Smart Dispersant Formulations for Reduced Environmental Impact of Crude Oil Spills

by

Emmanuel Nyankson

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Approved by

Ram B. Gupta, Chair, Professor of Chemical Engineering
Virginia A. Davis, Professor of Chemical Engineering
Allan E. David, Assistant Professor of Chemical Engineering
Prabhakar Clement, Professor of Civil Engineering

Abstract

The traditional chemical dispersant formulations used in combating oil spills are comprised of mainly hydrocarbon solvents, petroleum-derived surfactants, and additives. The toxicity of these chemical dispersants to aquatic life and marine habitats has necessitated the search for alternative dispersant formulations that are environmentally benign. In this dissertation, low toxicity dispersants with high dispersion effectiveness were formulated for their application in crude oil spill remediation.

In chapter 2, the effectiveness on oil dispersions of a composite particle made of paraffin wax and the surfactant dioctyl sodium sulfosuccinate (DOSS) was compared to that of the same DOSS dissolved in a liquid solvent using the U.S. EPA's baffled flask procedure. The solid dispersant composite particles are expected to release the surfactant exactly at the oil-water interface hence reducing surfactant wastage and toxicity. Solid dispersant composite particles were prepared by ultrasonically spray freezing paraffin wax and DOSS molten solution while varying the mass ratio. The amount of DOSS in the composite particle was determined by the methylene blue complexation procedure. Liquid delivery of DOSS was accomplished by dissolving the surfactant in propylene glycol (PG). The results from the study showed that the dispersion effectiveness of the DOSS-paraffin wax composite particles were dependent on particle size, the solubility of the matrix material (paraffin wax) in the crude oil and the DOSS-to-oil ratio (DOR, mg/g). This is because the paraffin wax would have to dissolve in the crude oil to release DOSS, which is then used for the dispersion of the crude oil. At 23 mg/g DOR, which was the maximum DOR used in the study, the dispersion effectiveness of the dispersant composite particles was 60 vol.% and 62.6 vol.% in the heavy Texas crude (TC) and the light crude (LC) oils, respectively. The dispersion effectiveness of the solubilized DOSS on TC was significantly higher than that of the dispersant composite particles; however, at DOR of 23 mg/g, the effectiveness of the dispersant composite particles on LC was just 1.8 vol.% below that of the solubilized DOSS. There was a significant increase in the dispersion effectiveness when the mixing energy was increased from 150 to 200 revolutions per minute (rpm); nevertheless, the effectiveness was almost the same at 200 and 250 rpm. Dispersion effectiveness was analyzed at different salinity environments, that is in brackish water (1.6 and 2.8 wt.% salt concentration) and saline water (3.5 wt.% salt concentration). The dispersant composite particles performed better at low salinities, however, the dispersion effectiveness almost leveled off at 2.8 and 3.5 wt.% salt concentrations. The dispersion effectiveness values of the formulated dispersant composite particles on light crude oil were almost the same as that of solubilized dispersants.

The possibility of formulating oil spill dispersants from food grade surfactants were explored in chapter 3. Soybean lecithin was used to formulate dispersants for crude oil spill application. Soybean lecithin was fractionated into phosphatidylinositol (PI) and phosphatidylcholine (PC) enriched fractions using ethanol. The fractionated PI was deoiled and characterized with Fourier Transform Infrared Spectroscopy (FT-IR). The crude soybean lecithin (CL) and the fractionated PI and PC were solubilized in water and their dispersion effectiveness determined using the U.S. EPA's baffled flask test. The dispersion effectiveness of these solubilized dispersants was compared with that of solid crude lecithin (SL). The dispersion effectiveness of PC was found to be higher than SL, CL, and PI at all the dispersant-to-oil ratios (DORs) tested. However, when the fractionated PI was modified or "functionalized" (FPI) with additional hydroxyl groups to alter the hydrophilic-lipophilic balance (HLB), its dispersion effectiveness improved remarkably and was higher than that of PC. Comparing the dispersion effectiveness of FPI to that of the traditional chemical dispersant formulations (solubilized dioctyl sodium sulfosuccinate (DOSS) and Tween 80 in propylene glycol), it was observed that the dispersion effectiveness of solubilized DOSS and Tween 80 were higher than that of FPI at lower DORs (≤ 12.5 mg/g). However at higher DORs (>28 mg/g), the dispersion effectiveness of FPI was slightly higher than that of solubilized DOSS and Tween 80. The dispersion effectiveness of PC on Texas (TC) and light crude (LC) oil samples were almost the same. The same observation was made for FPI on TC and LC. The dispersion effectiveness of PC and FPI were also tested in different salinity environments. PC and FPI performed better at the higher salinity of 3.5 wt.% than the lower salinities of 0.8 and 1.5 wt.%. At higher DORs, oil spill dispersants formulated from soybean lecithin (FPI) were effective than solubilized DOSS and Tween 80 in propylene glycol.

To reduce the aqueous solubility and toxicity of oil spill dispersants and increase dispersion effectiveness, halloysite clay nanotubes (HNTs) loaded with different combination of surfactants were studied for possible application in crude oil spill remediation in chapter 4. Halloysite nanotubes were loaded with the surfactants; Tween 80, dioctyl sodium sulfosuccinate (DOSS, D), Span 80 (S) and modified soybean lecithin phosphatidylinositol (Lecithin FPI, LFPI) by vacuum suction method. The HNT loaded with the surfactants were then characterized with scanning electron microscopy (SEM), Fourier Transform Infrared Spectroscopy (FT-IR) and Thermogravimetric analysis (TGA). The release kinetics of nonionic and anionic surfactants from HNT were respectively studied with the cobalt thiocyanate and methylene blue active substance tests. The dispersion effectiveness of the raw HNT and the HNT loaded with the surfactant(s) were examined with the U.S. EPA's baffled flask test procedure. The release kinetics of DOSS from HNT was slower than that of Tween 80 due to the interaction of the anionic head group of DOSS with the positively charged lumen of the HNT. The dispersion effectiveness of the raw HNT was lower than HNT loaded with surfactant(s) signifying the release of surfactants during the baffled flask test. For the dispersant formulated with a single surfactant loaded onto HNT, the highest and the lowest dispersion effectiveness were recorded by HNT loaded with Tween 80 (HNT-Tween 80) and HNT loaded with Span 80 (HNT-Span 80), respectively. Loading the HNT with binary surfactant mixtures improved the dispersion effectiveness. Notable among them was HNT loaded with DOSS and Tween 80 (HNT-DOSS-Tween 80) and HNT loaded with Lecithin FPI and Tween 80 (HNT-Lecithin FPI-Tween 80). The highest dispersion effectiveness values for all the dispersants formulated in this study were attained by HNT loaded with ternary surfactant mixtures. 100 and 99 vol.% dispersion effectiveness were obtained from HNT loaded with DOSS, Tween 80 and lecithin FPI (HNT-DOSS-Tween 80-Lecithin FPI) and HNT loaded with Span 80, Tween 80 and lecithin FPI (HNT-Span 80-Lecithin FPI), respectively. The petroleum based surfactant blend of DOSS, Span 80 and Tween 80 (HNT-DOSS-Tween 80-Span 80) recorded 96.2 vol.% dispersion effectiveness. An environmentally friendly oil spill dispersant was therefore formulated using naturally occurring HNT and FDA

approved food grade surfactants (Span 80, Tween 80 and Lecithin FPI) with 99 vol.% dispersion effectiveness.

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List of Abbreviations

AOCS	American Oil Chemists' Society
CH	Cyclohexanol
CL	Crude lecithin solubilized in water
Cryo-SEM	Cryo-Scanning Electron Microscopy
CTAS	Cobalt Thiocyanate Active Substance
D	DOSS
DCM	Dichloromethane
DLS	Dynamic Light Scattering
DOR	Dispersant-to-Oil Ratio
DOSS	Dioctyl Sodium Sulfosuccinate
EPA	Environmental Protection Agency
FPI	Functionalized (Modified) Phosphatidylinositol
FT-IR	Fourier Transform Infra-Red
GC-MS	Gas Chromatography-Mass Spectrometer
HLB	Hydrophilic-Lipophilic Balance
HNT	Halloysite Nanotube
HOR	Halloysite-to-Oil Ratio
LC	Light Crude Oil
IV	Iodine Value

LFPI	Lecithin Modified Phosphatidylinositol
NCP	National Contingency Plan
NEBA	Net Environmental Benefit Analysis
o/w	oil-in-water emulsions
PC	Phosphatidylcholine
PE	Phosphatidylethanolamine
PG	Propylene glycol
PI	Phosphatidylinositol
PS	Phosphatidylserine
S	Span 80
SEM	Scanning Electron Microscopy
SL	Solid (Powdered) Lecithin
SOR	Surfactant-to-Oil Ratio
T	Tween 80
TC	Texas Crude Oil
TGA	Thermogravimetric Analysis
vol. %	Volume percent
w/o	water-in-oil emulsions
wt. %	weight percent

Chapter 1

Introduction

1.1 Oil Spills

An oil spill is a discrete event in which oil is discharged through neglect, by accident, or with intent over a relatively short time. [1] The rate at which oil spills occur increased especially in the early part of the 20th century and this was due to increased demand for energy and the negligence on the side of the oil production companies.

The major energy sources in the United States are petroleum (oil), natural gas, coal, nuclear and renewable energy. Among these energy sources, petroleum remains the most consumed energy source with a consumption of 35 quadrillion BTU in 2012.[2] Increased consumption of petroleum products has inevitably resulted in the release of crude oil onto our marine waters. From historical perspective, some oil spills had occurred as a result of vessel failure, pipeline rupture, explosion of storage facilities and by the occurrence of a natural disaster. [3] Figure 1.1 shows the map of some of the world's largest oil spills.

Literature on oil spills has been characterized with inconsistencies in the amount and number of spilled oil. This is attributed to the numerous data base available for oil spills with its inherent errors. The merging of the different results is difficult since some data were reported considering oil spills of at least 700 tons,[3a] while others considered oil spills with a minimum of 34 tons of spilled volume.[1, 4]

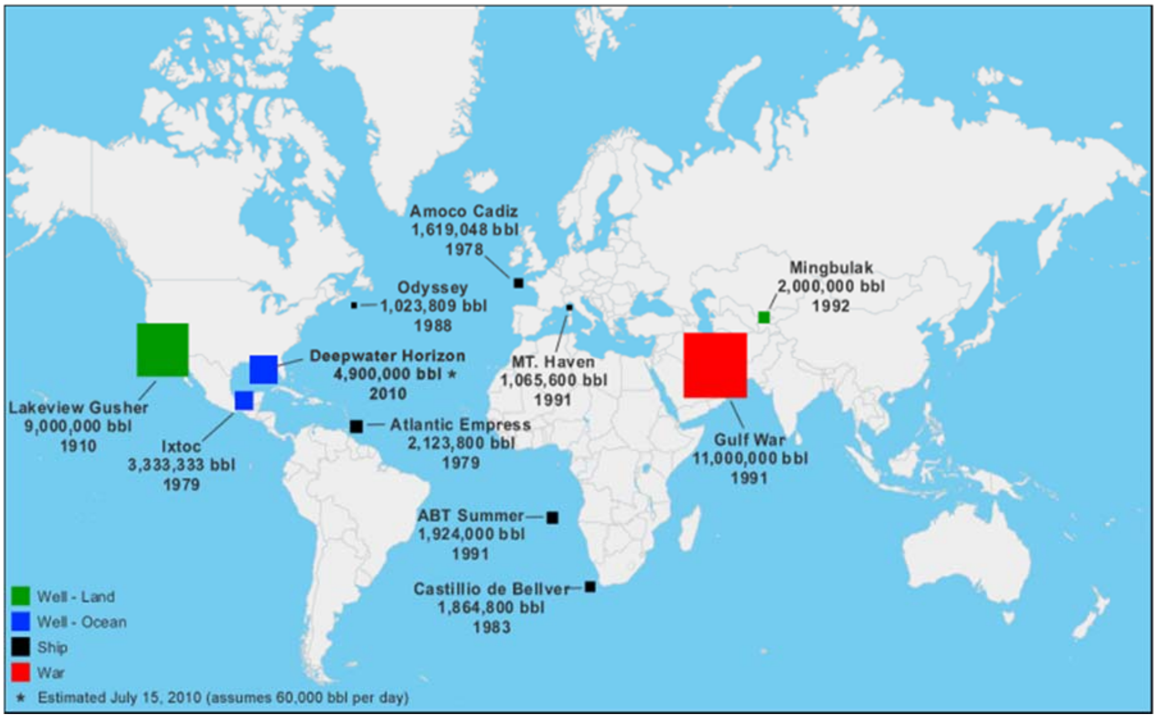


Figure 1.1 Some of the world's largest oil spills (www.geology.com)

Peter Burgherr [3a] reported a global overview of accidental oil spills from all sources considering oil spills of at least 700 tons from 1970 to 2004 (Figures1.2 and 1.3).

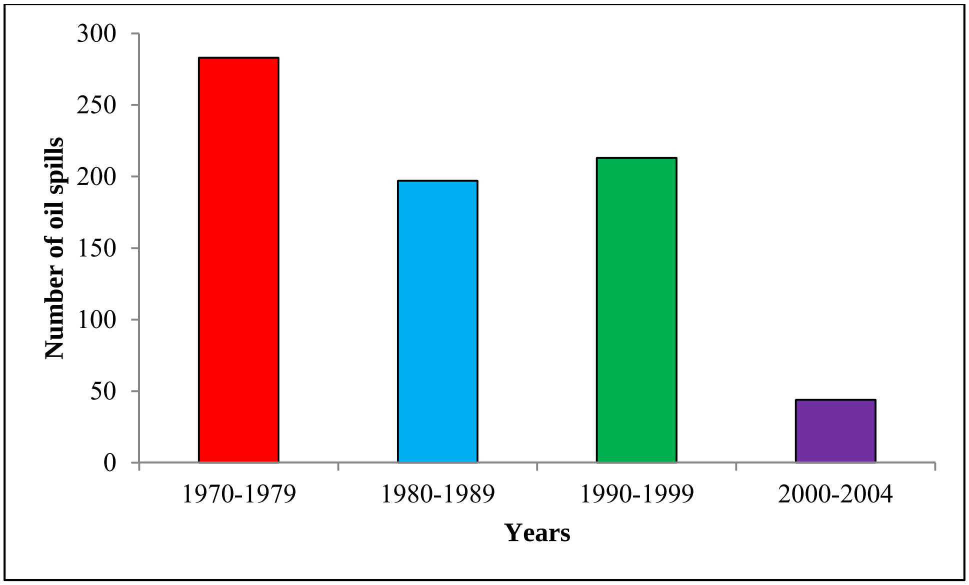


Figure 1.2 Number of oil spills of 700 tons or more worldwide (1970-2004) [3a]

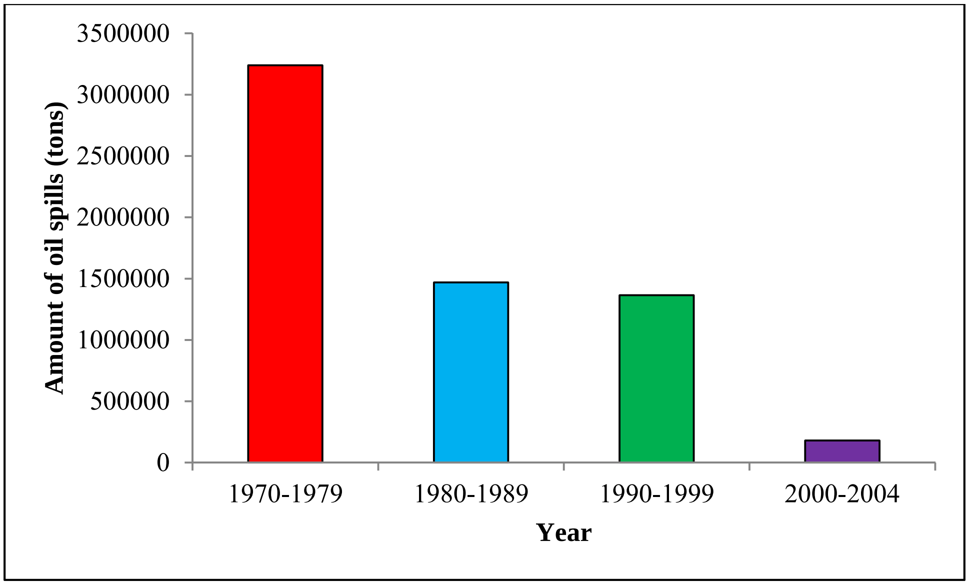


Figure 1.3 Amount of oil spills of 700 tons or more worldwide (1970-2004) [3a]

From the data reported by Burgherr[3a], it can be deduced that, the number and amount of oil spill has reduced drastically over the years and the trend was similar to that observed by Etkins.[1]

Anderson et al.[5], also reported on the oil spill trend by considering oil spills with at least 136 tons of spillage (Figure 1.4). His studies considered oil spills in port and at sea and his analysis was based on data reported by BP Amaco.[6] The number of oil spill at sea has seen over 50 % reduction since 1974. The decreased spillage attests to the effectiveness of oil spill prevention programs and measures and increased concern over escalating financial liabilities. [1, 7]

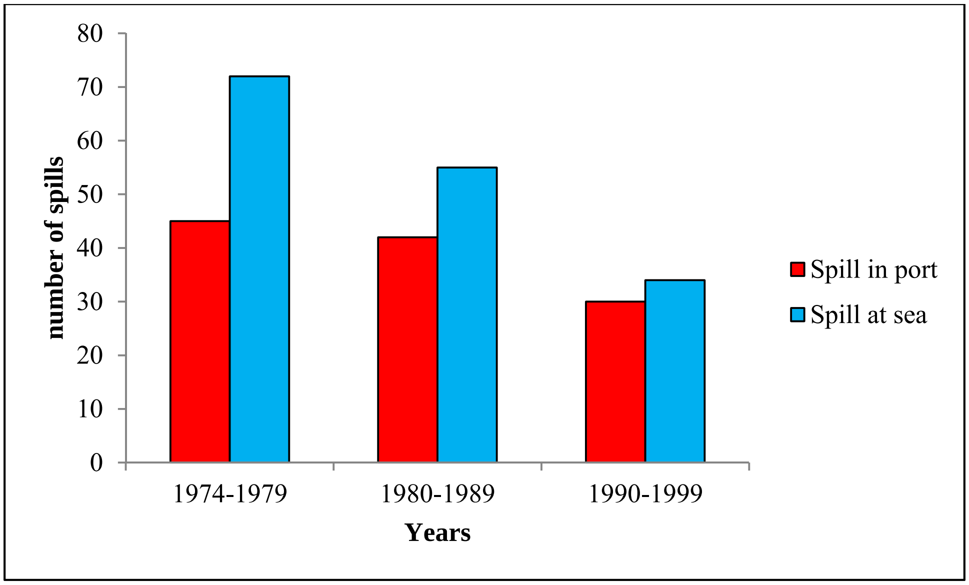


Figure 1.4 Number of oil spills of at least 136 tons (1974-1999). Data source [5]

1.2 The Fate of Spilled Oils

After an oil spill has occurred, several natural processes begin to operate on the oil. These processes can be physical, chemical or mechanical. At the early stages of the oil spill, the oil undergoes natural spreading, evaporation, emulsification, dissolution and mechanical transport by winds, waves and ocean current. The later stages of an oil spill is characterized by other processes such as dispersion, microbial decomposition (biodegradation) , photo-oxidation, sedimentation etc. [8] These processes are summarized in Figure 1.5.

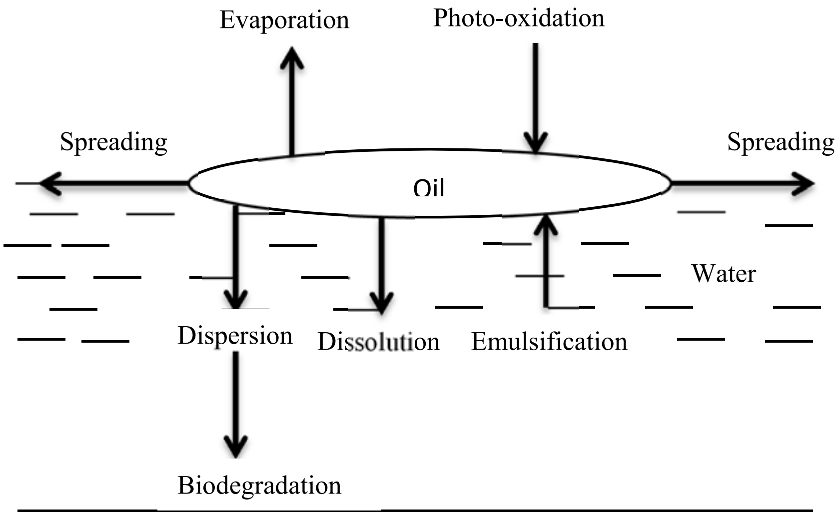


Figure 1.5 Processes that operate on the oil after oil spill [9]

1.2.1 Spreading of Oil

When oil spill occurs, there is an immediate need to determine how rapidly the oil will spread, and where it will go in a given time[10] due to the devastating and obnoxious effects of marine oil pollution.[11] Spreading makes the oil thin and as a result knowledge of where the oil goes after it is spilled and the area covered by the oil at a given time is also necessary to make decision about the type of response strategy to use since it determines the weathering of the oil.[10, 12] Weathering of the oil makes its dispersion very difficult and hence limits the response options available.

The physicochemical parameters of the crude oil that determines spreading are its pour point, density and spreading coefficient.[13] A pre-requisite for the spreading of a particular crude oil after spillage is that, its pour point must be lower than the ambient seawater temperature, otherwise the oil will solidify immediately or shortly after the spillage. At the initial stage, the spreading rate of oil for a large oil spill is dependent on the volume and density of the oil. Therefore oil spill on the surface of calm water will spread in the form of thin continuous layer due to the effect of gravity. Though the force of gravity acts downwards, it causes a sidewise spreading motion of a floating oil film by creating an unbalanced pressure distribution. After some time interval, surface tension and viscosity forces become the principal determinants that is the slick spread over the water surface due to a balance between the gravitational, viscous and surface tension forces. [13-14] At the front edge of the expanding slick, an imbalance exists between the surface tension, water and the oil, and the interfacial surface tension of the oil-water phase. Whether the oil will spread or form lenses is dependent on whether or not the spreading coefficient (S_o/w) is positive or negative.[8, 14b]

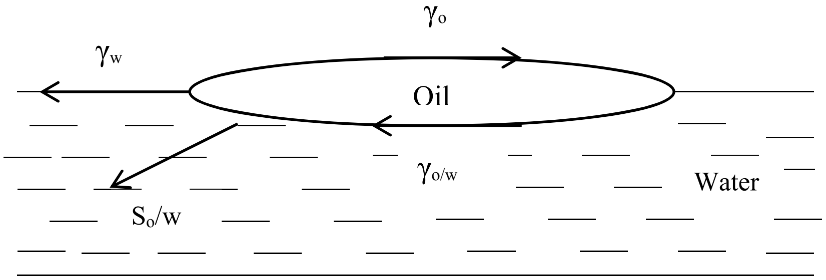


Figure 1.6 Spreading of oil on water [14a]

From Figure 1.6, spreading coefficient is defined as:

$$S_{o/w} = \gamma_w - \gamma_{o/w} - \gamma_o \tag{1}$$

Where: $S_{o/w}$ is the spreading coefficient, γ_w is the surface tension of water, γ_o is the surface tension of the oil and $\gamma_{o/w}$ is the interfacial surface tension at the oil/water interface. If the spreading coefficient is positive, the oil will spread but if it is negative, it will not spread and will remain as lens of liquid.[14a]

Langmuir studied the formation of lenses on water by pure hydrocarbons and derived an equation that can be used to predict the equilibrium thickness of the oil lens;[8]

$$h_\infty^2 = \frac{-2S_{o/w}\rho_w}{g(\rho_w - \rho_o)\rho_o} \tag{2}$$

h_∞ is the equilibrium thickness of the oil lens; $S_{o/w}$ is the spreading coefficient; ρ_o, ρ_w is the density of water and oil, respectively and g is the acceleration due to gravity. From the above equation, it can be deduced that, h_∞ can only be determined when $S_{o/w}$ is negative.

Considering the spreading of oil on water surfaces, Fay developed a theory that indicates that, spreading progresses through three phases namely: gravity-inertia, gravity-viscous and viscous-surface tension.[15]

1.2.2 Evaporation

When oil spill occurs, the composition of the oil is altered by a series of processes which includes evaporation, which is the primary initial process involved in the removal of oil from the surface of the sea. [13, 16] Typical crude oil can lose between 5 to 75 % of their volume depending on its light, medium and heavy crude content.[17] It was estimated that at least 38,600 tons of the oil spilled by Exxon Valdez was lost through evaporation and as much as 265,000 was lost in the same way during the Amoco Cadiz oil spill.[18] Evaporation of light hydrocarbon from the crude oil increases its density and viscosity and as a result, the spreading rate of the oil is decreased. The increase in density may cause the oil to sink into the water column.[19] Understanding of evaporation is important both from the practical view point of cleaning up spills and for developing predictive models since the oil may weather through evaporation and make the adoption of certain cleaning up strategies impossible.[20] Another important fact is that, evaporation may modify the toxicological properties of the spilled oil since during evaporation the surface films become less toxic due to the loss of polycyclic aromatic hydrocarbon and the water soluble fraction becomes more toxic.[21]

The evaporation mechanism of crude oils is very complex due to numerous compounds that can be found in crude oils. These compounds have different physical and chemical properties such as vapor pressure and therefore respond to changes in the environment differently. There are therefore several fundamental differences that exist between the evaporation of pure liquids such as water and that of a multi-component system such as crude oil. For example, the evaporation rate for a single liquid such as water is a constant with respect to time while the evaporation rate of crude oils is not linear with time. [17a, 17c, 22]

Factors such as wind speed, composition of the crude oil, temperature, humidity and formation of water-in-oil (w/o) emulsion determine the rate of evaporation of oil slick from the surface of the sea.[13, 16b, 23] After an oil spill occurs, the oil lighter components are evaporated and these molecules move into the layer of air above the evaporation surface. This layer of air is known as the boundary layer and the characteristics of this layer can affect the evaporation rate. For instance, if the boundary layer does not move and there is low turbulence, the rate of evaporation is expected to reduce since the air above the evaporation surface becomes saturated.[17c, 24] But extensive studies by Mervin F. Fingas[17c] led to the conclusion that, oil evaporation is not strictly boundary layer regulated, that is increasing the wind speed and the area will not change the evaporation rate significantly. These observations were contrary to predictions resulting from boundary-layer regulated evaporation.[17a, 17c]

1.2.3 Dissolution

An appreciable quantity of crude oil can be dissolved into the water column due to the polar nature of some of the low molecular weight compounds present in crude oil.[19] This dissolution is aided by the ocean current and waves and therefore, the rate of dissolution is lower for calm seas. Though the Dissolution of petroleum hydrocarbons in water is very small, with less than 1 % of spilled oil dissolved, it poses risks to aquatic species due to the acute toxicity of these hydrocarbon compounds. [18, 23a]

1.3 Oil Spills Response Methods

Due to the complex nature of oil spills, no perfect solution exists when they occur. Since the technologies that work for one situation may not work for another, different response technologies or methods are needed.[25] That is the nature of the oil spilled determines whether or not any action should be taken and if so, which response method should be applied. In cases where the spilled oil has very high API gravity no action may be required since such oils are made up of very light hydrocarbons and will evaporate on its own. Also, in a situation where spilled oil is not moving ashore, no action may be taking. The trained personnel will have to monitor the movement of the oil slick by paying particular attention to the ocean current and waves so that an appropriate action is taking should the direction of the oil changes. The response options available during a major offshore oil spill includes but not limited to mechanical containment and recovery, chemical dispersant application, in situ burning, natural biodegradation[26] and the use of solidifiers. The choice of the response option depends on the nature of the spill, the environment condition, availability of personnel and equipment,[27] the nature of the sea, road access to oil spill location and the human population around the oil spill location. In real life situations, for effective remediation, all the response method mentioned in this section should be combined.

1.3.1 In Situ Burning

The in situ burning of oil spills has historically been regarded as a response method of last resort. This method involves burning the spilled oil on the surface of the water (Figure 1.7). As with mechanical containment and collection method, burning is applicable only in certain circumstances. Since the dynamics of ignition and sustained burning of spills has not been well understood, igniting and keeping a slick ablaze is often difficult.[25, 28] In spite of this, in situ burning is reported to have been used to remove oil in several countries such as Canada, U.S.A., some European and Scandinavian countries.[26] Availability of equipment, less labor intensive and its suitability for large scale cleanup are some of the advantages of in situ burning as an oil spill response option.[29] Though as high as 98 % efficiency in just an hour of burning has being reported,[30] this value is dependent on the state of the oil and the sea on which the oil spill occurred.[29a, 31]

Figure 1.7 In situ burning of spilled oil [32]

As already discussed by Allan,[27] a lot of operational conditions need to be taking into consideration when adopting in situ burning as an oil spill response measure.

One most important operation condition is the slick thickness. Findings from laboratory experiments have shown that, the oil will burn only if it is of significant thickness. That is if the oil is thick enough, it acts as an insulation and keeps the burning slick surface at a high temperatures by reducing the heat loss to the underlying water.[33] The thickness of the slick is dependent on the nature of the oil and ranges from 1 to 5mm.[26, 33]

The presence of indigenous surfactants such as asphaltene, metallopophyrins and wax in crude oil usually leads to the formation of w/o emulsion.[34] The evaporation of lighter volatiles leads to the weathering of the oil. Weathering reduces the amount of surface oil, decreases the total extractable hydrocarbon and changes the composition of the hydrocarbon.[35] The mousse formation and weathering of the oil affects its ignition. For weathered crude that has formed w/o emulsion, the upper limit for successful ignition is about 25 % water. Paraffinic crude which is able to form metastable water-in-oil emulsions is able to ignite at a much higher water content.[33]

The decision to burn spilled oil is strongly related to the location of the spilled oil and the region of influence throughout the burning period.[27] This is necessary because incomplete combustion of the oil leads to the formation of smoke which creates a whole of health problems to the population close by. There may also be the formation of some residue after the burning which may sink and affects the aquatic habitat. In addition to air pollution, the effect of in situ burning on the ocean itself and its inhabitants is considerable. Therefore to decide on whether or not in situ burning should be adopted, it is necessary to ensure that, the spill is located not less than 6 miles away from human population as stipulated in the National Contingency Plan (NCP) of the United States.[36]

Availability of trained personnel and equipment is another major issue.[27] In the case of contained burning, one of the major issues that need to be dealt with is the availability of equipment. Some of the equipment needed for effective controlled burning are vessels and aircraft, fire containment booms and igniters.[33] These booms can either be made of steel or thermally resistant fabrics.[26] Some examples of booms made of steel are Sandvik steel barrier, spilltain boom and dome stainless steel boom. 3M fire boom, sea curtain fireguard and pyroboom are some of the examples of booms made from thermally resistant fabrics.[33] All these equipment should be available before in situ burning can be used and the booms must be long enough to form a ‘U’ configuration to be able to contain the burning.[37] Though many are of the view that only highly trained personnel should carry out in situ burning, others think otherwise. With the probability of unwanted ignition of the spilled oil causing harm to the cleanup personnel and the fact that the theory underlining the ignition of the oil is not understood, it is highly recommended that professional firemen are employed to handle in situ burning.

The state of the sea is another factor that needs to be taken into consideration when deciding on whether or not to use in situ burning as a remediation method. That is for a successful and safe application of in situ burning as an oil spill remediation method, it has been reported that, the wind should be less than 20 knots, waves should be less than 2 m, and the currents should not exceed 1 knot. [26]

All these factors limits the adoption of in situ burning as an oil spill response method, that is when oil spill occurs, a quick study need to be carried out to examine the feasibility of in situ burning as an oil spill response method before any decision is taken.

1.3.2 Mechanical Containment and Recovery

Where possible, the recovery of spilled oil by mechanical means which involves the use of skimmers and booms to block the spreading oil, concentrate it and remove it from the water is used. Though this method is preferable, current technologies still has many limitations and only about 10 % of the oil has been recovered from most major spills.[25] Based on the low oil recovery recorded when this response method is applied, it is usually not feasible for large oil spills. Whether or not this method can be applied is dependent on some factors such as the nature of the sea and the location of the oil spill. It is not advisable to apply this method when the ocean current is greater than 1 knot and the wave height is above 2 m.[38] Location of the spill is also an important factor since the equipment (booms and skimmers) must be conveyed to the spilled site. Some major disadvantages of this method are the high cost associated with its application and the fact that the collected oil needs to be disposed of properly. This clean up method includes the use of booms, skimmers, heavy oil skimmers and skimmer vessels.[38]

Booms are mechanical barriers that encircle spilled oils and control the motion and the spreading of the oil. As reported by Ventikos et al.,[38] booms can be divided into four categories namely: curtain booms, fence booms, shore sealing booms and fire resistant booms. Some examples of booms are shown in Figure 1.8. One major problem with the use of booms is that, some of the encircled oil may sink to the column of the sea when they become concentrated and hence affect the aquatic life. In addition to this, as a result of the towing speed exceeding the critical value, the oil may leak beneath the boom.[39] After the oil is encircled and concentrated by booms, skimmers are used to remove the oil mechanically from the surface of the sea. The skimmers (Figure 1.9) recover the oil either by suction or adhesion. One major problem with the use of skimmers is their inefficiencies which results in the recovered oil being mixed with large volumes of water. This makes the whole response method expensive since the oil needs to be recycled and the water removed.[39b, 40]

Figure 1.8 Booms being used in mechanical recovery of oil [32]

Figure 1.9 Skimmers being used for oil recovery [32]

1.3.3 Solidifiers

Solidifiers are hydrophobic polymeric materials that gel the oil, immobilize it and reduce the rate of spreading and thinning. The reduction in the spreading rate of the oil protects wildlife and receptor areas. Solidifiers are usually applied in a form of a powder, gels or granules.[41] The gelled mass usually floats on the sea and is collected by some mechanical means. There are three types of solidifiers namely; polymer sorbent, cross-linking agents and polymers with cross linking agents. Solidifiers should have the following characteristics: have a low cost of production, should be hydrophobic and oleophilic, minimal environmental effect upon application, high efficiency in the recovering of the oil and should be recyclable.[41a, 42]

1.3.3.1 Polymer Sorbent

When a polymer sorbent is applied, the oil binds to the polymer by weak van der Waal forces (Figure 1.10). Since most polymeric materials are porous, the oil binds to the spaces in between the polymer linkage. The weak van der Waal forces allow the bound oil to be remove by an application of an external shear. The most commonly used commercial polymer sorbent materials for oil spills are polypropylene and polyurethane foam. The hydrophobic and oleophilic characteristics of these commercialized products make them very efficient as sorbent materials.[41b, 43] Slow degradation of these materials and the fact that most of the members of this group of solidifiers are not naturally occurring which makes their synthesis expensive are some of the known disadvantages associated with polymer sorbents.[43a, 44] However, polymer sorbents are known to have high sorption capacity, [39b] are relatively simple and less toxic when compared to the other type of solidifiers.

Figure 1.10 Application of polymer sorbent (polypropylene)[32]

1.3.3.2 Cross-linking Agents

Unlike polymer sorbent, cross-linking agents chemically reacts with the oil to form a solid mass. The reaction involving the oil and the cross linking agent can either be exothermic or endothermic. Some of the commonly used cross-linking agents are norbornene and anhydride. Because these type of solidifiers worked by chemically bonding the oil to itself, a fully solidified mass is formed and this makes it easier to recover the oil from the surface of the sea.

1.3.3.3 Polymers with Cross-linking Agents

This type of solidifier consists of a sorbent polymer and cross-linking agent hence, a better oil recovery is achieved since the product of this kind utilizes the advantages associated with sorbent polymers and cross-linking agents. A typical commercial example of this type of solidifier is RigidOil by BP.[45] An advantage of this solidifier is that, a high oil recovery is achieved however, the requirement that the polymer and the cross-linking agent should be mixed immediately before application is a major constraint.

1.3.4 Chemical Dispersants

When used judiciously and in the right circumstances, chemical dispersants can be an effective countermeasure technology for combating oil spills. Application of sufficient energy to the dispersant-oil mixture results in the slick being broken down into smaller oil droplets that diffuses to the water column by buoyancy effect and the action of the ocean current. Subsequently, the surface area of the oil is increased and this helps to accelerate dilution and biodegradation of the oil. [46]

Dispersants are made up of one or more surface active agents (surfactants) dissolved in one or more solvents. The surfactant can either be anionic and or nonionic surfactant while the solvent can be an aqueous, hydrocarbon and hydroxyl compounds. Some additives are also added to speed up the biodegradation process after the oil has been dispersed.[42b, 47]

Application of chemical dispersants as a response option is possible over a wide range of slick thickness and weather conditions such as rough sea and strong ocean current and wind [47a] than the other response strategies mentioned in the previous sections. The active seas are advantageous since they provide the energy needed for the dispersion process and also help to distribute the dispersed oil in the water column, thereby offsetting the buoyant forces acting to re-surface the oil. Chemical dispersants also makes it possible to treat a large volume of spilled oil within the shortest possible time since it is possible to use large aircraft during the application. This is advantageous over other responds methods such as mechanical containment and recovery and the use of solidifiers.

1.4 Dispersant Theory

Dispersants are made up of one or more surface active agents (surfactants) and solvents(s). Each of these components plays vital role in determining how effective the dispersant will be in dispersing oil slick.

1.4.2 Surface Active Agents (Surfactants)

Surfactants are substances that when present at low concentrations in a system, has the property of adsorbing onto the surface or interfaces of the system and altering to a marked degree the surface or interfacial free energy of those surface (interface).[48] They consist of a long alkyl chain, or hydrophobic portion, attached to a water-soluble functional group, or hydrophilic portion[49] as shown in Figure 1.11a. Due to this amphiphilic nature of the surfactant, it locates and arranges itself at the oil-water interface[14a, 50] (Figure 1.11b). The lipophilic group is generally made up of long hydrocarbon chains whiles the hydrophilic group is mainly ionic or polar in nature. The surfactant dioctyl sodium sulfosuccinate (DOSS) is shown in Figure 1.11(c) and it has one hydrophilic head group and two hydrophobic tails.

