediation, and petroleum production and products (Jeneil Biosurfactant Co, 2001).

3.5.1 Biosurfactants in Oil Industry and Oil Pollution Control

Biosurfactants have specific properties for particular applications because microbes produce them during their growth on a special water-immiscible substrate. Biosurfactants are very effective in lowering the oil-water interfacial tension and oil viscosity and therefore can be used in the oil industry, in enhanced oil recovery and crude oil transportation (Hayes et al., 1986). They should be potential candidates for enhancing oil dispersion in oil spill applications since many biosurfactants are able to lower the interfacial tension between oil and brine to less than 0.01 mN/m (Finnery and Singer, 1985; Singer, 1985; Shennan and Levi, 1987). For oil removal purposes, IFT value of 2 is high and values of less than 0.001 mN/m are ideal (Wilson, 1990). Chemical surfactants are suitable for hydrocarbon mobilization but they are not actually as effective as biosurfactants in enhancing hydrocarbon biodegradation (Cooper, 1986).

3.5.2 Rhamnolipids

Rhamnolipids are composed of glycolipids. Rhamnolipid is an anionic surfactant. Their structure is demonstrated in (Figure 3.10). They are produced by certain species of *Pseudomonas* (Desai and Desai, 1993). Generally, rhamnolipids are a mixture of up to four different rhamnolipids.

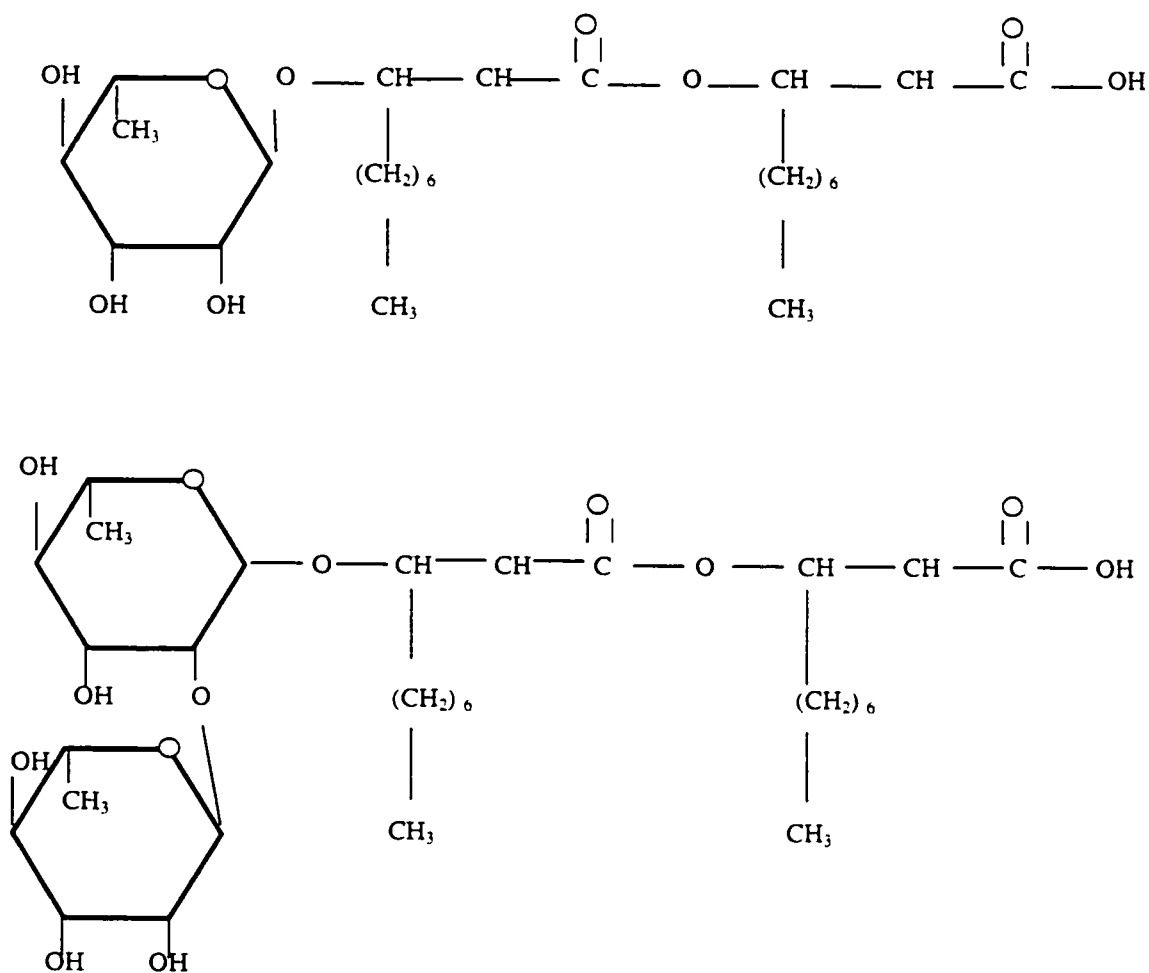


Figure 3.10 Structure of Rhamnolipids (Itoh et al., 1971)

Their emulsification properties for hydrocarbon-water mixtures, low interfacial tension (IFT) against oil and low CMC, have made them very useful in oil field applications and it is expected to be very effective in dispersing oil into water. They are effective in oil spill clean-up by enhancing bioremediation (Lang et al., 1986; Bernem, 1984). In many applications they are more effective than conventional surfactants in similar concentrations (Jenile Biosurfactant Co., 2001). Environmental applications include wastewater treatment, sludge treatment, and soil remediation to remove hydrocarbons and heavy metals (Jeneil Biosurfactant Co, 2000). Rhamnolipids have many other applications, as pesticides (Itoh et al., 1971; Sylдатk et al. 1985), concrete additives for higher strength and cement saving (Haferburg et al., 1988), and in enhanced oil recovery (Guerra-Santos, 1985; Sylдатk, 1984).

Depending on pH and salt concentration, pure rhamnolipids from *Pseudomonas spp.* can lower the interfacial tension against n-hexane to around 1 mN/m and the surface tension to 25-30 mN/m (Lang and Wangner, 1987; Itoh and Suzuki, 1972; Parra et al., 1989). Rhamnolipids have surface tensions of 29 mN/m and a CMC of 15 mg/L. Their IFT against oil is 0.5 (Mulligan and Gibbs, 1993).

A research study by Matsufuji, et al. (1997) showed *Pseudomonas aeruginosa*, grown on ethanol, produced a high amount of rhamnolipid. *Pseudomonas aeruginosa* uses water-soluble carbon sources, such as glucose or alcohols; to produce rhamnolipids to emulsify the water insoluble-carbon sources such as heavy oil compounds (Matsufuji, et al., 1997).

Sodium dodecyl sulphate (SDS) ($C_{12}H_{25}SO_4^-Na^+$) is an excellent anionic chemically synthesized surfactant. Its surface tension is 37 mN/m and CMC is 2023-2890 mg/L (Monmory-Hermosillo et al., 1994). Van Dyke et al., 1993, showed that sodium dodecyl sulfate (SDS) was less effective than the biosurfactants produced by *P. aeruginosa* UG2 in removing hydrocarbons. According to Deschenes et al. (1994), the rhamnolipids from the same strain could enhance the solubilization of 4-ring PAHs and significantly more 3-ring PAHs and in a bioslurry. The biosurfactants were five times more effective than SDS. Also, Burd and Ward (1996) found that the biosurfactants produced by *P. marginalis* could solubilize PAHs such as phenanthrene and enhance biodegradation.

CHAPTER FOUR

Experimental Materials and Methods

Introduction

In this chapter the material and the equipment set up that were used in this study will be described. Materials used include crude oil, saline solutions, Corexit 9500, biosurfactant JBR425, NaOH solution, ethanol, octanol, starch and cellulose. Saline, NaOH solutions, ethanol, and octanol were used as solvents to dilute JBR425. Starch and cellulose were used as additives to investigate if they can increase the stability of the dispersed oil. The stability of the emulsion was determined through a time study.

Effect of different solvents on the efficiency of JBR425 on dispersing oil was studied. The obtained formulation was also used to disperse two other types of oils: MX-50 and Mexican Sweet Crude. Also, effect of salinity and temperature was investigated and necessary modifications were made for applications at low temperatures and in fresh waters. The effectiveness of Corexit 9500 on dispersing oil was investigated and the results were compared.

4.1 Materials

4.1.1 Oil

The oil used in this study is Brut blend crude oil and was obtained from Shell Canada in Montreal. The effectiveness of JBR425 was also investigated on two other types of oil: MX-50 and Mexican sweet crude oil. They were both obtained from Petro Canada. Their technical information was obtained from the same company. Some characteristics of each of the crude oils used are in Table 4.1.

Table 4.1 Characteristics of the Oils

Characteristics	Brut	MX-50	Sweet crude
Origin	North Sea, UK	Mexico	Mexico
Density@15°C, kg/L	0.836	0.8956	N/A
Sulphur content, % m/m	0.35	N/A	Low
Wax content % m/m	6.3	N/A	N/A

4.1.2 Saline

Synthetic seawater with a salinity of 35‰ (or 3.5%) was prepared with kitchen seasalt and distilled water. The salinity is a measure of total dissolved salts in water and it is measured as grams of salt per kilogram of seawater denoted by “‰”. Generally seawater has salinities between 34‰ and 36‰ (Stowe, 1979).

The pH of the saline was adjusted to 7.7 by hydrochloric acid. pH of the saltwater before adjusting was around 10. pH of seawater is about 7.8. In warm temperatures, the pH of surface water is around 8.4 because warm temperatures and photosynthesis reduces the amount of dissolved CO₂ (Stowe, 1979).

4.1.3 Rhamnolipid (JBR425)

JBR425 is a 25% active ingredient (rhamnolipid) solution (Jeneil Biosurfactant Co., 2001). It was obtained from Jeneil Biosurfactant Co.

Table 4.2 Physical and Chemical Properties of JBR425

Type	Chemical Formula	M.W. (g/mol)	CMC (ppm)
Anionic	C ₂₆ H ₄₈ O ₉	504 ⁽¹⁾	60 ⁽²⁾

(1) Jeneil Bio. Surfactant. Co., 1999.

(2) Measured experimentally (Refer to section 4.3).

4.1.4 Solvents

Saline, NaOH solution, ethyl alcohol (HPLC Grade), and octanol were used as solvents to dilute JBR425. Some characteristics of ethanol and octanol are shown in Table (4.3). Ethyl alcohol and 1-octanol were purchased from Fisher Scientific.

The idea of NaOH as a solvent in oil spill dispersant originates from alkaline flooding in enhanced oil recovery (EOR) (PRI, 2001). Conventional methods of enhanced oil recovery are not able to recover the oil residual because of the high

viscosity of the crude oil (Hemond and Fechner-Levy, 2000). NaOH would react with the oil hydrocarbons and produce new surfactants (classic soap) on oil-water interface. These surfactants are anionic and can greatly decrease oil-water IFT (from 18 mN/m to 2 mN/m) and mobilize the oil. The combined effect of the surfactants and in situ produced surfactants can significantly reduce the interfacial tension (IFT) (Rudin and Wasan, 1991).

NaOH is also expected to stabilize oil-in-water emulsions. Surfactants containing *mono-valent* ions tend to stabilize oil-in-water emulsions while those containing polyvalent metal cations tend to stabilize water-in-oil emulsions (Payne and Philips, 1985). The reason is that each polyvalent metal cation coordinates with two surfactant molecules, with their polar group near the metal ion, and the hydrocarbon tails would adopt a V-shape orientation. With such orientation in a closed-packed interfacial layer, it would be easier for the surfactant molecules to accommodate in the oil phase (Schramm, 2000).

Table 4.3 Characteristics of Ethanol and 1-Octanol

CHARACTERISTICS	Ethanol	1-Octanol
Physical State & Appearance	Colorless liquid, clear	Colorless liquid, clear
Odor	Typical wood alcohol odor	Strong fresh orange or rose-like
LD50 (mg/kg mouse)	3450	1790
Solubility in water	Miscible	Immiscible
Density, g/cm ³ (Water = 1)	0.8074	0.834
Molecular formula	C ₂ H ₆ O	C ₈ H ₁₈ O
Molecular weight, g/mol	41	130

4.1.5 Additives

Two polymeric additives, kitchen pure cornstarch and microcrystalline cellulose powder were used as natural polymeric additives to enhance the emulsion stability. The starch was obtained from grocery shop and cellulose from Aldrich Chemical Company, Inc.

4.1.6 Corexit 9500

Corexit 9500 is a commercial dispersant and was obtained from OHMSETT Co., New Jersey, US. Corexit 9500 is a high performance, biodegradable oil spill dispersant. It is effective on many types of oils. It is either applied in a neat form or diluted with seawater to 5 to 10 percent. The performance of Corexit 9500 may be degraded if applied diluted. It should be applied as droplets, not fogged or atomized (EPA, 2001).

A dispersant to oil ratio of 1:50 to 1:10 is recommended for Corexit 9500. This rate varies depending on the type of oil, degree of weathering, temperature, and thickness of the slick. Usually a DOR of 1:20 is recommended (Belore, 2001). In these experiments, it was used at a DOR of 1:20.

Exxon, the Corexit manufacturing company, does not disclose the ingredients of Corexit 9500 because they are trade secrets. All is known is that it contains 3 commercial surfactants, one of which is an emulsion breaker, and all are dissolved in a solvent (Cunneff, 2001).