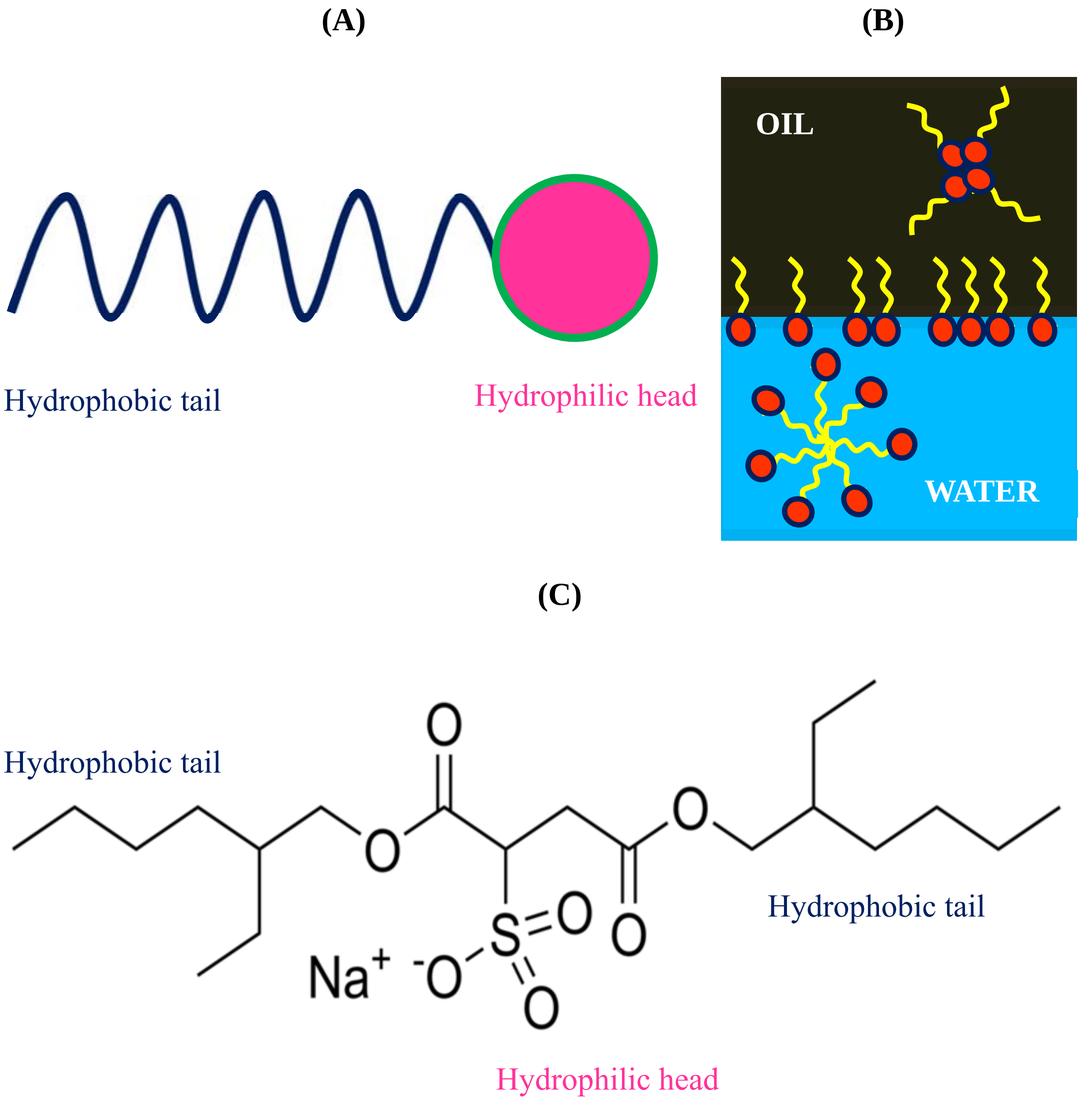


Figure 1.11 (A) surfactant molecule (B) arrangement of surfactant at the oil-water interface (C) the surfactant dioctyl sodium sulfosuccinate (DOSS)

The orientation of the surfactant at the interface leads to a reduction in the interfacial free energy. Surfactants find applications in almost every chemical industry. They play a vital role in the oil industry by enhancing tertiary oil recovery and oil slick dispersion for environmental protection.[51] The properties of surfactants that influences their efficacy include charge (anionic, nonionic, cationic), hydrophilic – lipophilic balance (HLB) and critical micelle concentration.[52] Depending on the nature of the hydrophilic groups of surfactant, they can be divided into four major categories namely: anionic, nonionic, cationic and amphoteric surfactants.[53]

1.4.2.1 Anionic Surfactants

Anionic surfactants are used in greater volume than any other surfactant because of their relatively low cost and high potency.[54] The hydrophobic group of the anionic surfactant is a linear alkyl group with a chain length in the region of 12-16 Carbon atoms. The hydrophilic groups on the other hand consist of sulfonate, phosphate, sulfate or carboxyl groups [50-51] and bears an ionic charge.

One of the most common anionic surfactant in dispersant formulation is dioctyl sodium sulfosuccinate (DOSS).[55] DOSS is diester of sulfosuccinate acid and is very stable against hydrolysis because the sulfur atom is directly bonded to the carbon atom. COREXIT EC9500A and COREXIT EC9527A which were used during the Gulf of Mexico oil spill[56] is known to contain approximately 10-30 wt.% organic sulfonic acid salt which speculated to be DOSS.[57] Lecithin phosphatidylinositol is another example of anionic surfactant.

1.4.2.2 Nonionic Surfactants

The surface active portions of nonionic surfactants bear no apparent ionic charge and are synthetized by the addition of ethylene oxide or propylene oxide to alkyl phenols, fatty acids, or fatty amides. The most common of these are those based on ethylene oxide, referred to as ethoxylated surfactants.[48, 51] Nonionic surfactants found major application as dispersing agents and as a result are one of the major components in dispersant formulations.[58] Studies by Brochu et al.,[59] has suggested that, nonionic surfactants can be used to disperse large portions of crude oil and their dispersion efficiency is dependent on their HLB values.[59]

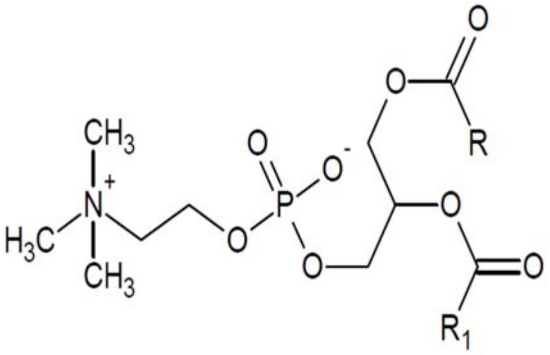
Studies have shown that, COREXIT line of products contains Tween 80, Tween 85 and Span 80; which are ethoxylated nonionic surfactant.[60] Nonionic surfactants adsorbs onto surfaces with the hydrophobic or hydrophilic group oriented towards the surface depending upon the nature of the surface. If polar groups capable of hydrogen bonding with the hydrophilic group of the surfactant are present on the surface, then the surfactant will adsorb with its hydrophilic group oriented towards the surface.[48]

1.4.2.3 Cationic Surfactant

When the hydrophilic group of the surface active agents consists of a positively charged head, the molecule is known as a cationic surfactant.[61] Most of the cationic surfactants contain quaternary ammonium ion, which serves as the hydrophilic part and an alkyl chain which imparts hydrophobicity to the surfactant. Since most surfaces are negatively charged, cationic surfactants can be used to make them hydrophobic.[48-49, 62] NEOS AB3000, which is a product listed on the U.S. EPA NCP product schedule was made with a blend of nonionic surfactants and cationic surfactants. This product recorded a dispersion effectiveness of 89.8 vol.% for South Louisiana crude oil and therefore showed the effectiveness of cationic surfactants in dispersing spilled crude oil.[63]

1.4.2.4 Amphoteric Surfactants

The hydrophilic group of amphoteric surfactants possesses both positively and negatively charged head groups. A typical example of amphoteric surfactant is lecithin phosphatidylcholine (Figure 1.12).



R and R_1 are fatty acid chains

Figure 1.12 Chemical structure of lecithin phosphatidylcholine

1.4.3 Solvents

The two main components in dispersants are surfactants and solvents.[60b, 64] In COREXIT 9500 and 9527, propylene glycol and 2-butoxyethanol are the main solvent components of the mixture, along with dipropylene glycol monobutyl ether and petroleum distillates.[65] In general, dispersant products contain about 40 to 80 % solvent.[66] Some of the dispersant products listed on the U.S. EPA NCP product schedule [63]are listed in Table 1.1 including their solvent component.

Table 1.1: Dispersants with their solvents

Dispersants	**Solvents**
MARE CLEAN 200	Paraffinic hydrocarbons
NOKOMIS 3-AA	Propylene glycol and water
SUPERSPERSE^{TM} WA02500	Distillates, hydrotreated light, water, ethanol
SEA BRAT #4	Propylene glycol
BIODISPERS	Water
JD-109	Ester based
DISPERSIT SPC 1000^{TM}	Non-petroleum based
COREXIT® EC9527A	Water, propylene glycol, 2-butoxyethanol
NEOS AB3000	Paraffins

These solvents have important role in ensuring high performance of the dispersant product.[66] The solvents in the dispersants play the following functions:

- It solubilizes the blend of surfactants, that is they acts as carriers for the surfactants.[42b, 66-67]
- Since most surfactants are viscous, the solvents help reduce their viscosity for easy application.[42b, 66-67]

- The solvent helps the surfactants to penetrate into the oil slick so that it can be released at the oil-water interface. [42b, 66-67]

Fiocco et al.,[66] reported that, solvents used in formulating chemical dispersant should have the following characteristics:

- It should be less dense than sea water to avoid sinking and allow spreading at the oil-water interface.
- It should have low toxicity. This is necessary so that it does not pose any danger to aquatic species.
- Have low vapor pressure to avoid rapid evaporation from sprayed drops.
- Have a flash point greater 60 °C.

1.5 The Need for Alternative Dispersant Formulations

Effective use of dispersants can accelerate oil biodegradation by naturally occurring microorganisms, preventing the oil spill from drifting ashore and damaging sensitive coastal ecosystems.[46a, b] However, indiscriminate application of dispersant to subsea and surface oil spills results in a significant amount of dispersant not coming into contact with the oil and wasted. The aqueous solubility and miscibility of oil spill dispersants and inevitable sea currents cause dispersant to be washed away and wasted. To compensate for this inefficiency, large amounts of dispersants are used resulting in high costs and a large environmental load. For example, an estimated 2.1 million gallons of dispersant were applied to the Gulf of Mexico during the Deepwater Horizon oil spill of 2010 to disperse approximately 205 million gallons of crude oil.[68]

The release of such high volume of chemical dispersants into our marine waters is worrisome since the chemical surfactants and the solvents used in formulating these dispersants are toxic. As an example, 2-butoxyethanol which was used in formulating Corexit 9580 and 9527 is known to be carcinogenic. In addition, most if not all of the chemical surfactants used in their formulation are synthetized chemically and are of petroleum origin and as a result are toxic to aquatic species, not easily biodegradable and the byproducts of their manufacturing processes can be environmentally hazardous.[69] Therefore environmental and human toxicity issues arose when such voluminous amount of chemical dispersants are applied. Studies conducted after the Gulf of Mexico oil spill revealed that the chemical dispersant, Corexit 9500A which was used for the Gulf of Mexico oil spill, was moderately toxic to Gulf of Mexico aquatic species and had adverse dermal and pulmonary effects on cleanup workers.[60b, 70] Although most dispersants are considered inexpensive, sheer volume leads to significant costs. The estimated 2.1 million gallons of dispersant applied during the Gulf of Mexico oil spill cost British Petroleum (BP) over $80 million.[70b]

To increase dispersant efficiency, reduce environmental toxicity and wastage, alternative oil spill dispersants were formulated in this work.

1.6 Summary of Chapters

The objective of this work is to demonstrate the effectiveness and applicability of new environmentally benign oil spill dispersant formulations. This objective was accomplished through: (1) the synthesis of DOSS-paraffin wax dispersant composite particles, (2) the formulation of oil spill dispersants using food grade surfactant (phospholipids in lecithin), and (3) the formulation of oil spill dispersant using naturally occurring halloysite nanotubes.

1.6.1 Chapter 2

To decrease surfactant wastage and dispersant toxicity, the use of solid water-insoluble paraffin wax particles containing the surfactant DOSS was proposed in chapter 2 as a potential oil spill dispersant for crude oil spill remediation. In such a formulation the surfactant is only released when the paraffin wax dissolves in the oil upon contact (Figure 1.13).

The ability of microparticles to adhere to the fluid interface (oil-water interface) may allow for continuous release of surfactant directly where it is needed and as a result reduce surfactant wastage. In addition, before dissolution takes place particles that adhere to the water-oil interface essentially reduce the unfavorable contact between the oil and water[71] and thus may lower the interfacial energy. This is expected to reduce the amount of energy needed to disperse the oil.

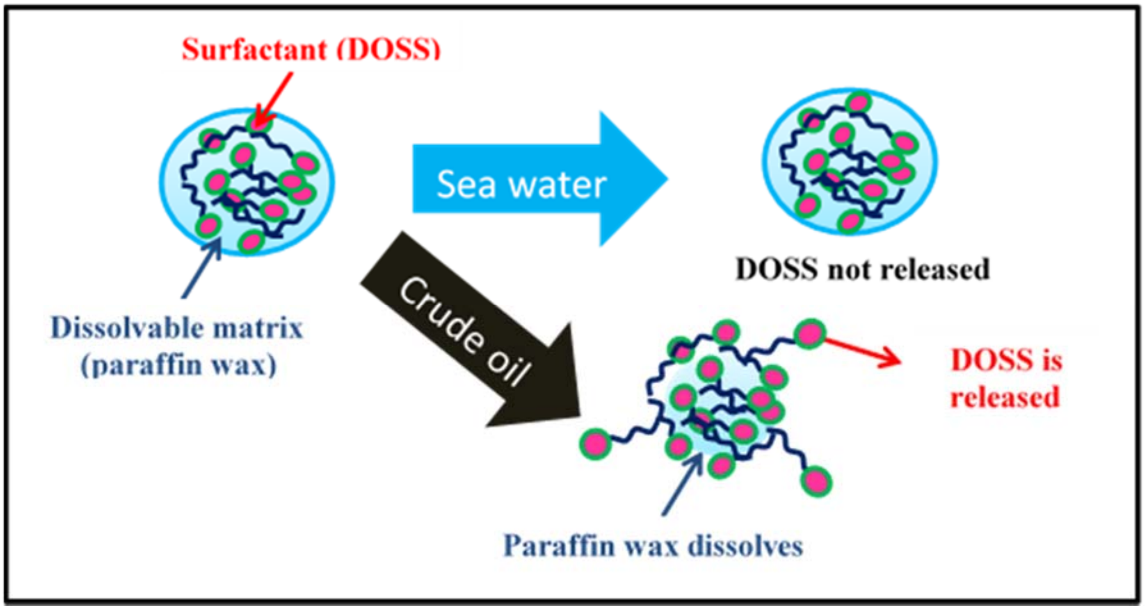
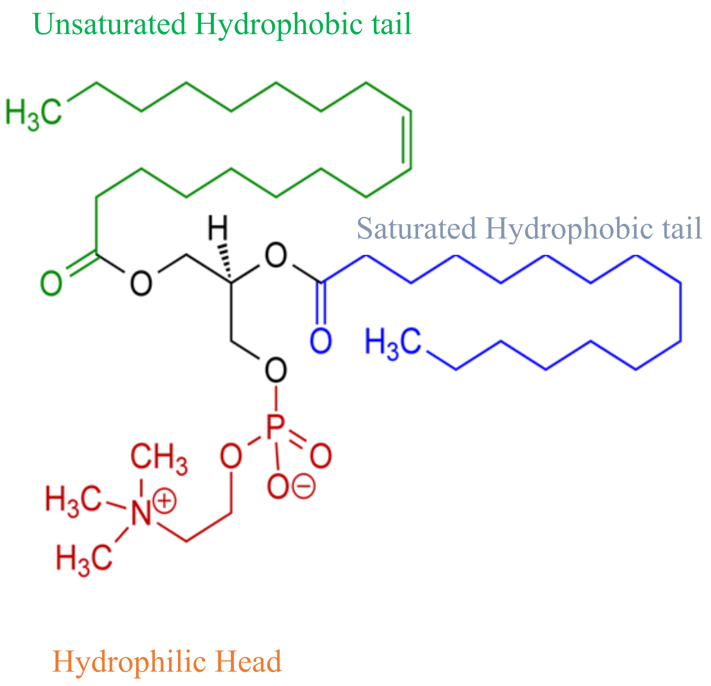


Figure 1.13 Mechanism of surfactant release from composite particle

The hydrocarbon based solvents (e.g. 2-butoxyethanol) used in dispersants formulations are known to be toxic to aquatic species and cleanup workers, the dispersant composite particle formulation will eliminate the use of these solvents and hence makes the dispersant less toxic. Furthermore, the different blend of solvents used for formulating traditional liquid dispersants may reduce the potency of the surfactants.

1.6.2 Chapter 3

The use of food grade surfactant; e.g. soybean lecithin solubilized in an aqueous solvent; water as a dispersant for crude oil spill application was formulated in chapter 3. Such a dispersant formulation is expected to be environmentally benign since soybean lecithin is biodegradable, less toxic and ecologically acceptable. Lecithin has been used to increase the biodegradation rate of dispersed oil since it contains phosphorus and nitrogen which are known to speed bacteria activity (Figure 1.14).[69, 72]



The hydrophilic and hydrophobic ends give lecithin a surface active property.

The phosphorus (P) and Nitrogen (N) increase biodegradation rate since they serve as nutrients for bacteria.

Figure 1.14 Chemical structure of lecithin

Therefore such a dispersant formulation will not only disperse the spilled oil but it will also aid in the biodegradation of the dispersed oil. The use of water as the medium of delivery will also result in a less toxic dispersant formulation and hence, it will help address the health concern raised by cleanup workers whenever oil spills occur. Again, the aquatic species will not be exposed to more toxic surfactants and solvents used in formulating liquid traditional dispersants.

1.6.3 Chapter 4

Halloysite nanotubes loaded with natural and synthetic surface active agents were formulated as a dispersant for crude oil spill application in chapter 4. The toxic hydrocarbon based solvents in traditional chemical dispersant formulations were replaced with environmentally benign and naturally occurring halloysite nanotubes. In addition to substituting the solvent with halloysite, the surface active agents used in the formulation were a blend of natural surfactants, surfactants that are used in the food processing industry (such as Tween 80 and Span 80) and a small percentage of the anionic surfactant DOSS. Surfactants used in the food industry are less toxic and with halloysite nanotubes being natural, non-toxic, biocompatible and an EPA 4A listed material, such a dispersant formulation is expected to be less toxic to aquatic species and cleanup workers. The continuous release of the embedded surfactants at the oil-water interface is expected to maintain the emulsion stability and result in high dispersion effectiveness.

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Chapter 2

Comparison of the Effectiveness of Solid and Solubilized Dioctyl Sodium Sulfosuccinate (DOSS) on Oil Dispersion Using the Baffled Flask Test, for Crude Oil Spill Applications

2.1 Introduction

Millions of gallons of crude oil and refined products are spilled into our marine waters worldwide each year. For example, over a period of 3 decades (1970-2000), over 3 billion gallons of crude oil and refined product were spilled into various marine waters.[1] The Gulf of Mexico and the Exxon Valdez oil spills are some of the most recent spill disasters, in which an estimated 205 and 11 million gallons of oil were released, respectively.[2]

Remediation strategies include mechanical containment and collection, in situ burning, shoreline clean up, natural biodegradation and the application of chemical dispersants. Since every oil spill is unique, technologies that work well in one situation may not work at all in another.[3] The limitations and concerns of some of the response options are summarized in Table A.1 (Appendix A.1) and were adopted from reference 4.[4] Where possible, oil is recovered by mechanical means, which involves the use of skimmers and booms to block the spread of oil, to concentrate it, and to remove it from the water. Though this method is preferable, mechanical containment still has many limitations. Only about 10 % of oil has been recovered from most major spills using mechanical containment [3] and as a result, this method is not feasible for large oil spills.

The in situ burning of oil spills has historically been regarded as a response method of last resort. As with the mechanical containment and collection method, burning is applicable only in certain circumstances; that is when the ocean current is less than 1 knot and the wave height is below 2 meters. Since the dynamics of ignition and sustained burning of oil spills has not been understood, igniting and keeping a slick ablaze is often difficult. Another limitation is that incomplete combustion of the oil results in the transfer of pollutants into the surrounding air and as a result creates environmental problems. In drift ice and open water, oil spills can rapidly spread to become too thin to ignite. The application of specific surfactant sometimes called herders or oil collecting agents to the water around the perimeter of the oil slick changes the surface chemistry of water forcing slick into smaller area. As a result, the thickness of the oil increases and this makes ignition much easier.[3, 5]

Many microorganisms possess the enzymatic capability to degrade petroleum hydrocarbon. Some microorganisms degrade alkanes (paraffin), others aromatics, and others both paraffinic and aromatic hydrocarbons. Seeding with oil degraders has not been demonstrated to be effective, but addition of nitrogenous fertilizers has been shown to increase the rate of petroleum biodegradation.[6] Because natural processes are generally slow and a large amount of nitrogenous fertilizers must be used to adequately accelerate the biodegradation process, this method has proved cost ineffective.

The application of chemical dispersants is one of the few feasible response measures for minimizing the impact of a large oil spill at sea. Chemical dispersants have many characteristics that make them attractive for use in oil spill response. These include:

- Enhancing the rate of oil dispersion and biodegradation by creating finer oil droplets and increasing surface area. This also results in a reduction of coalescence and resurfacing of the oil.[7]
- Feasibility in harsh weather conditions. Unlike mechanical containment and collection, and burning of oil in situ, dispersants can be used in harsh weather conditions. In fact the turbulent weather conditions promote the dispersion effectiveness.[8]
- Decreasing the exposure of the spilled oil to marine birds.[9]
- Countering the formation of water-in-oil emulsions which result from the presence of naturally occurring surfactants such as asphaltene in the crude oil. The formation of water-in-oil emulsions makes the natural dispersion of the crude oil very difficult.[9-10]

Effective use of dispersants can accelerate oil biodegradation by naturally occurring microorganisms, preventing the oil spill from drifting ashore and damaging sensitive coastal ecosystems.[11] However, indiscriminate application of dispersant to subsea and surface oil spills results in a significant amount of dispersant not coming into contact with the oil and wasted. The aqueous solubility and miscibility of oil spill dispersants and inevitable sea currents cause dispersant to be washed away and wasted. To compensate for this inefficiency, large amounts of dispersants are used resulting in high costs and a large environmental load. For example, an estimated 2.1 million gallons of dispersant were applied to the Gulf of Mexico during the Deepwater Horizon oil spill of 2010 to disperse approximately 205 million gallons of crude oil.[12] Environmental and human toxicity issues arose when such voluminous amount of chemical dispersants are applied. The chemical dispersant, Corexit 9500A which was used for the Gulf of Mexico oil spill, was moderately toxic to Gulf of Mexico aquatic species and had adverse dermal and pulmonary effects on cleanup workers.[13] Although most dispersants are considered inexpensive, sheer volume leads to significant costs. The estimated 2.1 million gallons of dispersant applied during the Gulf of Mexico oil spill cost British Petroleum (BP) over $80 million.[13c]

To decrease surfactant wastage and reduce dispersant toxicity, this study proposes the use of solid water-insoluble paraffin wax particles containing the surfactant, as chemical dispersants for their potential in oil spill dispersion. In such a formulation the surfactant (DOSS) is only released when the paraffin wax dissolves in the oil upon contact (Figure 2.1).

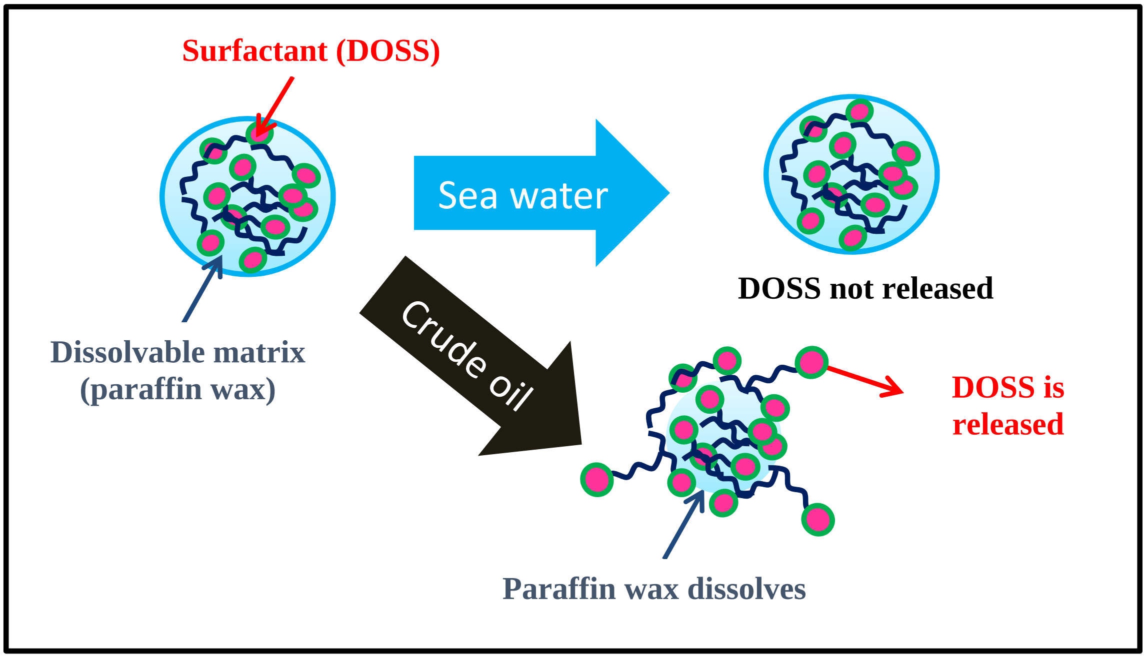


Figure 2.1 Mechanism of surfactant release from composite particle

The ability of microparticles to adhere to the fluid interface (oil-water interface) may allow for continuous release of surfactant directly where it is needed and as a result reduce surfactant wastage and the amount of surfactant needed. In addition, before dissolution takes place particles that adhere to the water-oil interface essentially reduce the unfavorable contact between the oil and water[14] and thus may lower the interfacial energy, further increasing the dispersion effectiveness. The hydrocarbon based solvents (e.g. 2-butoxyethanol) used in dispersants formulations are known to be toxic to aquatic species and cleanup workers, the dispersant composite particle formulation will eliminate the use of these solvents and hence makes the dispersant less toxic. Furthermore, the different blend of solvents used for formulating traditional liquid dispersants may reduce the potency of the surfactants. Therefore in this study, the dispersion effectiveness of dispersant composite particles prepared by spray freezing DOSS with paraffin wax was compared with that of DOSS dissolved in propylene glycol. We examined how various factors, such as mixing energy, salinity, particle size, crude oil type and solubility of the matrix material (paraffin wax) in the crude oil influences the effectiveness of the composite dispersant particles. Heavy crude (Texas crude, TC) and Light crude (LC) oils were used in this study.

2.2 Experimental Section

2.2.1 Materials

Sodium hydroxide pellets and concentrated sulfuric acid solution were obtained from Fisher Scientific, and methylene blue solution (1 % w/v) was obtained from RICCA Chemical Company. The following chemicals were all obtained from Sigma Aldrich: sodium phosphate dibasic, dioctyl sodium sulfosuccinate salt (DOSS), cyclohexanol (99

%) and paraffin wax. Dichloromethane and propylene glycol were obtained from Macron Chemicals and Spectrum Chemicals respectively. The Instant Ocean salt was obtained from Instant Ocean (Blacksburg, VA).

The heavy crude oil (Texas crude) was obtained from Texas Raw Crude International (Midland, TX) while the light crude was obtained from Ohmsett (Atlantic Highlands, NJ). The major compounds present in the crude oil samples and the properties of the crude oil are shown in Table A.2 (Appendix A.2) and Table 2.1 respectively.

Light crude oil has low viscosity and flows freely at room temperature. It has low density, low specific gravity and high API gravity due to the presence of a high proportion of light hydrocarbon fractions. The Light crude oil sample used in this study is made up of mainly alkanes (i.e., paraffin) and has an API gravity of approximately 40. The API gravity of the crude oil samples was determined with ASTM D287. On the other hand, heavy crude oil has high viscosity and cannot easily flow freely at room temperature. Heavy crude oil is highly dense and has low API gravity, mainly due to the presence of high proportions of aromatics and naphthenes. The Texas crude (heavy crude) used for this study is mainly made up of aromatics and napthenes and has an API gravity of approximately 32. The asphaltene content of the crude oil samples was determined by ASTM D3279 to be 6 and 4.1 wt.% for the heavy and the light crude, respectively.

Table 2.1 Properties of the crude oil

Crude oil	API Gravity	Solubility of Wax (g/l)	Asphaltene content (wt. %)
Texas Crude (TC)	32	25	6
Light Crude (LC)	40	12	4.1

A schematic diagram of the spray freezing setup used for making solid particles is shown in Figure 2.2. The setup consists mainly of a high temperature pump (Fluid Metering, Inc.), a sonication horn and controller, spray coater vessel, filter, chiller and air source. The suction and delivery lines of the pump were heated with heating tapes (Briskheat® Heating tape with percentile control) to ensure the paraffin wax-Doss mixture remained in a molten state. The chiller aided in the rapid cooling of the particles.

2.2.2 Experimental Procedure

2.2.2.1 Dispersant Composite Particles Preparation

An amount of paraffin wax was heated to approximately 80 ℃ containing an appropriate amount of DOSS. The molten paraffin wax-DOSS mixture was delivered onto a sonication horn via high temperature pump. The mixture was atomized and cooled to room temperature at a rate of $6\ ℃/s$ to form DOSS-paraffin wax composite particles. Five different particle formulations were made, namely: P1.61D, P3.73D, P5.12D, P6.33D and P8.10D. The spray freezing method used for the preparation of the particles resulted in the formation two major types of particles as can be seen in the last column of Table 2.2. The DOSS in particles with less than 5.12 wt.% DOSS were fully covered by the paraffin wax while the DOSS in the particles with more than 5.12 wt.% DOSS were not fully covered and were exposed on the surface of the particles. The compositions of these composite particles are shown in Table 2.2.

Table 2.2 Particle formulations used in this study

Particle	**Composition**	**Type of Particles**
P1.61D	Paraffin wax particles with 1.61 wt.% DOSS	Composite particle without DOSS on its surface
P3.73D	Paraffin wax particles with 3.73 wt.% DOSS	Composite particle without DOSS on its surface
P5.12D	Paraffin wax particles with 5.12 wt.% DOSS	Composite particle without DOSS on its surface
P6.33D	Paraffin wax particles with 6.33 wt.% DOSS	Composite particle with DOSS on its surface
P8.10D	Paraffin wax particles with 8.1 wt.% DOSS	Composite particle with DOSS on its surface

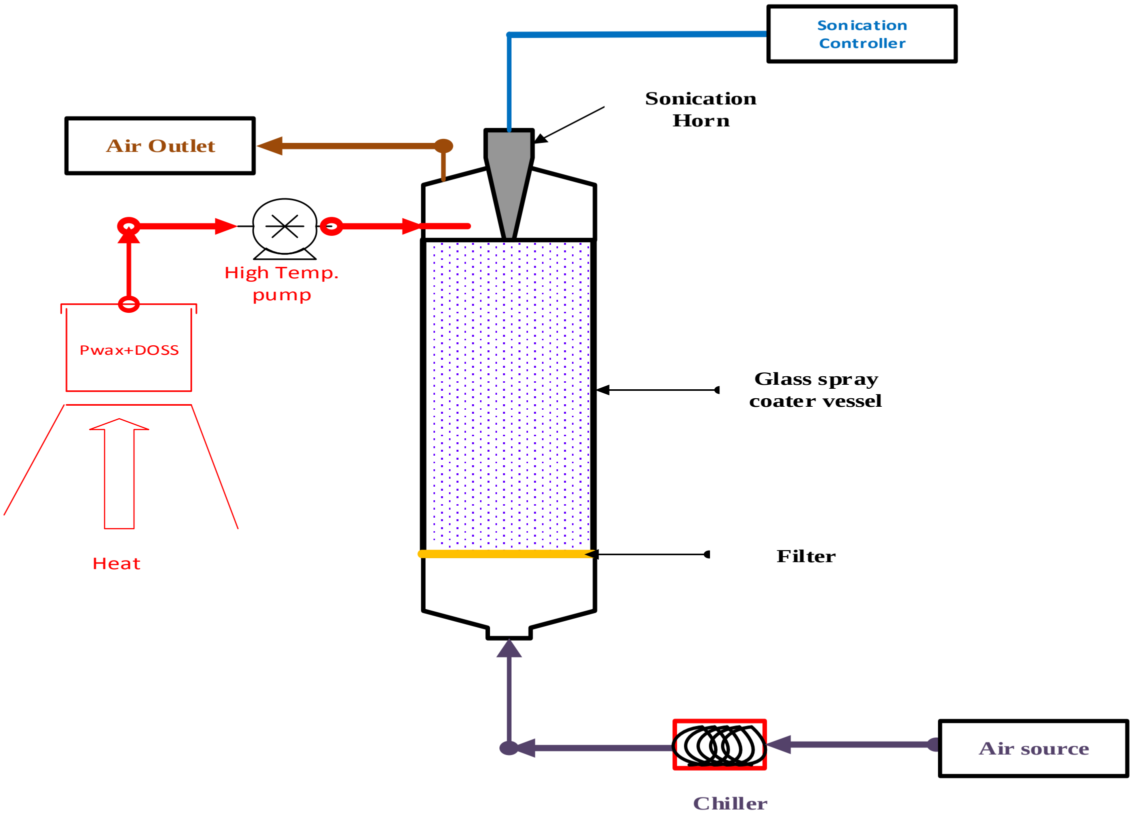


Figure 2.2 Spray freezing set up

2.2.2.2 Solubilized DOSS Preparation

Different concentrations of solubilized DOSS (0.05, 0.1, 0.2 and 0.3 mg/µl) were prepared by dissolving an appropriate amount of DOSS in equal volume of solvents; in this case propylene glycol, cyclohexanol (CH), dichloromethane (DCM), or water.

2.2.2.3 Synthetic Sea Water Preparation

Different concentrations, that is 35, 28 and 16 g/l (representing 3.5, 2.8 and 1.6 wt.%), of synthetic sea water were prepared by dissolving appropriate amounts of Instant Ocean sea salt in 1 L of distilled water and leaving it on a magnetic stirrer for 72 hours to dissolve all the salt. The chemical composition of instant ocean sea salt is presented in Table A.3 in Appendix A.3 and was adopted from reference 15.[15]

2.2.3 Product Characterization

2.2.3.1 Dissolution Trial

To examine whether or not some of the DOSS were exposed on the surface of the DOSS-paraffin wax composite particle after the spray freezing process, some weighed amount was used in a dissolution trial. In the analysis, 100 mg of the composite particles were added to 200 ml of water and stirred at 150 rpm with a Caframo® stirrer for 30 minutes after which 5 ml samples were drawn at 5 minutes interval and analyzed for DOSS using the methylene blue test. It should be noted that 5 ml of water was added anytime the 5 ml sample was drawn to maintain the concentration.

2.2.3.2 Methylene Blue Test

The methylene blue test is the analytical method used to quantify anionic surfactants in water. If some of the DOSS were exposed on the surface of the composite particles, DOSS will be released into the water during the dissolution trial. The procedure used for this test was the same as that described in the hand book of water analysis.[16] That is, 2 ml of the water sample drawn during the dissolution trial was added to 48 ml of distilled water in a separating funnel. 10 ml alkaline phosphate solution, 5 ml of neutral methylene blue solution and 15 ml of chloroform were then added. The extraction process was carried out by shaking the separating funnel gently for 1 minute. The phases were allowed to settle, and the chloroform extract drained off into another separating funnel containing 110 ml of distilled water and 5 ml acid methylene blue solution. The first separating funnel was then rinsed with 5 ml of chloroform and shaken for 1 minute. The phases were allowed to separate and the chloroform extract drained into the second separating funnel. The second separating funnel was then shaken for 1 minute and the phases allowed to separate. The chloroform extract was drained through a chloroform-moistened cotton wool on a funnel into a 50 ml graduated cylinder. The second separating funnel was then rinsed with 5 ml chloroform and shaken for 1 minute. The phases were allowed to separate and the chloroform extract drained into the same 50 ml graduated cylinder. The chloroform extract in the 50 ml graduated cylinder was topped up to the 50 ml mark with pure chloroform. The amount of DOSS was quantified at an absorbance difference of 650-400 nm. This analytical method is based on the formation of ionic pairs between the anionic surfactant and cationic methylene blue dye (Equation 1).

$$[C_{20}H_{37}O_7S]^- + [C_{16}H_{18}N_3S]^+ \rightarrow [C_{20}H_{37}O_7S]^-[C_{16}H_{18}N_3S]^+ \tag{1}$$

2.2.3.3 Baffled Flask Test

The baffled flask test, which is a revised protocol,[17] is used to evaluate dispersion effectiveness of chemical dispersants and is being considered by the EPA to replace the swirling flask test. The consideration is necessary due to the lack of reproducibility of the results obtained from the swirling flask test in the hands of different analyst[18] and also because the mixing exhibited by the swirling flask test does not resemble the mixing at sea.[19] The baffles make it possible to create breaking waves which are similar to the ones observed at sea.

To analyze the dispersion effectiveness of the solubilized DOSS, 100 µl of crude oil was added to 120 ml of synthetic sea water in a baffled flask. 4 µl of the solubilized DOSS was added directly on top of the oil and the baffled flask placed on a shaker (VWR advanced digital shaker, Model 3500) set at 200 rpm for 10 minutes. A settling time of 10 minutes was allowed after which 30 ml of the aqueous media with dispersed oil was drawn and then the dispersed oil was extracted with DCM and quantified with UV-Vis at an absorbance difference of 300-400 nm. The baffled flask procedure for determining the dispersion effectiveness of the dispersant composite particles was the same as described above but instead of the 4 µl of solubilized DOSS, an appropriate amount of composite DOSS-paraffin wax particles was used.

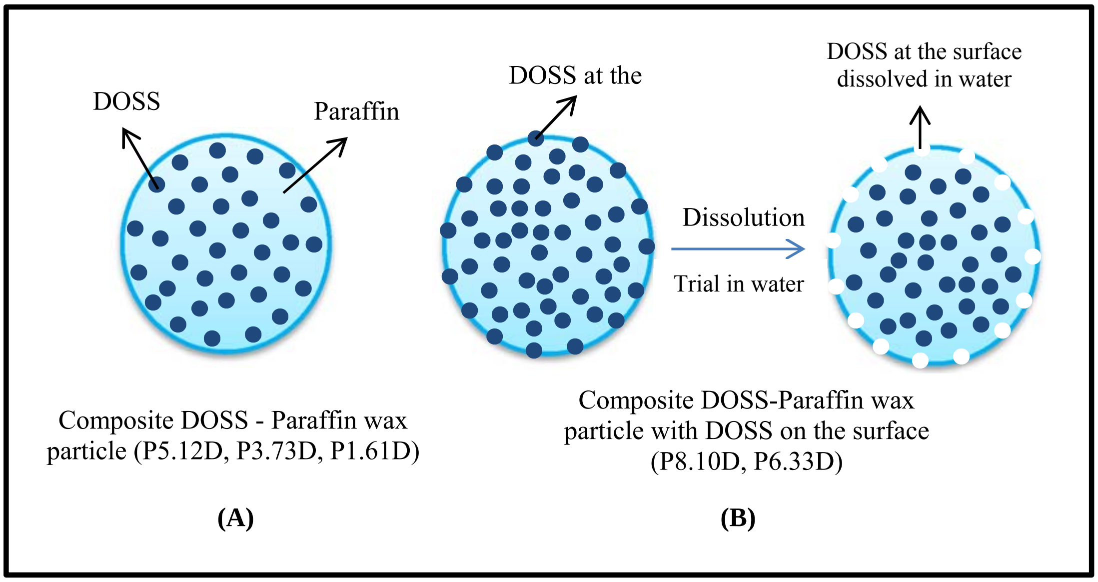
All the experiments were conducted at least in duplicates. The error bars in all the plots are the standard error of the mean (SEM).

2.3 Results and Discussion

2.3.1 Size and Morphology of Prepared DOSS Particles

The spray freezing method used for the preparation of the composite DOSS-paraffin wax particles in this study resulted in the formation of matrix particles as shown in Figure 2.3. In a matrix particle, the active agent; DOSS is distributed within the matrix (paraffin wax). Whether or not the entire DOSS will be fully covered by the paraffin wax is dependent on the weight percent of DOSS used during the formulation. As can be seen in Table 2.2 and Figure 2.3, some of the DOSS that were present in particles with more than 5.12 wt.% of DOSS were exposed on the surface of the composite particle. Particles

P8.10D and P6.33D were therefore designated as "composite particles with DOSS on its surface" whereas P5.12D, P3.73D and P1.61D were designated as "composite particles without DOSS on its surface" in Table 2.2.



Composite DOSS - Paraffin wax particle (P5.12D, P3.73D, P1.61D)

(A)

Composite DOSS-Paraffin wax particle with DOSS on the surface (P8.10D, P6.33D)

(B)

Figure 2.3 Schematic representation of the cross section of the matrix particles: (A) Composite DOSS-Paraffin wax particles (B) Composite DOSS-Paraffin wax particle with DOSS on its surface

The composite particles prepared had spherical shape (Figure 2.4) and tended to agglomerate with time in air during storage which can be attributed to the waxy nature of the particles. The extent of agglomeration was pronounced for particles P8.10D and P6.33D due to the presence of DOSS on the surface of those particles. Further agglomeration of the particles occurred in the solvents (organic) used for dynamic light scattering (DLS) analysis and as a result, large standard deviations in mean particle size were detected during the DLS analysis. To address this problem, mean particle sizes were determined with the help of SEM images of the particles and are recorded in Table 2.3. That is SEM images from 10 different scanned areas of each composite particle formulation were obtained and then the diameter of 21 randomly selected particles in each area were measured for computing the average particle size and standard deviation. The histogram for P1.61D, P3.73D and P5.12D are shown in Appendix A.4 in Figures A.1, A.2 and A.3.

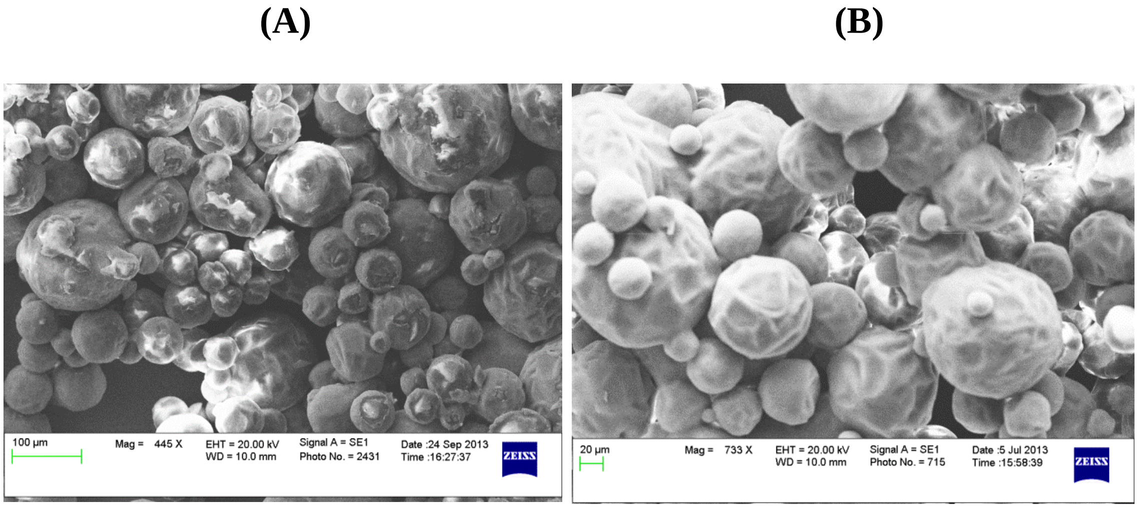


Figure 2.4 SEM of prepared particles: (A) P1.61D, and (B) P5.12D

Table 2.3 Mean particle sizes of the composite particles used for the US EPA's baffled flask test

Particle	Mean Particle Size (µm)
P1.61D	89.64 ± 7.32
P3.73D	97.07 ± 9.85
P5.12D	95.17 ± 9.03

2.3.2 Dissolution Trial and Methylene Blue Test

Since the ultimate aim of this research is to examine how effectively dispersant composite particles can be used to disperse oil slicks, there was the need to investigate whether or not the DOSS were indeed fully covered by the paraffin wax matrix. This was achieved by carrying out the dissolution trials and methylene blue test as stipulated in section 2.2.3. The results obtained from the methylene blue test are shown in Figure 2.5.

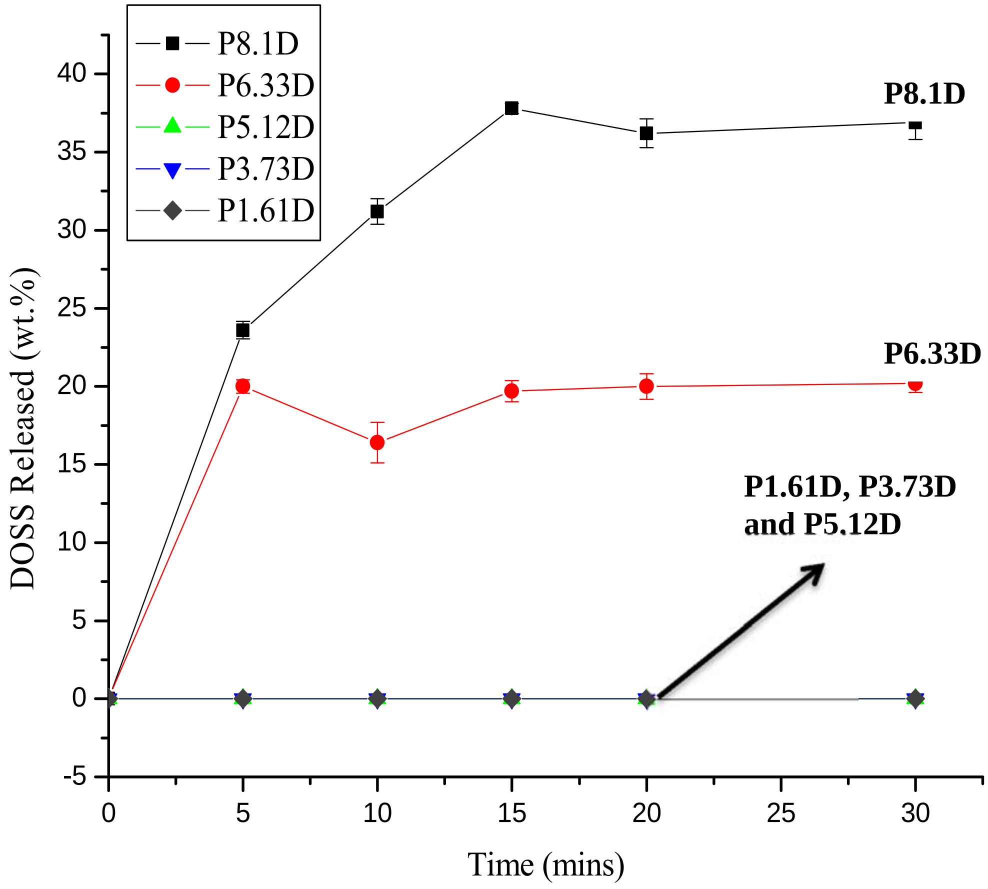


Figure 2.5 DOSS released in water versus time for various composite DOSS-paraffin wax particle formulations.

Figure 2.5 shows that the DOSS in P.161D, P3.73D and P5.12D were fully covered with zero weight percent (0 wt.%) release of DOSS in water from 5 to 30 minutes. On the other hand, the DOSS in P6.33D and P8.1D were not fully covered and released 20.2 and 36.9 wt.% DOSS into water in 30 minutes, implying that some of the DOSS was exposed on the surface of those composite particle. During the dissolution trial, only the DOSS exposed on the surface of the composite particle is dissolved in the water. After the dissolution trial, some of the DOSS in particles P8.1D and P6.33D remained in paraffin wax due to the matrix nature of the DOSS-paraffin wax particles as can be seen in Figure 2.3. This explains why there was no 100 wt.% release of DOSS in water though the concentrations were below the solubility limit of DOSS in water. The release rate is governed by the Noyes-Whitney equation:

$$Dissolution\ Rate = \frac{dC}{dt} = \frac{AD}{h}[C_s - C_b] \tag{2}$$

where, A is the surface area (m^2), D is the diffusivity (m^2/s), h is the boundary layer thickness (m), C_s is the saturation solubility (kg/m^3) and C_b is the bulk concentration (kg/m^3). This equation describes the rate of dissolution of spherical particles when the dissolution process is diffusion controlled and involves no chemical reaction. Physiochemical properties such as solubility and particle size affect the dissolution rate in the Noyes-Whitney's equation.[20] The fast release rate of the uncoated particles is due to the aqueous solubility of DOSS and also the increased surface area stemming from the micro-sized particles. Zero release rates were recorded by the composite particles P5.12D, P3.73D and P1.61D because paraffin wax is insoluble in water. Particles P1.61D, P3.73D and P5.12D were therefore used in the baffled flask test.

2.3.3 Dispersion Effectiveness of Composite Particles

Using the baffled flask test, the dispersion effectiveness of the different composite particle formulations was compared. Though it is possible for micro-sized particles to disperse crude oil through the formation of Pickering emulsion observations made during the study led to the conclusion that, the dispersion of the crude oil was mainly due to the release of the surfactant DOSS from the composite particle. It was observed that the composite particles adhered to the oil-water interface before the agitation of the baffled flask. After the agitation and settling step in baffled flask test, the particles settled on the surface of the oil-water emulsion. This is possible, when the density of the composite particles is less than that of water. Therefore, there was a good contact between the oil and the particles before the agitation of the baffled flask and as a result, allowed for the release of the DOSS after the oil dissolved the paraffin wax. The agitation of the baffled flask also allowed the particle to intermittently find the oil and this might have resulted in additional release of DOSS. The dispersion of the crude oil can therefore be attributed to the release of DOSS which subsequently resulted in a reduction in the oil-water interfacial tension during the baffled flask test. This concept works well for the dispersion of oil spill on the sea surface. The particles would have contributed to the emulsion formation and hence the dispersion of the oil, if they adhered to the oil droplet-water interface after the baffled flask test but observation of the emulsion under an optical microscope proved otherwise. From both Figures 2.6 and 2.7, it was observed that, for a particular composite particle formulation, the dispersion effectiveness increased as the DOSS amount increased. Increase in the amount of the surface active agent (i.e., DOSS) led to a reduction in the interfacial tension ($\gamma_{o/w}$) which enhanced the spreading of the oil. This made it easier for the oil to break into droplets upon the application of an external source of energy during the baffled flask test, as given by the following equation 3.[21]

$$A_{O/W} = \frac{W_k}{\gamma_{o/w}} \tag{3}$$

Where, $A_{O/W}$ is the interfacial surface area (cm^2) between the oil and the water, W_k is the mixing energy (ergs) and $\gamma_{o/w}$ is the interfacial tension ($dynes/cm$) between the oil and water. Since the total energy input for the baffled flask test is constant, a variation in interfacial surface area is therefore due to the differences in interfacial tension. Increasing the amount of DOSS resulted in a decrease in the interfacial tension causing the interfacial surface area to increase which results in the formation of a more stable oil-in-water emulsion due to smaller oil droplets with low rising velocity. The stable oil-in-water emulsion resulted in a much higher dispersion effectiveness as the dispersed oil droplets remain stable in the water and do not coalesce.

Different composite particle formulations have differing dispersion effectiveness, with P1.61D giving the highest dispersion effectiveness of 60 vol.% at DOR of 23 mg/g with TC as can be seen in Figure 2.6. However, in Figure 2.7, it was observed that, P5.12D provided the highest dispersion effectiveness of 62.6 vol.% at 23 mg/g DOR with LC. The dispersion effectiveness for TC was different than for LC for a given particle formulations, which can be attributed to differences in the solubility of paraffin wax in the TC versus LC (Table 2.1). Since wax has lower solubility in the LC compared to TC, increasing the amount of wax in the particles affected the dispersion of the LC much more than the TC. Increasing the amount of wax within a specified amount of oil led to a reduction in the solubility of wax and hence reduced the rate at which the paraffin wax dissolved in the oil, which subsequently affected the amount of DOSS released for dispersion. In Figure 2.7, at 23 mg/g DOR, P5.12D gave a dispersion effectiveness of 62.6 vol.% compared to 61.7 and 56.3 vol.% for P3.73D and P1.61D, respectively. This is attributed to the fact that, P1.61D contained more wax than P3.73D which also contained more wax than P5.12D. Since the solubility of wax in LC is very low, increasing the amount of wax had a negative effect on dissolution rate of the paraffin wax in the oil and dispersion effectiveness. However, a different observation was made in Figure 2.6 for dispersing TC. Though P1.61D contained more wax than P3.73D and P5.12D, it recorded a dispersion effectiveness of 60 vol.% compared to the 52.5 and 53.8 vol.% for P3.73D and P5.12D respectively. Therefore, particle size may be influencing the dispersion effectiveness. From Table 2.3, P1.61D has smallest mean particle size than P5.12D and P3.73D. With the TC having a much higher solubility of wax, addition of more wax did not affect the release of DOSS during dispersion to a greater extend compared to the LC. Because of the high solubility of the paraffin wax in TC, the effect of the particle size on the dispersion effectiveness is pronounced. Furthermore, the particle with the smallest size tends to dissolve more easily than the larger particles due to high surface area which enhanced the dissolution rate in the oil.

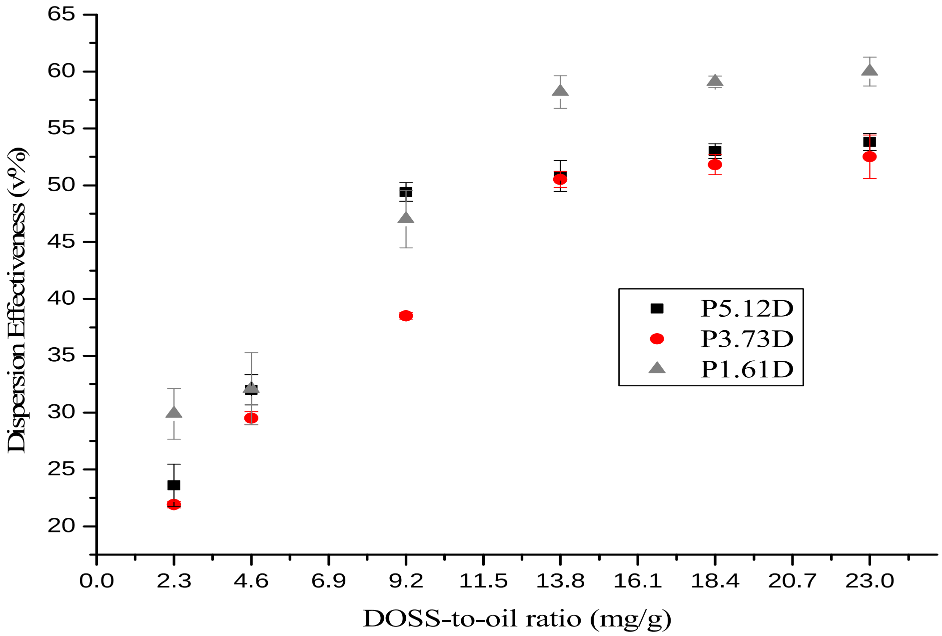


Figure 2.6 Dispersion effectiveness of composite particles in TC

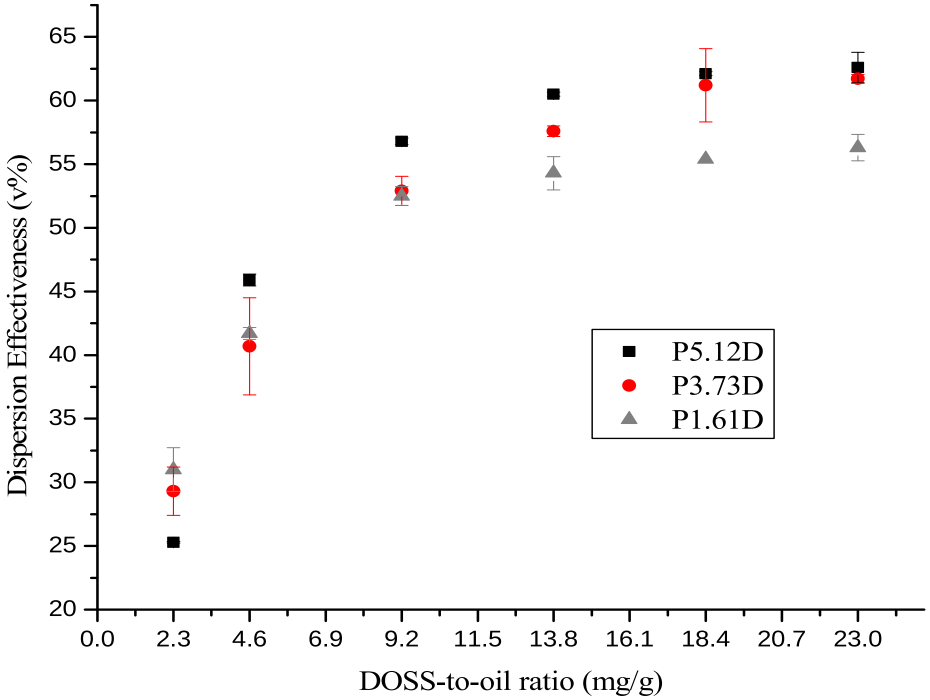


Figure 2.7 Dispersion effectiveness of particles in LC

2.3.4 Dispersion Effectiveness of Composite Particles and Solubilized DOSS

The dispersion effectiveness of the composite particles (P5.12D) and solubilized DOSS were compared in both TC and LC. From Figure 2.8, the dispersion effectiveness of the solubilized DOSS was 5-12 vol.% higher than those of the particles (P5.12D) in TC at all the DOR's used in the study. For dispersion to occur, the DOSS will have to diffuse from the solvent or the coating material to the oil-water interface. Diffusion from the solid state particle is much slower than from the liquid state when dealing with viscous TC. Despite this observed trend, the dispersion effectiveness of the particles recorded at 23 mg/g DOR was 53.8 vol.% , which meets the criteria set by EPA; that is for a dispersant to be used in oil spill remediation, it should be able to disperse at least 50±5 vol.% of the oil in the laboratory test. Therefore, the particles prepared in this study can still be used as a dispersant for oil spill remediation.

Shown in Figure 2.8, the dispersion effectiveness of the solubilized DOSS in LC was 1-11 vol.% more than that of the composite particle at all the DOR's investigated. This trend can be attributed to the ease with which the released DOSS migrated to the oil-water interface due to the high API gravity (40) and low viscosity of LC. A comparative study from Figure 2.8 showed that P5.12D dispersed 56.8 and 60.5 vol.% of the LC oil at 9.2 and 13.8 mg/g DOR, respectively compared to 49.4 and 50.8 vol.% of TC oil at 9.2 and 13.8 mg/g DOR, respectively. In general, the dispersion effectiveness of the particle and solubilized DOSS were higher in LCs than in TC. This observation stemmed from the fact that TCs are difficult to disperse due to their ability to form water-in-oil emulsions as a result of the presence of porphyrin and metallopophyrin complexes,[10] asphaltene and wax.[22] Analysis of the crude oil samples (Table 2.1) showed that TC contains more asphaltene than LC. In addition to this, the GC-MS analysis results (Table A.2 in Appendix A.2) show the presence of mainly aromatics and naphthenes in TC which makes crude oil very difficult to disperse. However, LC used in this study is made up of mainly alkanes and alkane/aromatic ratio is known to influence the emulsification behavior of the crude oil.[23]

The composite DOSS-paraffin wax particle delivery was expected to have resulted in an increase in dispersion effectiveness since the DOSS was delivered at the exactly where it is needed, that is the oil-water interface. As already mentioned in the discussion above, the dispersion effectiveness of the solubilized DOSS was higher than that of the composite particle. The matrix nature of the composite particles may have affected their effectiveness in dispersing the crude oil. With the high fraction of paraffin wax (>95 wt.%) in each particle used for the baffle flask test, which exceeded the solubility limit of paraffin wax in the LC and TC, not all the DOSS for each of the DOR analyzed was released for dispersion. In the case where solubility limits were not exceeded, since the baffled flask test was carried out for only 10 minutes, the DOSS released within that period was used for dispersion. Since less amount of DOSS may have been released from the composite particle for dispersion, the reduction of the interfacial tension was minimal compared to the solubilized DOSS. In view of this, a new particle preparation method will be developed in the future that would result in a core-shell particle with a thin layer of coating material as elaborated in chapter 6. The core-shell particle would allow for the release of the entire encapsulated surfactant as soon as the shell dissolves in the oil and this is expected to increase the dispersion effectiveness.

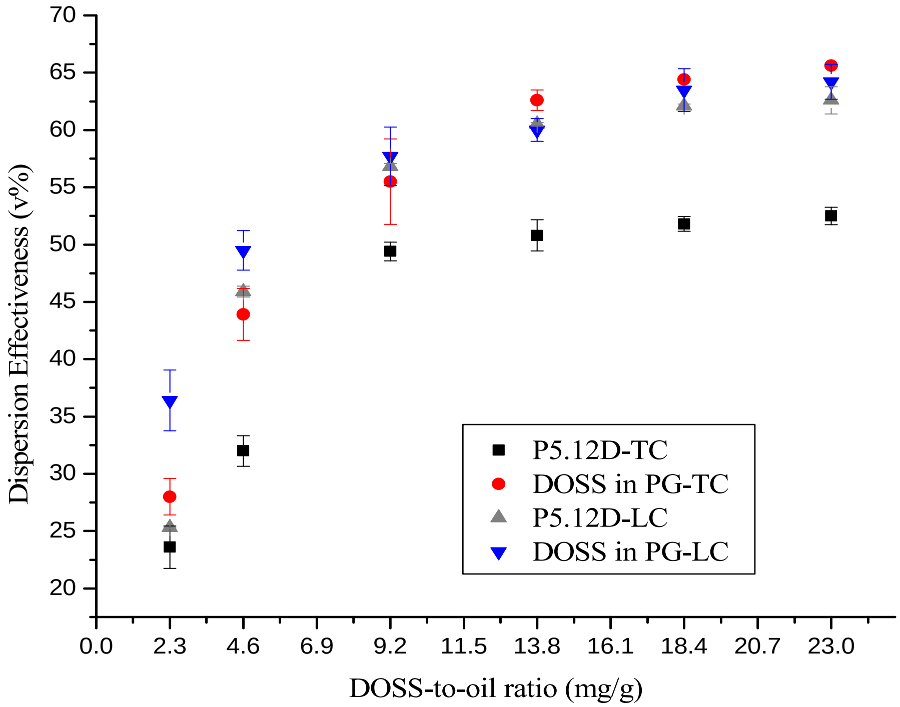


Figure 2.8 Dispersion effectiveness of particles (P5.12D) and solubilized DOSS in TC and LC

Since the study was about Comparing the dispersion effectiveness of solubilized DOSS and composite DOSS-paraffin wax particles, there was the need to investigate into how various solvents influences the dispersion effectiveness. Solvents with varying viscosities and solubility in water were used to prepare solubilized DOSS. The objective was to examine the effects that viscosity, density and water solubility have on the dispersion effectiveness. The viscosity and density of the solvents and their solubility in water are shown in Table A.4 (Appendix A.5). The dispersion effectiveness was examined by varying the DOR from 2.3 to 13.8 mg/g. Higher DOR could not be examined because it was not possible to prepare solution of higher concentrations of DOSS in water. That is

0.4 g/ml which would have resulted in DOR of 18.4 mg/g resulted in the formation of a solid mixture of DOSS and water.

From Table A.4 in Appendix A.5 and Figures 2.9 and 2.10, it was observed that the solvent with the highest viscosity, least solubility in water, and lowest density recorded the highest dispersion effectiveness. However, though DCM has the lowest solubility in water among all the solvents used, it recorded the lowest dispersion effectiveness. The high volatility of DCM resulted in a sizeable volume of solvent being lost when conducting the baffled flask test. Thus, solvents used in dispersant formulations should have low vapor pressure to avoid rapid evaporation.[24] For a better dispersion, the solvent should be able to "carry" the DOSS to the oil-water interface. Aqueous solubility of the solvent affects the spreading of the DOSS at the oil-water interface, causing most of the DOSS to dissolve in water instead of reducing interfacial tension. Again, high solvent viscosity enhanced the shearing effect during the baffled flask test, increasing the dispersion effectiveness. However, application of a highly viscous chemical dispersant to oil slick will inhibit the penetration of the dispersant through the slick and may reduce the dispersion effectiveness. Fiocco et al. [24] stated the importance of the solvent density on the dispersion process. Solvent should be less dense than sea water to avoid sinking and to allow for the spreading at the oil-water interface. Also, Solvents with density lower than that of the sea water are likely to record a higher dispersion effectiveness due to lower density by enhancing spreading of the oil and contributing to the reduction of the interfacial tension. These factors accounted for the trend observed in Figures 2.9 and 2.10: the solvent with the highest viscosity, lower density, lower solubility in water and less volatility contribute to higher dispersion effectiveness. That is, the dispersion effectiveness of DOSS in cyclohexanol (CH) >DOSS in PG>DOSS in water>DOSS in DCM. A balance of the factors highlighted above and toxicity of the solvents should serve as a guideline for the selection of solvent (from the ones used in this study) when formulating solubilized dispersants.

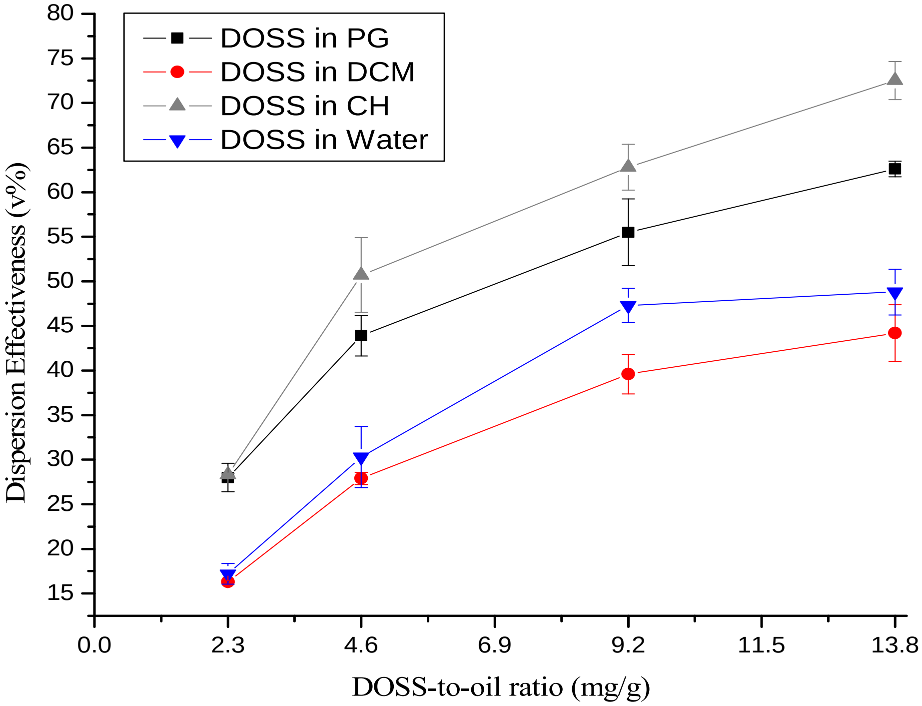


Figure 2.9 Dispersion effectiveness of solubilized DOSS in TC

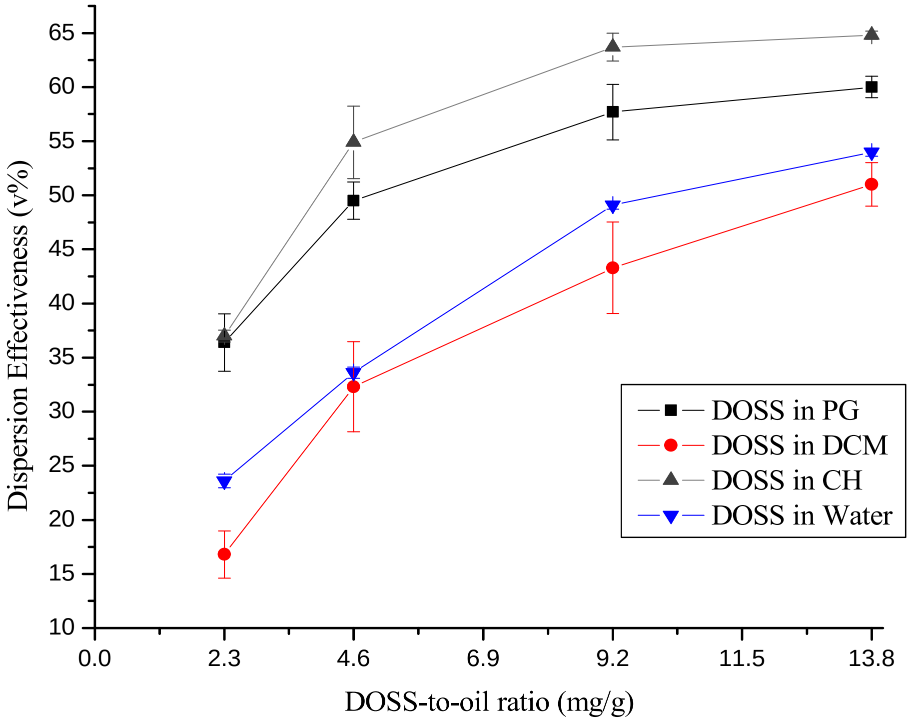


Figure 2.10 Dispersion effectiveness of solubilized DOSS in LC

2.3.5 Effect of Energy on Dispersion Effectiveness

2.3.5.1 Effect of Energy on Dispersion Effectiveness (composite particle-solubilized DOSS)

The baffled flask test, which is a revised protocol for testing the dispersion effectiveness of chemical dispersant, requires the use of 200 rpm as the mixing energy.[17, 25] This standard was set for solubilized DOSS, not for dispersants in the form of particles as it was used in this study. Therefore it is necessary to examine whether or not the standardized rpm can also be used for particulate dispersants.

The dispersion of oil slick into droplets is governed by a positive change in Gibbs free energy as,[26]

$$\Delta G = \gamma_w + \gamma_{o/w}\left(3\frac{\delta}{r} - 1\right) - \gamma_o \tag{4}$$

where, ΔG is the free energy change, r is the dispersed oil radius, γ_o is the oil's surface tension, γ_w is the water's surface tension, $\gamma_{o/w}$ is the interfacial tension (IFT) between the oil and water, and δ is the thickness of floating oil on a unit water area. In equation 4, γ_o and γ_w are fairly constant however, the IFT can be reduced by the addition of dispersant but no matter the amount of dispersant added, studies have shown that the free energy change will always be positive.[26] The only way that the dispersion process can be carried out is by the application of an external source of energy. In real life oil spill situations, this energy is supplied by the ocean current and waves but in the laboratory is achieved by the aid of an orbital shaker set at 200 rpm.

From the observations made in Figures 2.11 and 2.12, at 9.2 mg/g DOR, increasing the mixing energy resulted in a corresponding increase in dispersion effectiveness. One notable observation from both figures is that, while the dispersion effectiveness was very low at 150 rpm depicting the inadequacy of the mixing energy to produce a stable emulsion, the dispersion effectiveness was comparably high at 200 and 250 rpm for both the composite DOSS-paraffin wax particle and Solubilized DOSS. However, at 200 rpm, the dispersion effectiveness was almost the same as at 250 rpm within a standard error of margin of ± 0.82 for LC and ± 4 for TC. This affirms that the standardized rpm set for solubilized DOSS is also applicable to composite particulate DOSS. Hence, 200 rpm was used through-out this study.

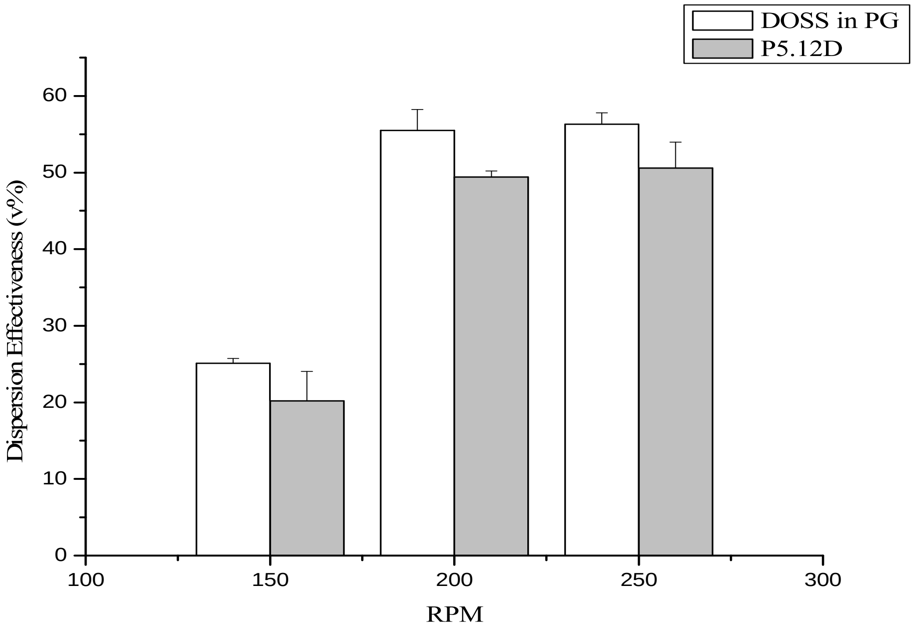


Figure 2.11 Dispersion effectiveness of particle (P5.12D) and solubilized DOSS in TC at DOR of 9.2 mg/g

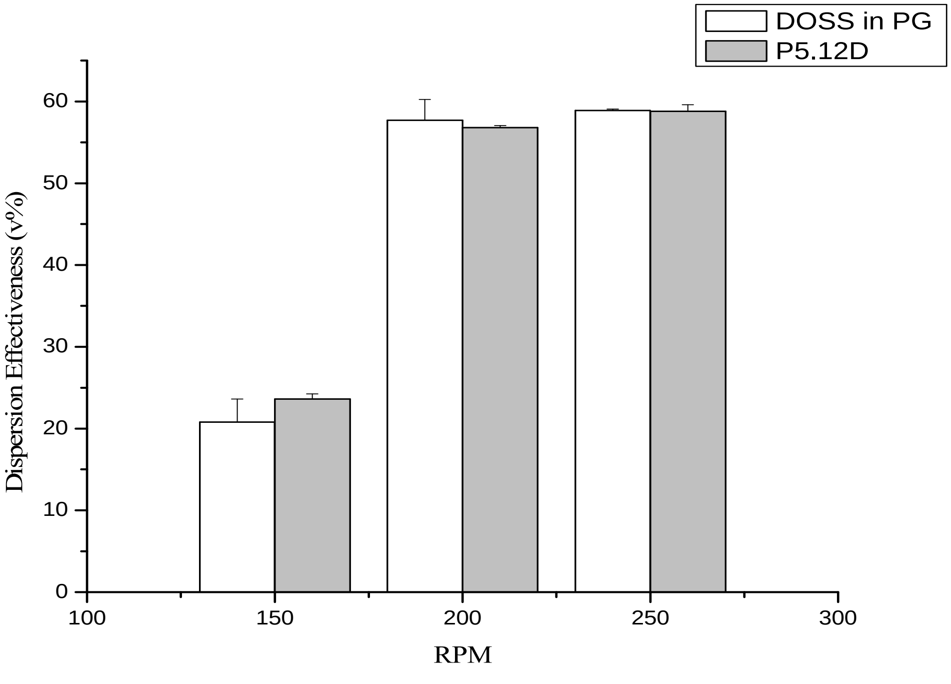


Figure 2.12 Dispersion effectiveness of particle (P5.12D) and solubilized DOSS in LC at DOR of 9.2 mg/g

2.3.5.2 Effect of Energy on Dispersion Effectiveness (composite DOSS-paraffin wax particles)

The next step was to examine how the dispersion effectiveness of the composite particle formulation varies with energy. This examination was done with particles P1.61D (Figure 2.13) and P3.73D (Figure 2.14) using TC. From Figures 2.13 and 2.14, it was observed that increasing DOR and the mixing energy led to a corresponding increase in the dispersion effectiveness.