4.2 Experimental Method

Before running final experiments, several experiments were done which led to the final protocol. The method and results of the preliminary experiments will be explained in addition to the final experiment results.

4.2.1 Preliminary Experiment- Swirling Funnel Test

Sweet crude was used for the preliminary experiments. The experiments were conducted at 25°C using 60 ml funnel, 50 ml saline, 0.1 ml oil, and 0.1 ml surfactant solution (DOR=1). Oil was gently added to the surface of the water and surfactant was applied drop-wise to the slick. The funnel then was placed on a New Brunswick Scientific shaker table (INNOVA model 2000) and set to 150 rpm for 90 minutes, followed by a 10 minutes settling time. 40 ml samples were taken.

Samples were analyzed by UV spectrometry and they were all corrected for their blanks. Dispersant blanks were made using 0.1 ml surfactant in 50 ml saline. Controls were made to investigate naturally dispersed oil and were made by 0.1 ml oil in 50 ml saline. The method of UV analysis is presented in section 4.5.1.1.

Since the CMC of JBR425 was not known, the solutions were made at relatively high concentrations and the surfactant drops passed through the oil slick right after applying. No significant dispersion occurred. In order to eliminate the effect of drops, oil and surfactant solutions were premixed and then applied to the surface of the water. The

results of the premixed experiments are presented in section 5.1. Effect of different levels of surfactant, NaOH solution, methanol, and ethanol were investigated.

The main impediment for oil dispersion was the funnels. Funnels, due to their conical shape, produce an outward force while rotating. This force would impede oil dispersion. Therefore final experiments were conducted with cylindrical bottles.

4.2.2 Final Experiment- Swirling Bottle Test

Container: A 1 litre cylindrical open bottle (diameter = 10 cm) with an outlet valve at the bottom to take the samples (Figure 4.1).

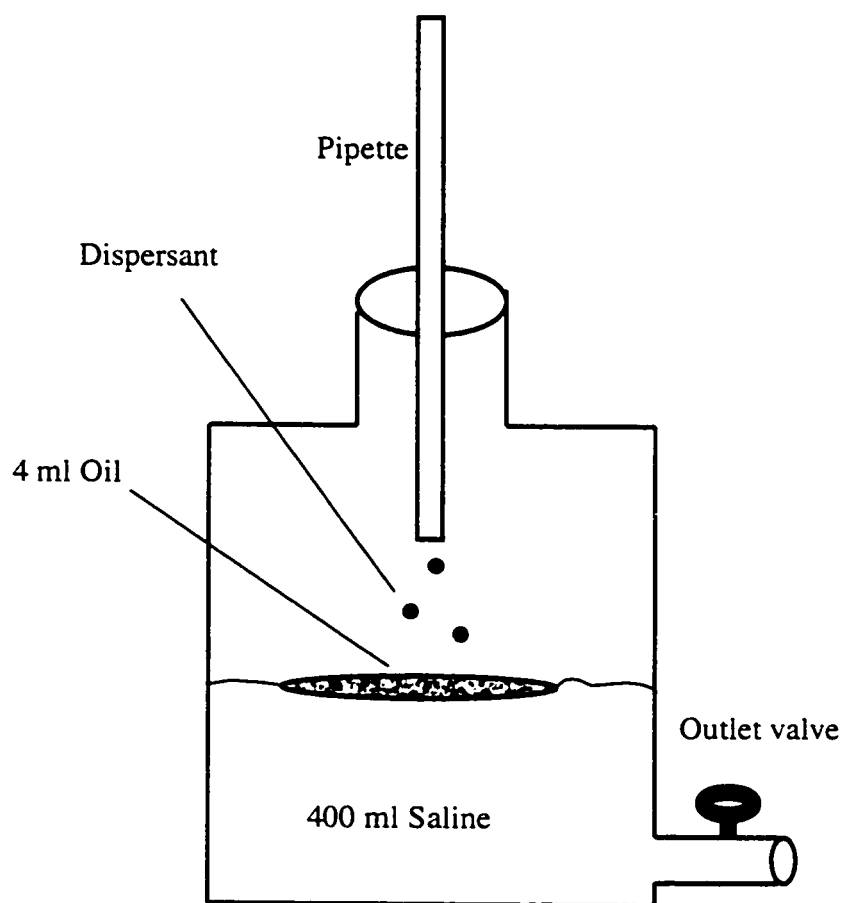


Figure 4.1 Schematic of the Bottle Test

400 ml saline was used and 4 ml oil was gently added to the surface of the water. The JBR425 solution was evenly added over the slick with a pipette. The bottle was placed on New Brunswick Scientific shaker table (INNOVA model 2000) to induce a swirling motion in the water content of the bottle. Shaker speed was 150 rpm and for a period of 10 minutes followed by a 1 to 2 minute settling time to let the bigger size droplets return to surface (Refer to section 4.2.2.1).

A 100 ml sample was taken, out of which 50 ml was set aside for further extraction by hexane. Each sample was extracted right after the experiment. Before each experiment, the pH of the saline was checked and adjusted to 7.7 with hydrochloric acid if it had dropped. All the experiments were triplicated. The equation to calculate the standard deviation is in Appendix C.

4.2.2.1 Time Study

The stability of the O/W emulsions is of great importance since unstable emulsions coalesce and reform the slick. To investigate the stability of the dispersed oil in water, samples were taken at different settling times of zero, 0.5 min, 1 min, 1.5 min, and 2 minutes.

Comparing the percentage dispersion of samples without settling time and after two minute settling indicates whether any solvent or additive could enhance the stability of the dispersed oil.

4.2.2.2 Effect of Solvents and Additives on JBR425 Efficiency

Four solvents (saline, NaOH, ethanol, and 1-octanol) were used to dilute JBR425, and two additives (cornstarch and cellulose) were used to increase the stability of JBR425. Every surfactant solution was prepared at least 15 minutes before the experiments. To stir the surfactants solutions, they were placed on a vortex shaker at high speed for 3 minutes. Also, they were shaken right before the application since rhamnolipid precipitated in saline. Solution of 2%, 4%, 8%, and 16% of JBR425 in saline was prepared and a volume of 2 ml of the 2% and 4% solution, and 0.5 ml of the 8% and 16% was applied to oil, i.e. DOR=1:2 and 1:8 respectively.

JBR425 (2%) with 4%, 2%, and 1% starch and 4%, 2%, and 1% cellulose in saline were made. In order to solubilize starch, before adding JBR425 the solution was heated at low temperature for a about a minute and stirred while heating. After it cooled down the surfactant was added. The cellulose did not become soluble in saline even by heating the solution.

NaOH were prepared at 0.05%, 0.2%, 0.5%, 1%, 1.5%, 2% concentrations and ethanol at 5%, 10%, 20%, 30%, 40%, 50%, and 60%. JBR425 (2%) was made with these solutions and applied at DOR=1:2. Octanol was used either pure or together with ethanol at different concentrations, from 10% to 80%. For all the experiments involving octanol, the solutions were made with 8% JBR425 and applied at DOR = 1:8.

4.2.2.3 Effect of Environmental Factors and Oil Type

Salinity of receiving waters and temperature has a great influence on the effectiveness of dispersants (Clayton, 1993). To investigate the effect of salinity, 4 ml oil and 400 ml distilled water were used and 0.5 ml JBR425 (8%) was added to the oil.

For the temperature study, 0.5 ml JBR425 (8%) was added to 4 ml oil and 400 ml saline at 10°C. For this study, saline, oil, and the bottle were placed in the incubator at 10 °C, 24 hours in advanced. The shaker was also placed in the incubator and the experiments were done at 10 °C.

The JBR425 formulation was also tried on dispersing two other types of oil, MX-50 and Mexican Sweet crude oil. The experiment was done with saline and at 25°C. The efficiency of the dispersants also depends on the type of the oil and is higher for lighter oils.

4.2.2.4 Foam-surfactant Application

In order to provide more surfactant-oil contact time, prevent surfactant from roll-off into the water, and cover a larger area, surfactant solution was delivered as foam to the oil slick. Droplets of dispersants that are big may easily wash off the slick and be lost to the surrounding water. Dispersant rapidly passes through thin and less viscous oils. Usually before applying dispersants to thin slicks, the slick is concentrated by deploying booms to sufficiently increase the thickness of the slick. If foam could be effective then there would be no need to concentrate thin layers before surfactant application.

Foams consist of thousands of tiny bubbles that can be generated by a liquid. Foams are very unstable because of their high specific surface areas. Liquid properties such as surface tension, viscosity, and ionic strength greatly affect the foam behavior. Foaming ability of liquids has strong relation with the surface activity of the solutes (Vardar, 1998). Surface activity of a solute is the ability of solutes molecules to transfer from the bulk phase to the surface (Thomas et al, 1977).

To generate foam, the surfactant solution and air should flow simultaneously through a porous media (Figure 4.2). JBR425 (2%) was used to make foam. Foam was made at three different air pressures, 34.5 kPa, 68.95 kPa, and 103.4 kPa (5, 10, and 15 psi, respectively) and at an intermediate flow rate of 45 on scale, which is equal to 40 ml/min (Appendix A).

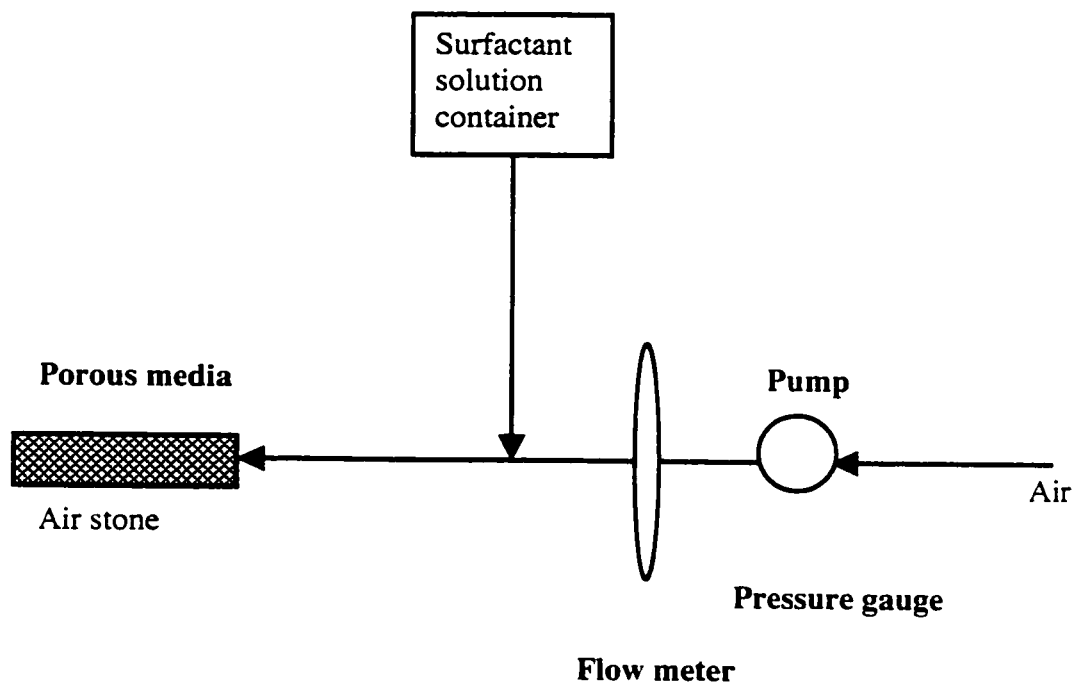


Figure 4.2 Schematic of the Setup to Generate Foam

4.2.2.5 Efficiency of Corexit 9500

The capability of Corexit 9500 was also investigated for salinity, temperature, and oil type. It is not really appropriate to compare the efficiency of Corexit with the JBR425 because Corexit 9500 contains three surfactants. In this study a DOR of 1:20 was chosen since this is the ratio usually used in real applications (Belore, 2001). 0.2 ml Corexit was applied drop-wise to 4 ml oil.

4.3 Critical Micelle Concentration (CMC) Measurement

To measure the CMC, a FISHER SCIENTIFIC Surface Tensiometer (model 21) was used. The CMC value for JBR425 in saline 35 ‰ and at 25°C, was 60 ppm (Table 4.4 and Figure 4.3).

Table 4.4 CMC Value of JBR425 in Saline

pH	Temperature	Salinity	CMC
7.7	25 °C	35 ‰	60 ppm

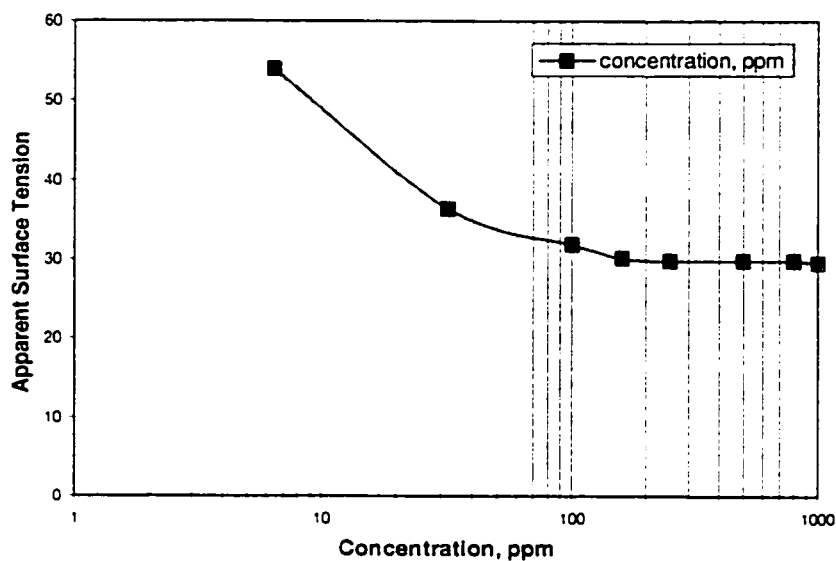


Figure 4.3 JBR425 in Saline, Surface Tension vs. JBR425 Concentration

4.4 Sampling and Extraction Procedure

Liquid-liquid extractions of samples were performed using hexane because rhamnolipids are not soluble in the hexane. Three extractions, using 25 ml of solvent each, were performed, with the final combined extracts adjusted to 100 ml. The extracts were filtered by WHATMAN # 40 filter paper before adjusting the volume. The extracted samples transferred to 45 ml glass vials and stored at 4°C until analysis to prevent possible evaporation of oil components.