From equation 3, it can be deduced that, at a fixed mixing energy, increasing the DOSS amount resulted in an increase in dispersion effectiveness which stemmed from the reduction in IFT. This trend was observed for both P1.61D and P3.73D. Again it can be deduced from the same equation 3, that for a constant DOSS amount (i.e., constant IFT), increasing the energy led to a corresponding increase in the oil-water interfacial area, which depicts the production of much smaller oil droplets. Smaller oil droplets lead to the formation of a more stable oil-water emulsion and this resulted in higher dispersion effectiveness.

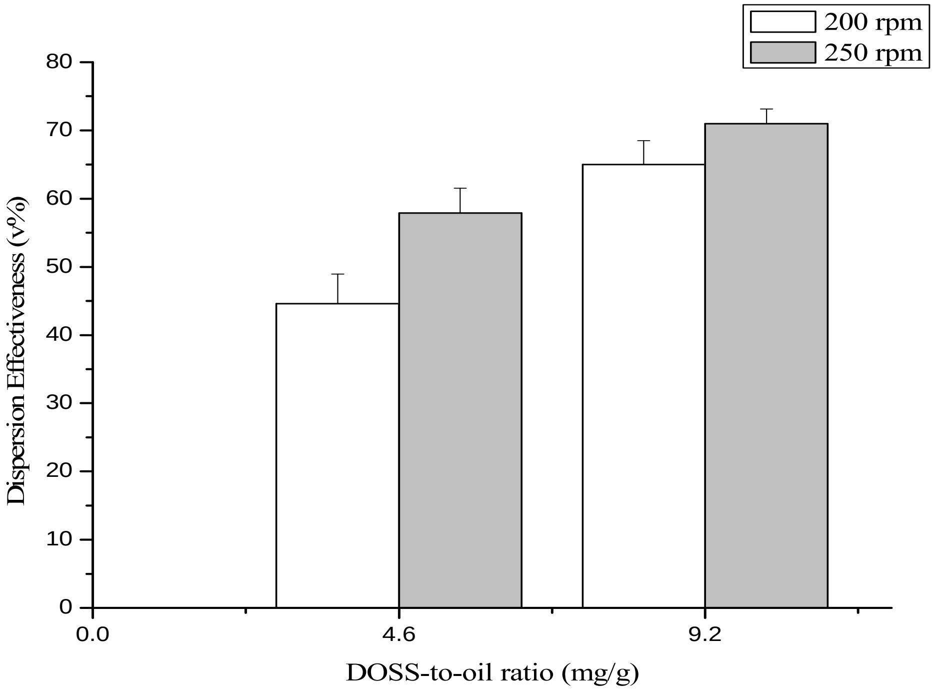


Figure. 2.13 Dispersion effectiveness of composite particle (P1.61D) in TC

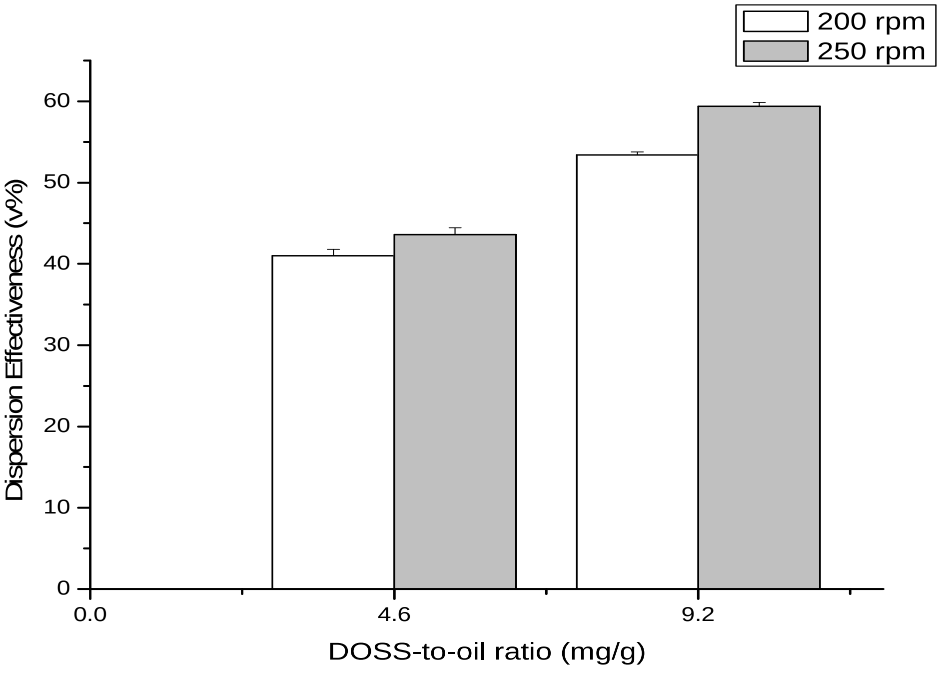


Figure. 2.14 Dispersion effectiveness of composite particle (P3.73D) in TC

2.3.6 Effect of Salinity on Dispersion Effectiveness

The composite particle dispersants were tested at different salinities to determine the effect of salt concentration on dispersion effectiveness. Since the salinity of sea water is usually around 3.5 wt.%, the dispersion effectiveness for synthetic sea water of salinities 1.6, 2.8 and 3.5 wt.% were tested. The dispersion effectiveness was tested at lower salinity (1.6 and 2.8 wt.%), to examine the possible application of the particulate formulation in oil spills that occur on seas with much lower salinity such as the Baltic sea. From the observations made in Figure 2.15, the dispersion effectiveness decreased with increasing salinities, however, it can be noted that, the dispersion effectiveness for 2.8 and 3.5 wt.% salinity were almost the same (within a standard error of ±1.83) depicting the independence of dispersion effectiveness on salinities close to that of sea water. The variation of dispersion effectiveness with salinity can be attributed to the variation of the critical micelle concentration with salinity.[27] The behavior of the surfactant in the presence of salt ions makes the effect of the salinity difficult to explain since the effect of these ions on dispersion effectiveness is dependent on the hydrophilic-lipophilic balance (HLB) value of the surfactant present in the dispersant.[28] DOSS has an HLB value of approximately 10. Therefore a different trend may result for surfactant with HLB value different from 10. The more hydrophilic the dispersant (higher HLB value), the more soluble it is in water and the vice versa. The presence of the salt ions alters the solubility of the dispersant in water and subsequently affects the dispersion effectiveness. For example, addition of calcium salt to Corexit 9500 dispersant (dispersant with maximum efficiency in marine environment) increased its effectiveness compared to that of other dispersants designed for fresh water use.[29]

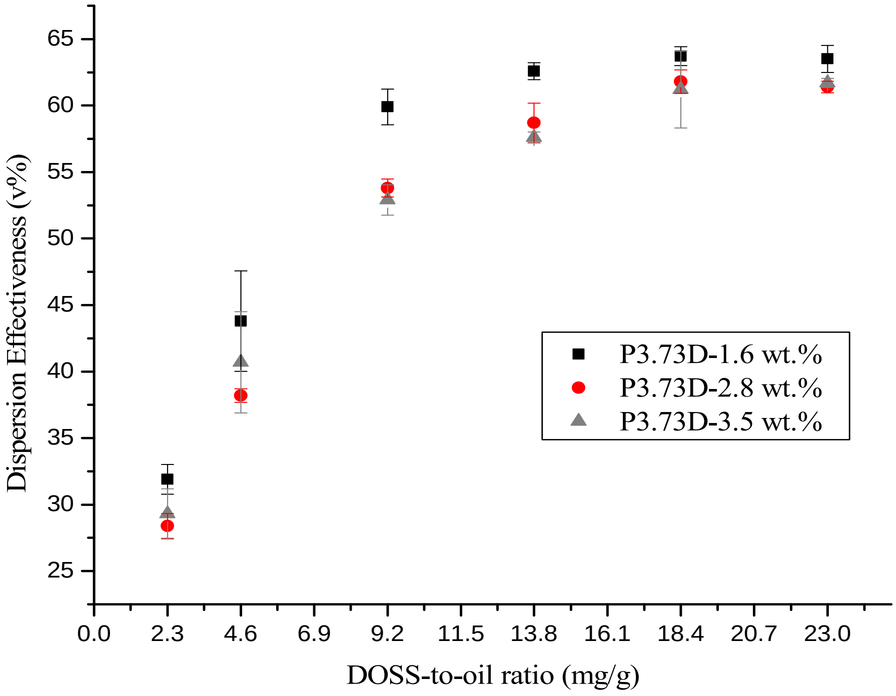


Figure. 2.15 Effect of salinity on dispersion in LC

2.4 Conclusions

The dispersion effectiveness of the dispersant composite particles is dependent on the solubility of the matrix material (paraffin wax) in the crude oil and the particle size of the dispersant particles. The solubilized DOSS dispersed TC and LC slightly better than the particulate dispersant. The trend observed for the variation of the dispersion effectiveness with energy was the same for both solubilized and particulate dispersants. The standardized rpm for the baffled flask test can also be used when analyzing the dispersion effectiveness of particulate dispersants. The dispersion effectiveness remained almost constant at sea water salinities of 2.8 and 3.5 wt.% and the dispersion effectiveness values recorded at these salinities were slightly lower than those at 1.6 wt.%.

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Chapter 3

Soybean Lecithin as a Dispersant for Crude Oil Spills

3.1 Introduction

The accidental release of natural crude oil and its refined products into marine waters is a major problem for the coast guards of most countries worldwide. An oil spill is defined as discrete event in which oil is discharged through neglect, by accident, or with intent over a relatively short time.[1] Different response measures such as; the application of chemical dispersants, burning of oil in situ, shoreline cleanup, and the use of mechanical containment and collection are adopted whenever oil spills occur. Among these oil spill response methods, chemical dispersant application is one of the few response measures that when adopted under the right circumstances and with judicious use of dispersants, leads to reduced environmental and economic impact of the oil spill.[2] Dispersants are one of the only feasible response options for large-scale oil spills.

A chemical dispersant is a mixture of surfactants (anionic and/or nonionic) and a hydrocarbon solvent.[3] When chemical dispersants are applied to an oil spill and sufficient energy is exerted to the dispersant-oil mixture, the slick is broken down into smaller droplets due to the reduction of the oil-water interfacial tension.[4] The oil droplets diffuse both vertically and horizontally by the action of the sea waves and remain in the water column since they possess very little rising velocity.[5] The increased surface area which arises from the smaller oil droplet size helps to accelerate biodegradation of the oil by bacteria action and hence reduces the environmental impact of the spilled oil.[2, 6]

The use of chemical dispersants as a means of combating oil spills is being accepted worldwide due to improvement in dispersant formulations and the use of Net Environmental Benefit Analysis (NEBA) in deciding whether or not dispersants should be used. With over three decades of research, it is now clear that the use of chemical dispersants to counter the effects of oil spills have led to a reduction in toxicity and the environmental problems that first generation chemical dispersants caused.[7]

However, indiscriminate application of chemical dispersant during oil spills has increased concerns about the environmental impact of using chemical dispersants.[8] For example, an estimated 2.1 million gallons of dispersant were applied to the Gulf of Mexico during the Deepwater Horizon oil spill of 2010 to disperse approximately 205 million gallons of crude oil.[3] Environmental and human toxicity issues arose when such a voluminous amount of chemical dispersant was applied. The chemical dispersant used for the Gulf of Mexico oil spill, Corexit 9500A was moderately toxic to cleanup workers and Gulf of Mexico aquatic species.[9] Four thousand gallons of Corexit 9580 were also applied to disperse part of the 11 million gallons of crude oil spilled during the Exxon Valdez Oil Spill, which occurred on Prince Williams Sound, Alaska. Though Corexit 9580 helped disperse some of the spilled oil, its use was discontinued since scientific data on its toxicity was incomplete. Corexit 9580 contains 2-butoxyethanol which was known to be carcinogenic.[10] The dispersant formulations used during the 1967 Torrey Canyon and 1996 Sea Empress oil spills were devastating to aquatic species.[8, 11]The chemical surfactants and the solvents used in formulating these dispersants are responsible for their toxicity. Some of the chemical surfactants (e.g. dioctyl sodium sulfosuccinate-DOSS) used in their formulation are synthetized chemically, are of petroleum origin, are toxic to aquatic species, are not easily biodegradable, and the byproducts of their manufacturing processes can be environmentally hazardous.[12]

The popular perception that natural products are always better for the environment has led to the suggestion that petrochemical surfactants should be replaced with surfactants based on renewable oil seeds or animal-fat-derived materials because the change would minimize the environmental impact of surfactant containing products.[13] Although this popular perception is not always correct, the natural surfactants are indeed better for the environment. Soybean lecithin is a well-known natural surfactant in the food, cosmetics, and paints industry. It use in these industries stemmed from its availability and excellent emulsifying behavior.[14] Soybean lecithin has been used to form food emulsions such as milk, butter, margarine, cheese, chocolate, and ice cream.[15] The emulsification properties of soybean lecithin can be associated with its phospholipid constituents which are well known emulsifiers, wetting, and dispersing agents. The most common types of phospholipids are phosphatidylcholine (PC), phosphatidylinositol (PI), phosphatidylethanolamine (PE), and phosphatidylserine (PS). Ethanol can be used to fractionate PI and PC from the lecithin, each of which has different solubility in this solvent.[14, 16] Research has shown that, PI and PC have different emulsification properties and can be used to form either water-in-oil (w/o) emulsions or oil-in-water (o/w) emulsions. [17]

Increased environmental awareness and strict legislation has made environmental compatibility of dispersants an important factor in their applications.[12, 18] To reduce the toxicity and environmental impact of dispersants, there is a need to look into the way dispersants are formulated. To this end, this study aims at formulating a more environmentally friendly dispersant for crude oil spill applications. Recent studies have shown that a blend of 60 wt.% lecithin and 40 wt.% Tween 80 is an effective emulsifier.[19] This study proposes the use of a natural surfactant, soybean lecithin dissolved in water, as a dispersant for crude oil spill applications. Such a dispersant formulation is expected to be environmentally benign since soybean lecithin is biodegradable, less toxic, and ecologically acceptable. Lecithin has been used to increase the biodegradation rate of dispersed oil since it contains phosphorus and nitrogen which are known to speed bacteria activity.[12, 20] Therefore such a dispersant formulation will not only disperse the spilled oil, but it will also aid in the biodegradation of the dispersed oil. The use of water as the delivery medium will eliminate the use of hydrocarbon solvents and result in a less toxic dispersant formulation. In this study, PI and PC were fractionated from crude soybean lecithin using ethanol. PI and PC were solubilized in water and their dispersion effectiveness compared with that of solubilized crude soybean lecithin in water (CL), powdered soybean lecithin (SL), solubilized Tween 80, and dioctyl sodium sulfosuccinate (DOSS) in propylene glycol. Various factors such as ethanol fractionation of crude soybean lecithin into PC and PI, structural modification of PI, salinity, crude oil type (Texas crude, TC and light crude, LC) and PI-to-PC ratio in the formulated dispersant were examined for influences on the dispersion effectiveness.

3.2 Experimental Section

3.2.1 Materials

Soybean lecithin was purchased from Stakich Inc. (Bloomfield Hills, MI) and Koptec ethanol 200 proof was obtained from VWR. The following chemicals were obtained from Sigma Aldrich: dioctyl sodium sulfosuccinate salt (DOSS) and Tween 80. Sodium thiosulfate (0.1N) and propylene glycol were obtained from Macron Chemicals and Spectrum Chemicals respectively. Hanus (Iodine monobromide) solution and chloroform were purchased from RICCA and EMD Chemical Company, respectively. Potassium iodide (10 w/v %) and starch indicator were obtained from BDA Chemicals. Instant Ocean salt was obtained from Instant Ocean (Blacksburg, VA). The heavy crude oil (Texas crude-TC) was obtained from Texas Raw Crude International (Midland, TX) while the light crude (LC) was obtained from Ohmsett (Atlantic Highlands, NJ). The major compounds present in the crude oil samples, the properties of the crude oil as well as the composition of the Instant Ocean salt have been reported by Nyankson et al.[21]

3.2.2 Experimental Procedure

3.2.2.1 Fractionation of Crude Soybean Lecithin with Ethanol

The method used to fractionate the soybean lecithin is similar to the one described by Wu et al..[14] Approximately 3 g of crude lecithin was weighed into a centrifuge tube, then 9 g of ethanol (95 %) was added. The tube was closed and heated in a water bath at 60 °C for 60 minutes, stirring every 15 minutes during heating to enhance the dissolution of the PC in ethanol. After heating for 60 minutes, the mixture was centrifuged for 5 minutes. The ethanol phase was poured off into a glass vial and the ethanol evaporated at 70 °C. The solid residue that remained after evaporation was labelled as PC (PC-enriched fraction). The solid residue that remained in the centrifuge tube after centrifugation was then deoiled with acetone according to the AOCS official method Ja 4-46 [22] and was labelled as PI (PI-enriched fraction). The PI was characterized by Fourier transform infrared spectroscopy (FT-IR).

To evaluate the effect of structural modification of PI on its dispersion effectiveness, some of the PI samples were stored in vials over a period of 10 weeks before they were solubilized to form dispersants. Changes that occurred in the PI structure during storage were examined by FT-IR and iodine value (IV) determination. The dispersants formulated from the freshly fractionated PI was designated as PI while those formulated from the modified or "functionalized" PI was designated as FPI.

3.2.2.2 Solubilized Dispersant Formulations

The PC and PI obtained from fractionating crude lecithin with ethanol have different solubility properties. While PC could be dissolved in water and propylene glycol, PI could only be dissolved in water. In view of this, different dispersant formulations were made in water and in propylene glycol. Different concentrations of solubilized DOSS, Tween 80, and PC (0.05, 0.1, 0.2 and 0.3 mg/µL) were prepared by dissolving an appropriate amount of DOSS, Tween 80 or PC in an appropriate volume of propylene glycol. The soybean lecithin dispersants were formulated by dissolving PC, PI, FPI, and the crude soybean lecithin in water (CL). That is a solubilized dispersants of 0.1 mg/µL concentration were prepared by dissolving appropriate amounts of each sample in an appropriate volume of water.

Soybean lecithin dispersants were also formulated by varying the FPI-to-PC ratios but keeping the concentration of FPI and PC in the water as 0.1 mg/μL.

3.2.3 Product Characterization

3.2.3.1 Fourier Transform Infrared (FT-IR) Spectroscopy

A Nicolet IR100 FT-IR spectrometer with infrared spectra 400 – 4000 cm^{-1} was used for the analysis. The equipment used a TGS/PE detector and a silicon bean splitter with 1 cm^{-1} resolution. Approximately 100 mg of KBr was mixed with 1 mg of the sample to prepare the sample discs. The KBr background spectrum was subtracted from the spectrum of each individual sample.

3.2.3.2 Iodine Value Determination

To investigate whether or not the number of C=C double bonds were reduced after storage, the PI samples were tested for their iodine value (IV) just after fractionation (PI) and also after it has been stored for 10 weeks (FPI). Two hundred and fifty milligram (250 mg) of the samples were weighed and dissolved with 10 mL of chloroform in a 500 mL stopper flask. 25 mL of Hanus solution was added to the flask and cocked immediately. The mixture was then swirled to ensure good mixing and was immediately placed in the dark for 60 minutes. The blank solution was simultaneously prepared by adding 10 mL of chloroform to 25 mL of Hanus solution in another 500 mL flask. After the 60 minutes, 20 mL of 10 % potassium iodide solution was added together with 100 mL of deionized water. The resulting solution was titrated with 0.1 N sodium thiosulfate using 3 mL of starch solution as an indicator. The burette reading was taken at the end of the titration.

3.2.3.3 Synthetic Sea Water Preparation

Different concentrations, that is 35, 15 and 8 g/L (representing 3.5, 1.5 and 0.8 wt.%), of synthetic sea water were prepared by dissolving appropriate amounts of Instant Ocean sea salt in 1 L of distilled water and leaving it on a magnetic stirrer for 48 hours to dissolve all the salt

3.2.3.4 Baffled Flask Test

The baffled flask test, which is a revised protocol,[4] is used to evaluate dispersion effectiveness of chemical dispersants and is being considered by the U.S. EPA to replace the swirling flask test. To analyze the dispersion effectiveness of the solubilized PC, DOSS, and Tween 80 in propylene glycol, 100 μL of crude oil was added to 120 mL of synthetic sea water in a baffled flask. Four microliters (4 μL) of the solubilized dispersant was added directly on top of the oil and the baffled flask placed on a shaker (VWR advanced digital shaker, Model 3500) set at 200 rpm for 10 minutes. A settling time of 10 minutes was allowed after which 30 mL of the aqueous media with dispersed oil was drawn and then the dispersed oil was extracted with DCM and quantified with UV-Vis at an absorbance difference of 300-400 nm.

The baffled flask procedure for determining the dispersion effectiveness of the solubilized PI, FPI, PC and CL in water was the same as described above but instead of using 4 μL of the solubilized dispersant for the analysis, different volumes were used that is 5, 10, 15, 20, 25 and 30 μL.

The baffled flask test procedure for determining the dispersion effectiveness of the powdered crude lecithin (SL) was the same as described above but instead of taking a specific volume of the solubilized samples, an appropriate amount of the solid crude lecithin particles was weighed and used for the analysis.

3.2.3.5 Optical Microscopy of Emulsions

The emulsions were prepared as described in the baffled flask test procedure and the optical microscopy images were taking with EVOS® FL auto imaging system just after the 10 minute settling time.

All experiments were conducted in at least triplicate. The error bars in all the plots are the standard error of the mean (SEM).

3.3 Results and Discussion

3.3.1 Dispersion Effectiveness of Solubilized PI, FPI, PC, CL and Solid Crude Lecithin (SL)

Lecithin is a widely used commercial term for a complex mixture of phosphatides produced from a vegetable source such as soybeans or an animal source such as eggs.[15b] Soybeans are the major source of lecithin owing to its unique functionality and availability.[14] The major components in soybean lecithin are phosphatidylcholine (PC), phosphatidylethanolamine (PE) and phosphatidylinositol (PI). These phospholipids are responsible for the emulsification properties exhibited by lecithin.

Generally, the dispersion effectiveness of SL, CL, PI, FPI and PC increased with increasing DOR as can be seen in Figure 3.1. The increase in dispersion effectiveness with increasing DOR can be attributed to the production of more stable emulsions due the generation of emulsions with smaller droplets and lower rising velocity. A decrease in droplet diameter with increasing DOR is well established in literature, and can be attributed to a number of factors such as faster adsorption of surface active agents at the oil-water interface and its subsequent reduction in interfacial tension thereby facilitating droplet breakup.[23] In addition to this, more surfactant is available to completely cover the oil droplets and this results in a more stable emulsion.[24] A significant phase separation was observed at low DOR, and this was attributed to the instability of the emulsions formed at low DOR which resulted in coalescence and creaming of the emulsion droplets. Oiling-out was pronounced for CL, SL and PI at low DOR. However, negligible oiling-out was observed at high DOR especially for PC and FPI.

The possibility of solid dispersant particles being used for oil spill remediation has already being reported. Henceforth, the dispersion effectiveness of crude powdered soybean lecithin (SL) was examined using TC as the crude oil sample and the result reported in Figure 3.1. By varying the dispersant-to-oil ratio (DOR), it can be seen that the dispersion effectiveness of SL increased from 6.4 vol.% at DOR of 0 mg/g to 49.8 vol.% at DOR of 37.5 mg/g. However, a slightly higher dispersion effectiveness value of 55.6 vol.% was obtained at DOR of 37.5 mg/g when the crude powdered soybean lecithin was solubilized in water (CL) at 0.1 mg/uL concentration. This trend was expected since for dispersion to occur, the phospholipids should be able to diffuse to the oil-water interface. With liquid state diffusion being faster than solid state diffusion, more phospholipid molecules are likely to settle at the oil-water interface and hence this resulted in the relatively higher dispersion effectiveness values obtained with CL at higher DORs. The lower dispersion effectiveness obtained for SL and CL compared to the fractionated PC is not surprising since current studies has suggested that SL solubilized in ethanol is not an excellent emulsifier.[19]

To improve on the dispersion effectiveness values recorded by SL and CL, the crude soybean lecithin was fractionated into PC and PI-enriched fractions. The ethanol soluble fraction is mainly made up of concentrated PC and only a small fraction of PI while the ethanol insoluble fraction is made up of concentrated PI and a small fraction of PC. The PE is evenly distributed between the PC and PI-enriched fractions.[15b] Further de-oiling of the PI-enriched phase with saturated acetone resulted in oil-free PI. The chemical structure of the PI and PC are shown in Figure 3.2.

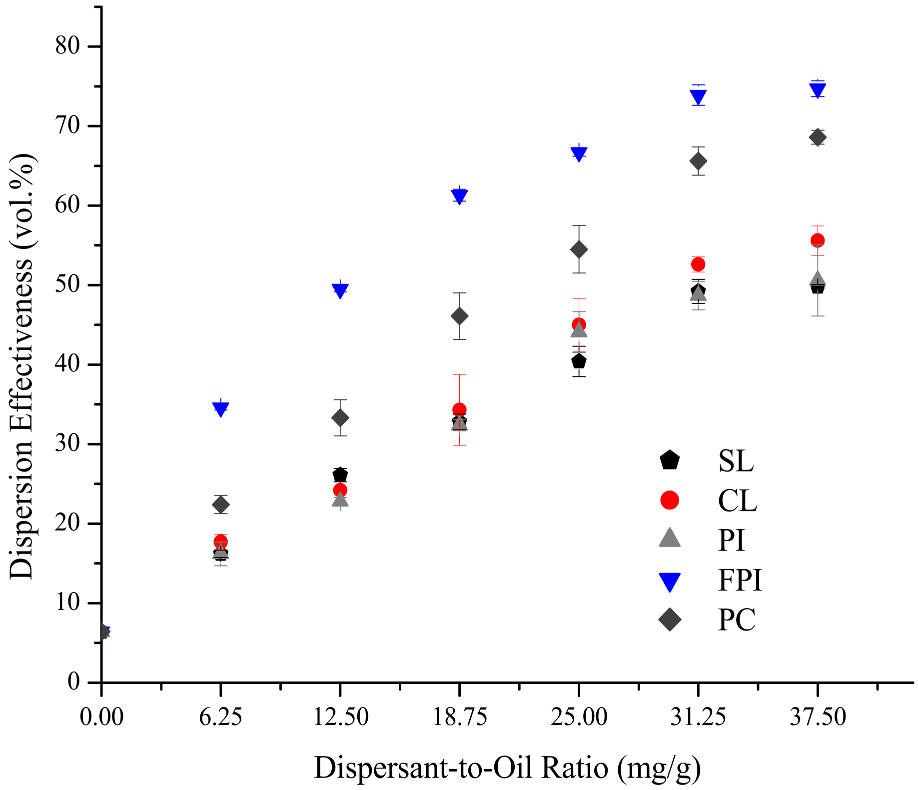
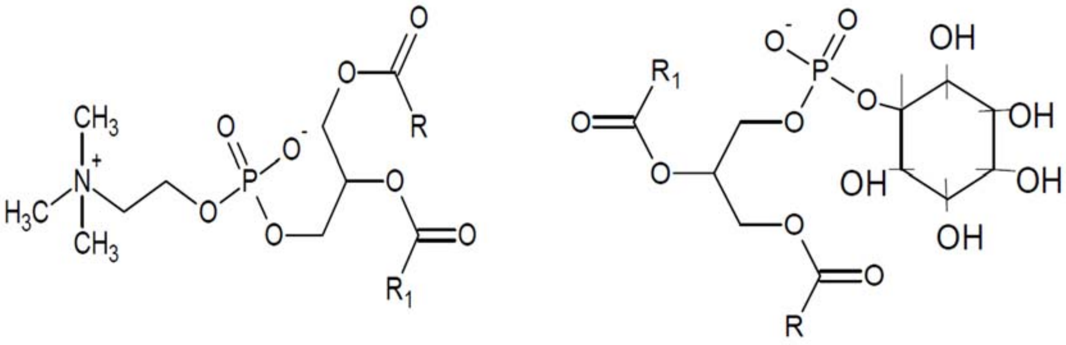


Figure 3.1 Dispersion effectiveness of PI, FPI, PC, CL and SL

Figure 3.2 shows that, phosphatide molecules contain 2 long-chain fatty acids esterified to glycerol and a phospho-diester bonding a choline or inositol. The hydrophilic portion of the molecules is the phospho-diester portion while the hydrophobic portion is the fatty acid end,[15b] which are R and R_1. The phospholipids appear to be made up of fatty acids of the C16 and C18 series. Some of the fatty acids present in phospholipids are palmitic acids, linoleic acids and oleic acids. [15b, 25] PC is known to contain approximately 58 and 20 wt.% linoleic and palmitic acids, respectively while PI is made up of 25 and 44 wt.% linoleic and palmitic acids, respectively.[7] These values suggest that, both PI and PC contain a higher amount of unsaturated fatty acids.



(A) (B)

Figure 3.2 (A) Chemical structure of PC and (B) Chemical structure of PI

The amphiphilic nature of these molecules is responsible for their emulsification property. PC and PI were solubilized in water and their dispersion effectiveness determined by the baffled flask test. Three different observations were made with these dispersant formulations.

Firstly, the dispersion effectiveness of the solubilized PC in water (PC) was higher than that of SL and CL at all the DORs tested. For example, at DOR of 37.5 mg/g the dispersion effectiveness of PC, CL and SL were 68.6, 55.6 and 49.8 vol.%, respectively. The hydrophilic-lipophilic balance (HLB) of crude soybean lecithin has been reported to be about 4.[26] Crude lecithin is more lipophilic and therefore based on the Bancroft rule which states that a surfactant which preferentially partitions into water favors the formation of oil-in-water (o/w) emulsions and that a surfactant which preferentially partitions into oil favors the formation of water-in-oil (w/o) emulsions,[27] crude lecithin is expected to favor the formation of w/o emulsions which would explain the comparatively lower dispersion effectiveness values observed for CL and SL. The use of lecithin to form o/w emulsions requires modification of the lecithin to increase its hydrophilicity and this was achieved through solvent fractionation. The results showed that, the PC-enriched fraction has a better o/w emulsification property. Fractionation of the crude lecithin into PI and PC enriched fractions resulted in the distribution of the components present in the crude lecithin between the various fractions. This distribution resulted in PI and PC having different physical and chemical properties from the crude lecithin. A change in the relative concentrations of its constituent molecules will result in a change in its HLB. The HLB of purified PC has been reported to be around 7,[26] that is the HLB of the fractionated PC is close to the range that favors the formation of o/w emulsion.[28] This observation is in agreement with other results in the literature that suggests that PC is an excellent o/w emulsifier.[17b]

Secondly, the dispersion effectiveness of the PC dispersant formulation was higher than that of PI formulation. It has been stated that, while the ethanol soluble fraction (PC-enriched) supports the formation of o/w emulsion, that of the ethanol insoluble fraction (PI-enriched) supports the formation of w/o emulsion.[26] Since the dispersion effectiveness of the freshly fractionated PI is almost the same as that of SL and CL (Figure 3.1), the HLB of deoiled PI is expected to be lower than or probably around 4 and therefore, freshly fractionated PI is expected to favor the formation of w/o emulsion. Fractionating the crude lecithin resulted in the formation of anionic PI and zwetterionic PC. Since PC is zwetterionic, it forms a monomolecular interfacial film that binds water molecules at the surface and serves as a physical barrier against coalescence.

An interesting observation was made when the PI was stored for a period of 10 weeks before it was used to formulate the dispersant. Since polar lipids are insoluble in acetone while neutral lipids are, deoiling of the PI with acetone removed the neutral lipids which comprised of triglycerides and tocopherols from PI. Tocopherols are antioxidants present in lecithin hence its removal resulted in a PI which is less oxidatively stable.[10] Acetone may be considered to be the solvent of crystallization since the deoiled PI has a higher degree of crystallinity and hence the deoiled PI was crystalline, granular, powdery and had high surface/volume ratio which also contributed to its reduced stability.[15] The C=C double bonds in the unsaturated fatty acids present in PI are known reactive sites for hydroxylation. With these unique properties of the deoiled PI and the fact that the deoiled PI is slightly hygroscopic, it was prudent to store them in air over a period of time to examine whether or not it was possible to alter the hydrophilicity of the deoiled PI through natural oxidative process without using any chemical treatment. That is the hydrophilicity of PI can be modified by the introduction of additional hydroxyl groups onto the PI structure and this can be achieved by either hydroxylation or by hydrolysis. The storage of the PI over such a period was to examine how natural oxidation (hydroxylation) of the PI affected its emulsification properties. As can be seen in Figure 3.1, the dispersion effectiveness of the dispersant formulated from PI, which has been modified by storing for 10 weeks (FPI) were higher than that of the PC, SL, CL and PI. At DOR of 37.5 mg/g, the dispersion effectiveness of FPI, PI, PC, SL and CL were 74.7, 50.6, 68.6, 49.8 and 55.6 vol.%, respectively. From Figure 3.2, it can be seen that, PI contains a bonded hydroxyl group in its chemical structure. Hydroxylation of PI will result in the introduction of additional hydroxyl groups into its structure. To investigate this, equal amounts of PI that have been stored for two days (PI-2days), 3 weeks (PI-3weeks) and 10 weeks (PI-10weeks) in the same environmental conditions (temperature of 298 K and an average relative humidity of 65 %) were analyzed with FT-IR. The area under the bonded hydroxyl peak represents the concentration of the hydroxyl group in the compound. The FT-IR spectra are shown in Figure 3.3.

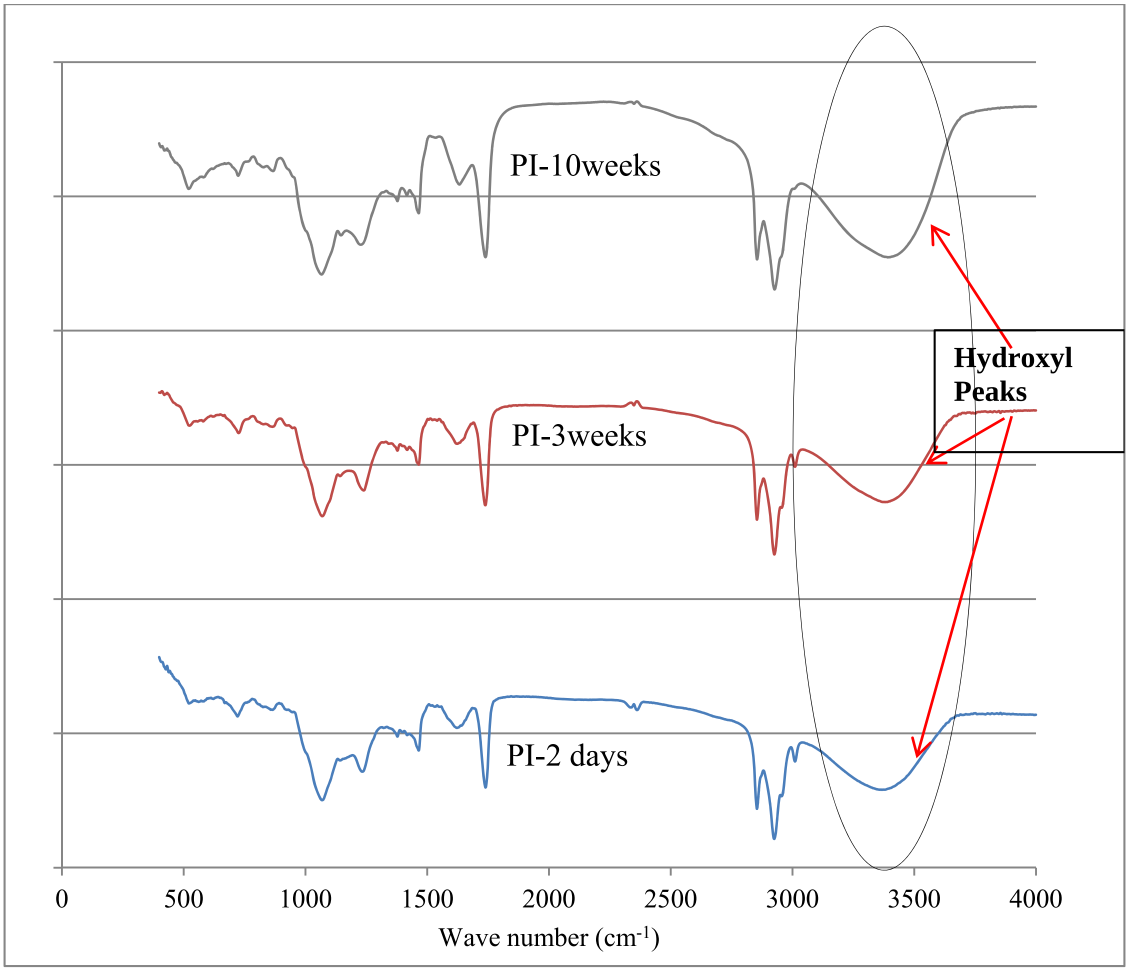
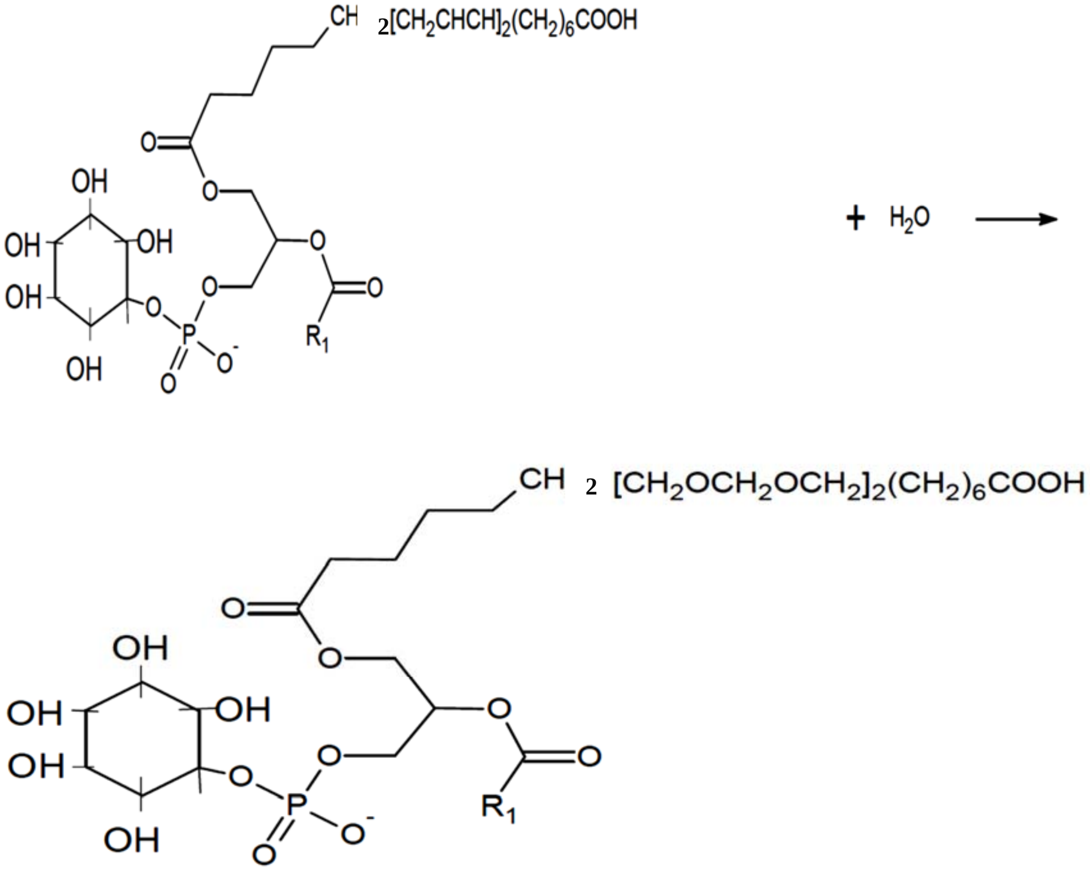


Figure 3.3 FT-IR spectra for PI-2 days, PI-3 weeks and PI-10 weeks

The peak between wavenumbers 3200 and 3600 cm^{-1} represents the bonded hydroxyl group in the PI structure. As can be seen in the Figure 3.3, the area under the bonded hydroxyl group increased with storage time. That is the concentration of the bonded hydroxyl group is greater in PI-10 weeks and least in PI-2 days. Therefore more hydroxyl groups were introduced into the PI structure during storage. Both hydrolysis and hydroxylation reactions will introduce additional hydroxyl groups into the PI structure. However, hydrolysis reaction is not likely to occur during storage since this reaction is known to occur in lecithins in the presence of strong acids or bases.[7-8] The possible reaction occurring during storage may be a hydroxylation reaction. In hydroxylation reaction, water molecule reacts at the double bonds of the unsaturated fatty acids in the phospholipid structure. It should be noted that, the average relative humidity over the storage period was 65 %. Assuming that R_1 and R are palmitic and linoleic acids in the PI structure in Figure 3.2, the following reaction may occur:



The above reaction will result in the reduction of the number of C=C double bond that is the degree of unsaturation will be reduced. To examine if the reaction that occurred resulted in the reduction of C=C double bonds, the iodine values (IV) of PI-2 days and PI-10 weeks were determined. The IV for PI-2 days was determined to be 96 and was within the range stated in literature [26] while that of the PI-10 weeks was 72. The significant reduction in the IV after storage depicts a reduction in the degree of unsaturation of PI-10 weeks compared to PI-2 days. There was therefore approximately 25 % reduction in IV after storing the PI for 10 weeks.