4.5 Analyzing for Oil Content

4.5.1 UV Spectrophotometry

UV (Ultraviolet) Spectrophotometric method was used to quantitatively analyze the dispersed oil content. A PERKIN ELMER, Lambda UV/VIS spectrophotometer (model: 40) was used.

4.5.1.1. Method of Water Sample Analyzing by UV, Preliminary Experiment

As a screening test, samples from the preliminary experiments were analyzed by UV/VIS spectrophotometry without extraction. They were scanned under the following method:

SLIT	2.0 nm
LAMP	UV+VIS
ORDINATE MODE	A
WAVE. MAX	500 nm
WAVE MINIMUM	190 nm
SPEED	960 nm/min
CYCLE TIME	0.1 min
ORD. MAX	1.00 A
THRESHOLD	0.01 A

Comparing the scans of the naturally dispersed and chemically dispersed oil, indicates the range of absorption of light and heavy oil compounds, since the heavier oil fraction cannot be dispersed naturally (Appendix B, Figure (a). UV absorbance at 204 nm

and 260 nm were selected and corrected for the absorbance of the blank (Appendix B, Figure (b)).

4.5.1.2 Range of UV Light Absorbency of Different Oil Fractions

To determine the range of absorbency of different fractions of the sweet crude oil, UV/VIS spectrophotometry was performed on oil dissolved in hexane. Four samples of the oil were kept at different temperatures for 30 minutes and the scans defined the peaks of the volatile, semi volatile, and heavy components. Boiling points of light oil fractions are below 200°C (Lang and Wagner, 1993).

First, 0.0225 g oil was weighed and dissolved in 100 ml hexane (i.e. 225 ppm), and then it was scanned for the whole range of 190 nm to 500 nm, with the method mentioned in Section 4.5.1.1. Since its concentration was too high, it was twelve times diluted to about 20 ppm and then it was scanned. This scan showed the absorbency of the whole oil fractions.

Then to determine the peaks of the volatile, semi-volatile, and non-volatile fractions, three scans were done on weathered samples at 25°C, 100°C and 200 °C. Each sample was weighed before and after being weathered and the weight of the remaining oil was determined to calculate its concentration in hexane. All the samples were diluted to 20 ppm.

By overlapping and comparing the scans of heated crude oil at different temperatures, it appears that peak A is volatile, B is semi-volatile and C is non-volatile (Appendix B, Figure (C)). UV absorbance at 204 nm and 260 nm was selected comprising volatile and non-volatile fractions.

4.5.1.3 Preparation of Standard Extracts and Calibration Curves

Standard extracts are necessary to create the calibration curves. Calibration curves are required for quantitating dispersed oil in samples. For each single experiment, a calibration curve was generated.

Standard extracts were developed by 0.5 ml oil, 50 ml saline, and surfactant was added at 1:8 the amount used in the relevant experiment, i.e. 0.25 ml for JBR425 (2%), 0.06 ml for JBR425 (8%), and 0.025 ml for Corexit 9500. Standard solutions were extracted with the same manner identical to a sample. A 0.5 ml volume of Brut weighed 0.3850 g. Therefore the concentration of the standard extract was 0.3850g Brut/ 100 ml hexane or 3850 ppm.

To generate each calibration curve, four dilutions of each standard extract were made. The first step to generate the calibration curve is to define a specific wavelength. Each standard extract and its blank extract were scanned over a wide range of UV+VIS, from 190 nm to 500 nm and a wavelength was chosen. For all the experiments a value of around 257 nm was selected, since this area represented a non-volatile region in the scans of distilled oil in hexane (Appendix B, Figure (C)).

4.5.3 Gas Chromatography (GC)

Samples were analyzed by GC to investigate if any component selectively disappears in the chromatographs, over time or from one dispersant to another. Samples were from Brut in hexane, Corexit 9500, JBR425 (2%) in saline, and [JBR425 (8%) + 60% ethanol + 32% octanol]. Samples taken without settling and after two minutes settling were analyzed. The chromatographs of the samples and their blanks are in Appendix C. A 3800 VARIAN Gas Chromatograph equipped with flame ionization detector (FID) was used. The column was bought from J & W SCIENTIFIC. The specifications of the GC column used was as follows:

Liquid Phase: DB-5

Film Thickness: 0.25 μm

Column Dimensions: 30m x 0.250 mm

Temperature Limits: -60 to 325 °C

Helium was used as carrier and make-up gas. The hexane peak was wide and the height of it was so big compared to the peaks from the oil. To narrow down the hexane peak in the chromatographs, split mode was tried as the first alternative. 90% of the sample in hexane was split to decrease the peak height for 10 times. Since the peaks from the oil were small relative to the peak of the hexane, by splitting 90% of the sample the oil peaks became so small to the range of noise. Therefore this method was not feasible to use. The splitless mode with a pressure pulse at the beginning was the second trial

method. The hexane peak became better and sharper and the separation improved. The splitless mode with the following method was used:

Oven: 50 °C [2 min] to 300 °C at 10 °C/ min

Carrier gas: Helium, 1 ml/min

Detector: FID, 250 °C

Injection: 1 µl [extracts in hexane], splitless, direct injection

FID oven: 250 °C

CHAPTER FIVE

Results and Discussions

5.1 Results of the Preliminary Experiments

Effect of Different levels of JBR425 on Oil Dispersion- To investigate the effect of surfactant concentration, 0.1 ml oil was premixed with 0.1 ml surfactant solution at different concentrations. The dispersion results are shown in Figure (5.1). The results show the more surfactant applied to the oil, the more dispersion occurred.

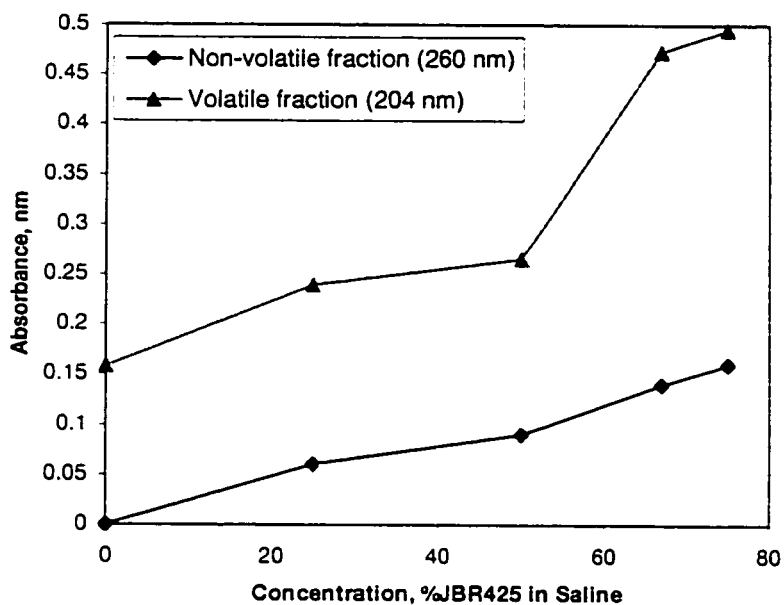


Figure 5.1 Effect of Concentration of JBR425 on Dispersing Light and Heavy Oil Fraction.

To investigate the effect of solvent salinity on the efficiency of JBR425 (2%), it was diluted with saline and distilled water. The results showed the efficiency is higher with distilled water because salinity affects micellization (Figure 5.2). Also, since the density of fresh water is less than saline, the JBR425 solution in saline is heavier and passes through the slick more quickly than the solution in fresh water, until at 75% JBR425 were the high surfactant concentration overcomes the effect of the salinity.

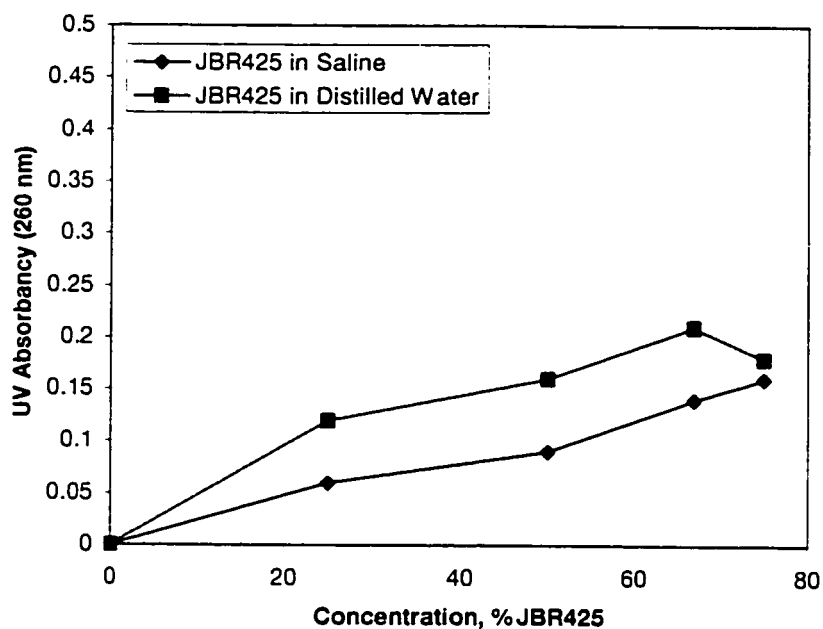


Figure 5.2 Effect of Salinity of Solvent on the Efficiency of JBR425 in Dispersing Oil.

Effect of NaOH on JBR425 Efficiency- To investigate the effect of alkaline, JBR425 was diluted with NaOH solutions. The results showed the higher %NaOH, the less effective became the efficiency of JBR425 in dispersing oil (Figure 5.3).

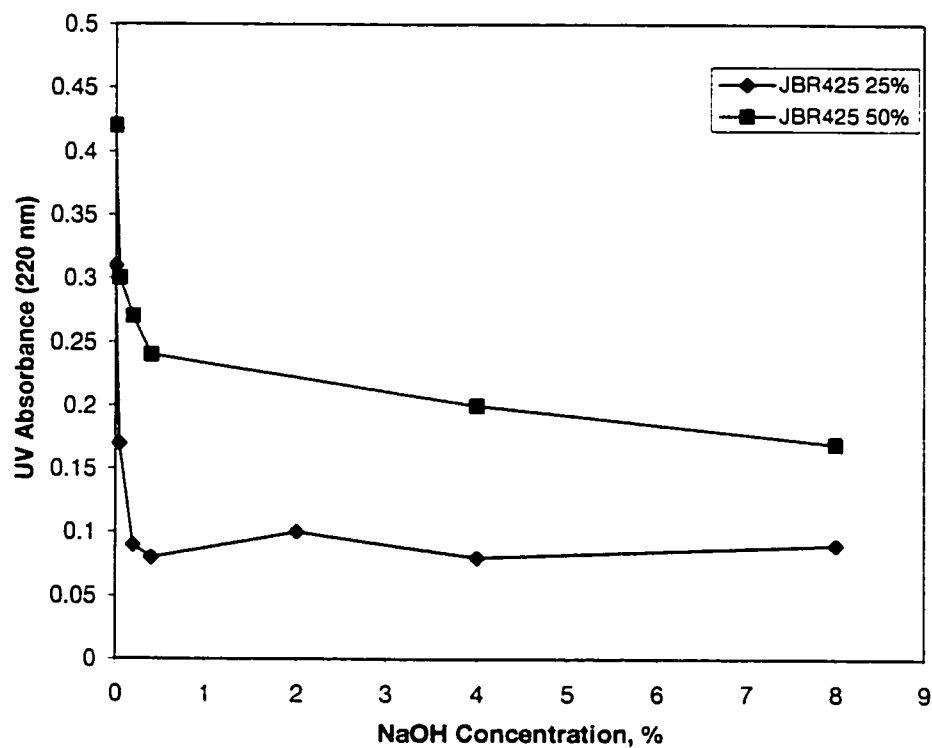


Figure 5.3 Effect of NaOH on the Efficiency of JBR425

Effect of Alcohols on JBR425 Efficiency- The effect of two alcohols, methanol and ethanol, as solvents were also investigated. The results showed that they have a negative effect on the efficiency of JBR425 (2%) (Figure 5.4).

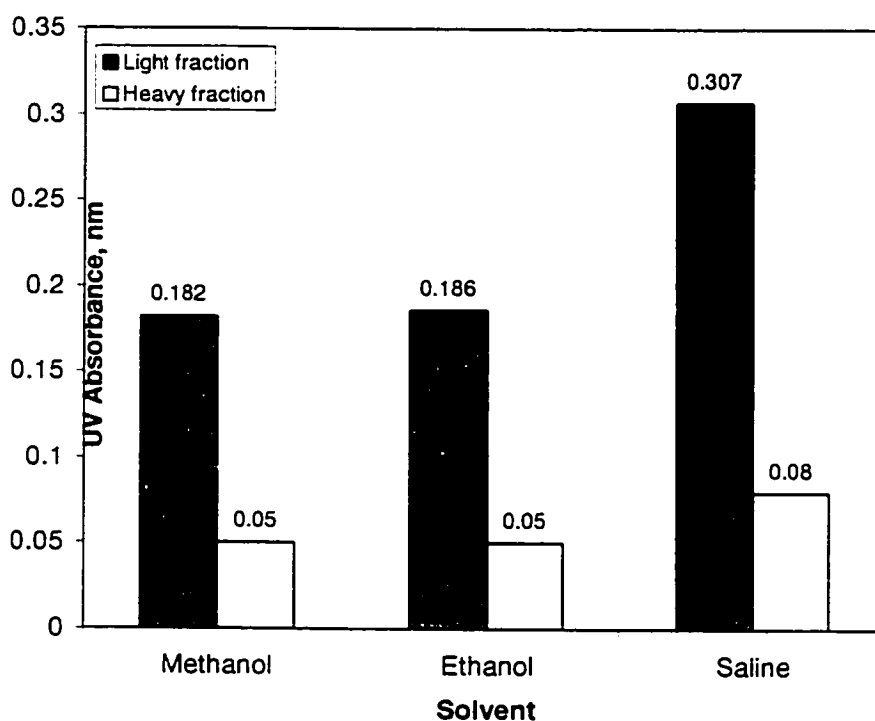


Figure 5.4 Effect of Methanol and Ethanol, in Comparison with Saline, on the Efficiency of JBR425.

5.2 Results of the Final Experiments, Swirling Bottle Test

5.2.1 Effect of Solvents

Effect of four different solvents on the efficiency of JBR425 was investigated. Yet it has to be remembered that a single surfactant cannot disperse oil and stabilize the emulsion like a mixture of surfactants do. Emulsions formed by a mixture of surfactants, with different water solubilities, are much more stable than emulsions formed with a single surfactant (Myers, 1999).

5.2.1.1 Saline

A 2%, 4%, 8%, and 16% solution of JBR425 in saline was used to investigate the efficiency of JBR425. The dispersion results are in Table (5-2). Higher levels of surfactant resulted in more dispersion because they form more micelles incorporating oil. But delivering the same amount of surfactant at higher concentrations (in order to decrease the DOR value) would decrease its efficiency because the surfactant solution becomes denser. Therefore, it readily passes through the slick without providing enough time for the surfactant to affect the oil-water interfacial tension. The efficiency of Corexit 9500 on dispersing oil is shown in Table 5.2.

JBR425 (2%) was selected to evaluate different solvents and additives since its ability to disperse oil was relatively high. The price was also a major factor in choosing this concentration (Refer to section 6.3).

Table 5.1 Percentage Oil Dispersion by JBR425 in Saline and Corexit 9500.
(SD = Standard Deviation, n=3)

	% Rhamnolipid	% Dispersion Without Settling Time	% Dispersion Settling Time: 2 min
JBR425 (2%) DOR=1:2	0.5	65.0 SD = ± 4.0	12.5 SD = ± 1.5
JBR425 (8%) DOR=1:8	2	61.0 SD = ± 3.3	11.5 SD = ± 1.3
JBR425 (4%) DOR=1:2	1	75.0 SD = ± 2.0	17.0 SD = ± 1.6
JBR425 (16%) DOR=1:8	4	68.5 SD = ± 4.0	15.0 SD = ± 1.8
Corexit 9500 DOR=1:20	0	84.0 SD = ± 4.2	45.0 SD = ± 3.7

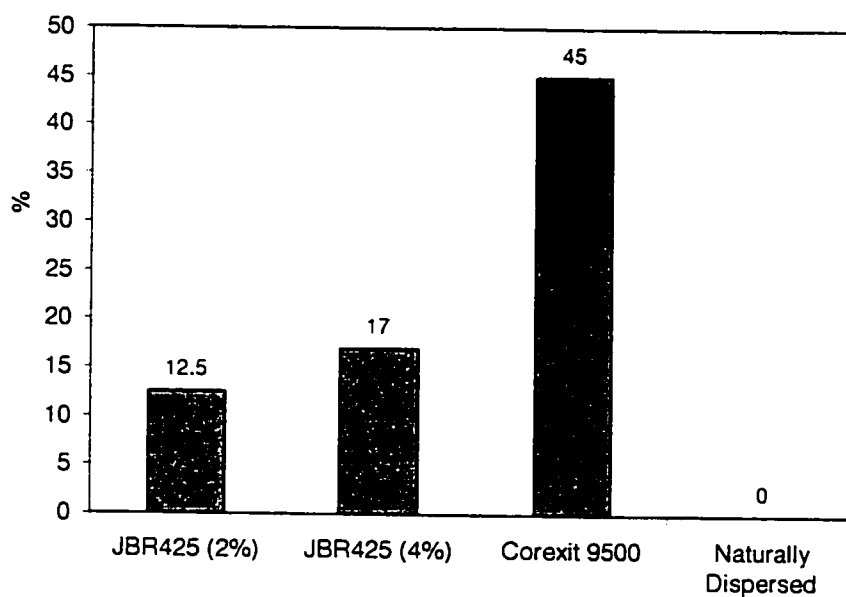


Figure 5.5 Comparison of the Efficiency of JBR425 (2%) and (4%) in Saline, and Corexit 9500 with Naturally Dispersed Oil (n=3). Settling time: 2 min

A time study on JBR425 (2%) and Corexit 9500 shows the stability of the dispersed oil (Figure 5.6, Table 5.2). This study shows that rhamnolipid, at such low concentration, is able to disperse oil but the emulsion is not much stable.

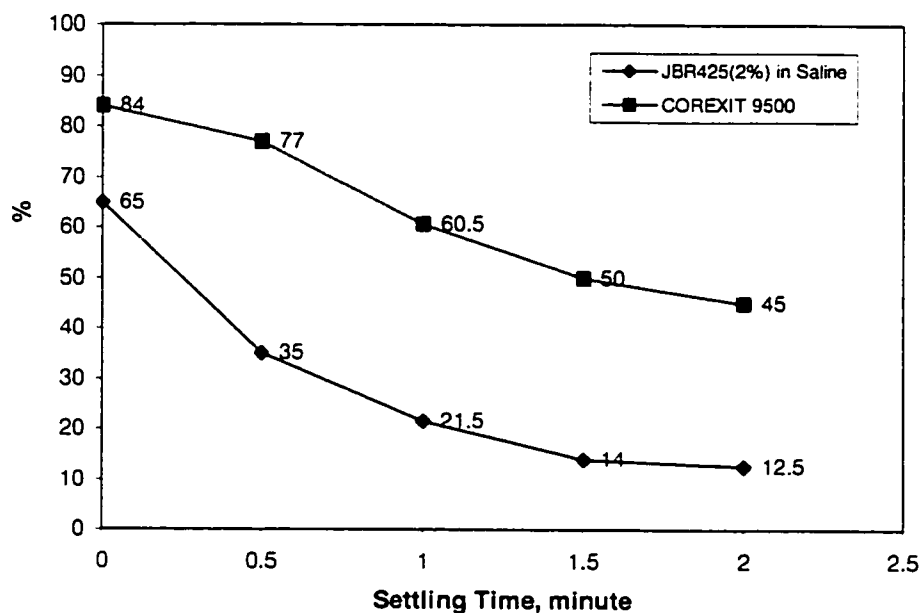


Figure 5.6 Time Study on JBR425 (2%) and Corexit 9500

Table 5.2 Time Study on JBR425 (2%) and Corexit 9500. Values are average, n=3.

Settling time (min)	JBR425 (2%)	Corexit 9500
0	65.0 SD = ± 4.0	84.0 SD = ± 4.2
0.5	35.0 SD = ± 2.5	77.0 SD = ± 2.8
1	21.5 SD = ± 1.8	60.5 SD = ± 3.1
1.5	14.0 SD = ± 1.3	50.0 SD = ± 2.5
2	12.5 SD = ± 1.5	45.0 SD = ± 3.7

5.2.1.2 NaOH Solutions

To evaluate the effect of NaOH solutions on the efficiency of JBR425, the study was done over time. The results indicate that NaOH did not increase the efficiency of JBR425, neither in terms of dispersion nor emulsion stabilization (Figure 5.7, Table 5.3). Because rhamnolipids become ionized at high pHs and react with NaOH, therefore they become even more water soluble and exhibit less tendency for oil phase. They may also leave the oil and enter into the water; therefore the emulsion is less stable.

Dropping the pH of saline from 7.7 to 6.2 in JBR425 (2%) in saline, indicates that the rhamnolipids are slightly acidic due to their carboxylic functions. Also, comparison of the pHs of NaOH solutions before and after adding JBR425, shows rhamnolipids have neutralized the alkaline (Table 5.4). JBR425 does not precipitate in alkaline solutions because rhamnolipids become ionized.

Table 5.3 Effect of Rhamnolipids on pH of Alkaline Solutions.

% NaOH	pH JBR425 (2%) in NaOH	pH NaOH Solution
0.05	11.1	11.9
0.2	12.2	12.5
0.5	12.3	12.6
1.0	12.7	12.8
2.0	13.4	13.3

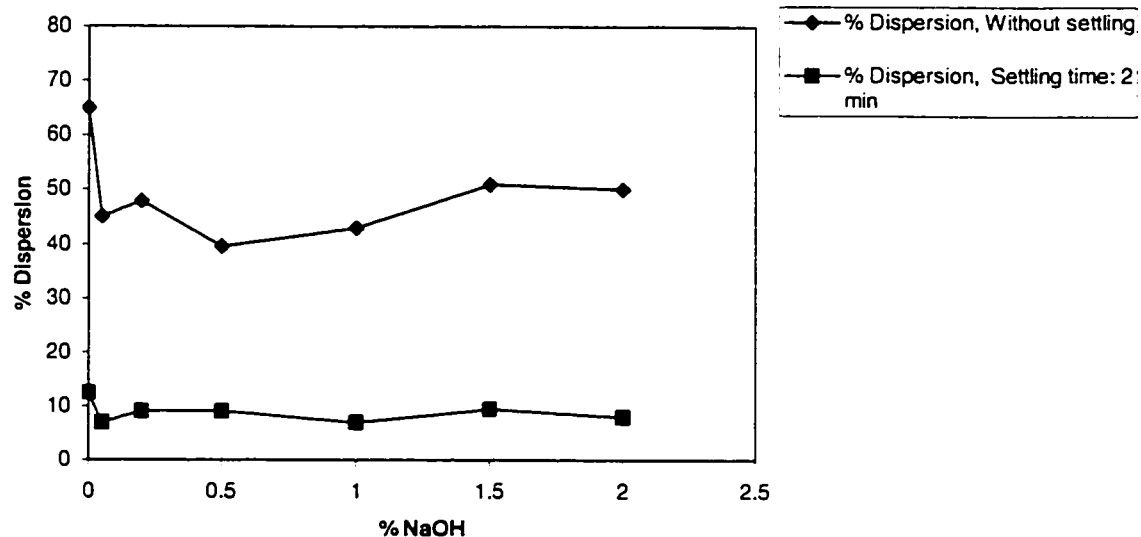


Figure 5.7 Effect of NaOH on the Efficiency of JBR425 (2%), n=3.

Table 5.4 Effect of NaOH on the Efficiency of JBR425

% NaOH	Sample pH	% Dispersion	% Dispersion	% Dispersion
		Without settling time	Settling time: 1 min	Settling time: 2 min
2.0	10.9	50.0 SD = ± 2.8	16.0 SD = ± 1.8	9.0 SD = ± 1.3
1.5	10.9	51.0 SD = ± 2	16.0 SD = ± 2.4	7.5 SD = ± 0.5
1.0	10.7	43.0 SD = ± 2.6	12.5 SD = ± 1.0	7.0 SD = ± 1.0
0.5	10.1	39.5 SD = ± 4.2	14.5 SD = ± 1.0	9.0 SD = ± 1.3
0.2	9.2	48.0 SD = ± 6.8	15.0 SD = ± 2.6	9.0 SD = ± 1.0
0.05	7.7	45.0 SD = ± 1.8	12.0 SD = ± 1.8	7.0 SD = ± 1.6
0.0	7.7	65.0 SD = ± 4	21.5 SD = ± 1.8	12.5 SD = ± 1.5

5.2.1.3 Ethanol

Alcohols are known as co-solvents and co-surfactants and are used in dispersants to increase the solubility of surfactants and decrease dispersant viscosity for different application systems (Fiocco and Lewis, 1999).

Ethanol did not increase the efficiency of JBR425. The results of the experiments are shown in Figure (5.8) and Table (5.5). JBR425 is soluble in ethanol and ethanol is highly miscible in water. Therefore, ethanol increases the tendency of the JBR425 solution towards water and provides less contact time between oil and surfactant. In the water, alcohols as co-surfactants may leave the oil droplet and reduce the stability of the dispersed oil.