It can be deduced from the area under the hydroxyl peak in the FT-IR spectra that, this reaction is very slow since the bonded hydroxyl group concentration for the PI stored for 3 weeks (PI-3 weeks) was almost the same as that of PI-2 days. Therefore enough storage time should be allowed for the reaction to take place. Preliminary studies not reported in this paper showed that, 10 weeks was enough to allow this reaction to take place since the iodine value reduction for samples stored for 10 to 18 weeks were similar and were between 25 to 27 % which is within the 25 to 30 % recorded in literature.[15] As a result, the storage time used in the study was enough to introduce an adequate amount of hydroxyl groups into the PI structure. Instead of allowing the hydroxylation reaction to occur naturally, this reaction can be induced by reacting the PI with hydrogen peroxide and water in the presence of lactic acid as a catalyst.[8] The 25-27 % reduction in IV recorded in this study which fell within the range of IVs obtained by chemical treatment of crude lecithin proves that the emulsification behavior of PI can be improved by storing it in air over a long period of time. Hydroxylation reactions introduce additional hydroxyl groups into the PI structure and as a result, hydrophilicity is increased. An increase in hydrophilicity subsequently shifted the HLB of PI towards the range (8-18)[16] that favors the formation of an o/w emulsion and this shift is responsible for the increase in the dispersion effectiveness observed with FPI. A typical HLB of chemically hydroxylated lecithin has been reported to be around 8[16] which is more hydrophilic than that of the freshly fractionated PI.

The introduction of additional hydroxyl groups onto the PI structure affected the structural arrangement of PI at the oil-water interface. The additional hydroxyl groups make it possible for the PI to attain the "loop worm" structure at the oil-water interface which improved the emulsion stability.[29] The additional hydroxyl groups help increase the interaction at the oil-water interface and hence reduced the tendency of the emulsion droplets to coalesce (Figure 3.4). The reduction in the tendency of the emulsion droplets to coalesce will enhance the emulsion stability and hence increase the dispersion effectiveness. In addition to the improvement in the interaction between the hydroxyl groups and the liquid film at the oil-water interface, the additional hydroxyl groups are likely to increase the surface potential at the oil-water interface since emulsion formed by FPI, which is anionic surfactant, will be stabilized by the negative charge formed by the polar head group at the oil-water interface. The increment in the surface potential due to the presence of additional hydroxyl groups will increase electrostatic repulsion between the emulsion droplets, protecting the emulsion from processes such as creaming and coalescence.[30,31,31b] In addition, the crowding of the anionic head group will introduce electrostatic repulsion among the charged head groups and this will affect the characteristics of the monolayer at the oil-water interface. The introduced hydroxyl groups which are less hydrophilic than the anionic head will moderate the electrostatic interactions among the anionic head groups. The net result will be a densely packed interfacial layer which will make it possible to attain high dispersion effectiveness. This is responsible for the high dispersion effectiveness values observed for FPI.

Optical microscopy images of the emulsions formed with FPI are shown in Figure 3.5 (D-F). It can be seen that as the DOR increases, the emulsion droplet density increases. It was also observed that, an increase in emulsion droplet density was accompanied with flocculation of the droplets. The droplet sizes of the FPI emulsion were relatively smaller than that of the PC as can be seen from the histogram represented in Figure 3.6. The histogram was obtained by taking optical microscopy images of the emulsion droplets after the 10 minutes settling time in the baffled flask test and analyzing the images for droplet size using the ImageJ software. The smaller droplet sizes and the higher droplet density further substantiate why the emulsion formed with FPI was more stable and hence resulted in a higher dispersion effectiveness than PC.

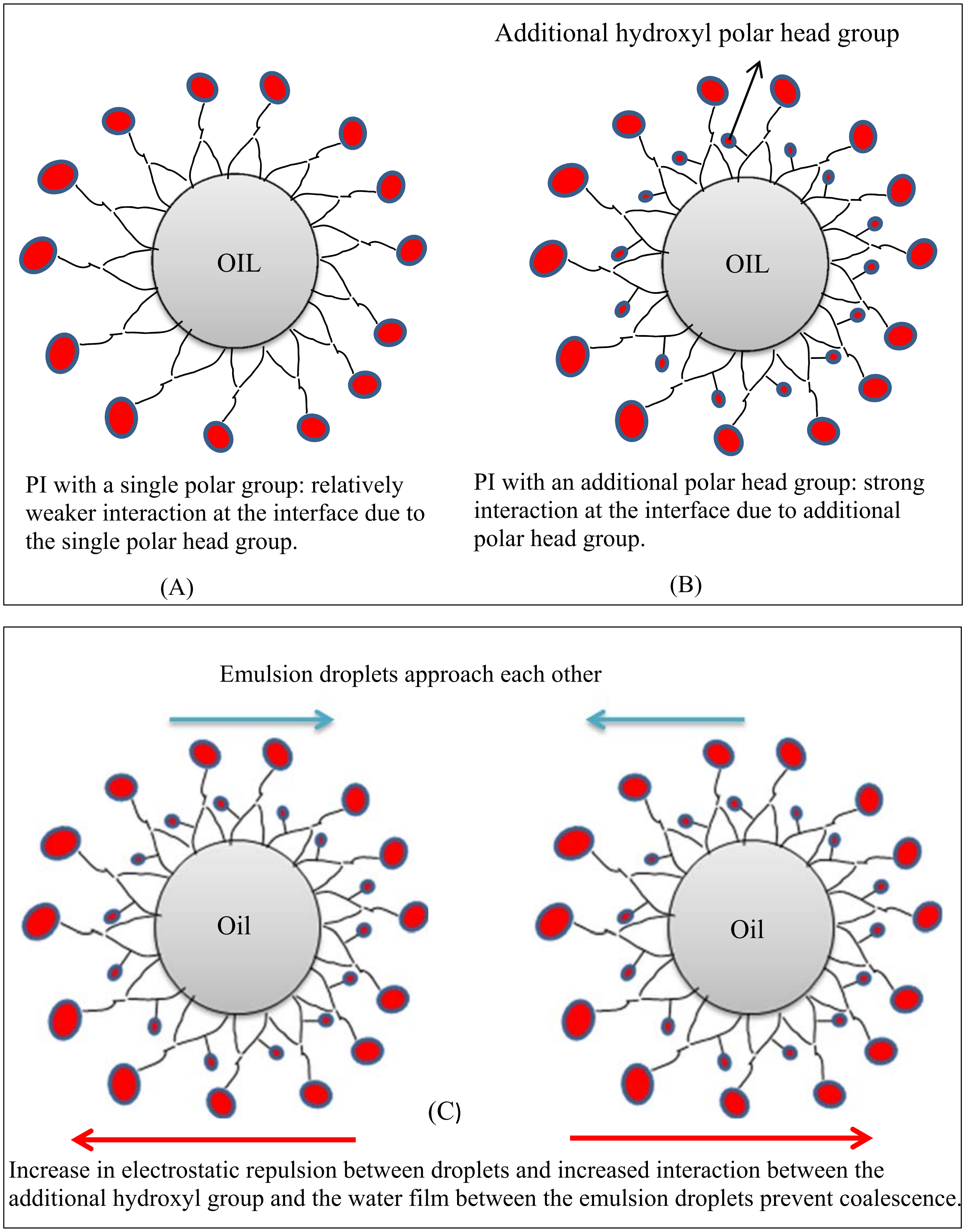


Figure 3.4: Mechanism for emulsion stabilization: (A) structural arrangement of freshly fractionated PI molecules at the oil-water interface, (B) structural arrangement of fractionated PI that has additional hydroxyl groups (FPI) at the oil-water interface and (C) contribution of the additional hydroxyl group in stabilizing emulsion droplets.

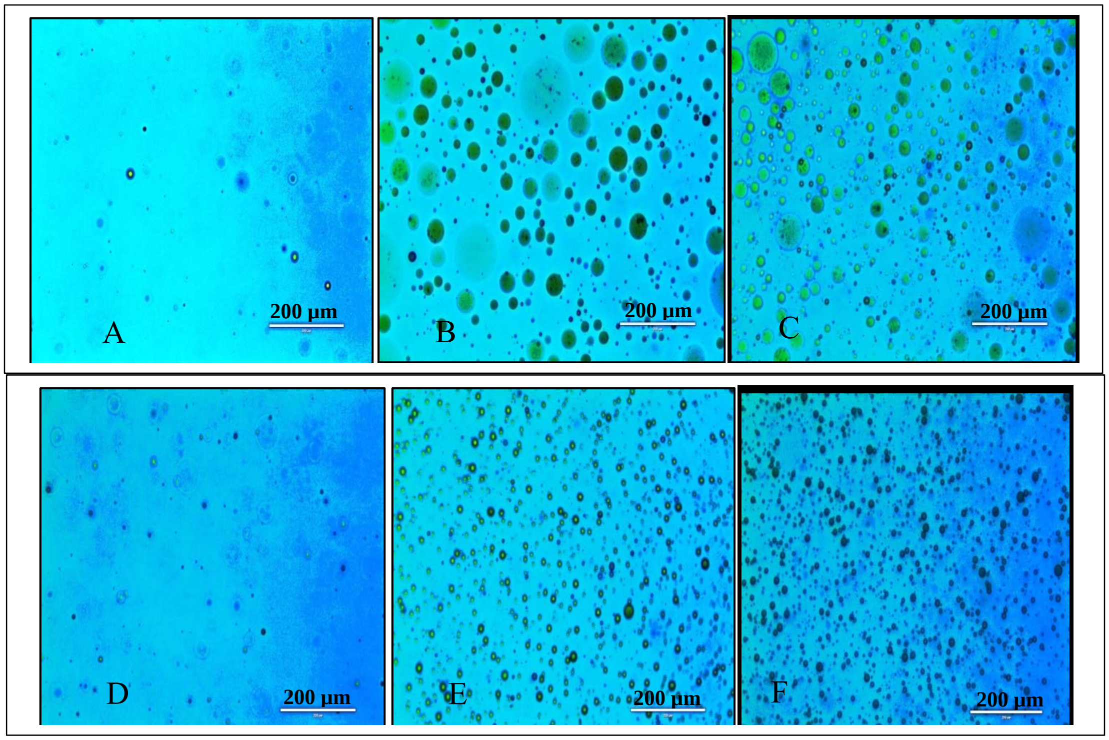


Figure 3.5 Optical microscopy of TC oil-in-water emulsions: (A) PC at 6.25 mg/g DOR (B) PC at 18.75 mg/g DOR (C) PC at 37.5 mg/g DOR (D) FPI at 6.25 mg/g DOR (E) FPI at 18.75 mg/g DOR (F) FPI at 37.5 mg/g DOR

The emulsification property of the PC however remained constant over the same storage time depicting that the hydroxylation reaction did not naturally occur in PC. This can be attributed to the nature of the fractionated PC compared to that of the PI. While the PI-enriched fraction was hygroscopic, granular and flowable, that of the PC was tacky. As a result, there was more surface area available for the hydroxylation reaction to occur in PI than in PC. The optical microscopy images of the emulsions formed with PC are shown in Figure 3.5 (A-C) and it can be seen that, the emulsion droplet density increases with increasing DOR but the droplet density were lower than that of FPI. It was also observed that at DOR of 18.75 and 37.5 mg/g, some of emulsion droplets flocculated.

For a dispersant formulation to be listed on the National Contingency Plan (NCP) Product Schedule, it should be able to disperse at least 50±5 vol.% of the oil used in the laboratory test. As can be seen in Figure 3.1, PC and FPI at DOR of 25 mg/g meet this criterion, therefore our dispersant formulations can be used to combat oil spills should they occur.

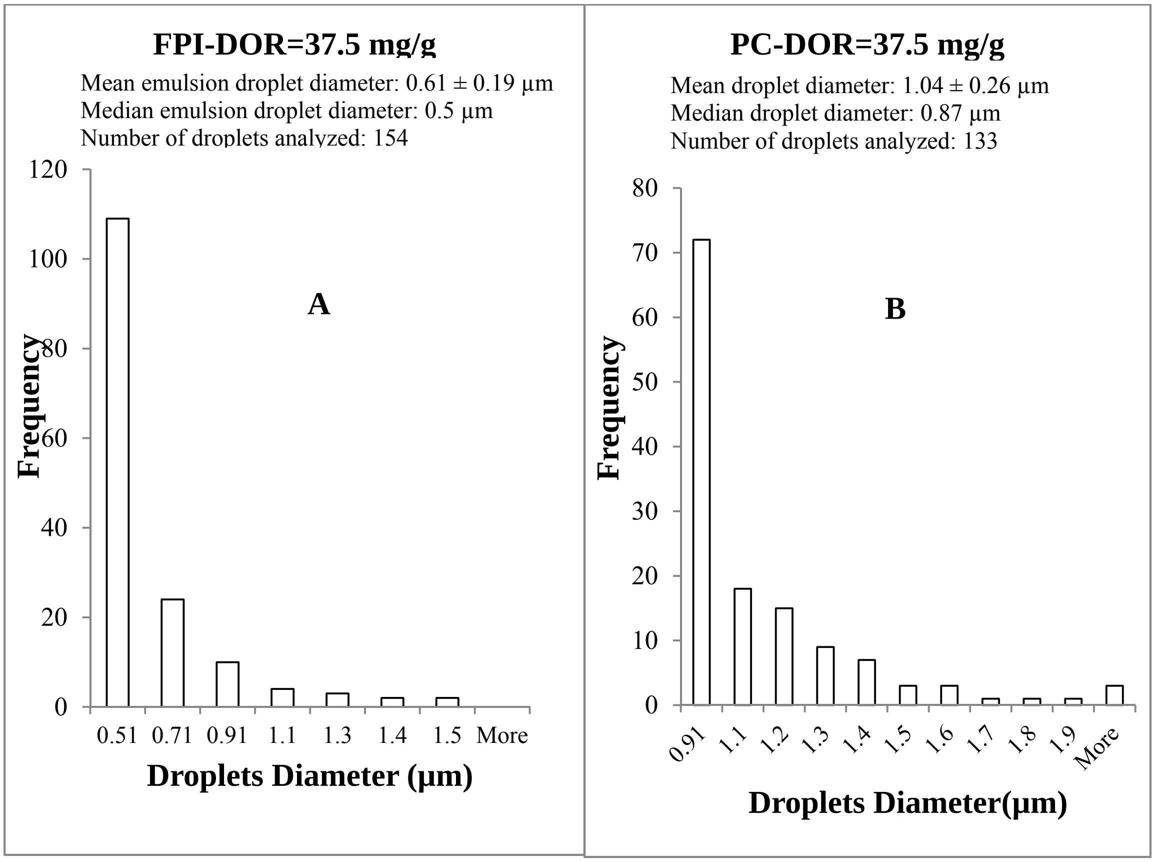


Figure 3.6 Histogram for emulsion droplets diameter (with TC) for: (A) emulsions obtained from PI at DOR=37.5 mg/g, and (B) emulsions obtained from PC at DOR=37.5 mg/g.

3.3.2 Comparing the Dispersion Effectiveness of Solubilized FPI and PC with Solubilized DOSS and Tween 80

The dispersion effectiveness of the natural surfactants (FPI and PC) was compared with that of synthetic chemical surfactants (DOSS and Tween 80) and the results are shown in Figure 3.7. From Figure 3.7, it can be seen that, the dispersion effectiveness of Tween 80 and DOSS were higher at lower DORs compared to that of PC and FPI. However, at higher DORs, the dispersion effectiveness of FPI was slightly higher than that of Tween 80 and DOSS (within a standard error of ±1), the dispersion effectiveness of PC solubilized in propylene glycol was almost the same as that of DOSS and the dispersion effectiveness of PC solubilized in water was slightly higher than that of DOSS (within a standard error of ±0.57).

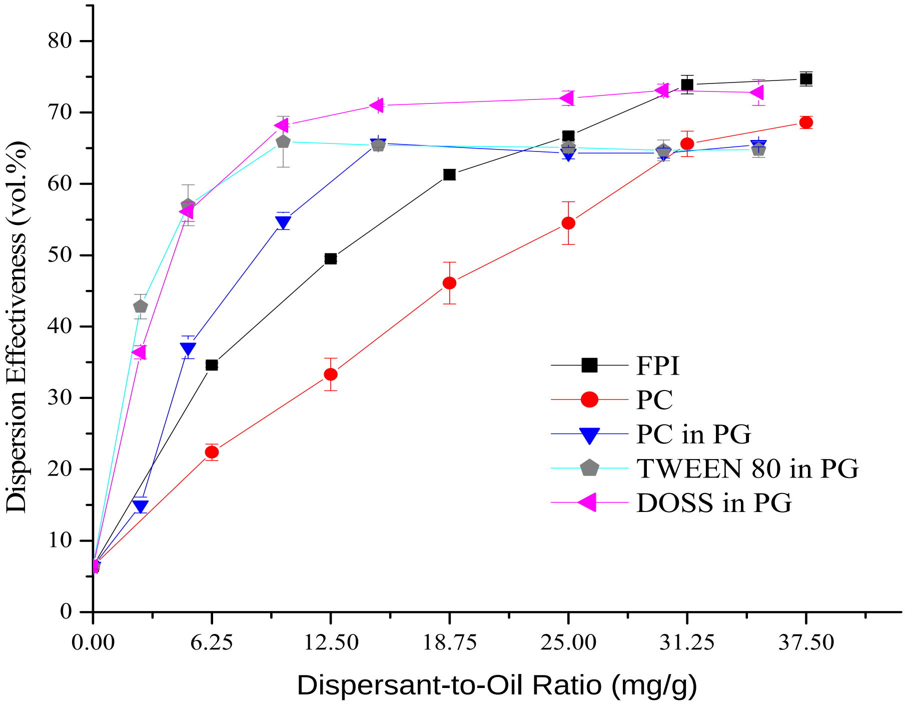


Figure 3.7: Comparing the dispersion effectiveness (with TC) of solubilized FPI and PC with solubilized DOSS and Tween 80

These observations can be explained in terms of the efficiency of the surfactants used in the formulation of the dispersants in forming emulsions and the structural arrangement of the surfactants molecules at the oil-water interface.

Below a DOR of 12.5 mg/g, the dispersion effectiveness of DOSS and Tween 80 were significantly higher than that of FPI and PC. This trend can be attributed to the excellent efficiency of the surfactants DOSS and Tween 80 in forming emulsions. The surfactant efficiency is defined as the bulk phase concentration necessary to reduce the interfacial tension by a predetermined amount.[13] Smaller amount of DOSS and Tween (lower DOR) is enough to create a more stable o/w emulsion than when using the same amount of FPI and PC. This can be attributed to the significant reduction in interfacial tension by Tween 80 and DOSS at lower DORs. Nevertheless, solubilized PC in PG recorded much higher dispersion effectiveness than PC in water at lower DOR. This can be related to the effect that solvents used in formulating dispersants have on dispersion effectiveness. In previous studies, we concluded that dispersants formulated in propylene glycol usually give higher dispersion effectiveness and this can be related to solvent viscosity, density and its solubility in water.[21] The propylene glycol may also serve as a co-surfactant by adsorbing at the oil-water interface and further reducing the interfacial tension. From Figure 3.7 it can be seen that, the shape of the dispersion effectiveness versus DOR plot was the same for the dispersants formulated in PG that is the dispersion effectiveness was higher at lower DOR but leveled off at higher DOR. On the other hand, the dispersion effectiveness of PC and FPI in water kept on rising steadily from lower DOR to higher DOR, further proving the impact of the choice of solvents on interfacial tension reduction.

Emulsion formation is influenced by the shear forces and the interfacial tension forces. At a lower DOR, the droplets sizes are larger and the shear forces are larger than interfacial tension forces. The droplet radius will decrease (Figure 3.8) as long as DOR is increased until the interfacial tension forces balance or exceed the shear forces,[32] that is increasing the surfactant concentration will decrease the droplet size up to the point where the hydrodynamics of the system becomes the limiting factor.[33] The leveling off of the dispersion effectiveness of DOSS and Tween 80 at higher DOR is probably due to excessive amount of interfacial forces generated at higher DOR due to their excellent surfactant efficiency. With a standardized energy being supplied at 200 rpm during the baffled flask test analysis, such an energy can easily be surpassed with an increase in surfactant concentration. In addition to this, high concentration of non-adsorbed surfactants may influence emulsion stability.[34]

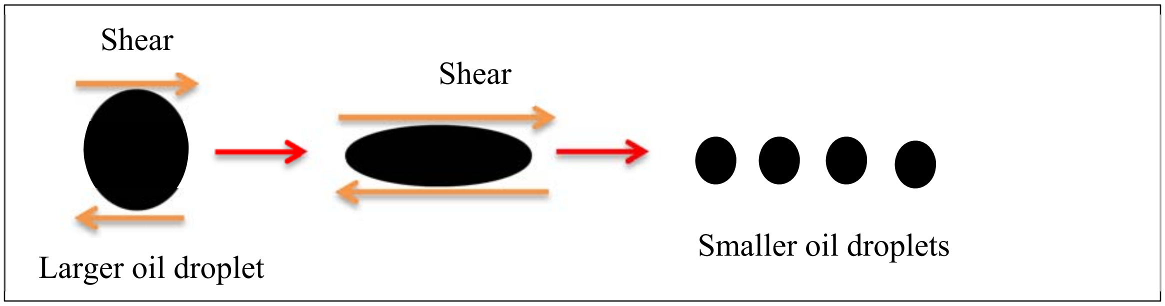


Figure 3.8 Breaking of larger liquid droplets into smaller droplets by shear

The gradual increase in dispersion effectiveness of PC and FPI is probably due to the gradual impact of these dispersants in reducing the interfacial tension. This might have kept the interfacial tension forces well below the shear forces, which resulted in the generation of emulsion droplets with lower rising velocity. The stability of the emulsions formed from this dispersant is responsible for the higher dispersion effectiveness recorded.

Though the dispersion effectiveness for DOSS and Tween 80 leveled off at higher DOR, it can be seen that, the dispersion effectiveness of DOSS is lower than that of Tween 80. With DOSS being an anionic surfactant, a possible repulsion between the polar head group while adsorbing at the oil-water interface may have accounted for the reduction in the dispersion effectiveness. Studies have shown that, DOSS easily desorbs into salt water after emulsion formation[35] and this desorption results in the coalescence of smaller emulsion droplets into larger ones. Visual observations made during the baffled flask test attest to this fact since there was oiling-out and creaming of the emulsions formed with solubilized DOSS. The formation of larger emulsion droplets increases their rising velocity and as a result, these oil droplets fell out of the sampling zone during the analysis done with the baffled flask test. The oxyethylene "hairs" in Tween 80 are important for providing steric stabilization to the oil droplets and preventing their coalescence.[36] The rate of desorption of Tween 80 from the oil-water interface has therefore been reported to be much slower than that of DOSS[37] and this is responsible for the much higher dispersion effectiveness recorded for Tween 80 at higher DOR.

From the above paragraphs, it can be concluded that a larger amount of lecithin (FPI and PC) will be required to attain higher dispersion effectiveness. Usually, it is better to use a lower amount of dispersant (lower DOR) since it reduces cost and toxicity. However, soybean lecithin is less toxic and is not expected to have any negative impact on aquatic species and cleanup workers. In addition to this, the cost of DOSS and Tween 80 per gram is respectively 36 and 12 times that of lecithin [38] , which suggests that dispersants formulated with lecithin PI and PC will be less costly when compared to those formulated with DOSS and Tween 80.

3.3.3 Effect of FPI/PC Ratio on Dispersion Effectiveness

With the fractionated PC and FPI recording much higher dispersion effectiveness than the crude lecithin, it was worth examining how the dispersion effectiveness will change by varying weight percent or ratios of FPI and PC. Varying the FPI-to-PC ratios resulted in dispersion effectiveness values that were almost the same as those recorded for 100 wt.% PC (Figure 3.9). The HLB of FPI and PC are probably similar, hence combining them in different ratios did not have a dramatic impact on the combined HLB and the dispersion effectiveness. Though lecithin is known to be zwetterionic, fractionating lecithin resulted in the formation of an anionic PI and zwetterionic PC. With PC having both positive and negative charge head groups, these groups are likely to interact with the negative charge head groups of the PI. These interactions which may be attractive or repulsive will affect the structural arrangement of the surfactants at the oil-water interface. This arrangement will result in the formation of an "expanded" monomolecular film at the oil-water interface[13] which will subsequently has a negative impact on the dispersion effectiveness.

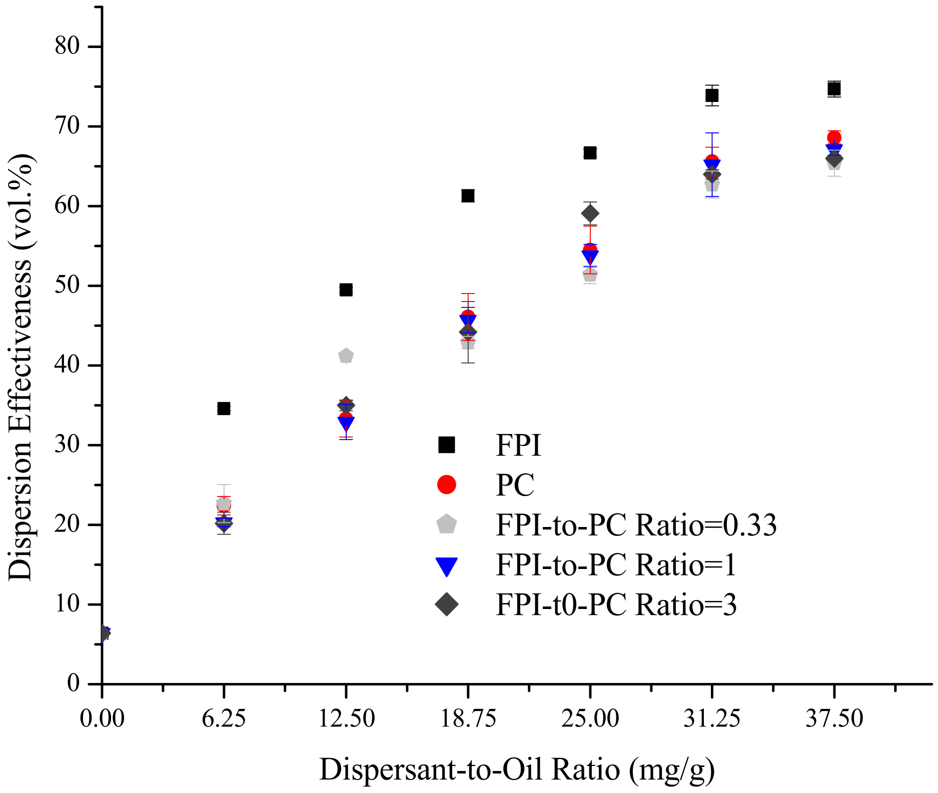


Figure 3.9 Effect of FPI-to-PC ratio on dispersion effectiveness (with TC)

3.3.4 Effect of Texas Crude (TC) and Light Crude (LC) Oil Samples on Dispersion Effectiveness

The effect of crude oil type on the dispersion effectiveness was investigated with solubilized PC and FPI in water. Previous studies with these oil types showed that, particulate dispersants formulated with DOSS disperses the LC much better than the TC, and thus it was worth examining how phospholipids (PC and PI) would disperse these crude oil types.

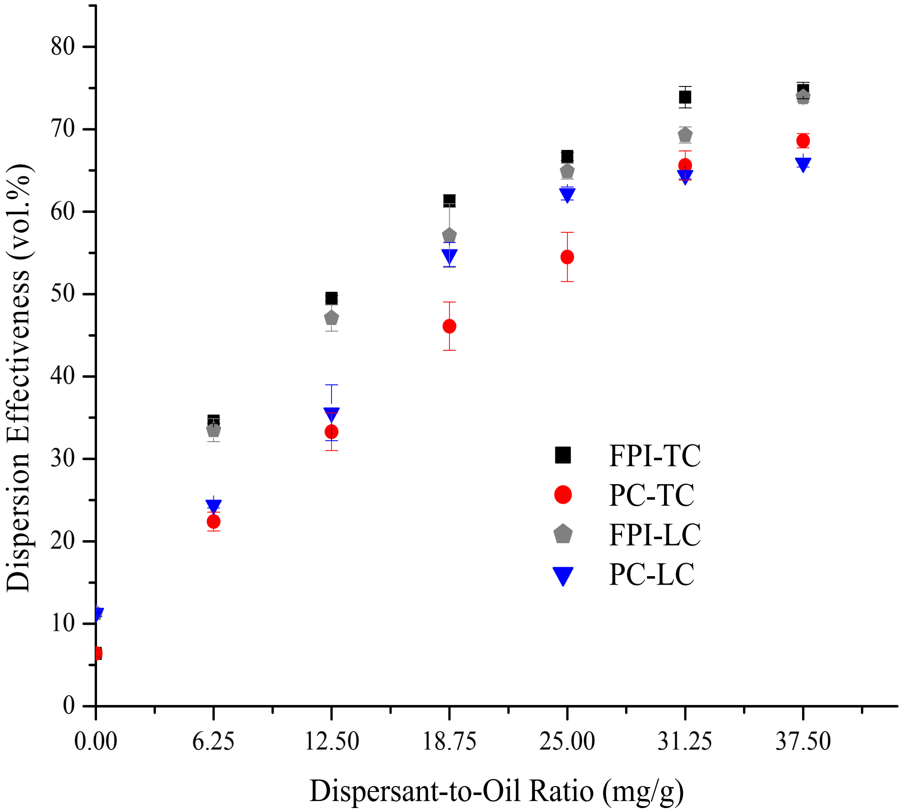


Figure 3.10 Effect of Texas crude and Light crude on dispersion effectiveness

The asphaltene content, API gravity, and chemical composition of these oil types were determined in a previous study.[21] The TC was much heavier with lower API gravity than the LC and the asphaltene content of the TC and LC were 6 and 4.1 wt.%, respectively. With these values, one would expect the dispersion effectiveness for the LC to be higher than that of the TC but as can be seen in Figure 3.10, the dispersion effectiveness on LC and TC were almost the same for both PC and FPI. As the composition of oil varies, it is reasonable that a particular dispersant formulation could be more effective with one oil type than another, but as can be seen PC and FPI dispersed both the LC and TC almost equally. That is FPI and PC can produce stable emulsion irrespective of the asphaltene content, API gravity and chemical composition of LC and TC. PC and FPI were therefore less sensitive to the composition of the crude oils used in this study. This observation gives FPI and PC a significant advantage over other synthetic surfactants such as DOSS which in our previous studies dispersed LC better than TC.

3.3.5 Effect of Salinity on Dispersion Effectiveness.

The stability of emulsions formed by anionic surfactants can be influence by the presence of salt ions since the concentration of the salt ions can influence the droplet size of the emulsion.[39] Since different surfactant systems respond differently to the presence of salt ions, the dispersion effectiveness of the dispersant formulations were tested in different salinity environment using Texas crude (TC) oil.

From Figures 3.11 and 3.12, it can be seen that the dispersion effectiveness of PC and FPI in TC increased with increasing salinity.

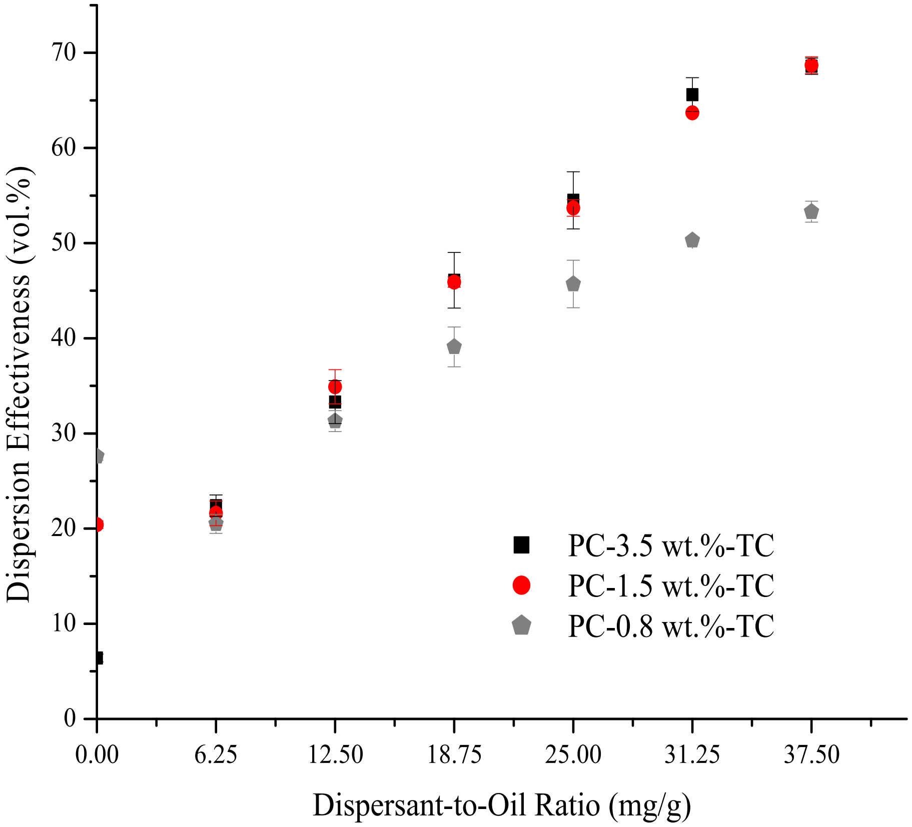


Figure 3.11 Effect of salinity on dispersion effectiveness of PC in TC

PI and PC are anionic and zwetterionic surfactants respectively and therefore the polar head groups of these surfactants are likely to interact or bind with the salt ions. However, binding of these salt ions are competitively inhibited by water and at 4:1 molar ratio of water to the phospholipid, ion binding is inhibited completely.[15b] The molar ratio of water to FPI or PC used in the baffled flask test was more than 4 since the amounts of phospholipids were varied from 0.5 to 3 mg which corresponds to DOR of 6.25 and 37.5 mg/g respectively. It is therefore unlikely that the change in dispersion effectiveness observed with salinity is due to the binding of the ions to polar head groups. Binding of the ions to the polar head group will affect the hydrophilicity and the arrangement of FPI and PC molecules at the oil-water interface. This is because the bound neutral ions will reduce the electrostatic repulsion among the charged head groups. The presence of the neutral electrolyte will also affect micelle formation since the critical micelle concentration will change.