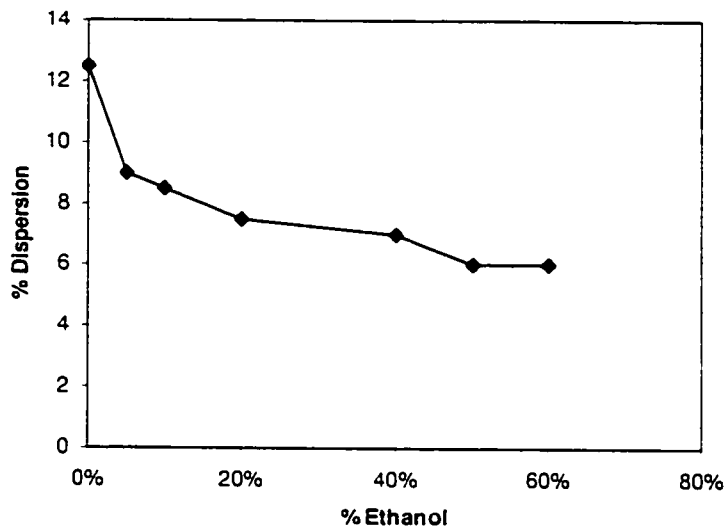


Figure 5.8 Effect of Ethanol on the Efficiency of JBR425 in Dispersing Oil
Settling time: 2 min

Table 5.5 Effect of Ethanol on the Efficiency of JBR425 (2%) in Saline, n=3.

% Ethanol	% Dispersion Without Settling	% Dispersion Settling Time: 2 min
0	65.0 SD = ± 4.0	12.5 SD = ± 1.5
5	57.5 SD = ± 3.3	9.0 SD = ± 0.5
10	56.0 SD = ± 2.0	8.5 SD = ± 1.3
20	52.5 SD = ± 3.8	7.5 SD = ± 1.3
40	45.0 SD = ± 2.5	7.0 SD = ± 0.3
50	44.0 SD = ± 2.8	6.0 SD = ± 0.9
60	41.0 SD = ± 3	6.0 SD = ± 0.7

5.2.1.4 Octanol

When applying all kinds of JBR425 solutions in saline, they just washed off and passed through the slick and entered into the water. The surfactant solution first broke the oil slick into big droplets and then into smaller droplets over time, while being on the shaker. The bottle test is comprised of a batch system but it is not the same in actual situations. If drops are not small enough at the beginning, there will be no chance for surfactants to break the oil into small droplets, since the dispersant has already been lost into the seawater and have no more contact with the dispersed oil.

Passing quickly through the slick would not provide enough time for dispersant to reduce oil-water interfacial tension. To keep the surfactant solution in the oil phase, there is a need for an oily solvent. Octanol is an oleophilic alcohol.

0.5 ml JBR425 (8%) in octanol was added to the slick, i.e. DOR=1:8. The drops did not pass through the slick and once the shaker was on, the oil dispersed into very tiny droplets. Its efficiency is compared with JBR425 (8%) in saline in Table (5.6) and Figure (5.10). Dispersion was just enhanced at the beginning.

Table 5.6 Effect of Octanol on the Efficiency of JBR425 (8%), n=3.

	% Dispersion Without settling	% Dispersion Settling time: 1 min	% Dispersion Settling time: 2 min
JBR425 (8%) in Octanol	70.0 SD = ± 2.1	20.5 SD = ± 1.3	9.0 SD = ± 0.3
JBR425 (8%) in Saline	61.0 SD = ± 3.3	22.0 SD = ± 2.1	11.5 SD = ± 1.3

5.2.1.5 Mixed Ethanol and Octanol

Neither ethanol nor octanol could increase dispersion. Since octanol tend to keep the JBR425 solution in the oil phase and ethanol tends to drag the solution into the water column, it was expected that a combination of both could make a balance between the hydrophobic and hydrophilic properties of the formulation. The mixture of JBR425 (8%), ethanol, and octanol is quite miscible in each other and makes an even homogenous phase. The results are shown in Figure (5.9) and Table (5.6). A 60% ethanol in formulation resulted in the best dispersion.

To investigate the effect of alcohols without surfactants, 0.5 ml of (60% ethanol + 40 % octanol) was added to oil. No dispersion occurred. The alcohols did not affect the interfacial tension.

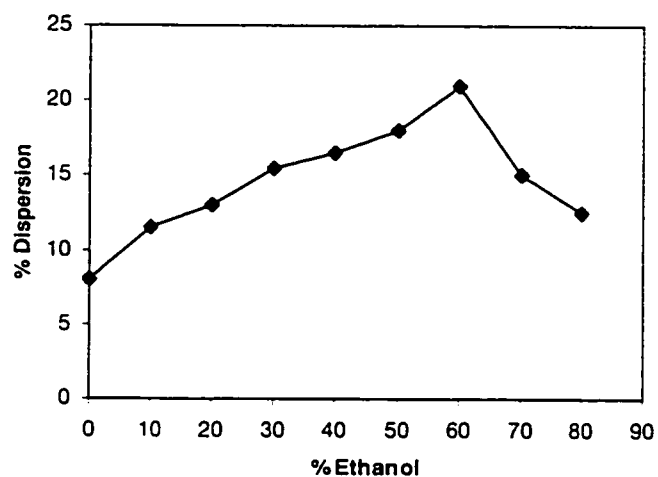


Figure 5.9 Effect of Ethanol on the Efficiency of JBR425 (8%) in Octanol

**Table 5.7 Effect of Ethanol on the Efficiency of JBR425 (8%) in Octanol, n=3.
Settling time: 2 min**

% Ethanol	% Dispersion
0	8.0 SD = ± 0.3
10	11.5 SD = ± 1.3
20	13.0 SD = ± 0.8
30	15.5 SD = ± 0.5
40	16.5 SD = ± 1.3
50	18.0 SD = ± 0.5
60	21.0 SD = ± 1.3
70	15.0 SD = ± 2.0
80	12.5 SD = ± 0.5

Table 5.8 Time Study on (JBR425 (8%) + 60% Ethanol + 32% Octanol), n=3.

	% Dispersion Without settling	% Dispersion Settling time: 1 min	% Dispersion Settling time: 2 min
JBR425 (8%) DOR=1:8	82.0 SD = ± 2	34.5 SD = ± 2.3	21.0 SD = ± 1.3

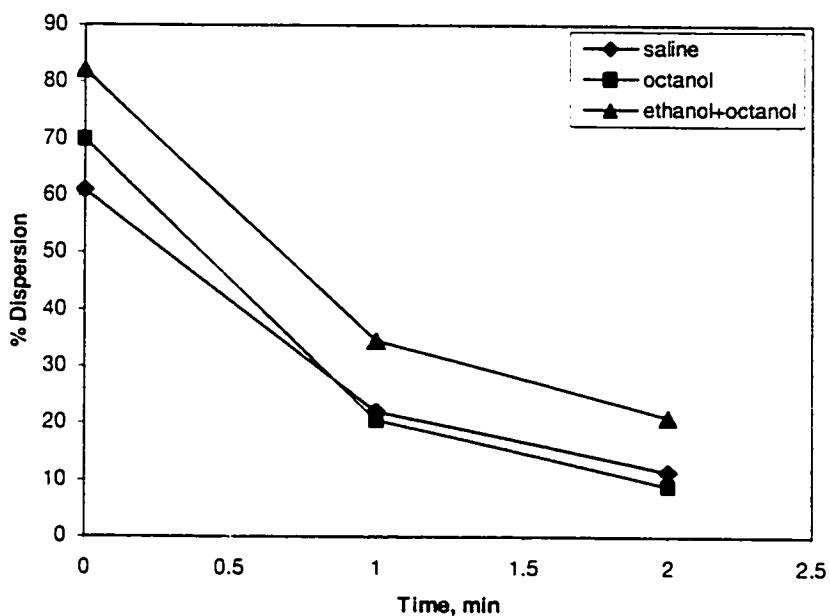


Figure 5.10 Comparing the Effect of Saline, Octanol, and (60% Ethanol + 32% Octanol) as Solvents, on the Efficiency of JBR425 (8%).

Comparing the GC chromatographs of JBR425 in saline, JBR425 in (ethanol + octanol), and Corexit 9500, at two minute settling and without settling, shows that after two minutes a fraction of the dispersed oil resurface or is lost to air (Appendix D). No specific peak or group of peaks disappeared after 2 minutes, and this indicates that rhamnolipid dissolved not only light compounds but also medium and heavy fraction.

5.3 Foam-surfactant Application

JBR425 (2%) in saline was used to make foam. Foam was made at three different air pressures, 34.5 kPa, 68.95 kPa, and 103.4 kPa and at an intermediate flow rate of 45 on scale, which is equal to 40 ml/min (Appendix A). At 98.95 kPa the quality of foam was good (Table 5.9). Corexit did not make any foam due to its oily solvent that impede formation of bubbles.

The results of dispersion are shown in Table (5.9). The foam was applied in two ways, from top and under the slick by submerging the delivery pipe under the slick. The results showed that foam could not improve oil dispersion. The bubbles were too weak to penetrate into the oil and were deflected by the oil. It could not pass through the slick to reach oil-water interface.

Table 5.9 Air Pressure and Foam Quality, JBR425 (2%) in Saline

Air Pressure (kPa)	Foam Quality
34.5	Small unstable bubbles
68.95	Good foam
103.4	Big unstable bubbles

Table 5.10 Surfactant-foam Efficiency. A comparison of delivering surfactant as foam and drop-wise, n=3.

Method of Application	% Dispersion Without Settling Time	% Dispersion Settling Time: 2 min
JBR425 (2%) as Foam Applied onto the Slick	38.5 SD = ± 6.9	6.0 SD = ± 1.6
JBR425 (2%) as Foam Applied under the Slick	43.0 SD = ± 5.4	7.5 SD = ± 1.3
JBR425 (2%) Drop-wise	65.0 SD = ± 4.0	12.5 SD = ± 1.5

5.4 Effect of Polymeric Additives

Neither starch nor cellulose enhanced the stability of the emulsion because they are not soluble in water (Table 5.11 and 5.12). Starch became soluble after heating the solution prior to adding JBR425. Still the efficiency of JBR425 was not enhanced. The cellulose did not become soluble in saline even by heating the solution.

Table 5.11 Effect of Starch on the Efficiency of JBR425 (2%) in Saline, n=3.
Settling time: 2 min

% Starch	% Dispersion
4	10 SD = ± 0.8
2	12 SD = ± 2.2
1	13 SD = ± 0.9
0	12.5 SD = ± 1.5

Table 5.12 Effect of Cellulose on the Efficiency of JBR425 (2%) in Saline, n=3.
Settling time: 2 min

% Cellulose	% Dispersion
4	10 SD = ± 1.6
2	10.5 SD = ± 1.3
1	12 SD = ± 1.3
0	12.5 SD = ± 1.5

Table 5.13 Effect of Solubilized Starch on the Efficiency of JBR425 (2%) in Saline, n=3. Settling time: 2 min

% Starch	% Dispersion Starch	% Dispersion Soluble Starch
1	13.0 SD = ± 0.9	12.0 SD = ± 1.0
2	12.0 SD = ± 2.2	14.5 SD = ± 1.5
4	10.0 SD = ± 0.8	14.0 SD = ± 1.3

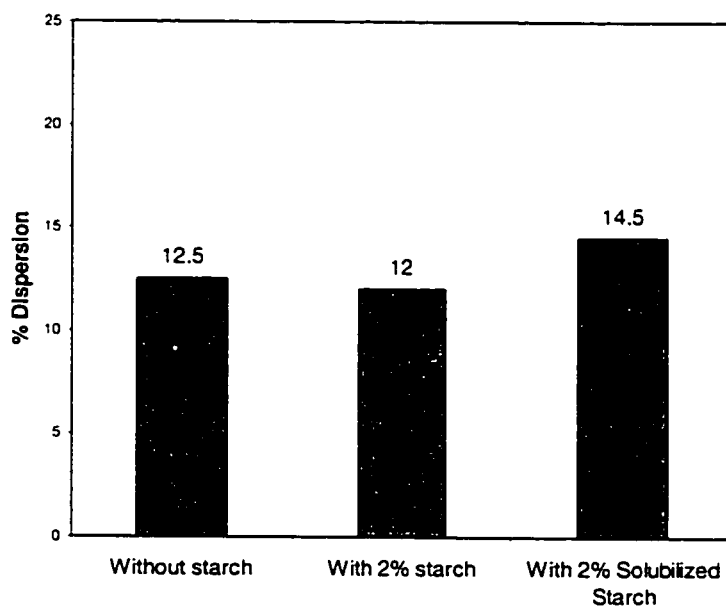


Figure 5.11 Effect of 2% Starch on the Efficiency of JBR425 (2%) in Saline. Settling time: 2 min

A solution of JBR425 (2%) with starch was applied as foam to investigate if the strength of bubbles improved. The dispersion was not enhanced (Table 5.13).

Table 5.14 Effect of Starch on the Efficiency of Foam-surfactant.

Settling time: 2 min

Foam-surfactant	% Dispersion
JBR425 (2%) + 2% starch	6.0 SD = ± 1.2
JBR425 (2%) Without Starch	6.0 SD = ± 1.6

Starch was also used in [(JBR425 (8%) + 60% ethanol) in octanol]. The stability of the emulsion was not improved (Table 5-14). Starch is not soluble in either of the alcohols which deteriorates the efficiency of the solution.

Table 5.15 Effect of Starch on the Stability of Dispersed oil with (JBR425 (8%) + 60% ethanol + 32% Octanol). Settling time: 2 min

% Dispersion Without Starch	% Dispersion With 1% Starch	% Dispersion With 2% Starch	% Dispersion With 4% Starch
21.0 SD = ± 1.3	21.0 SD = ± 2.0	20.0 SD = ± 0.8	18.5 SD = ± 1.5

5.5 Effect of Salinity

Salinity of receiving waters greatly impacts dispersants effectiveness. The efficiency of (JBR425 (8%) + 60% ethanol) in octanol dropped dramatically from 21% in saline to 8.5 in fresh water (Table 5.16). Efficiency of Corexit 9500 on dispersing oil into fresh water also dropped significantly (Table 5.16).

Salinity slightly prevents migration of the dispersants into the water phase. It increases water density, therefore keeps the dispersant afloat in the oil phase to influence the oil-water interfacial tension. Salinity may also affect the critical micelle concentration and the solubility of dispersants by altering the HLB values of its surfactants (Clayton et al., 1993).

In order to account for the effect of salinity, less ethanol and more octanol could decrease the tendency of the solution towards water. The dispersion results are in Figure (5.12) and Table (5.17). 40% ethanol in the formulation was the most effective percentage in dispersing oil into fresh water.

Table 5.16 Efficiency of Corexit 9500 and (JBR425 (8%) + 60% Ethanol + 32% Octanol) in Fresh Water, n=3. Settling time: 2 min

	% Dispersion Saline 35‰	% Dispersion Fresh water
JBR425 (8%) + 60% ethanol + 32% octanol	21.0 SD = ± 1.3	11.5 SD = 1.3
Corexit 9500	45.0 SD = ± 3.7	28.0 SD = ± 1.5

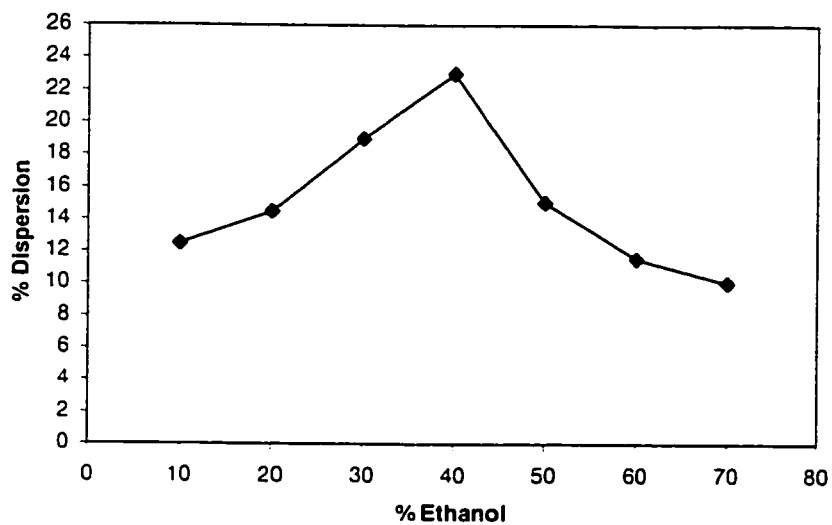


Figure 5.12 Effect of Ethanol on the Efficiency of JBR425 (8%) in Fresh Water

Table 5.17 Effect of Ethanol on the Efficiency of (JBR425 (8%) in Octanol) in Fresh Water, n=3.

% Ethanol	% Dispersion
70	10.0 SD = ± 1.4
60	11.5 SD = ± 1.3
50	15.0 SD = ± 1.3
40	23.0 SD = ± 1.9
30	19.0 SD = ± 1.3
20	14.5 SD = ± 1.0
10	12.5 SD = ± 0.3

5.6 Effect of Temperature

Temperature plays an important role on the effectiveness of dispersants. It affects viscosity and pour point of oil and dispersant and also the solubility of the surfactants (Clayton et al., 1993). Higher viscosities increases roll-off impacts.

The effectiveness of [(JBR425 (8%) + 60% ethanol) in octanol] dropped dramatically to 9%. Higher levels of ethanol resulted in better dispersion since the solution became less viscous (Table 5.17). The efficiency of Corexit 9500 also dropped to about half at 10°C. The results are shown in Table (5.18)

Table 5.18 Efficiency of Corexit 9500 and JBR425 (8%) at 10°C, n=3.

	% Dispersion at 25°C	% Dispersion at 10°C
JBR425 (8%) + 60% ethanol	21.0	8.0
+ 32% octanol	SD = ± 1.3	SD = ± 0.8
Corexit 9500	45.0	22.0
	SD = ± 3.7	SD = ± 3.8

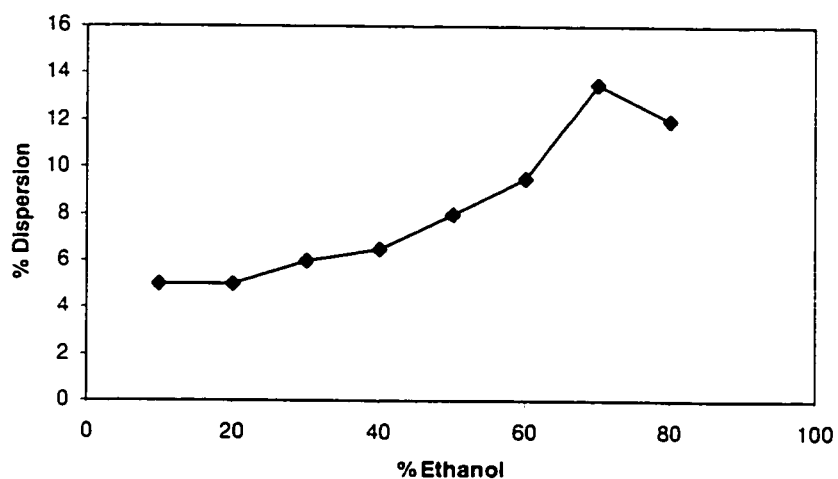


Figure 5.13 Effect of Ethanol on the Efficiency of JBR425 (8%) at 10°C.

Table 5.19 Effect of Ethanol on the Efficiency of JBR425 (8%) in Octanol at 10 °C, n=3. Settling time: 2 min

% Ethanol	% Dispersion
10	5.0 SD = ± 0.7
20	5.0 SD = ± 0.3
30	6.0 SD = ± 0.7
40	6.5 SD = ± 0.5
50	8.0 SD = ± 0.5
60	9.5 SD = ± 1.3
70	13.5 SD = ± 1.0
80	12.0 SD = ± 1.0

5.7 Effectiveness of JBR425 on Dispersing MX-50 and Mexican Sweet Crude Oil

Effectiveness of JBR425 (8%) formulation and Corexit 9500 was investigated on two other types of oils, MX-50 and Sweet Crude Oil. The results are in Table (5.19). Both dispersants show less effectiveness for MX-50 because it is heavier than Sweet crude and Brut crud oil.

Table 5.20 Effectiveness of Corexit 9500 and [(JBR425 (8%)+60% Ethanol+ 32% Octanol] on Dispersing MX-50 and Mexican Sweet Crud Oil, n=3.

Settling time: 2 min

Type of Oil	% Dispersion by JBR425(8%)	% Dispersion by Corexit 9500
MX-50	14.0 SD = ± 0.9	36.0 SD = ± 2.4
Sweet Crude	19.5 SD = ± 0.9	51.0 SD = ± 2.6
Brut Crude	21.0 SD = ± 1.5	45.0 SD = ± 3.7

5.8 Economic Study

The chances of oil spillage will never diminish and a need for a more effective, environmentally friendly, and less expensive response action is high. Dispersants are one of the practical response methods that is fast, easy, cheap, and more effective in comparison to mechanical recovery. A spill of over 10,000 tons is considered as a catastrophic spill and in Canada may happen every 15 years. Currently in Canada there are over 100 small oil spills, 10 moderate spills and at least one major spill that occur offshore each year. Also each year, there are more than 1,000 inland spills in Canada (Government Publication of Canada, 1994).

Biosurfactants are potential candidates for wide spread use in commercial oil spill dispersants since they not only clear concerns about toxicity, but also can be produced economically. They can be produced easily from readily available, renewable, and less expensive substrates such as sugars, vegetable oil, and waste (Mulligan and Gibbs, 1993). Process optimization and wide scale production may even lower the production prices. The higher the purity of biosurfactants, the more expensive is the product (Table 6.3). JBR215 is suitable for oil spill applications (Schniepp, 2001). At the same rate, a solution of JBR215 (14%) provides the same amount of rhamnolipid as JBR425 (8%) for a lower price. The prices for ethanol and octanol are in Table 6.5.

Table 6.4 Bulk Pricing of JBRs

Commercial product	Bulk Price, \$/gallon	Bulk Price, \$/ litre
Corexit 9500 (1)	15.5 CANS ~ 10.3US \$	3.4 CANS ~ 2.3 US \$
JBR215 (2)	22.0 US\$	4.84 US\$
JBR325 (3)	100.0 US\$	22.0 US\$
JBR425 (4)	134.0 US\$	29.5 US\$
JBR515 * (5)	351.0 US \$	77.2 US \$

(1) Camros Environment Co., Oak Ville, Ontario. 2001.

(2), (3), (4), and (5): Jeneil Biosurfactant Co. Saukville, Wisconsin. 2001.

* JBR515 is a highly purified product used by pharmaceutical, cosmetics, etc. industries (Schniepp. 2001)

Table 6.5 Bulk Price of Ethanol and Octanol

	US \$/ litre
Ethyl alcohol	0.46
1-octanol*	1.70

(Chemical Market Reporter, Dec. 2000. Volume 258, issue 25)

* The price of synthetic 1-octanol is 0.925\$/ lb = 2.04 \$/ kg (Chemical Market Reporter, 2000). The density of 1-octanol is 0.834 (based on the MSDS), therefore the price would be 1.70\$ /litre.

For the best formulation obtained for JBR425 (8%), the ethanol-to-octanol ratio (EOR) was 1.875. Therefore for JBR215 (14%), the same ratio should be maintained, i.e. 56% ethanol and 30% octanol. The price of JBR215 (14%) and JBR425 (8%) is in Table (6.8).

Table 6.6 Comparing the Prices of JBR215 (14%) and JBR425 (8%)

	US \$/ liter
14% JBR215 + 56% ethanol + 30% octanol	1.44
8% JBR425 + 60% ethanol + 32% octanol	3.18

Corexit 9500 is usually used at DOR= 1:20 and JBR425 (8%) was used at DOR = 1:8. Considering the application rates, the prices are in Table 6.7.

Table 6.7 Price of JBR and Corexit 9500 for Every Litre Spilled Oil.

	DOR	US \$/ litre spilled oil
JBR215 (14%) EOR=1.87	1:8	0.18
JBR425 (8%) EOR=1.87	1:8	0.40
Corexit 9500	1:20	0.11

CHAPTER SIX

Conclusions

Introduction

In this research, biosurfactant rhamnolipid showed promising capability on dispersing oil into the water but still need improvements in terms of stability of the dispersed oil in water. Biodispersants are better candidates than chemical dispersants for areas of high spillage where we cannot expose the marine environments to frequent chemical dispersants. Although for areas of frequent spills and shallow waters, the best method is to mechanically remove the oil from the surface of the water, if possible.

In this chapter the most important conclusions obtained from this investigation have been summarized. The most important factors affecting the efficiency of JBR425 will be discussed. Also, suggestions for future work, that may increase dispersion or stability of the O/W emulsion, will be mentioned.

6.1 Oil Dispersion Efficiency

This study showed the importance of solvents on the efficiency of surfactants. Solvents help the surfactants to penetrate through the oil and reach the oil-water interface. The surfactant molecules must attain a certain concentration at the oil-water interface and remain for a sufficient period of time to sufficiently reduce the interfacial surface tension.

Alkaline and ethanol (as solvents) did not increase the effectiveness of JBR425 compared to saline. JBR425 is water-soluble but does not mix with oil phase. It simply rolls off the oil and enters into surrounding water. Ethanol and octanol did not either increase the efficiency of JBR425 because one increased the tendency of the solution towards water and the other towards oil, respectively. A mixture of (60% ethanol + 32% octanol), i.e. an ethanol:octanol ratio of 1.875, could greatly improve the effectiveness of the JBR425 (8%) (Table 6.1). The efficiency of this formulation dropped dramatically in dispersing oil into fresh waters and at low temperatures. For such applications, the formulation was modified to 40% ethanol for fresh water and 70% for low temperature applications. With this formulation, the efficiency of the JBR425 (8%) for fresh water applications significantly increased (Table 6.2 and 6.3). Corexit 9500 also showed great sensitivity to salinity and temperature. There is more room to improve the efficiency of JBR425, in terms of dispersion and emulsion stabilization.

Table 6.1 Dispersion Results

	% Dispersion Without Settling	% Dispersion Settling time: 2 min
8% JBR425 in saline	61.0	11.5
8% JBR425 in octanol	56.0	9.0
8% JBR425 + 60% ethanol + 32% octanol	82.0	21.0
Corexit 9500	84.0	45.0

Table 6.2 Effect of Salinity of Receiving Water on Dispersant Efficiency. Settling time: 2min

	Saline 35‰	Fresh water
8% JBR425 + 60% ethanol + 32% ethanol	21.0%	11.5%
8% JBR425 + 40% ethanol + 32% ethanol	16.5%	23.0%
Corexit 9500	45.0%	28.0%

Salinity: 35‰, Temperature: 25°C

Table 6.3 Effect of Temperature on Dispersant Efficiency. Settling time: 2min

	25 °C	10°C
8% JBR425 + 60% ethanol + 32% octanol	21.0%	8.0%
8% JBR425 + 70% ethanol + 32% octanol	15.0%	13.5%
Corexit 9500	45.0%	22.0%

6.3 Future Work

- To investigate the efficiency of the formulation with more JBR425 and less alcohols, in order to decrease the dispersant-to-oil ratio, expose the marine environment to less alcohols and reduce the price (Table 6.8).