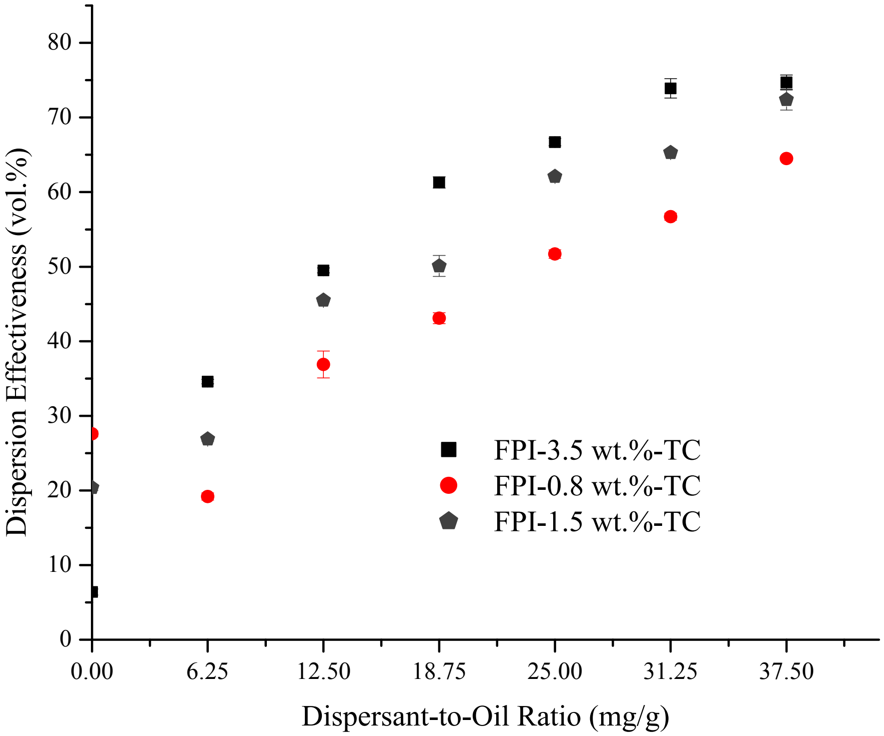


Figure 3.12 Effect of salinity on dispersion effectiveness of FPI in TC

Therefore, it is likely that the salt ions present screened the polar head groups and hence resulted in the reduction in electrostatic repulsion that existed between them. A reduction in the repulsion between the polar head group will allow a condensed or close packed arrangement of surfactant molecules at the oil-water interface. As a result, the stability of the emulsions was improved and higher dispersion effectiveness observed at higher salinity. Though there is the tendency for droplet aggregation to occur at higher salinity[40] as can be seen in Figure 3.5 at DOR of 18.75 and 37.5 mg/g, this did not result in a reduction in dispersion effectiveness. A visual observation of the emulsions formed at salinity environments of 0.8 and 1.5 wt.% indicated that there was oiling-out due to the coalescence of oil droplets depicting the instability of the emulsions formed at these salinities.

3.4. Conclusions

The results from this study show the potential of dispersants formulated with Lecithin (FPI and PC) to replace the traditional liquid chemical dispersant formulations. This study showed that PC and PI obtained by fractionating crude soybean lecithin with ethanol disperse crude oil to different extents. The dispersion effectiveness of freshly fractionated PC was higher than that of the crude soybean lecithin (CL) and freshly fractionated PI. However, after structural modification of PI (FPI), its dispersion effectiveness improved remarkably and was higher than that of PC. This was attributed to the introduction of additional hydroxyl groups into the PI structure which increased its hydrophilicity and resulted in improved dispersion effectiveness. The dispersion effectiveness of the FPI was lower than that of solubilized DOSS and Tween 80 in propylene glycol at lower DORs whiles at higher DORs, the dispersion effectiveness of FPI was higher than that of solubilized DOSS and Tween 80 in propylene glycol. Dispersants formulated by varying the ratio of FPI and PC resulted in a dispersion effectiveness that was almost the same as that of PC. The dispersion effectiveness of FPI and PC in both LC and TC oil samples were similar despite differences in the composition of these oil samples. Varying the salinity environment during the analysis resulted in higher dispersion effectiveness at a salinity of 3.5 wt.% and a lower dispersion effectiveness at 0.8 wt.%.

3.5 Acknowledgement

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Chapter 4

Halloysite Clay Nanotubes Loaded with Surfactant(s) as a Dispersant for Crude Oil Spill Remediation

4.1 Introduction

Over 120 million gallons of crude oil are spilled into the environment worldwide each year.[1] In 2014 alone, about 8 major oil spills occurred which resulted in a spillage of millions of gallons of crude oil. [2] The Deepwater horizon oil spill, which is considered to be the worst spillage in history resulted in the release of over 200 million gallons of crude oil into the Gulf of Mexico.[3] The increase in the number and amount of crude oil spillage can be associated with increased industrial activities due to the emergence of different petrochemical, food, pharmaceutical, and metallurgical industries.[4] The effect of oil spill on the environment is enormous since it causes great harm to the vegetation, food crops and aquatic species.[5]

To minimize the impact of oil spills on the environment, different remediation strategies are being developed. Some of the most commonly used oil spill response options are in situ burning, mechanical containment and recovery and chemical dispersant application. Recently, oil spill absorbents as an oil spill response option has attracted the attention of many researchers since this allows for the recovery of the spilled oil.[6] Among these oil spill response methods, chemical dispersant application is one of the few response measures that when adopted under the right circumstances and with judicious use of dispersants, leads to reduced environmental and economic impact of the spilled oil.[7] Dispersants are one of the only feasible response options for minimizing the impact of large-scale oil spills.

The traditional liquid chemical dispersant formulation is comprised of surface active agent(s), and solvent(s) as the delivery medium. The surface active agents used in the traditional liquid chemical dispersant formulations are mainly petroleum based surfactants such as dioctyl sodium sulfosuccinate salt (DOSS) which is known to be relatively toxic when compared with food grade surfactants such as Tween 80 and Span 80. Hence current studies have proposed the use of food grade surfactants such as lecithin and Tween 80, as the active agents in dispersant formulation.[8] Possible replacement of the solvents in the traditional dispersant formulation with other materials such as halloysite nanotubes, iron oxide nanoparticles and dissolvable polymer matrix has been studied.[9] Chemical dispersant application:

- Counters the formation of water-in-oil emulsions which result from the presence of some compounds such as metallopophyrins and waxes in the crude oil. The formation of water-in-oil emulsions makes the natural dispersion of the crude oil very difficult.[10]
- Enhances the rate of oil dispersion by creating finer oil droplets and increasing surface area. This also results in a reduction of coalescence and resurfacing of the oil.[11]
- Allows for the dispersion of the oil in harsh weather conditions. [12]
- Decreases the exposure of marine birds to the spilled oil.[10a]

Despite these advantages, chemical dispersant applications has some associated disadvantages. The major limitations of chemical dispersant application as an oil spill response option are the solubility of the surface active agents in water and the toxicity of the petroleum based surfactants, and hydrocarbon based solvents used in their formulation. The aqueous solubility of the dispersant and the ocean current cause the dispersant to be washed away and wasted. To compensate for this inefficiency, large amounts of dispersants are used resulting in high costs and a large environmental load. The hydrocarbon based solvents such as 2-butoxyethanol used in the traditional chemical dispersant formulations are toxic to humans and aquatic species. To reduce the solubility and toxicity of the dispersant during application, this study proposes the use of halloysite nanotubes as nanocontainers for surface active agents.

Halloysite clay nanotube (HNT), which belongs to the smectite group of nanoclays is composed of tetrahedral sheets of silica fused to an octahedral sheet of alumina.[13] HNT is a natural 1:1 aluminosilicate clay mineral that can be mined from deposits as a raw material and it is a weathering product of volcanic rocks.[14] It has a rolled hollow tubular structure of many concentric layers with a chemical formula of $Al_2Si_2O_5(OH)_4.nH_2O$ as can be seen in Figure 4.1. The "n" can either be 0 or 2 depending on whether or not the halloysite tube is dehydrated or hydrated. The size of halloysite nanotube varies in length from 500-1000 nm and the lumen diameter varies from 15-100 nm and is characterized with high pore volume and specific surface area of 1.3 mL/g and 65 m^2/g, respectively.[14a, 15]

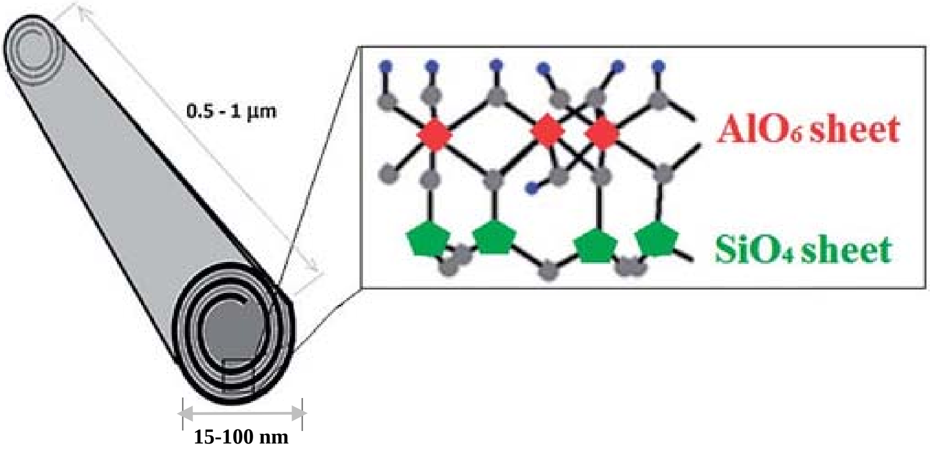


Figure 4.1 Schematic representation of halloysite nanotube.[16]

The unique properties of HNT such as: its strong surface charge, low cost, environmental friendliness, biocompatibility, high aspect ratio and its availability has made it possible for it to be used in a wide array of applications. HNT has been used as nanocomposite scaffold for tissue engineering,[15b] nanocontainers for drug delivery[16-17] and for the controlled release of anticorrosion and protective agents.[14a] [18] In addition to these, Hughes et al.[14b] used naturally occurring halloysite to enhance the capturing of flowing cells.

The toxicity of the formulated dispersant upon application can further be reduced by blending natural surfactant such as phosphatidylinositol (PI) with petroleum derived surfactants such as Tween 80 and DOSS. Current studies reported by Athas et al.[8] suggested that, a blend of lecithin and Tween 80 solubilized in ethanol is an excellent emulsifier when compared to lecithin and Tween 80 alone. A more stable emulsion has been attained by blending different fractions of DOSS, Span 80 and Tween 80.[19]

Owoseni et al.[9a] conducted a fundamental study into the possible application of HNT in oil spill remediation. They concluded that raw HNT can stabilize dodecane-in-water emulsions for at least 3 months. Cryo-scanning electron microscopy (Cryo-SEM) imaging of the oil-in-water emulsions showed that the HNT assemble in a side-on orientation at the oil-water interface and formed networks on the interface through end-to-end linkages. A constant dynamic interfacial tension of approximately 50 mN/m was observed for the emulsions stabilized by the raw HNT depicting that HNT stabilized the oil-in-water emulsions through steric hindrance. On the other hand, a much lower dynamic interfacial tension value of approximately 24 mN/m was observed when HNT was loaded with surfactants such as DOSS and Tween 80. The lower dynamic interfacial tension values was attributed to the release of the surfactant from HNT. Transmission electron microscopy (TEM) images of the HNT loaded with the surfactants showed that, the lumen of the HNT was occupied with the surfactants.

To reduce dispersant solubility and toxicity, and increase dispersion effectiveness, we report a blend of surfactants loaded onto halloysite nanotubes as a dispersant for crude oil spill remediation. In this study, the effectiveness of raw HNT and HNT loaded with surfactant(s) in dispersing Texas crude oil was examined with the U.S. EPA's baffled flask test. PI was fractionated from crude lecithin and its structure modified through natural hydroxylation process. The modified PI (FPI), DOSS, Span 80 and Tween 80 were loaded individually onto HNT by vacuum suction. DOSS-Tween 80, DOSS-Lecithin FPI, DOSS-Span 80, Tween 80-Span 80, Lecithin FPI-Span 80 and Lecithin FPI-Tween 80 blends were also loaded onto the HNT. Ternary mixtures comprising of DOSS-Lecithin FPI-Tween 80, DOSS-Span 80-Tween 80 and Tween 80- Lecithin FPI-Span 80 loaded onto HNT were also formulated. The HNT loaded with the surfactants were characterized with thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FT-IR). The release of Tween 80 and DOSS from HNT were also studied and the dispersion effectiveness of the HNT loaded with the surfactant(s) examined with the baffled flask test.

4.2. Experimental Section

4.2.1 Materials

Soybean lecithin was purchased from Stakich Inc. (Bloomfield Hills, MI) and Koptec ethanol 200 proof was obtained from VWR. Halloysite nanotubes were purchased from Naturalnano Inc. (Rochester, NY). The following chemicals were obtained from Sigma Aldrich: dioctyl sodium sulfosuccinate salt (DOSS), ammonium thiocyanate (ACS reagent, ≥97.5) and Tween 80. Sodium thiosulfate (0.1N) was obtained from Macron Chemicals. Cobalt (II) nitrate hexahydrate (ACS reagent 98+ %) was purchased from Acros Organics. Hanus (Iodine monobromide) solution and methylene blue solution (1% w/v) were purchased from RICCA Chemical Company while chloroform and dichloromethane were purchased from EMD Chemical Company. Potassium iodide (10 w/v %) and starch indicator were obtained from BDA Chemicals. Instant Ocean salt was obtained from Instant Ocean (Blacksburg, VA). Sodium hydroxide pellets and concentrated sulfuric acid solution were obtained from Fisher Scientific. The heavy crude oil (Texas crude-TC) was obtained from Texas Raw Crude International (Midland, TX).

The major compounds present in the crude oil samples, the properties of the crude oil as well as the composition of the Instant Ocean salt have been reported by Nyankson et al.[20]

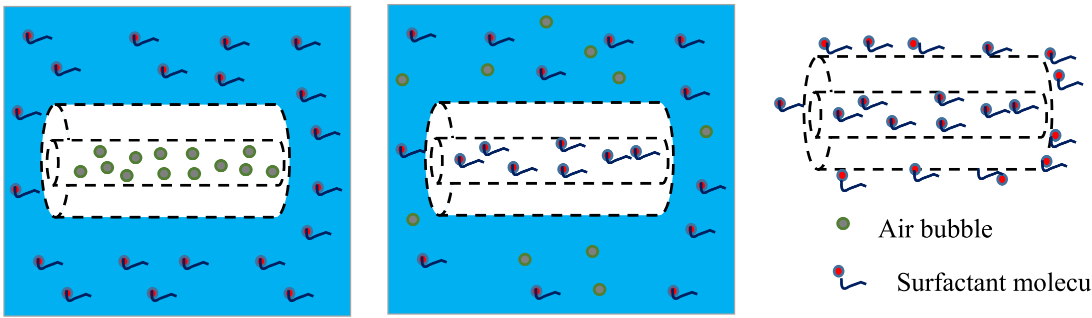
4.2.2 Experimental Procedure

4.2.2.1 Fractionation of Crude Soybean Lecithin with Ethanol

The method used to fractionate the soybean lecithin is similar to the one described by Wu et al..[21] Briefly, some amount of crude lecithin was weighed into a centrifuge tube, ethanol (95 %) was added. The tube was then heated in a water bath at 60 ℃ for 60 minutes, stirring every 15 minutes during heating to enhance the dissolution of the phosphatidylcholine (PC) in ethanol. After heating for 60 minutes, the mixture was centrifuged for 5 minutes. The ethanol phase was poured off into a glass vial. The solid residue that remained in the centrifuge tube after centrifugation was then deoiled with acetone according to the AOCS official method Ja 4-46 [22] and was labelled as PI (PI-enriched fraction). To structurally modify PI, some of the PI samples were stored in vials over a period of 14 weeks. Changes that occurred in the PI structure during storage were examined by FT-IR and iodine value (IV) determination. The structurally modified PI was labelled as FPI. A detailed discussion on the structural modification and characterization of FPI was reported by Nyankson et al..[23]

4.2.2.2 Surfactant Loading Method

The loading method was similar to the ones reported by Owoseni et al.[9a] and Ward et al.[17] Briefly, a nearly saturated surfactant(s) solution was mixed with the halloysite nanotubes which has been dried at 80 ℃ for 12 hrs. Specifically, 2g of the surfactant(s) was added to 100 ml of an ethanol:water (90:10 w/w) solution, resulting in a 20 mg/ml surfactant(s) solution. Approximately 2.5 ml of the surfactant solution was added to the dried HNT to form a nearly wet paste. The mixture was then placed in a vacuum jar and vacuum suction applied for 5 minutes after which the pressure was released. The vacuum suction procedure was repeated 5 times after which the mixture was vacuum dried. Another 2.5 ml of the surfactant(s) solution was then mixed with the dried HNT loaded with the surfactant(s) in the previous step. Vacuum suction was applied to the mixture for 5 minutes and then the pressure was released. The vacuum suction step was again repeated 5 times. The surfactant loading method is summarized in Figure 4.2. The HNT loaded with the surfactant(s) was then vacuum dried and characterized with TGA, SEM and FT-IR.



HNT in surfactant solution with air bubbles occupying the lumen

Surfactant molecules settles on the surface of the tube and also replace air bubbles in the lumen during vacuum suction

After vacuum drying, surfactants settle in the lumen and the outer surface of the HNT.

Figure 4.2 Surfactant loading method

4.2.3 Product Characterization

4.2.3.1 Thermogravimetric Analysis (TGA) of the HNT Loaded with Surfactants

Thermogravimetric analysis (TGA) of the raw HNT and the HNT loaded with surfactant was carried out using Pyris 1 TGA. The analysis was performed with nitrogen and at a heating rate of 10 ℃/min for 80 minutes.

4.2.3.2 Fourier Transform Infrared (FT-IR) Spectroscopy

A Nicolet iS10 FT-IR equipped with Smart itR ATR accessory with infrared spectra 400 – 4000 cm^{-1} was used for the analysis. The equipment uses deuterated triglycine sulfate (DTGS) detector and a KBr/Ge beam splitter. Approximately 2 mg of the sample was used for the analysis.

4.2.3.3 Surfactant Release Kinetics

A weighed amount of the HNT loaded with the surfactant was added to 100 ml of deionized water and stirred at 200 rpm with a Caframo® stirrer for 9 hours during which 4 ml samples were drawn at different time intervals and analyzed for surfactant released. The DOSS amount released was analyzed with methylene blue complexation procedure while the amount of Tween 80 released was analyzed with ammonium cobalt thiocyanate active substance test. It should be noted that 4 ml of water was added anytime the 4 ml sample was drawn to maintain the concentration.

4.2.3.4 Methylene Blue Test

The procedure used for this test was the same as that described in the hand book of water analysis.[24] That is, 2 ml of the water sample drawn during the dissolution trial was added to 48 ml of distilled water in a separating funnel. 10 ml alkaline phosphate solution, 5 ml of neutral methylene blue solution and 15 ml of chloroform were then added. The extraction process was carried out by shaking the separating funnel gently for 1 minute. The phases were allowed to settle, and the chloroform extract drained off into another separating funnel containing 110 ml of distilled water and 5 ml acid methylene blue solution. The first separating funnel was then rinsed with 5 ml of chloroform and shaken for 1 minute. The phases were allowed to separate and the chloroform extract drained into the second separating funnel. The second separating funnel was then shaken for 1 minute and the phases allowed to separate. The chloroform extract was drained through a chloroform-moistened cotton wool on a funnel into a 50 ml graduated cylinder. The second separating funnel was then rinsed with 5 ml chloroform and shaken for 1 minute. The phases were allowed to separate and the chloroform extract drained into the same 50 ml graduated cylinder. The chloroform extract in the 50 ml graduated cylinder was topped up to the 50 ml mark with pure chloroform. The amount of DOSS was quantified at an absorbance difference of 650-400 nm.

4.2.3.5 Cobalt Thiocyanate Active Substance (CTAS) Test

The CTAS test was used to study the release kinetics of HNT loaded with nonionic surfactants such as Tween 80. In the CTAS test, the nonionic surfactant reacts with ammonium cobalt thiocyanate in the aqueous phase and form colored ion association complex species. The ammonium cobalt thiocyanate reagent was prepared by dissolving 6 g of Cobalt (II) nitrate hexahydrate and 40 g of ammonium thiocyanate in a quantity of deionized water in a volumetric flask and topping it up to 200 ml. The reagent must be prepared on the same day of use to prevent oxidation, which can affect the absorbance readings. The Tween 80 quantification was carried out by adding 10 ml of DCM to a 100 ml separation funnel. Approximately 2 ml of the water sample drawn from the release trial in addition to 5 ml of ammonium cobalt thiocyanate was added. The two immiscible phases were allowed to separate after shaken the separation funnel for about 2 minutes. The lower portion of the DCM extract was ran through a plug of wool moistened with DCM. The absorbance of the DCM extract was obtained at an absorbance difference of 620-400 nm.

4.2.3.6 Baffled Flask Test

The dispersion effectiveness of the HNT loaded with the surfactant(s) was examined with the baffled flask test. To analyze the dispersion effectiveness of HNT loaded with surfactants, 100 µl of crude oil was added to 120 ml of 3.5 wt.% synthetic sea water in a baffled flask. An appropriate amount of the HNT loaded with the surfactant was weighed and added directly on top of the oil and the baffled flask was placed on a shaker (VWR advanced digital shaker, Model 3500) set at 200 rpm for 10 minutes. A settling time of 10 minutes was allowed after which 30 ml of the aqueous media with dispersed oil was drawn and the dispersed oil extracted with DCM and quantified with UV-Vis at an absorbance difference of 300-400 nm.

All the experiments were conducted at least in triplicates and the error bars on all the plots are the standard error of the mean (SEM).

4.3 Results and Discussion

4.3.1 Morphology and Dispersion Effectiveness of Raw HNT

The TEM images of the raw HNT used in this study are show in Figure 4.3. It can be seen that, the HNT used for the study had different lengths and diameters. The diameter of the HNT varies with a larger proportion of the HNT having lumen diameter of approximately 10-70 nm and length of 330-1500 nm. One notable observation from the TEM images was the fact that a smaller proportion of the HNTs were nanorods.

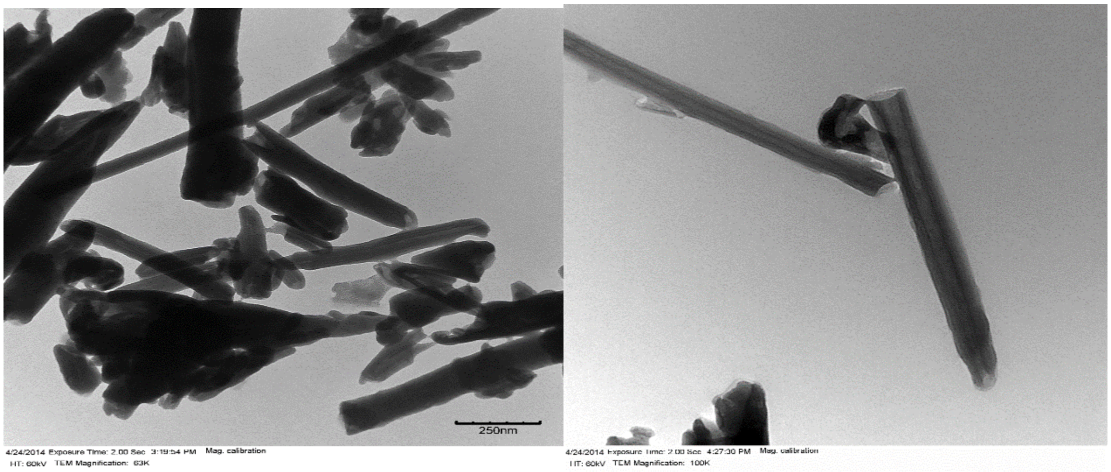


Figure 4.3 TEM images of the raw HNT

The dispersion effectiveness of the raw halloysite were examined at different halloysite-to-oil ratio (HOR) and the results are shown in Figure 4.4A. The dispersion effectiveness of the raw HNT were almost the same at lower HOR but increased at HOR of 194 mg/g. Nanomaterials stabilize emulsions through the formation of Pickering emulsion. Increased dispersion effectiveness at higher HOR can therefore be attributed to increased adsorption of the HNT at the oil droplet–water interface. The adsorbed HNT resulted in the formation of a rigid barrier (Figure 4.4B) at the oil droplet-water interface providing a mechanical barrier to droplet coalescence and creaming. A dense network structure of HNT is formed at the oil droplet-water interface resulting in the formation of a more stable emulsion at higher HOR.[9a, 25]

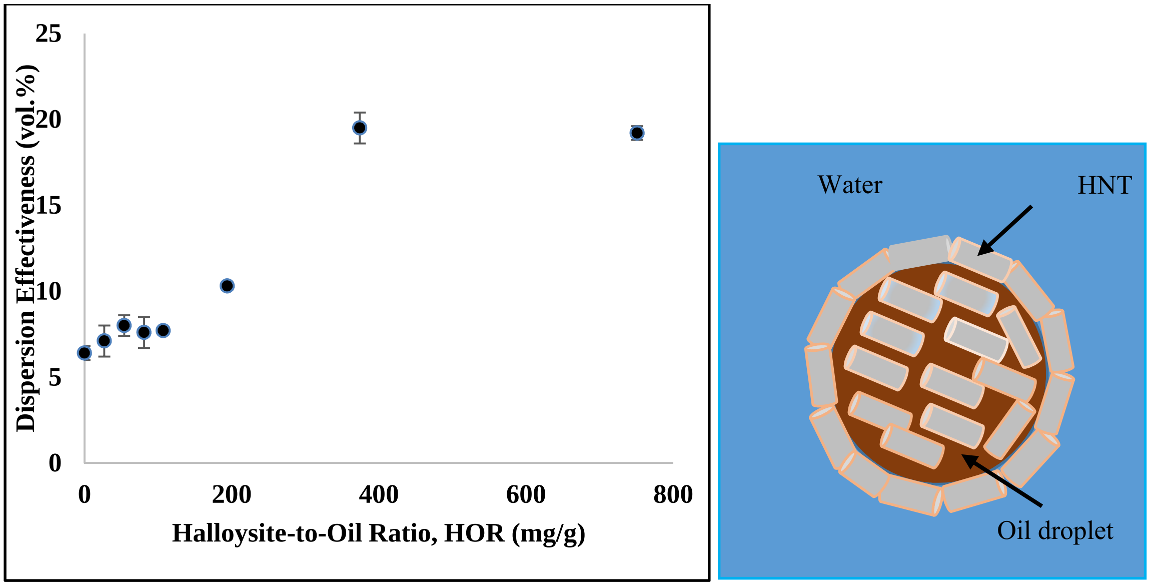


Figure 4.4 (A) Dispersion effectiveness of raw HNT at different HORs (B) Adsorption of HNT at oil-water interface.

However, comparing the highest dispersion effectiveness obtained at high HOR to that of surfactant DOSS, it was observed that the dispersion effectiveness of raw HNT was much lower than that of DOSS.[9b] Generally, higher energy is required to form very stable Pickering emulsion. The 200 rpm energy supplied during the baffled flask test was not enough to result in the formation of a very stable emulsion and therefore the lower dispersion effectiveness observed for raw HNT. The dispersion effectiveness values of nanoparticle stabilized emulsions are known to have been improved by the addition of a small quantity of surfactants.[9c, 25] To improve dispersion effectiveness, reduce toxicity and solubility of dispersants in water, different surfactant(s) were loaded onto HNT and their release amount and dispersion effectiveness examined.

The method adopted for loading the surfactant onto the HNT resulted in the surfactant settling in the interstitial spaces between the HNTs and in the lumen of the HNTs. The HNT agglomerated as a result of the surfactant settling in the interstitial spaces between the tubes as can be seen in the SEM images in Figure 4.5.

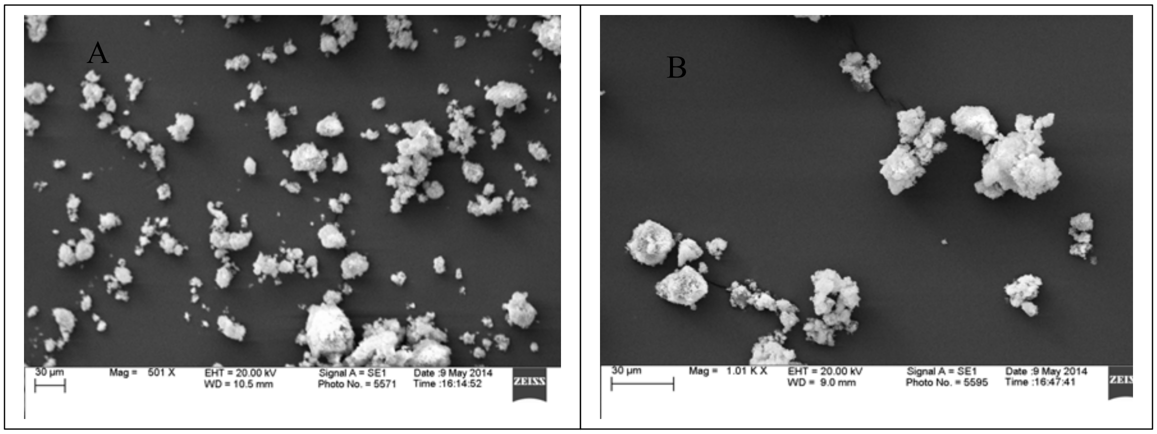


Figure 4.5 SEM images of HNT loaded with (A) 20 wt.% Tween 80 and (B) 20 wt.% DOSS

The degree of agglomeration was pronounced for DOSS than Tween 80 and this can be attributed to the tacky nature of DOSS compared to the slightly viscous Tween 80.

4.3.2 TGA of HNT Loaded with Surfactant

Figure 4.6 shows the TGA for (A) HNT loaded with tween 80 and (B) HNT loaded with DOSS. TGA analysis is used to determine the changes in sample weight with temperature. The nature of the curves in Figure 4.6 depict multistage decomposition with relatively stable intermediates.

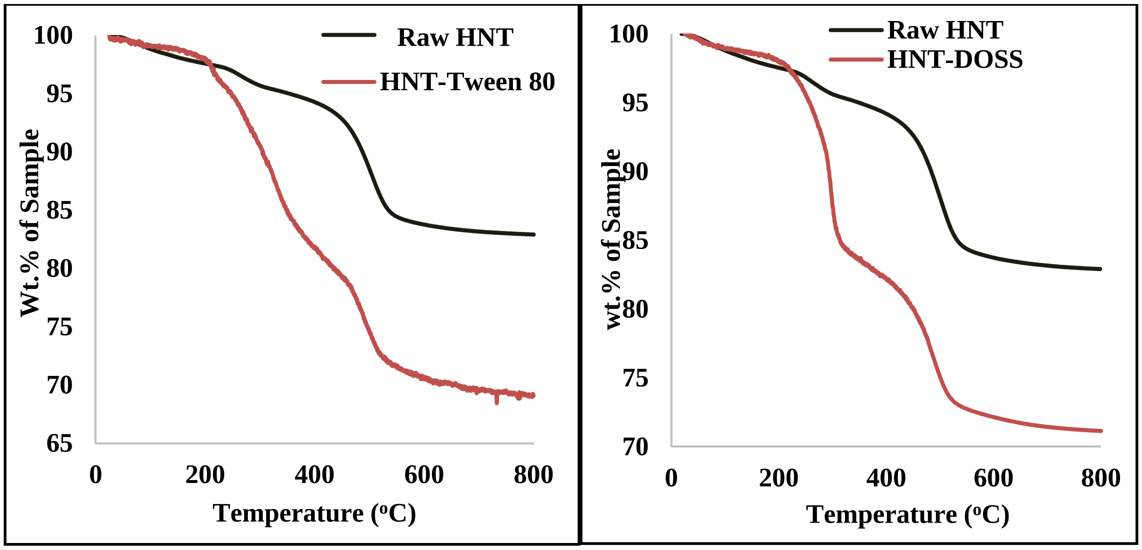


Figure 4.6 TGA for: (A) HNT loaded with 14 wt.% Tween 80 and (B) HNT loaded with 12 wt.% DOSS.

Two distinct decompositions were observed in the raw HNT samples at approximately 60 and 500 °C. The mass loss at 60 °C is due the decomposition of water molecules adsorbed onto the surface of the HNT while the mass loss at 500 °C can be attributed to dihydroxylation of HNT. The HNT loaded with the surfactants recorded a mass loss at approximately 300 °C which can be attributed to the thermal degradation of the surfactant as reported by Owoseni et al..[9a] The mass loss which occurred from the degradation of the surfactant was used to determine the actual amount of surfactant loaded onto the HNT.

The HNTs loaded with the surfactants were examined with FT-IR and 6 major peaks were observed as can be seen in Figure 4.7. The peak observed at 905 cm^{-1} is due to deformation vibrations of inner surface hydroxyl groups while the peak observed at1000 cm^{-1} is attributed to stretching vibrations of Si-O-Si. The stretching mode of epical Si-O resulted in a peak at 1118 cm^{-1} while peak at 1647 cm^{-1} is due to deformation vibration of the interlayer water. The peaks at 3691 and 3621 cm^{-1} is due to the stretching vibration of inner surface hydroxyl groups.[26]

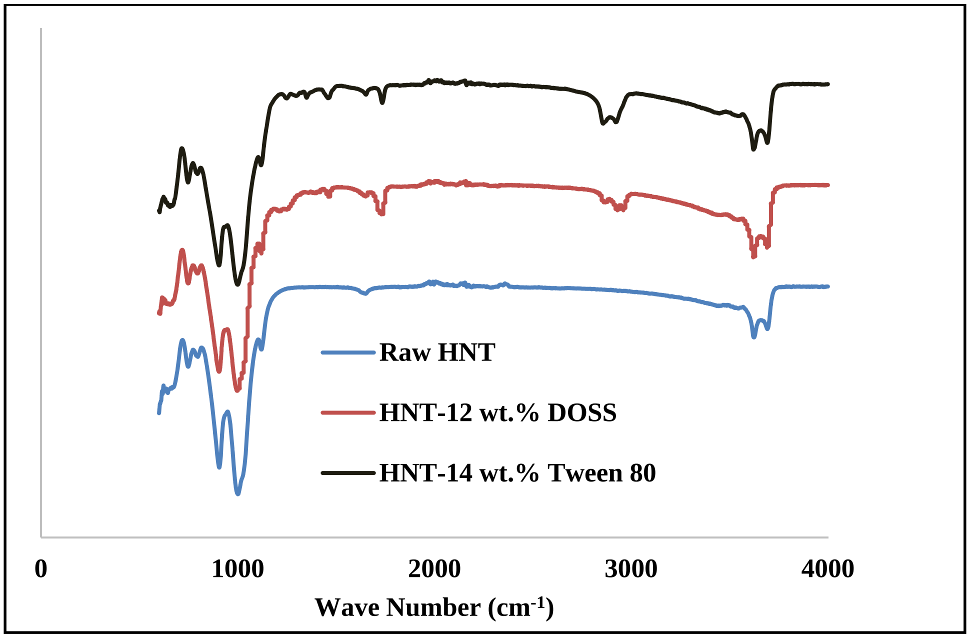


Figure 4.7 FT-IR spectra of raw HNT and HNT loaded with surfactant

Additional peaks were observed for the HNT samples loaded with the surfactants. The peaks observed at 2870 and 2940 cm^{-1} are respectively due to symmetric and asymmetric stretching of CH_2. The peak at 2960 cm^{-1} is due to the symmetric stretching of CH_3 while the peak at 1740 cm^{-1} is due to C=O stretching. Symmetric C-H vibration of CH_3 was observed with a peak at 1470 cm^{-1}. The sulfonation bond which is present in DOSS was observed with symmetric S=O stretching at 1050 cm^{-1}.[27]

4.3.3 Surfactant Release

The release of DOSS was examined with the methylene blue active substance test while that of Tween 80 was studied with the cobalt thiocyanate active substance test. Generally, the release of the DOSS and Tween 80 experienced an initial burst within the first 5 minutes but the release was gradual afterwards (Figure 4.8A).