Table 6.8 Comparing the Prices of JBR215 (14%) and JBR215 (28%)

	DOR	US \$/ litre dispersant	US \$/ litre spilled oil
JBR215 (28%) + 47% ethanol + 25% octanol	1:16	2.0	0.12
14% JBR215 + 56% ethanol + 30% octanol	1:8	1.44	0.21
Corexit 9500	1:20	2.27	0.11

- To investigate the effect of sophorolipid, an oleophilic biosurfactant produced by *Candida bombicola* which is a yeast. For better oil dispersion and more stable emulsion, a mixture of at least two surfactants with different solubilities in water is necessary.

- To investigate whether Corexit 9500 or the obtained formulation of JBR425 with ethanol and octanol enhances biodegradation.
- To enhance biodegradation of the dispersed oil through addition of nutrients in the dispersants like nitrogen and phosphorous which stimulate growth of the micro-organisms concerned.
- To use other emulsion stabilizers that are soluble in ethanol.
- To develop mathematical models.
- To perform experiments at larger scale.

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Appendix A

Calibration table for the flowmeter

Flowmeter

Calibration Data

Scale Readings	Flow (ml/min)
5	3.6
10	6.5
15	9.5
20	13.5
25	17.8
30	22.6
35	27.1
40	33.2
45	40.1
50	48.1
55	57.1
60	65
65	72.3

Appendix B

UV scans of the Sweet crude oil

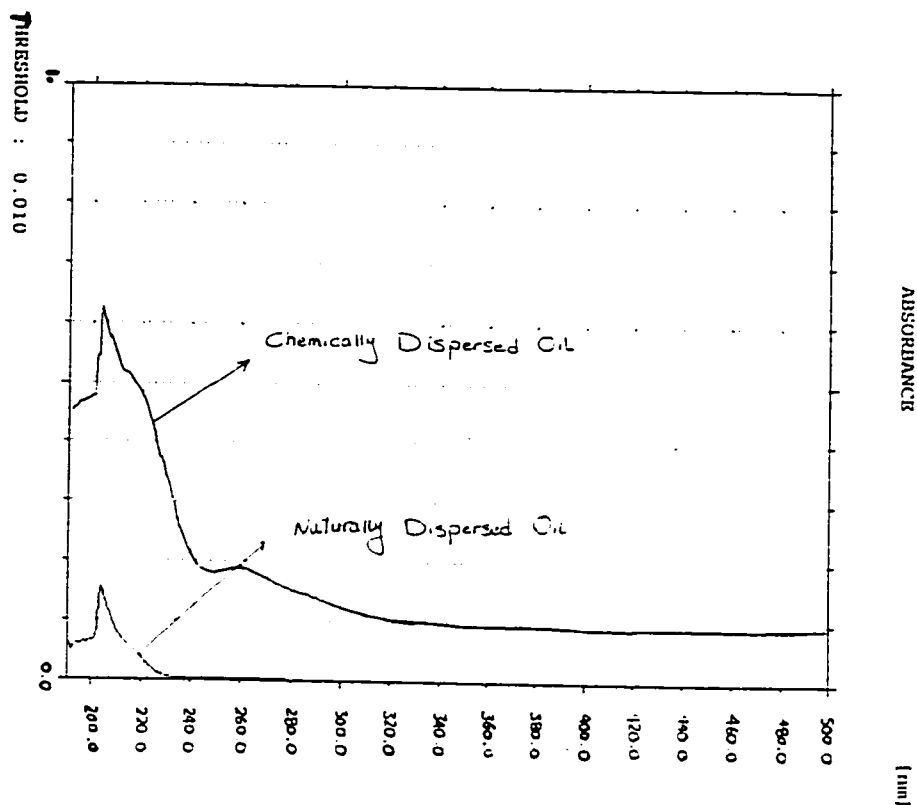


Figure (a) - Comparing the scans of chemically and naturally dispersed oil.

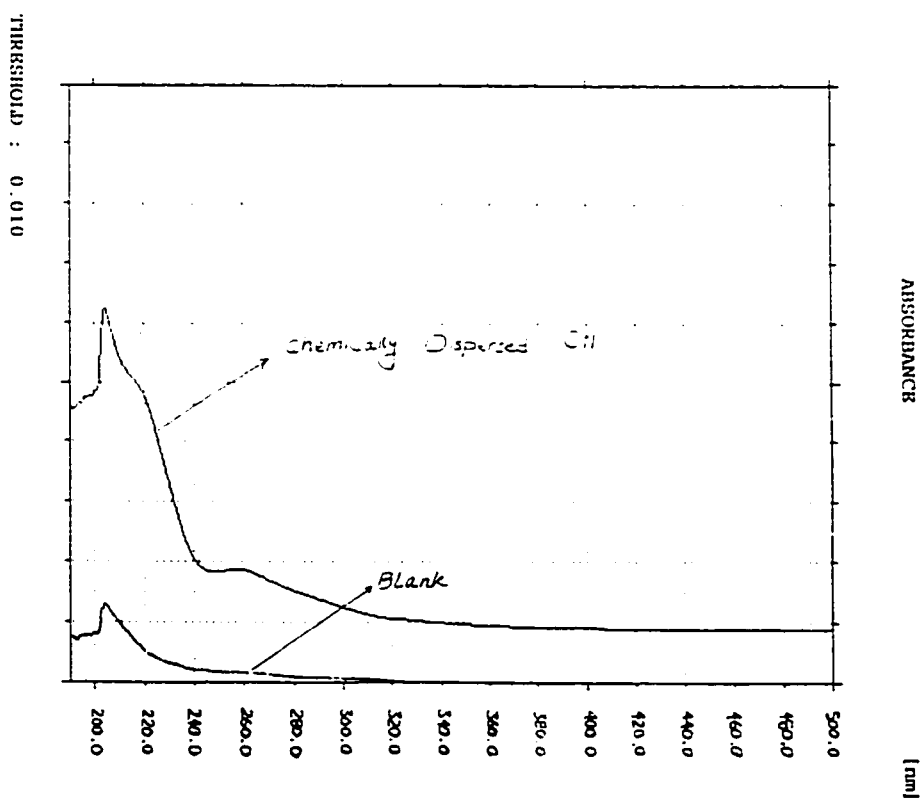
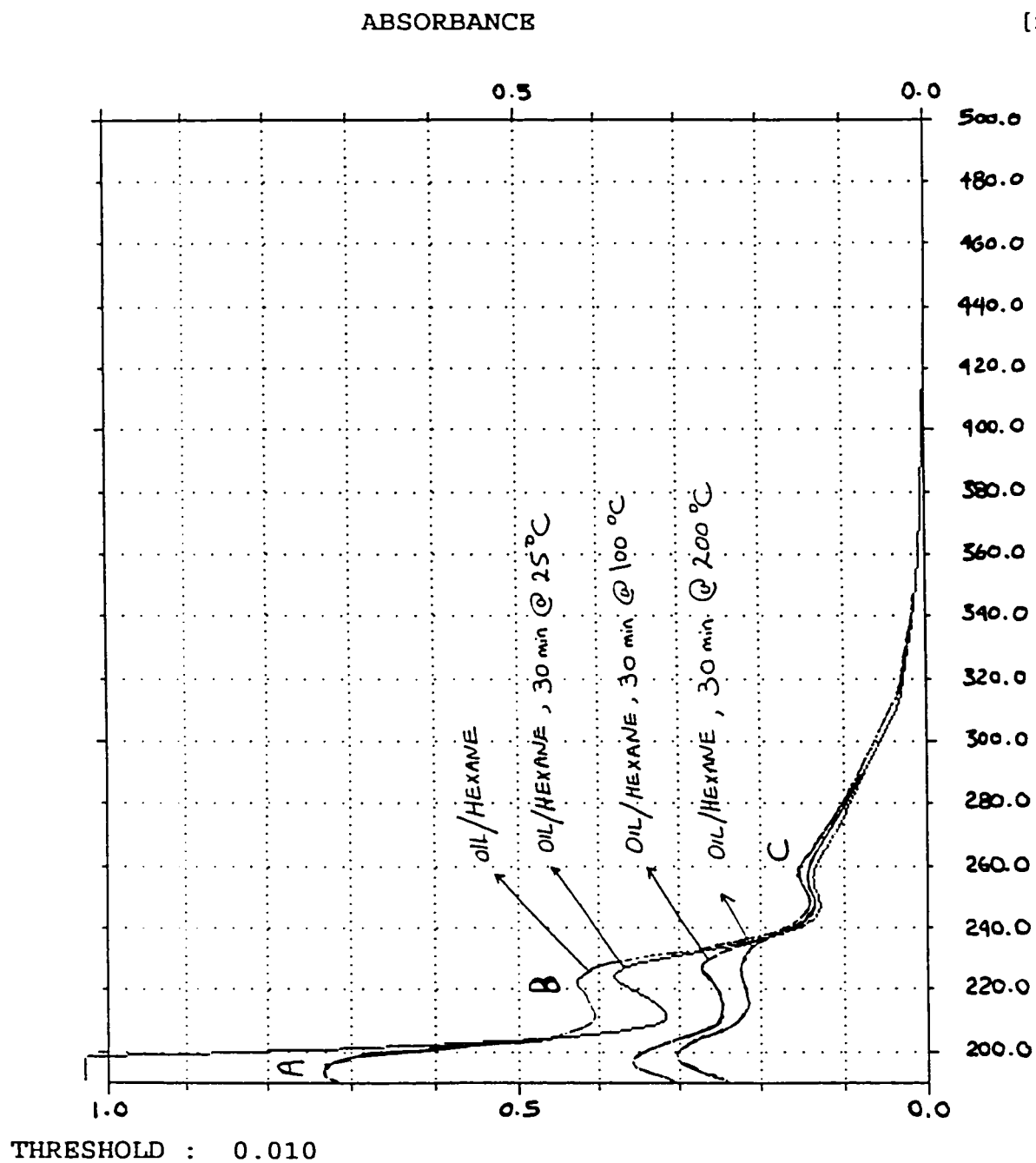


Figure (b) - Comparing the scans of chemically dispersed oil and its blank.



Figure(c) - Scans of oil at different temperature.

Appendix C

Equations for calculating the standard deviation

Equations for Calculating the Standard Deviation

$$S.D. = \sqrt{\frac{\sum_{s=1}^m \sum_{i=1}^n (y_{is} - M)^2}{(n_y - 1)}}$$

$$M = \frac{\sum_{s=1}^m \sum_{i=1}^n y_{is}}{n_y}$$

where:

S.D. = Standard Deviation

s = series number

i = point number in series s

m = number of series for point y in chart

n = number of points in each series

y_{is} = data value of series s and the i th point

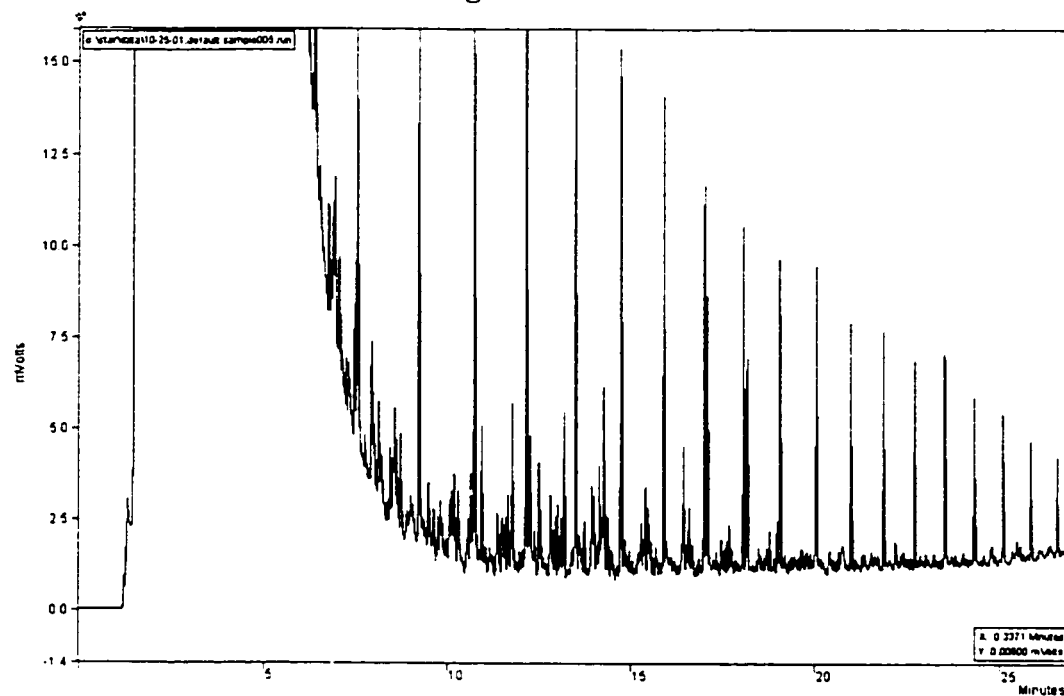
n_y = total number of data values in all series