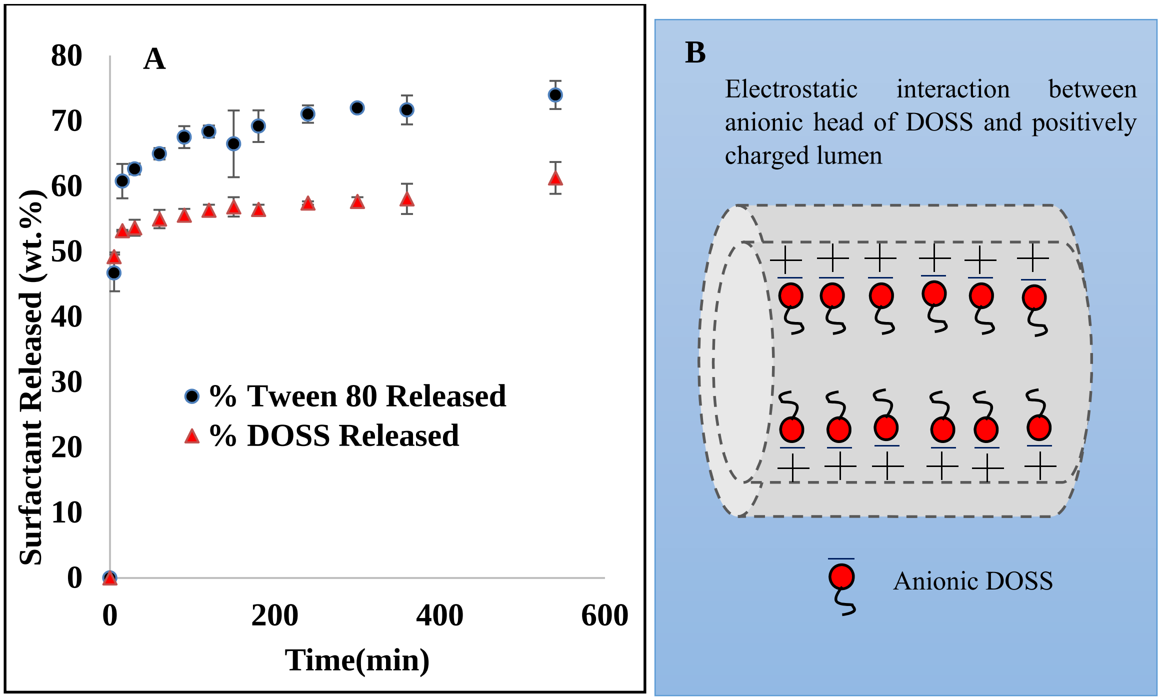


Figure 4.8 (A) Release kinetics of DOSS and Tween 80 from halloysite nanotubes (B) Electrostatic interaction between anionic head of DOSS and positively charged lumen

Significant portion of the surfactant release occurred as an initial burst within the first 5 minutes and this is in agreement with previous studies conducted into the release of different materials from HNT.[9a, 15c] According to Ward et al.,[15c] there are 3 places that the surfactant can be loaded; (a) inside the lumen (b) bound to the inner and or outside of HNT through electrostatic forces and (c) as crystallites in the spaces between adjacent HNTs. The initial burst can be attributed to the release of the surfactants occupying the interstitial spaces between adjacent HNTs while the gradual release can be attributed to the release of the surfactant trapped in the lumen. Since the release of the surfactant occurs by diffusion mechanism, the initial burst can also be attributed to the higher concentration gradient of the surfactant as depicted in Fick's 1st and 2nd laws of diffusion.[28] The release rate of the surfactants in the lumen is determined by the nature of the interaction between the surfactant and the HNTs. It can be observed from Figure 4.8A that, the release rate of DOSS was much slower than that of Tween 80 though both recorded a similar initial burst. In 9 hours, 61 wt.% DOSS was released compared to 74 wt.% for Tween 80. The fraction of the surfactant released is related to the strength of the interaction between the HNT and the surfactant, and also on the solubility of the surfactant in water.[15c] The aluminum-hydroxyl bonds on the inner surface of HNT makes inner surface of the lumen slightly positively charged, hence with DOSS being an anionic surfactant a much stronger electrostatic interaction is expected (Figure 4.8B). The stronger electrostatic interaction of DOSS with the slightly positively charged inner surface of the lumen is responsible for the relatively slower release rate of DOSS from HNT.

4.3.4 Dispersion Effectiveness of HNT, HNT-DOSS, HNT-Tween 80, HNT-Span 80 and HNT-Lecithin FPI

The dispersion effectiveness of the various surfactants loaded onto the HNT were determined with the baffled flask test and are shown in Figure 4.9. It is obvious from Figure 4.9 that, the dispersion effectiveness of HNT loaded with the surfactants was significantly higher than that of raw HNT. The higher dispersion effectiveness of the HNT loaded with the surfactant can be attributed to the release of surfactants from the HNTs which subsequently reduced the oil-water interfacial tension. The reduction in the oil-water interfacial tension allowed for easy break up of oil droplets resulting in the formation of a stable emulsion with its associated high dispersion effectiveness. The HNT contributed to the formation of a solid barrier which aided in the stabilization of the emulsion.[9a] It can be seen in Figure 4.9 that, the dispersion effectiveness of HNT loaded with Tween 80 was higher than that of Lecithin FPI, DOSS and Span 80 at all the surfactant-to-oil ratios (SORs) examined in the study. As an example, at SOR=25 mg/g, the dispersion effectiveness of HNT-Tween 80, HNT-Lecithin FPI, HNT-DOSS and HNT-Span 80 were 69.1, 62.8, 44.9 and 23.6 vol.%, respectively.

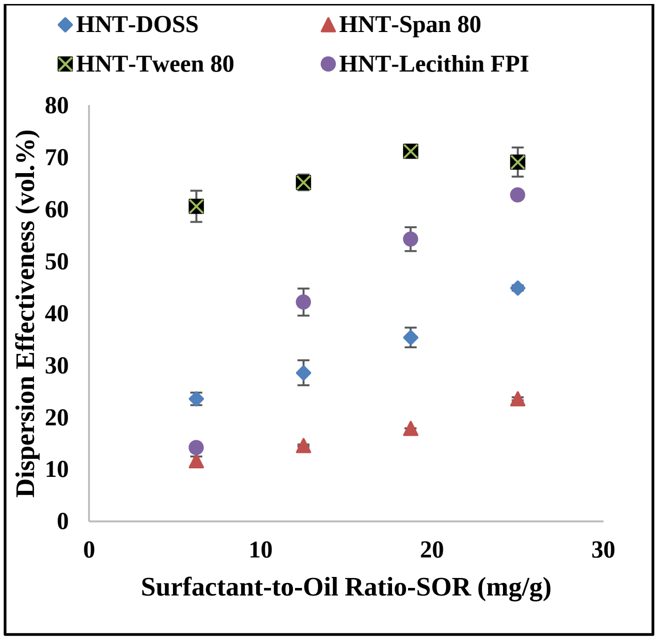


Figure 4.9 Dispersion effectiveness of HNT loaded with different surfactants.

The trend observed in Figure 4.9 can be related to the hydrophilic-lipophilic-balance of the various surfactants loaded onto HNT. The HLB system assigns a numerical value between 0 and 20 scale for nonionic surfactants, with 0 being more hydrophobic and 20 being more hydrophilic. Surfactants with HLB value in the range of 8-18 supports the formation of oil-in-water (o/w) emulsions while those with HLB values in the range of 4-6 supports the formation of water-in-oil (w/o) emulsions. The HLB of Span 80, Tween 80, DOSS and Lecithin FPI are 4.3, 15, 10 and 8, respectively.[29] From the HLB values, Span 80 is very hydrophobic and therefore has a much lower affinity for the continuous aqueous phase. Span 80 is therefore expected to favor the formation of w/o emulsion according to the Bancroft rule.[30] The hydrophobicity of Span 80 also slows down its adsorption kinetics at the oil-water interface and this inhibited oil break up[19b] resulting in the formation of an unstable emulsion which accounted for the lower dispersion effectiveness observed.

Though the HLB of DOSS is within the range that favors the formation of o/w emulsions, HNT-DOSS recorded a relatively lower dispersion effectiveness. Studies conducted into the emulsification behavior of DOSS and Tween 80 revealed that, unlike Tween 80, DOSS easily desorbs from the oil-water interface into the surrounding aqueous phase.[31] The oil droplets coalesce as DOSS desorbs into the aqueous phase leading to the formation of an unstable emulsion which can be related to the relatively lower dispersion effectiveness observed for HNT-DOSS. Tween 80 on the other hand persistently adsorbs from the aqueous phase to the oil-droplet interface and exhibits a much slower leaching rate into the surrounding aqueous phase.[32] The slower leaching rate results in the formation of a stable emulsion which accounts for the higher dispersion effectiveness for HNT-Tween 80. Lecithin FPI was obtained by fractionating PI from crude lecithin with ethanol and modifying the structure of PI by introducing hydroxyl groups onto its structure. The relatively higher dispersion effectiveness of HNT-Lecithin FPI is connected to the additional hydroxyl groups on the PI structure which increased its hydrophilicity resulting in the formation of a more stable emulsion.[23] It was reported in our previous work that the dispersion effectiveness of DOSS and Tween 80 solubilized in propylene glycol were higher than that of Lecithin FPI solubilized in water except at higher dispersant-to-oil ratios. However, from Figure 4.9 we observed that the dispersion effectiveness of HNT-Lecithin FPI was higher than that of HNT-DOSS but lower than that of HNT-Tween 80 at all the SORs examined. Both DOSS and Lecithin FPI are anionic surfactant and therefore are expected to interact with the positively charged lumen of HNT. The interaction of DOSS and Lecithin FPI with the positively charged lumen is expected to influence their release rate and subsequently impact their dispersion effectiveness. The higher degree of solvation of the sodium counter ion for DOSS makes its interaction with the positively charged lumen stronger resulting in a slower release of DOSS from HNT and hence the lower dispersion effectiveness observed for HNT-DOSS formulation.

The TEM images of the HNT loaded with the surfactant(s), Cryo-SEM images of the emulsions stabilized by HNT loaded with the surfactant(s) and interfacial tension measurements were reported in our previous article.[9a]

4.3.5 Dispersion Effectiveness of Binary Surfactant Mixtures Loaded onto HNT

The minimal dispersion effectiveness of HNT-100wt.% Tween 80 and HNT-100 wt.% DOSS compared to the different blends of HNT-DOSS-Tween 80 observed in Figure 4.10 (A) is consistent with data already published.[19b, 29c] At SOR=12.5 mg/g, a maximum dispersion effectiveness of 95 vol.% was attained with HNT loaded with 60 wt.% DOSS and 40 wt.% Tween 80. The minimum dispersion effectiveness values of 28.6 and 65.2 vol.% were attained at HNT-100wt.% DOSS and HNT-100wt.% Tween 80, respectively.

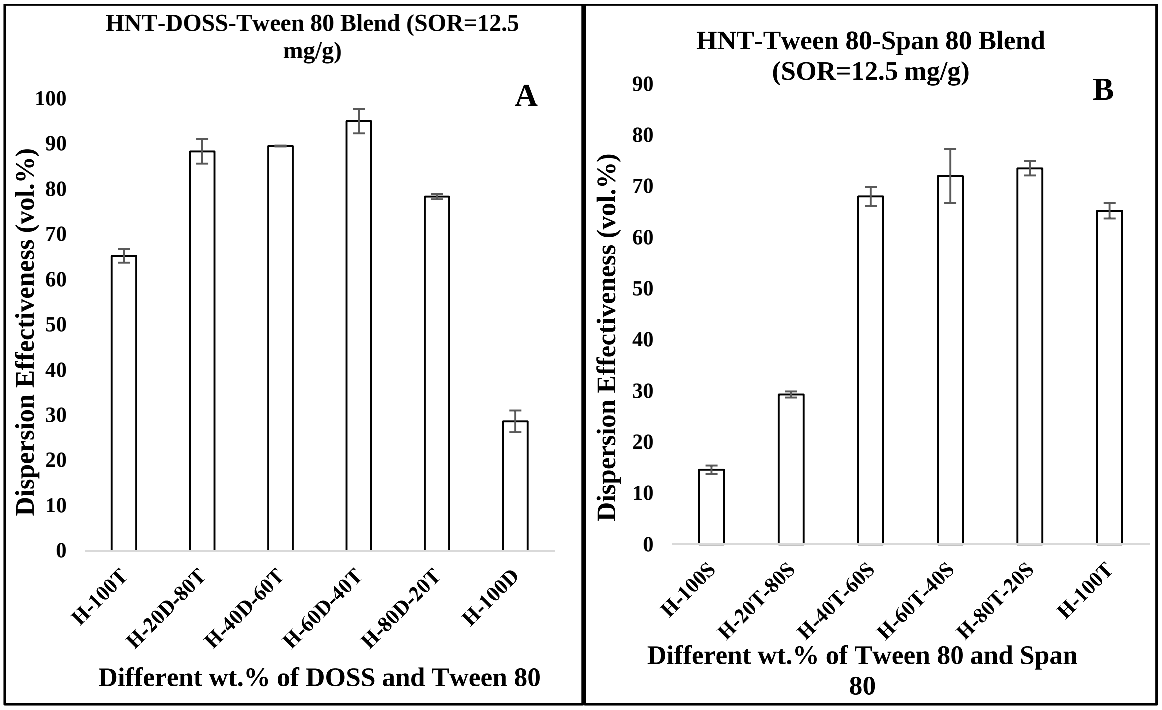


Figure 4.10 Dispersion effectiveness of: (A) HNT-DOSS-Tween 80 at different wt.% of DOSS and Tween 80 (B) HNT-Tween 80-Span 80 at different wt.% of Tween 80 and Span 80. [H=HNT, T=Tween 80, S=Span 80, D=DOSS]

This trend is consistent with those reported in prior work by Reihm et al.[25] who observed lower interfacial tension at 60 wt.% DOSS and 40 wt.% Tween 80. Addition of Tween 80 to DOSS increased the dispersion effectiveness remarkably due to the fact that, at the oil droplet-water interface, the sorbitan ring of Tween 80 with its long polyoxyethylene chains is maintained in the water phase far from the anionic head of DOSS. Such an arrangement reduced the electrostatic repulsion between the anionic head group of DOSS and resulted in a close packed arrangement of surfactants at the oil droplet-water interface.[29c] Dispersion effectiveness at higher SOR of 25 mg/g is reported in Figure B.1A (Appendix B.1).

Addition of Span 80 to Tween 80 resulted in a reduction of the dispersion effectiveness except when the wt. % of the loaded Span 80 was about 20-60 as can be seen in Figure 4.10(B). Compared to HNT-100 wt.% Tween 80, the increase in dispersion effectiveness with 20-60 wt.% Span 80 was marginal. Increase in the wt.% of Span 80 slowed down the adsorption of the dispersant at the oil droplet-water interface[8] and this resulted in the formation of an unstable emulsion which accounted for the low dispersion effectiveness. In addition to this, increasing the Span 80 concentration inhibits oil break up resulting in the formation of larger oil droplets which are unstable. Addition of Span 80, which is hydrophobic also increased the tendency to form w/o emulsions[19a] which impacted negatively on dispersion effectiveness. A similar trend was observed when Span 80 was added to DOSS (Figure 4.11A) and Lecithin FPI (Figure 4.11B). The plots for the dispersion effectiveness of HNT-Tween 80-Span 80, HNT-DOSS-Span 80 and HNT-Lecithin FPI-Span 80 formulations at higher SOR of 25 mg/g are shown in Figures B.1B, B.2A and B.2B, respectively (Appendix B.1).

The dispersion effectiveness of HNT loaded with different blends of Tween 80 and Lecithin FPI were higher than that of HNT loaded with 100 wt.% Tween 80 and 100 wt.% Lecithin FPI (Figure 4.12A).

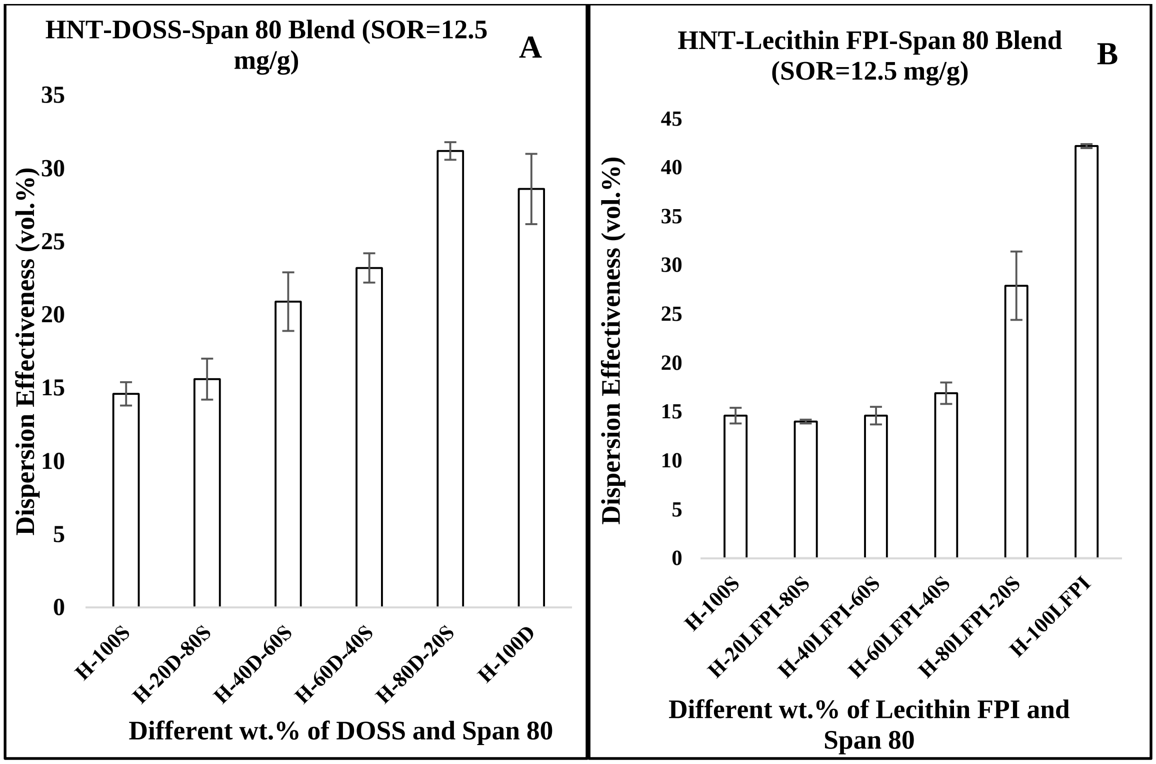


Figure 4.11 Dispersion effectiveness of: (A) HNT-DOSS-Span 80 at different wt.% of DOSS and Span 80 (B) HNT-Lecithin FPI-Span 80 at different wt.% of Lecithin FPI and Span 80. [H=HNT, D=DOSS, S=Span 80, LFPI=Lecithin FPI]

This result is also consistent with those reported by Athas et al.[8] The relatively faster desorption of Tween 80 into the surrounding aqueous phase is compensated by the slower tendency of Lecithin FPI to desorb from the oil-water interface. The oxyethylene "hair" in Tween 80 provided steric stabilization to oil droplet and prevented their coalescence.[19a] This resulted in the formation of a stable emulsion which accounted for the higher dispersion effectiveness values observed for HNT loaded with different fractions of Tween 80 and Lecithin FPI. The nonionic Tween 80 also reduced the electrostatic repulsion between the anionic head groups of Lecithin FPI resulting in a closed packed arrangement of surfactant at the oil droplet-water interface. Closed packed arrangement of surfactants at the oil droplet-water interface prevented oil droplet coalescence and provided a stable emulsion with high dispersion effectiveness. The dispersion effectiveness of HNT-Tween 80-Lecithin FPI at higher SOR of 25 mg/g is shown in Figure B.3A (Appendix B.1).

However, HNT loaded with a mixture of two anionic surfactants, that is DOSS and Lecithin FPI resulted in a dispersion effectiveness which was almost the same as HNT loaded with 100 wt.% DOSS and 100 wt.% Lecithin FPI. This result is consistent with data reported by Brochu et al.[29c] Unlike Tween 80–DOSS blend, the electrostatic repulsion between the anionic head groups was pronounced and this is responsible for the trend observed in Figure 4.12B. The dispersion effectiveness HNT-Lecithin FPI-DOSS formulation at SOR of 12.5 mg/g is shown in Figure B.3B (Appendix B.1).

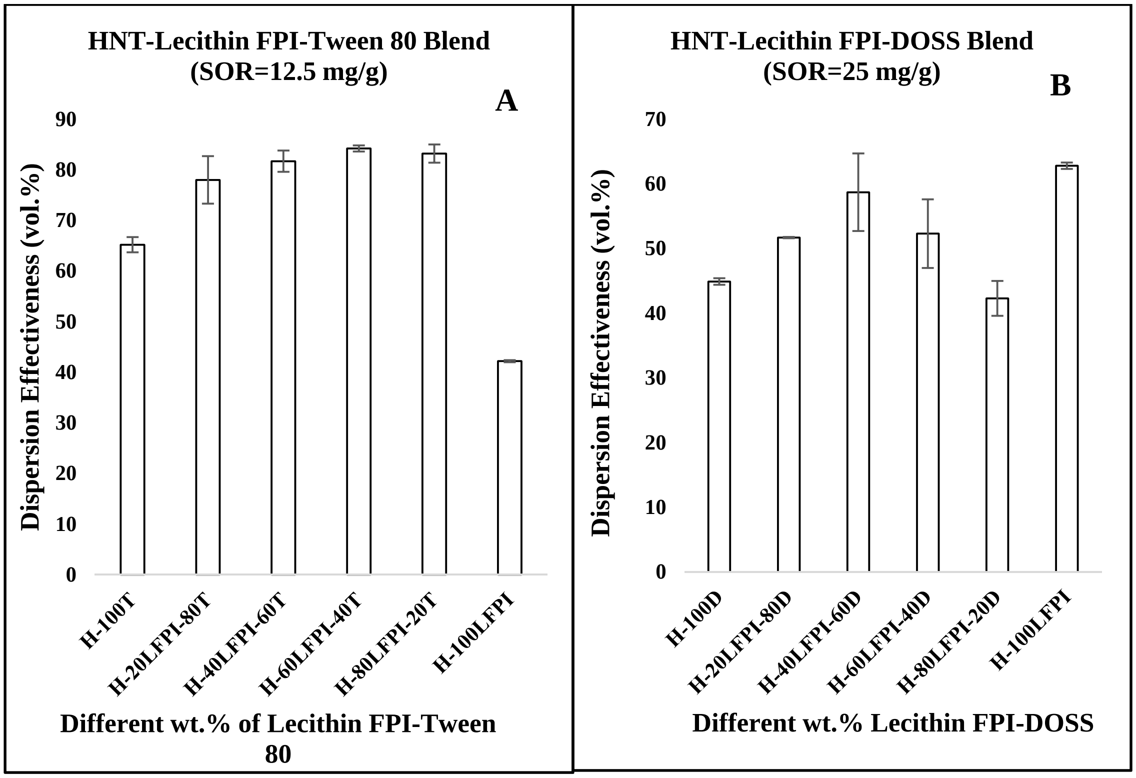


Figure 4.12 Dispersion effectiveness of: (A) HNT-Lecithin FPI-Tween 80 at different wt.% of Lecithin FPI and Tween 80 (B) HNT-Lecithin FPI-DOSS at different wt.% of Lecithin FPI and DOSS. [H=HNT, LFPI=Lecithin FPI, T=Tween 80, D=DOSS]

4.3.6 Dispersion Effectiveness of Ternary Surfactant Mixtures Loaded onto HNT

The dispersion effectiveness of HNT loaded with Tween 80-DOSS-Span 80 was examined with the baffled flask test and the results are shown in Figure 4.13. The right corner of the triangle represents 100 wt.% DOSS. When one moves upwards along the straight line to the top corner, the wt.% of DOSS decreases while that of Span 80 increases until 100 wt.% Span 80 is attained. The bottom left corner represents 100 wt.% Tween 80. Moving upwards along the straight line increases the Span 80 wt.% while the Tween 80 wt.% decreases. Moving from the left to the right along the bottom line increases DOSS wt.% while the Tween 80 wt.% decreases. Addition of a third component is represented by a point in the ternary diagram. The dispersion effectiveness at the three corners of the triangle, representing a single surfactant loaded onto HNT were relatively lower. However, the dispersion effectiveness increased upon the addition of a second and a third component. The 95-100 vol.% dispersion effectiveness occupied a smaller region at the center of the ternary plot. In that region, the maximum dispersion effectiveness value was 96.2 vol.% and was recorded at HNT-40 wt.% Tween 80-40.wt.% DOSS-20 wt.% Span 80.

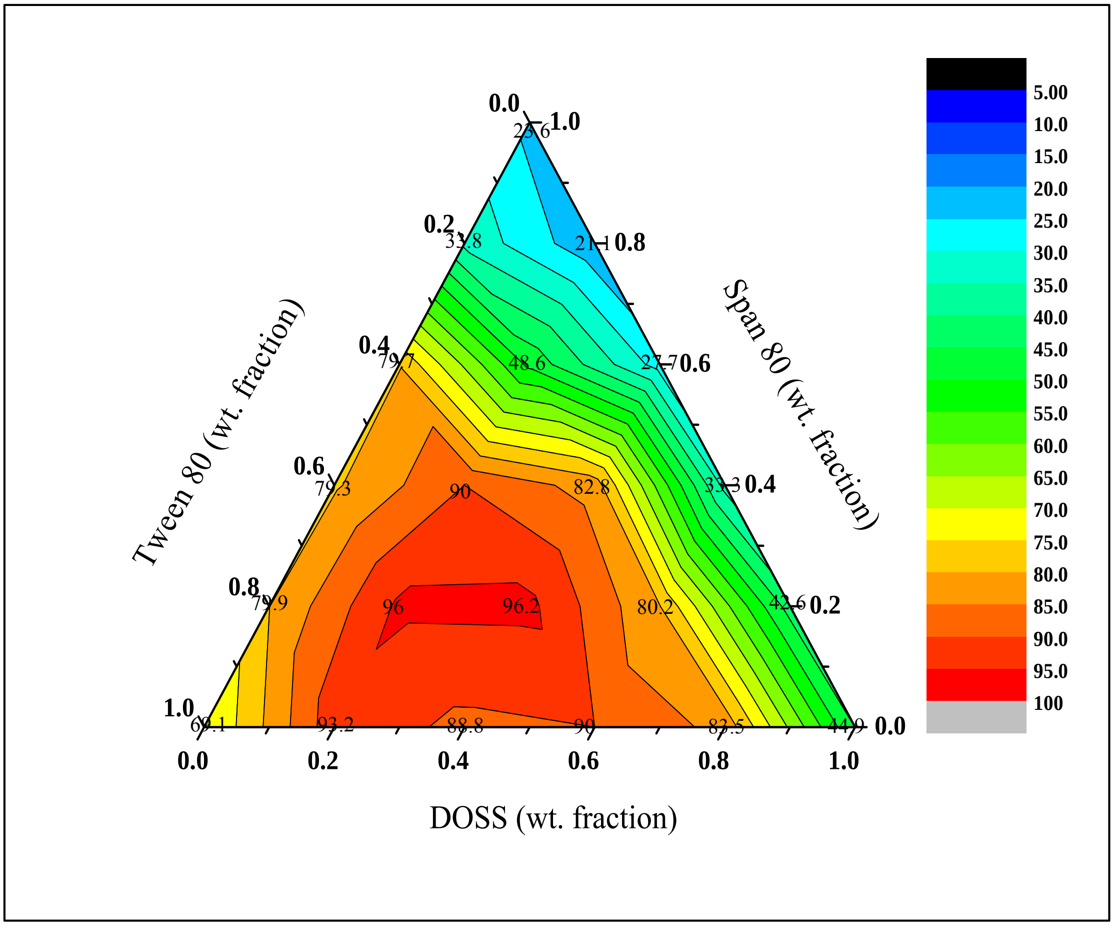


Figure 4.13 Ternary contour plot for HNT loaded with DOSS, Tween 80 and Span 80 (SOR=25 mg/g)

The maximum dispersion effectiveness attained at 40 wt.% Tween 80, 40 wt.% DOSS and 20 wt.% Span 80 is consistent with already published data.[19b, 29c] The higher dispersion effectiveness observed for HNT- 40 wt.% Tween 80-40 wt.% DOSS-20 wt.% Span 80 is attributed to reduction in interference between the head groups of DOSS and Span 80 by Tween 80.[29c] The moderation of the interaction between DOSS and Span 80 by Tween 80 allowed for a closed packed arrangement of surfactants at the oil droplet-water interface resulting in the formation of a stable emulsion. The closed packed arrangement of the surfactants at the oil droplet-water interface results in the lowering of the interfacial tension which favors droplet break up. A lower initial interfacial tension was observed by Riehm et al.[19b] at 40 wt.% Tween 80, 40 wt.% DOSS and 20 wt.% Span 80. High dispersion effectiveness values were recorded by the HNT-Tween 80-DOSS-Span 80 formulation even at lower SOR of 12.5 mg/g as can be seen in Figure B.4 (Appendix B.2).

One major concern with the above formulation is the fact that all the three surfactants are petroleum derived and so do not degrade easily. Food grade surfactants such as Lecithin FPI can replace any of the components in the above formulation. Considering the synergy between DOSS and Tween 80, and also between Tween 80 and Lecithin FPI, Span 80 which is a petroleum based food grade surfactant was replaced with a plant based biodegradable food grade surfactant, Lecithin FPI.

The dispersion effectiveness of HNT loaded with DOSS, Tween 80 and Lecithin FPI is reported in the ternary contour plot in Figure 4.14. It is obvious from Figure 4.14 that, HNT loaded with 100 wt.% DOSS, 100 wt.% Tween 80 and 100 wt.% Lecithin FPI recorded a relatively lower dispersion effectiveness than the binary mixtures of DOSS-Tween 80 and Tween 80-Lecithin FPI. The highest dispersion effectiveness was attained when a third component was added. 100 vol.% dispersion effectiveness was recorded with HNT-40 wt.% DOSS-20 wt.% Lecithin FPI-40 wt.% Tween 80 and HNT-20 wt.% DOSS-60 wt.% Lecithin FPI-20 wt.% Tween 80. The highest dispersion effectiveness was observed with 20-40 wt.% DOSS and 60-80 wt.% food grade surfactants (Tween 80 and Lecithin FPI). That is the wt.% of the most toxic component (DOSS) was reduced while the fraction of the food grade surfactant was increased. It should be noted that, Lecithin FPI is less toxic, biodegradable and also speed up biodegradation of the dispersed oil since it contains phosphorus. The 95 -100 vol.% dispersion effectiveness region occupied almost half of the triangle depicting the effectiveness of HNT loaded with DOSS-Tween 80-Lecithin FPI mixtures in dispersing crude oil.

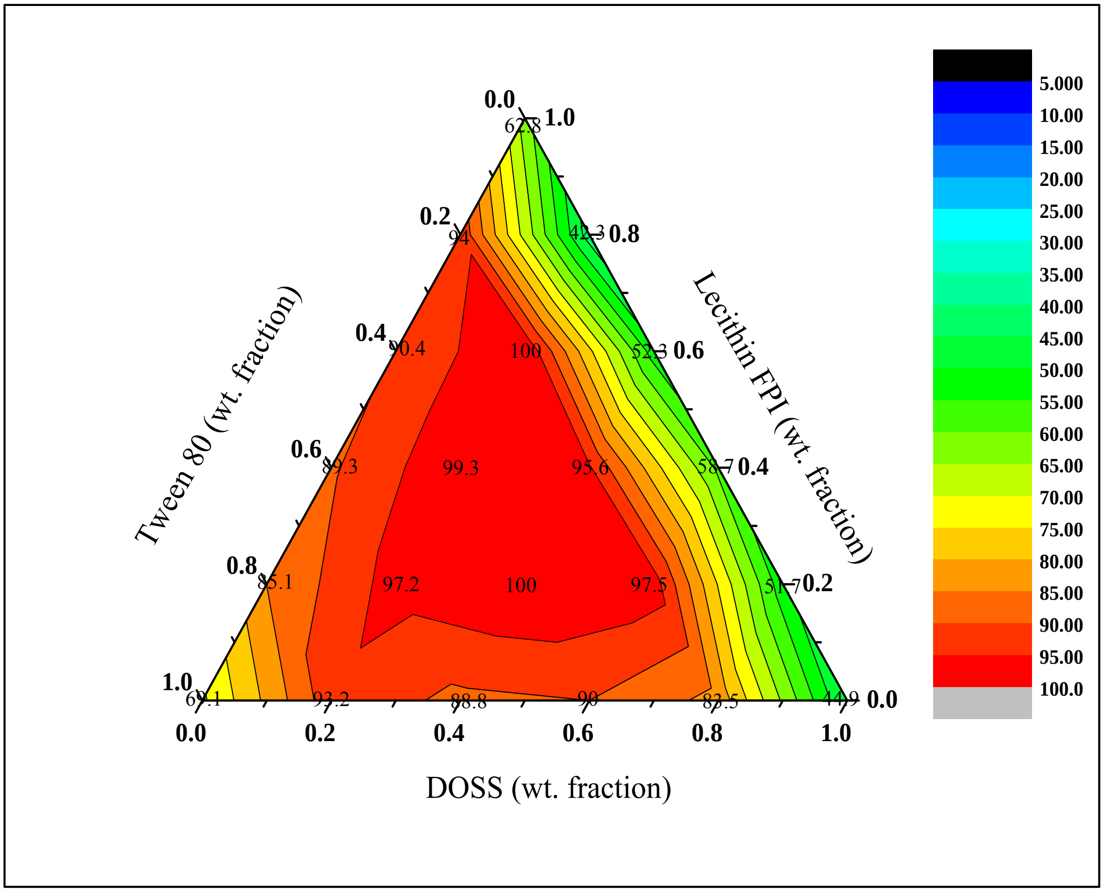


Figure 4.14 Ternary contour plot for HNT loaded with DOSS, Tween 80 and Lecithin FPI (SOR=25 mg/g)

The higher dispersion effectiveness attained with the HNT-DOSS-Tween 80-Lecithin FPI can be related to three factors. Firstly, as already stated earlier, a synergy exist between DOSS-Tween 80 and Tween 80-Lecithin FPI in forming o/w emulsions. This synergy can be seen in Figure 4.14, as dispersion effectiveness of HNT-DOSS-Tween 80 and HNT-Tween 80-Lecithin FPI were higher than HNT-100 wt.% DOSS, HNT-100 wt.% Tween 80 and HNT-100 wt.% Lecithin FPI. The electrostatic interaction between the anionic head groups of DOSS and Lecithin FPI were moderated by the nonionic Tween 80 resulting in the formation of a densely packed arrangement of surfactants at the oil droplet-water interface. The easy desorption of DOSS from the interface into the aqueous phase is also compensated for by the low tendency of Tween 80 and Lecithin FPI to desorb from the interface. Secondly, anionic surfactant stabilizes emulsion through the formation of surface charges at the oil droplet-water interface while Tween 80, which is nonionic stabilizes emulsion through steric effect. The combination of these two stabilization mechanisms is expected to impact positively on the emulsion stability. Thirdly, the inhibition of droplet break up by Span 80 was eliminated by replacing Span 80 with Lecithin FPI. This resulted in the formation of smaller emulsion droplet which were more stable and hence the high dispersion effectiveness observed. Very high dispersion effectiveness values were recorded by the HNT-DOSS-Lecithin FPI-Tween 80 formulation at lower SOR of 12.5 mg/g as can be seen in Figure B.5 (Appendix B.2).

Preliminary results from toxicological studies conducted in our lab with Artemia Salina showed that DOSS is more toxic than Lecithin FPI, Span 80 and Tween 80. Studies conducted with other organisms have shown that, DOSS is less non-toxic compared to Tween 80 and Span 80.[33] In view of this, DOSS in the HNT-DOSS-Tween 80-Lecithin FPI formulation was replaced with Span 80 which is a food grade surfactant. The dispersion effectiveness of HNT loaded with Tween 80, Lecithin FPI and Span 80 is shown in Figure 4.15. The ternary system of Tween 80, Span 80 and Lecithin FPI resulted in a much higher dispersion effectiveness than binary systems of Span 80-Tween 80 and Span 80-Lecithin FPI, and the single component systems of Span 80, Tween 80 and Lecithin FPI

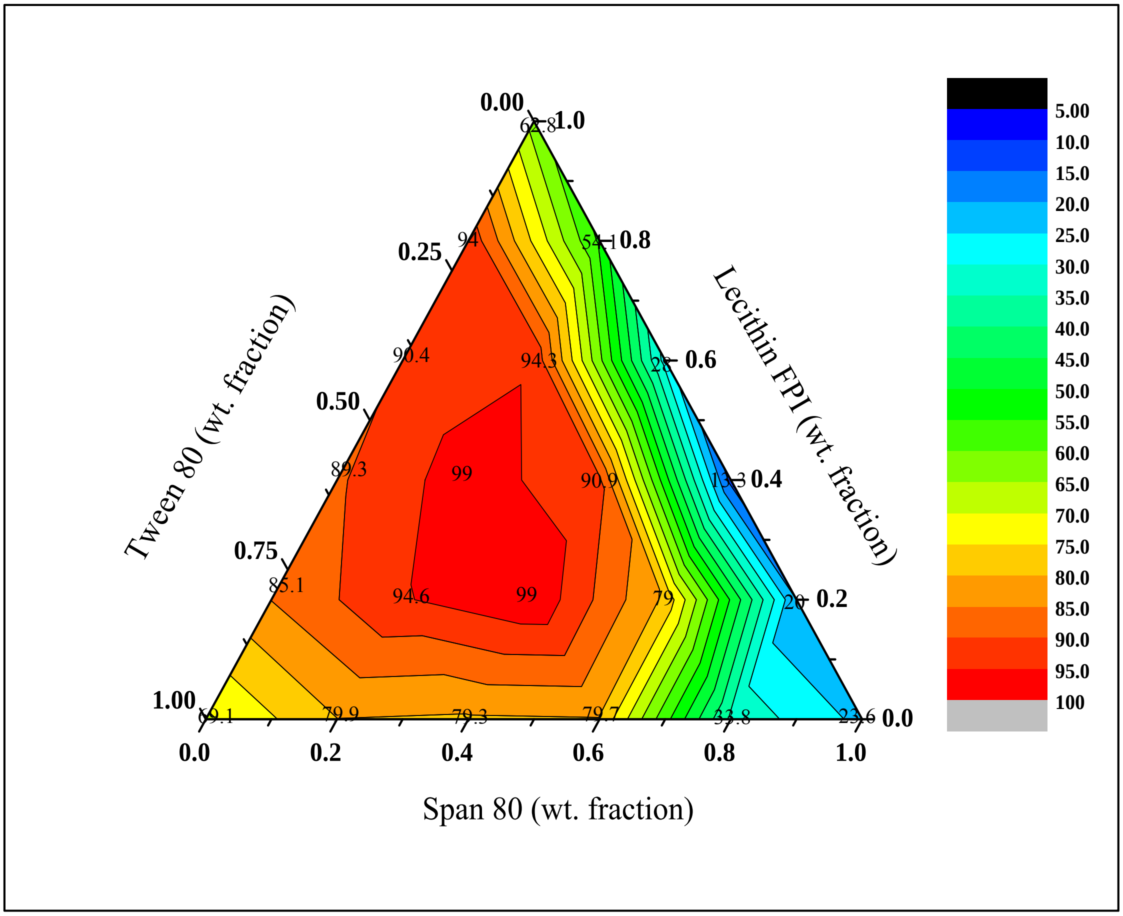


Figure 4.15 Ternary contour plot for HNT loaded with Span 80, Tween 80 and Lecithin FPI (SOR=25 mg/g)

The region occupied by the 95-100 vol.% dispersion effectiveness was larger than HNT-DOSS-Tween80-Span 80 formulation but smaller than HNT-Tween 80-Lecithin FPI-DOSS formulation. The highest dispersion effectiveness value of 99 vol.% was observed at HNT-40 wt.% Span 80-20 wt.% Lecithin FPI-40 wt.% Tween 80 and HNT-20 wt.% Span 80-40 wt.% Lecithin FPI-40 wt.% Tween 80. The Lecithin FPI in this formulation therefore acted as DOSS in HNT-DOSS-Span 80-Tween 80 formulation. The interaction between the head groups of Span 80 and Lecithin FPI was therefore moderated by Tween 80 and hence the observed dispersion effectiveness. The relatively lower dispersion effectiveness of the HNT-Span80-Tween 80-Lecithin FPI compared to that of HNT-DOSS-Lecithin FPI-Tween 80 formulation is due to the inhibition effect to droplet break up by Span 80.[19b] The dispersion effectiveness of HNT-Span 80-Tween 80-Lecithin FPI at a lower SOR of 12.5 mg/g were relatively smaller than that of HNT-DOSS-Lecithin FPI-Tween 80 and HNT-DOSS-Span 80-Tween 80 formulations as can be seen in Figure B.6 (Appendix B.2). The HNT-Tween 80-Span 80-Lecithin FPI formulation is therefore very effective in dispersing crude oil at higher SORs. This is in agreement with our previous findings which suggested that, Lecithin FPI is very effective in dispersing crude oil at higher concentrations.[23] This effect became pronounced in this formulation due to the ineffectiveness of Span 80 in dispersing crude oil. However, HNT-Tween 80-Span 80-Lecithin FPI formulation is expected to be more environmentally friendly since it is comprised of FDA approved food grade surfactants with Lecithin FPI being biodegradable.