M = arithmetic mean

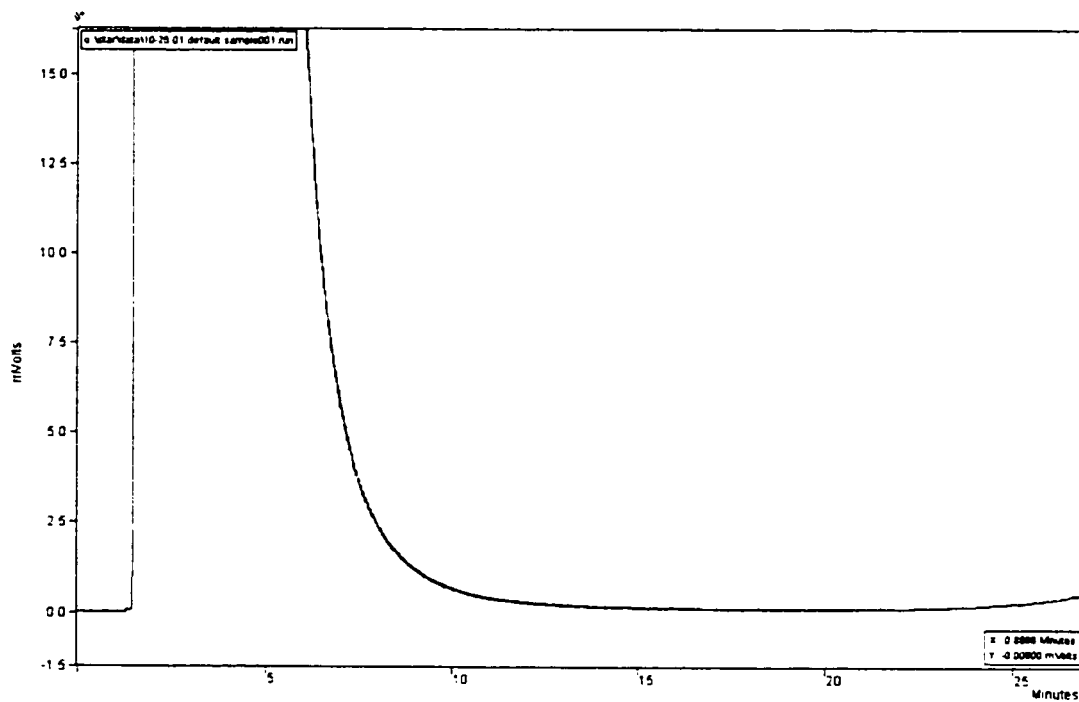
Appendix D

Gas Chromatographs of the Brut crude oil

Figure 1- Brut crude oil



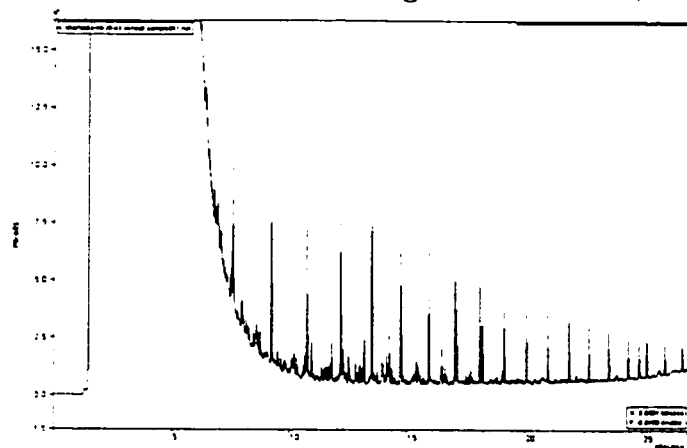
(a) Brut in Hexane



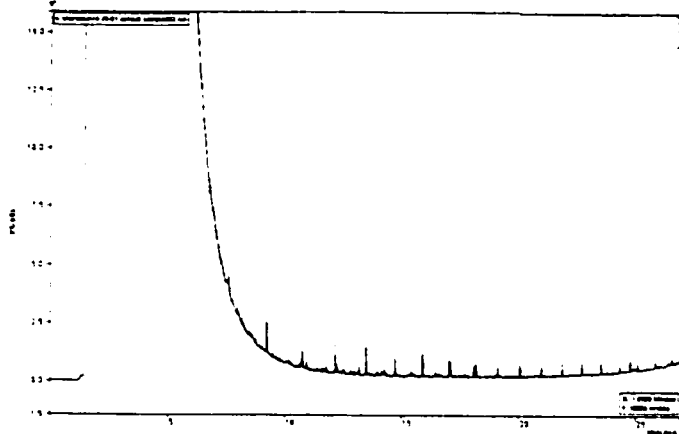
(b) Hexane

Figure 1- (a) is the GC graphs of Brut crude oil in Hexane and (b) is the hexane alone.

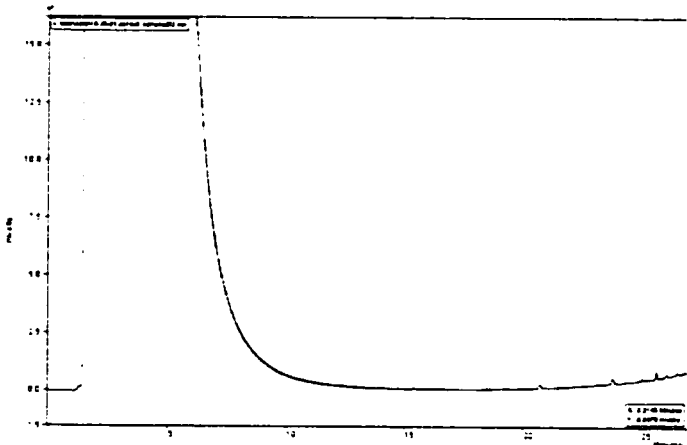
Figure 3- JBR425 (2%) in Saline



(a) Dispersed oil with JBR425 (2%), samples were taken right after shaking (without settling)



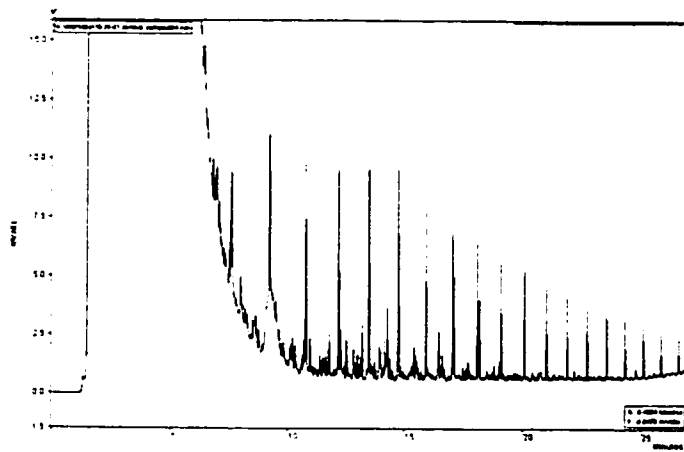
(b) Dispersed oil with JBR425 (2%) after 2 min of settling



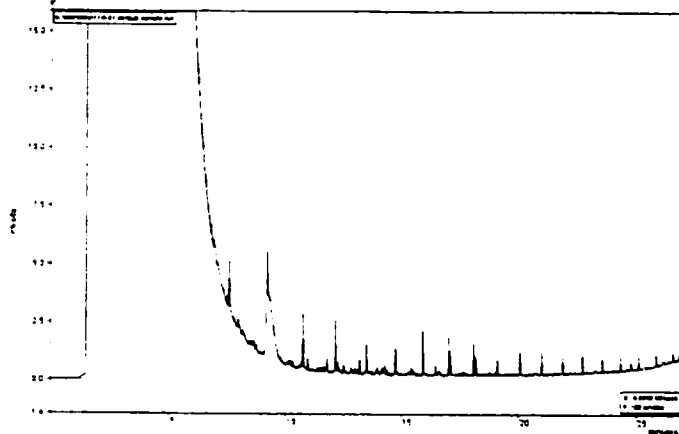
(c) Blank (JBR425 (2%) in Saline)

Figure 3- (a) is the dispersed oil with JBR425 (2%) diluted in saline as solvents. Comparing Figures (a) and (b) shows that after 2 minutes of settling most of the dispersed oil has resurfaced.

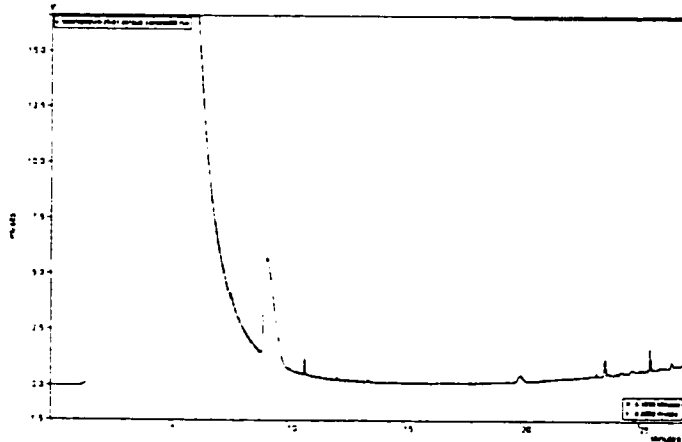
Figure 4- (JBR425 (8%) + 60% Ethanol + 32% octanol)



(a) Dispersed oil with (JBR425 (8%) + 60% ethanol + 32% octanol), samples were taken right after shaking, i.e. without settling.



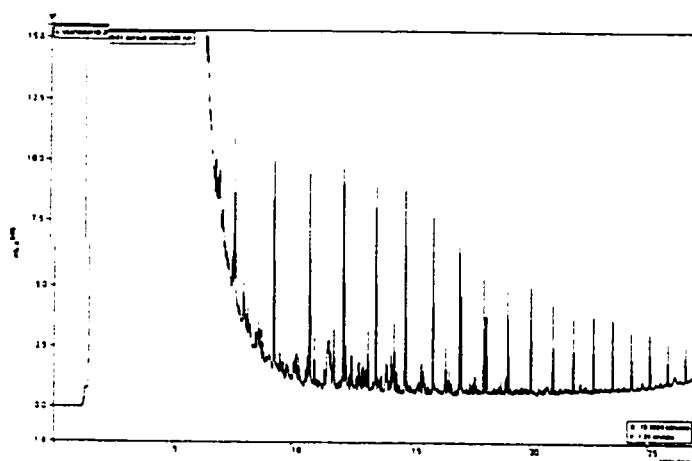
(b) Dispersed oil with JBR425 (8%) after 2 min of settling



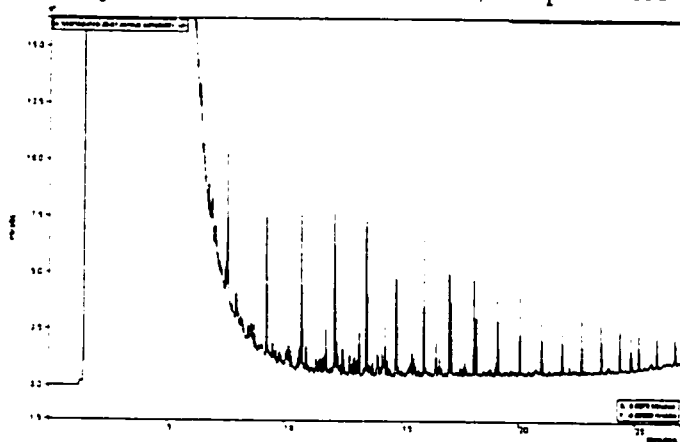
(c) Blank (JBR425 (8%) + 60% Ethanol + 32% octanol)

Figure 4- Comparing Figures (a) and (b) indicates that JBR425 (8%) was able to dispersed all fractions of oil since after 2 minutes of settling no specific peak or groups of peaks disappeared.

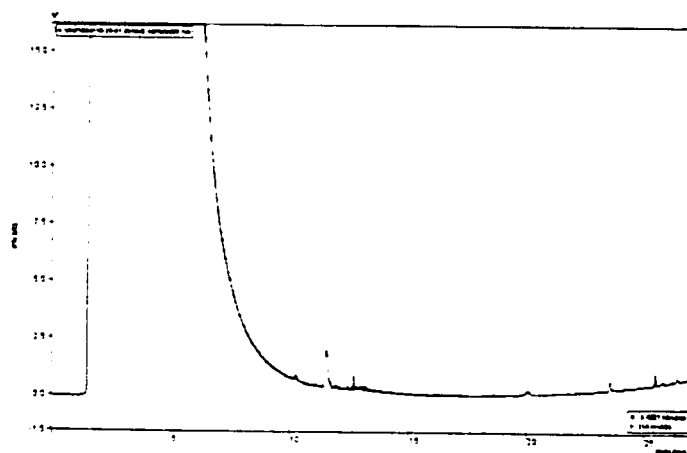
Figure 2- Corexit 9500



(a) Dispersed oil with Corexit 9500, samples were taken right after shaking



(b) Dispersed oil with Corexit 9500 after 2 min of settling



(c) Blank (Corexit 9500)

Figure 2- (a) is dispersed oil with Corexit 9500 right after shaking. Comparing the two graphs, (a) and (b), shows after 2 minutes of settling some dispersed oil has resurfaced.