The various HNT-Surfactant(s) mixtures that resulted in the highest dispersion effectiveness are summarized in Table 4.1. It can be deduced from Table 4.1 that, higher dispersion effectiveness can be attained by varying the wt.% of the anionic and nonionic surfactants in the dispersant formulation. This dispersant formulations are expected to be environmentally benign since hydrocarbon solvent is replaced with naturally occurring HNTs, the solubility of the surfactant is reduced through their controlled release from HNTs, Lecithin FPI is biodegradable and food grade surfactants are used with the exception of DOSS.

Table 4.1The various combinations of surfactants that resulted in the highest dispersion effectiveness for each ternary formulation.

Dispersant Formulation	**Total wt.% of anionic surfactant**	**Total wt.% of nonionic surfactant**	**Dispersion Effectiveness (vol.%)**
HNT-40wt.% DOSS-20 wt.% Lecithin FPI-40 wt.% Tween 80	60	40	100
HNT-20wt.% DOSS-60 wt.% Lecithin FPI-20 wt.% Tween 80	80	20	
HNT-40 wt.% DOSS-20 wt.% Span 80-40 wt.% Tween 80	40	60	96.2
HNT-40 wt.% DOSS-20 wt.% Span 80-40 wt.% Tween 80	20	80	
HNT-40 wt.% Span 80-20 wt.% Lecithin FPI-40 wt.% Tween 80	20	80	99
HNT-20 wt.% Span 80-40 wt.% Lecithin FPI-40 wt.% Tween 80	40	60	

4.4 Conclusions

The results from the study show the potential of HNT loaded with various combinations of anionic and nonionic surfactants in replacing traditional liquid oil spill dispersant formulations. It was successfully delineated in this chapter that the solubility of dispersants can be reduced through the controlled release of the dispersants from HNT. The interaction of anionic DOSS with the positively charged lumen slowed down the release kinetics of DOSS from HNT. The dispersion effectiveness of HNT loaded with the surfactant(s) were significantly higher than raw HNT and this was attributed to the release of the surfactants from HNT. Synergy existed between DOSS-Tween 80 and Tween 80-Lecithin FPI in forming o/w emulsions. Almost 100 vol. % dispersion effectiveness were attained with HNT-DOSS-Tween 80-Span 80, HNT-DOSS-Lecithin FPI-Tween 80 and HNT-Span 80-Lecithin FPI-Tween 80 formulations. The highest dispersion effectiveness values obtained from HNT-DOSS-Tween 80-Span 80 formulation was attributed to synergy that exist between DOSS and Tween 80, the moderation of the electrostatic repulsion between the DOSS and Span 80 by Tween 80 and the compensation of the faster desorption rate of DOSS from the oil droplet-water interface by slower tendency of Span 80 and Tween 80 to desorb. For the HNT-Tween 80-DOSS-Lecithin FPI, steric stabilization by the oxyethylene "hairs" of Tween 80 coupled with the ionic stabilization of DOSS and Lecithin FPI were responsible for the higher dispersion effectiveness values observed. The region in the ternary diagram representing the 95-100 vol.% dispersion effectiveness of HNT-Span 80-Tween 80-Lecithin FPI which is made up of only food grade surfactants was slightly smaller than that of HNT-DOSS-Lecithin FPI-Tween 80 formulation. This was due to the inhibition to droplet break up by Span 80.

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Chapter 5

Conclusions

Environmentally benign dispersant formulations with high dispersion effectiveness were developed throughout this work. Though oil spills may occur either on land or at sea, the objective of this work is to formulate dispersants that can be used to address the problems associated with large scale oil spill at sea. In the first part of the dissertation, DOSS-paraffin wax composite dispersant particles were synthesized by spray freezing method and their dispersion effectiveness examined with the baffled flask test. Particulate dispersant formulations is expected to reduce surfactant wastage and eliminate the toxic hydrocarbon based solvents used in traditional liquid dispersant formulations. The dispersion effectiveness of the DOSS-paraffin wax dispersant composite particles was dependent on the solubility of the matrix material (paraffin wax) in the crude oil and the particle size of the dispersant particles. The dispersion effectiveness varied with the different crude oil samples. The dispersant composite particles were more effectiveness in dispersing light crude (LC) oils than heavy crude (TC) oils. Energy influenced the dispersion effectiveness to a greater extent, with higher energy inputs resulting in a significantly higher dispersion effectiveness. The trend observed for the variation in dispersion effectiveness with energy was the same for both particulate and solubilized dispersant. The standardized rpm for the baffled flask test can also be used when analyzing dispersion effectiveness of particulate dispersants. The dispersion effectiveness remained almost constant at sea water salinities of 2.8 wt.% and 3.5 wt.%. The results from the study showed that the formulated dispersant composite particles were effective in dispersing crude oil. The surfactant loading mechanism adopted in the preparation of the dispersant composite particles allowed for a maximum surfactant loading of 5.12 wt.% and this affected the dispersion effectiveness. To increase the surfactant loading and also improve dispersion effectiveness, a core-shell dispersant particle formulation is proposed in chapter 6.

Dispersant for crude oil spill remediation was formulated from soybean lecithin, which is a food grade surfactant in chapter 3. Lecithin is less toxic, biodegradable and contains nutrients for bacteria. The phospholipids present in lecithin are responsible for their surface active property hence the phospholipids in lecithin were fractionated and their effectiveness in dispersing crude oil examined with the baffled flask test. The results from the study show the potential of dispersant formulated with lecithin to replace the traditional chemical dispersant formulations. Different dispersion effectiveness values were obtained from the different phospholipids fractionated from lecithin. The dispersion effectiveness of freshly fractionated phosphatidylcholine (PC) was higher than that of crude soybean lecithin (CL) and freshly fractionated phosphatidylinositol (PI). However, after structural modification of PI (FPI), its dispersion effectiveness improved remarkably and was higher than that of PC. This was attributed to the introduction of additional hydroxyl groups into the PI structure which increased its hydrophilicity and resulted in improved dispersion effectiveness. The dispersion effectiveness of the FPI was lower than that of solubilized DOSS and Tween 80 in propylene glycol at lower DORs whiles at higher DORs, the dispersion effectiveness of FPI was higher than that of solubilized DOSS and Tween 80 in propylene glycol. Dispersants formulated by varying the ratio of FPI and PC resulted in a dispersion effectiveness that was almost the same as that of PC. The dispersion effectiveness of FPI and PC in both light crude (LC) and Texas crude (TC) oil samples were similar despite differences in the composition of these oil samples. The dispersion effectiveness was dependent on the salinity of sea water. The dispersion effectiveness of soybean lecithin was therefore enhanced by fractionating it into its various phospholipids and by structural modification of the fractionated phospholipids. FPI and PC were effective in dispersing the crude oil at higher concentrations. Addition of excess nutrient (phosphorus) to the ocean may result in the formation of algae bloom. Assuming the fatty acid chains in PI and PC are linoleic and palmitic acids, the weight percent of phosphorus in PI and PC can be estimated to be 3.2 and 3.7, respectively. Since the dispersed oil will diffuse both horizontally and vertically by the action of the wave current, the concentration of phosphorus at the spilled site is expected to decrease with time and hence the tendency for algae bloom to occur may be reduced.

Naturally occurring halloysite nanotubes (HNTs) were studied for their potential application in oil spill remediation. HNT is biocompatible, naturally occurring, readily available and environmentally friendly. Various surfactants namely DOSS, Tween 80, Span 80 and modified lecithin phosphatidylinositol (Lecithin FPI) were loaded onto HNT by vacuum suction. The dispersion effectiveness of HNT loaded with the surfactant(s) were examined with the baffled flask test. The results from the study show the potential of HNT loaded with various combinations of anionic and nonionic surfactants to replace traditional liquid oil spill dispersant formulations. It was successfully delineated that, the solubility of dispersant can be reduced through the controlled release of the dispersants from HNT. The interaction of anionic DOSS with the positively charged lumen slowed down the release kinetics of DOSS from HNT. The dispersion effectiveness of HNTs loaded with the surfactant(s) were significantly higher than raw HNT and this was attributed to the release of the surfactas from HNT. Synergy existed between DOSS-Tween 80 and Tween 80-Lecithin FPI formulations in forming o/w emulsions. Almost 100 vol. % dispersion effectiveness were attained with HNT-DOSS-Tween 80-Span 80, HNT-DOSS-Lecithin FPI-Tween 80 and HNT-Span 80-Lecithin FPI-Tween 80 formulations. The high dispersion effectiveness values obtained from HNT-DOSS-Tween 80-Span 80 formulation was attributed to synergy that exist between DOSS and Tween 80 in forming o/w emulsions, the moderation of the electrostatic repulsion between DOSS and Span 80 by Tween 80 and the compensation of the faster desorption rate of DOSS from the oil droplet-water interface by slower tendency of Span 80 and Tween 80 to desorb. For the HNT-Tween 80-DOSS-Lecithin FPI formulation, steric stabilization by the oxyethylene “hairs” of Tween 80 coupled with the ionic stabilization of DOSS and Lecithin FPI was responsible for the high dispersion effectiveness values observed. The area in the ternary diagram representing the 95-100 vol.% dispersion effectiveness of HNT-Span 80-Tween 80-Lecithin FPI formulation which was made up of only food grade surfactants was slightly smaller than that of HNT-DOSS-Lecithin FPI-Tween 80 formulation. This was due to the inhibition to droplet break up by Span 80.

The dissertation has demonstrated the formulation of alternative dispersants for large scale marine oil spills. High dispersion effectiveness and low toxicity dispersant were formulated throughout this work. For a product to be listed on the NCP product schedule, it should be able to disperse at least 50±5 vol.% of the oil in a laboratory test. The maximum dispersion effectiveness for the formulated composite particles, Lecithin and HNT dispersants were 62.6, 74.7 and 100 vol.%, respectively. The high dispersion effectiveness values attained with the alternative dispersant formulations will reduce the overall cost of the oil spill remediation process. That is since a 100 vol.% dispersion effectiveness was attained with SOR of 0.025 (25 mg/g) for the HNT formulated dispersant, it implies that all the oil will be removed from the surface of the ocean. These high dispersion effectiveness formulated dispersants would reduce operational cost since less amount of the dispersant would be required. The remediation cost would further be reduced since the dispersant application rate will decrease. Environmentally benign materials were used in the newly formulated dispersants. The composite particles, Lecithin and HNT formulated dispersants are therefore expected to be less toxic and ecologically acceptable. The dispersants formulated in this work will address the environmental problems associated with the use of chemical dispersants as an oil spill response method.

Chapter 6

Future Directions

This dissertation has investigated several ways of formulating smart oil spill dispersants. There are a number of areas of future exploration stemming from this work and they are elaborated below.

6.1 Enhancing the Emulsification Properties of Lecithin through Chemical Treatment.

The hydrophilicity of surfactants influences their dispersion effectiveness. Hydrophobic surfactants support the formation of water-in-oil (w/o) emulsions while hydrophilic surfactants favors the formation of oil-in-water (o/w) emulsions. As already developed in chapter 3, the dispersion effectiveness of phosphatidylinositol (PI) can be enhanced by deoiling the PI to make it oxidatively unstable and storing it over a period of time. Chemical modification of lecithin could be an area of future exploration. Chemical treatment of lecithin by hydroxylation introduces hydroxyl groups into the lecithin structure. Hydroxylated lecithin is therefore expected to be more hydrophilic with improved emulsification properties. For the purpose of hydroxylation, lecithin can be reacted with hydrogen peroxide and lactic acid or hydrogen peroxide with sulfuric acid. Potassium permanganate solution can also be used. The chemical treatment of lecithin by hydroxylation is expected to save time and also, increase dispersion effectiveness.

6.2 Encapsulated Halloysite Nanotubes Embedded with Surfactants and Nutrients for Crude Oil Spill Application.

Indiscriminate application of dispersant to subsea and surface oil spills results in a significant amount of dispersant not coming into contact with the oil. The aqueous solubility and miscibility of oil spill dispersants and inevitable sea currents cause dispersant to be washed away and wasted. To compensate for inefficiency, large amounts of dispersants are used resulting in high costs and a large environmental load. To address these problems, DOSS-paraffin wax dispersant composite particles were synthesized in chapter 2. In chapter 4, the unique properties of naturally occurring halloysite nanotubes (HNTs) were explored in order to reduce the solubility and toxicity of dispersants. An area of future exploration could be the combination of the concepts developed in chapters 2 and 4 to formulate the next generation of dispersants with high dispersion effectiveness, low toxicity and enhanced biodegradation rate.

The next generation of dispersant formulation can be targeted directly to an oil spill, thereby reducing the environmental impact and consumption of the dispersant. The new generation dispersant formulation would involve the microencapsulation of solid surfactant(s), HNT and nutrients in a water-insoluble, oil-dissolvable shell for selective release of surfactant within an oil spill, as shown in Figure 6.1. The next generation of dispersant is applied using water as the media, this avoiding the use of solvent in contrast to the traditional Corexit formulations.

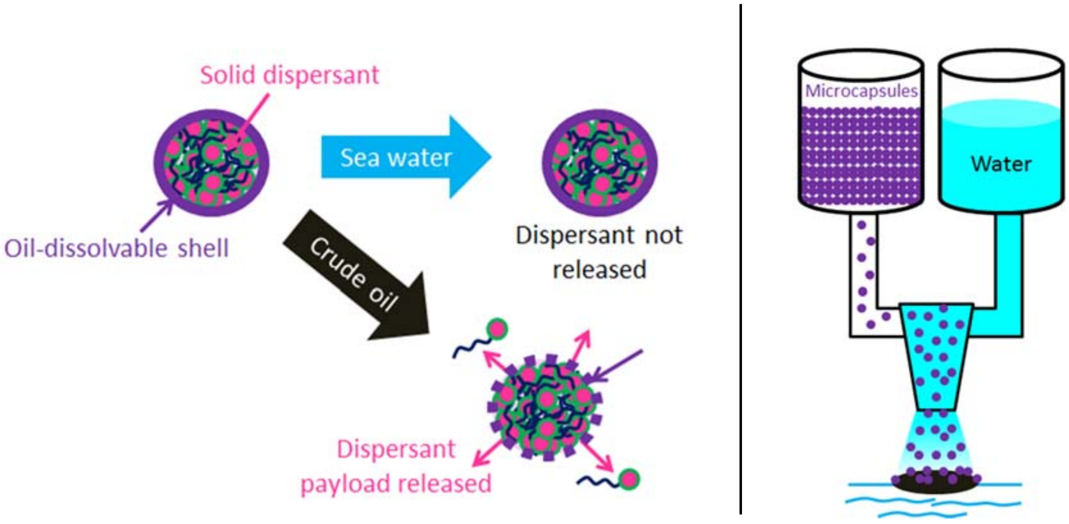

Figure 6.1 Next generation of dispersant: (A) mechanism of the dispersant release from smart microcapsules, and its (B) field application in oil spill.

The next generation design of the dispersion microcapsules include (Figure 6.2), (a) synthetic and natural surfactants, (b) natural halloysite nanotubes which “hardens” surfactants needed for microparticles making and provides an oil-dispersion synergy with surfactants in the final use, (c) a small dose of nutrient for oil-consuming bacteria which will enhance the degradation of dispersed oil, (d) a shell which is water-insoluble and crude-oil soluble (e.g., heavy petroleum wax), and (e) silica nanoparticle attached over the shell to allow for a good powder flowability of the solid microcapsules and a good wettability with water needed while spraying the aqueous suspension on the spill site.

Such a dispersant formulation will result in high dispersion effectiveness, low toxicity, reduced surfactant wastage and increased biodegradation rate.

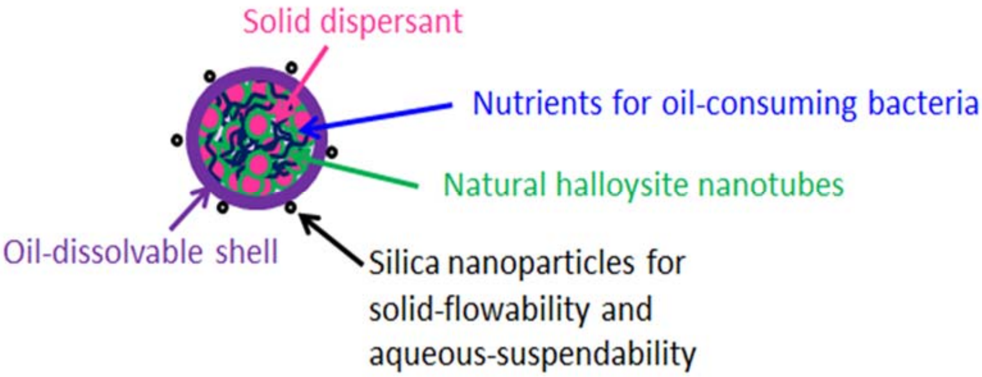

Figure 6.2 Next generation design of the dispersant microcapsules for utilization in oil spills.

6.3 Toxicological Studies of Different Dispersant Formulations.

One of the major concern of the current traditional liquid dispersant formulations is their toxicity. In view of this, it is would be necessary to analyze the toxicity of the various dispersant formulated in the chapters of this study to have a fair idea of how toxic they are to aquatic species though environmentally benign materials were used in their formulation. The Artemia salina (Artemiidae), the brine shrimp, is an invertebrate component of the fauna of saline aquatic and marine ecosystems. Artemia salina can be hatched within 24 hours and used for routine ecotoxicity testing. The availability of the eggs, its low cost, the ease of hatching them into larvae and the relative ease of maintaining a population under laboratory conditions, makes the brine shrimp a simple and effective test in animal bioassays and toxicological studies. Artemia salina has been used in a laboratory bioassay to estimate the mean lethal concentration (LC_{50}) of toxins and plant extracts.

The potential toxicity of chemical substances often is presented as their LC_{50}. LC_{50} is the concentration of a substance that is lethal to 50 % of the organisms in a toxicity test. LC_{50} can be determined for any exposure time, but the most common exposure period is 96 hours though 24, 48, and 72 hours can also be used. The longer the exposure time, the higher will be the lethality and hence the LC_{50} would be lower.

The brine shrimp can be exposed to different concentrations of the formulated dispersants for a specific exposure time. The percentage lethality can then be determined by comparing the mean surviving larvae of the test and control tubes. The LC_{50} value can be determined from the best-fit line plotted concentration verses percentage lethality.

Appendices

Appendix A

Comparison of the Effectiveness of Solid and Solubilized Dioctyl Sodium Sulfosuccinate (DOSS) on Oil Dispersion Using the Baffled Flask Test, for Crude Oil Spill Applications

A.1 Limitations of Oil Spill Response Options

The most common oil spill response options and their limitations are listed in Table A.1.

Table A.1 Limitations of response options (adopted from reference[4] in chapter 2)

Response Options	**Limitations**
Mechanical containment and recovery	o Limited to low current and waves o Not efficient when the slick is less than 1 mm thick o Requires storage for recovered oil and water
In situ burning	o Igniting of weathered oil is a problem o Transfer of pollutants into the environment due to incomplete combustion of the oil o The fire extinguishes at limiting thickness due to heat loss, and the remaining oil cannot be burned
Natural dispersion	o Natural processes are very slow o Natural dispersion of weathered oil can be difficult
Chemical dispersants	o Limited time window of opportunity o Viscosity and emulsification can reduce effectiveness

A.2 GC-MS Analysis of Light and Heavy Crude Oils

The major compounds in the crude oil samples detected by GM-MS analysis are shown in Table A.2.

Table A.2 Major compounds present in the Heavy and Light Crude oils from GC-MS analyses

Major Compounds	
Heavy Crude	**Light Crude**
Azulene, 4,6,8-trimethyl	Pentadecane
Cyclotetradecane, 1,7,11-trimethyl-4-(1-methylethyl)	Hexadecane
1,2,-Benzisothiole, 3-(hexahydro-1H-azepin-1-yl)-1,1-dioxide	Decane,3,8-dimethyl
	Naphthalene, 2,3,6-trimethyl
Dibenzothiophene, 4-methyl	Octadecane
Naphto[2,3-b] thiophene, 4,9-dimethyl	Nonadecane
2,8-Dimethyldibenzo (b,d) thiophene	Eicosane
Phenol,2-[5-2(-furanyl)-3-1H-Pyrozoly**]**	Heneicosane
	Docosane
	Tricosane
	Hexacosane
	Heptacossane

A.3 Chemical Composition of Instant Ocean Salt

The chemical composition of the Instant Ocean salt used to form the synthetic sea water is shown in Table A.3

Table A.3 Chemical composition of Instant Ocean sea salt at 35 ppt salinity (adopted from reference [15] in chapter 2)

Ionic Constituents	g/kg of sea water
Chloride (Cl^-)	19.290
Sodium (Na^+)	10.780
Sulfate (SO_4^-)	2.660
Magnesium (Mg^{2+})	1.320
Potassium (K+)	0.420
Calcium (Ca^{2+})	0.4
Bicarbonate (HCO_3^-)	0.200
Bromide (Br-)	0.056
Strontium (Sr++)	0.0088
Fluoride (F-)	0.001
Boric Acid ($B(OH)_3$)	0

A.4 Histograms for the Particle Size Distributions of the Dispersant Composite Particles

The images of the DOSS-paraffin wax dispersant composite particles were taken with SEM and 210 of the particles analyzed for their mean diameter. The histograms obtained from the image analysis are shown in Figures A.1, A.2 and A.3.

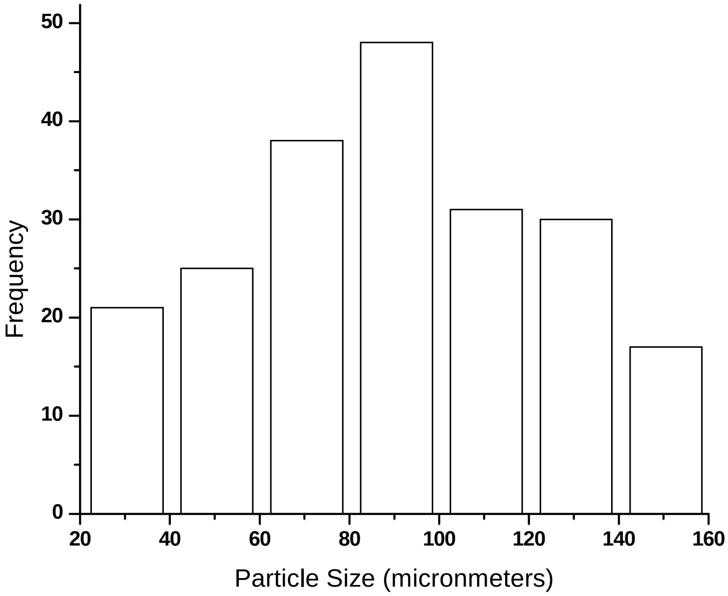

Figure A.1 Histogram of the particle size distribution for particle P1.61D

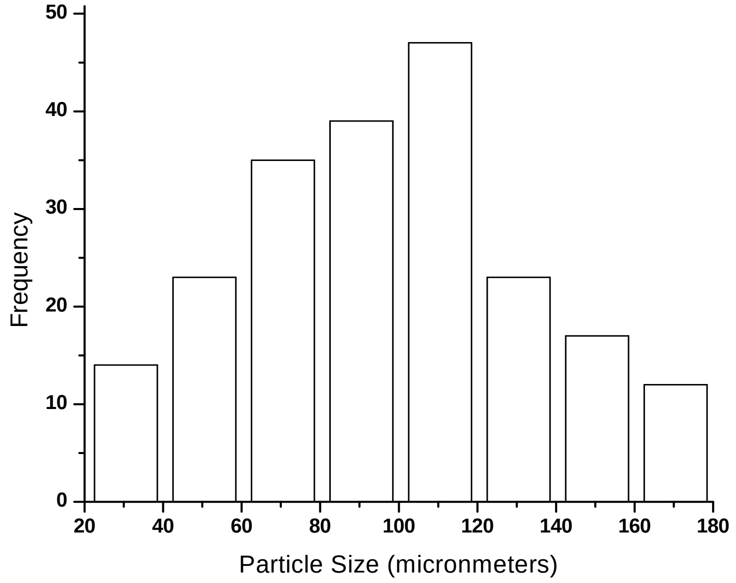

Figure A.2 Histogram of the particle size distribution for particle P3.73D

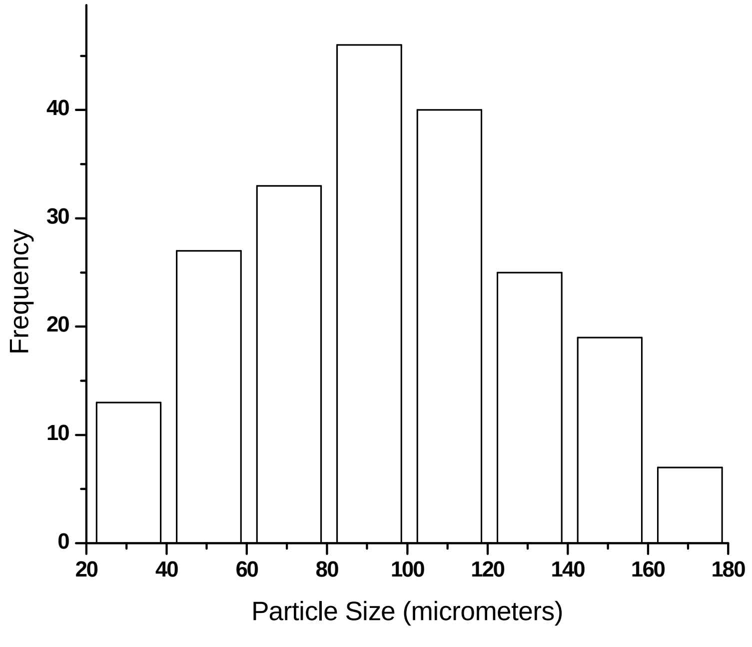

Figure A.3 Histogram of the particle size distribution for particle P5.12D

A.5 Properties of Solvents

The properties of the solvents used in formulating the solubilized DOSS dispersants are shown in Table A.4

Table A.4 Viscosity of the solvents and their solubility in water

Solvent	**Viscosity (cp)**	**Solubility in water**	**Density (g/cm^3)**
Dichloromethane	0.413	13 g/l	1.33
Water	1		1
Propylene glycol	40.4	miscible	1.04
Cyclohexanol (CH)	41.5	36 g/l	0.962

Appendix B

Halloysite Clay Nanotubes Loaded with Surfactant(s) as a Dispersant for Crude Oil Spill Remediation

B.1 Dispersion Effectiveness of Binary Surfactant Mixtures Loaded onto Halloysite Nanotubes (HNT)

The dispersion effectiveness of the various binary surfactant mixtures loaded onto HNT are shown in Figures B.1, B.2 and B.3.

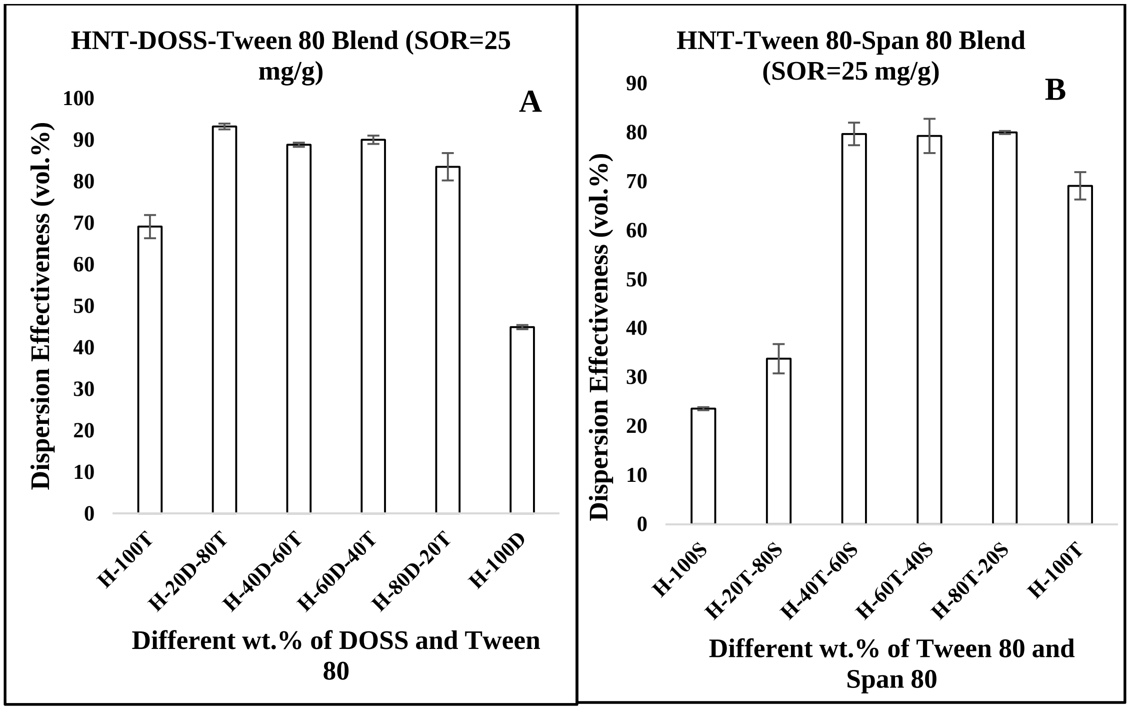

Figure B.1 Dispersion effectiveness of: (A) HNT-DOSS-Tween 80 at different wt.% of DOSS and Tween 80 (B) HNT-Tween 80-Span 80 at different wt.% of Tween 80 and Span 80. [H=HNT, T=Tween 80, S=Span 80, D=DOSS]

Minimal dispersion effectiveness of HNT-100 wt.% DOSS and HNT-100 wt.% Tween 80 compared to different blends of HNT-DOSS-Tween 80 was observed in Figure B.1A at Surfactant-to-oil ratio (SOR) of 25 mg/g. A similar trend was observed in Figure B.1B except at 20, 40 and 60 wt.% Span 80 for HNT-Tween 80-Span 80 formulation.

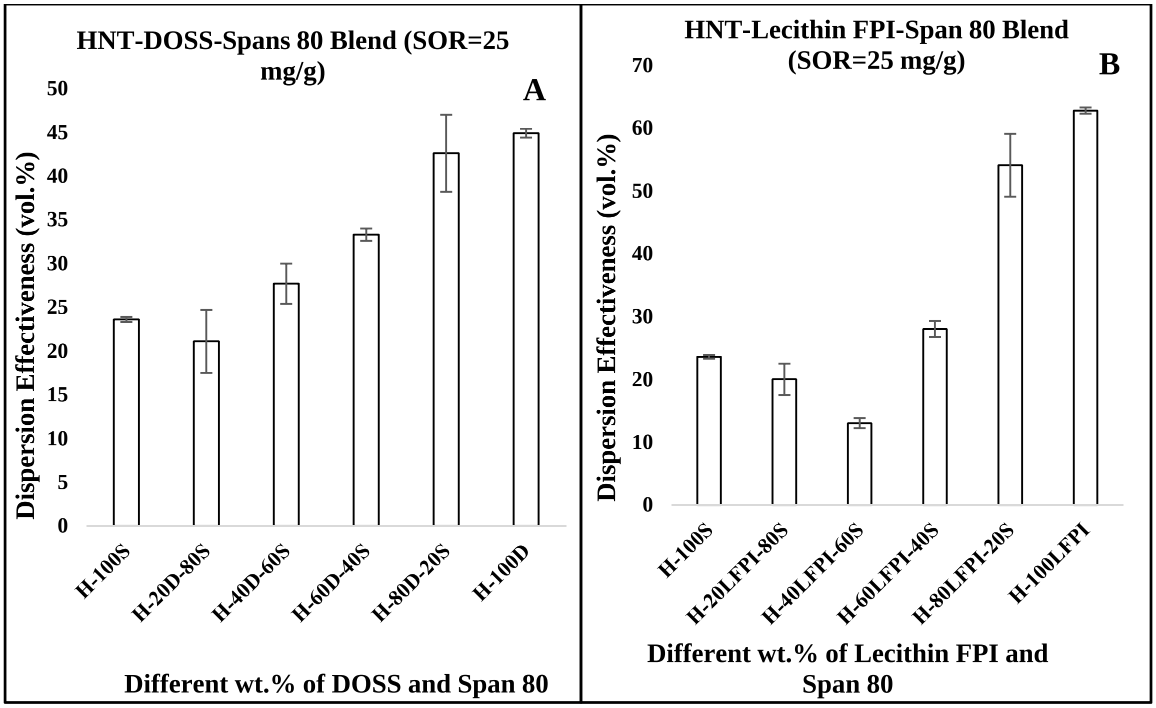

Figure B.2 Dispersion effectiveness of: (A) HNT-DOSS-Span 80 at different wt.% of DOSS and Span 80 (B) HNT-Lecithin FPI-Span 80 at different wt.% of Lecithin FPI and Span 80. [H=HNT, D=DOSS, S=Span 80, LFPI=Lecithin FPI]

The dispersion effectiveness of HNT loaded with different wt.% of DOSS and Span 80 were lower than that of HNT loaded with 100 wt.% of DOSS as can be seen in Figure B.2A. In Figure B.2B, the dispersion effectiveness of HNT loaded with different wt.% of Lecithin FPI and Span 80 were lower than that of HNT loaded with 100 wt.% Lecithin FPI.

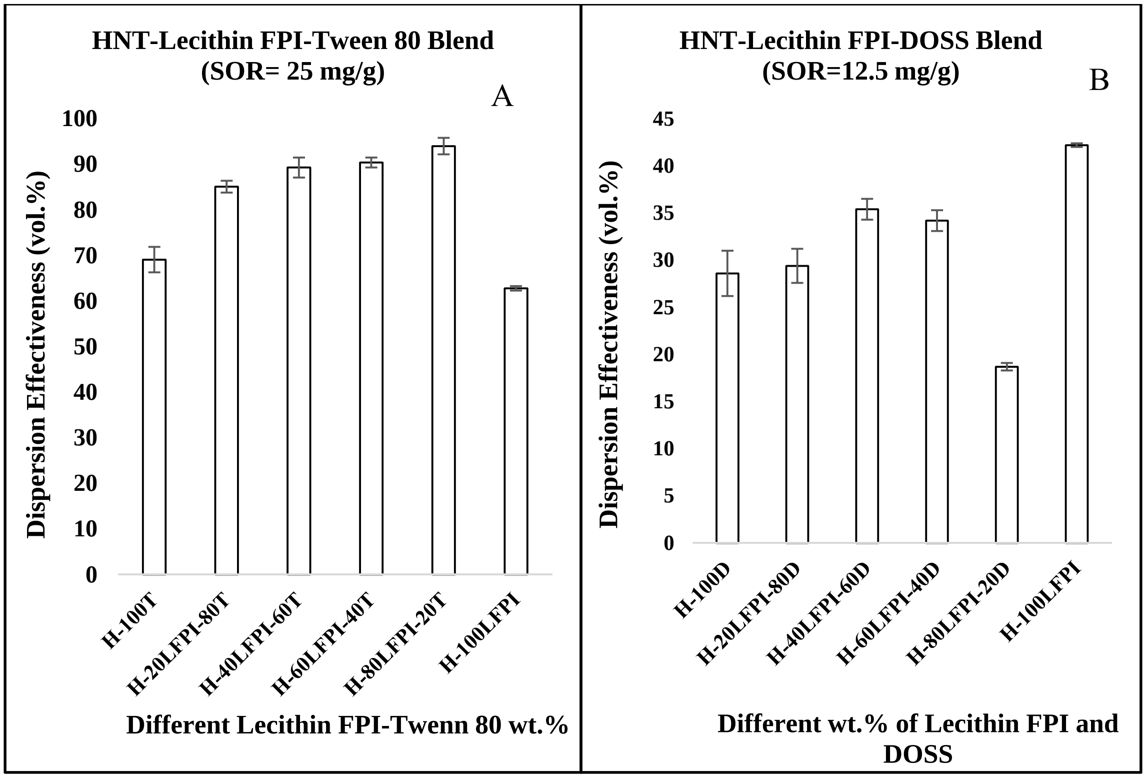

Figure B.3 Dispersion effectiveness of: (A) HNT-Lecithin FPI-Tween 80 at different wt.% of Lecithin FPI and Tween 80 (B) HNT-Lecithin FPI-DOSS at different wt.% of Lecithin FPI and DOSS. [H=HNT, LFPI=Lecithin FPI, T=Tween 80, D=DOSS]

The synergy of Lecithin FPI-Tween 80 blends in forming emulsions was observed in Figure B.3A. The dispersion effectiveness of HNT loaded with different wt.% of Lecithin FPI and Tween 80 was higher than HNT loaded with 100 wt.% Tween 80 and HNT loaded with 100 wt.% Lecithin FPI. No synergy exist between Lecithin FPI and DOSS in forming emulsions as can be seen in Figure B.3B. The dispersion effectiveness of HNT loaded with various mixtures of DOSS and Lecithin FPI were lower than that of HNT loaded with 100 wt.% Lecithin FPI.

B.2 Dispersion Effectiveness of Ternary Surfactant Mixtures Loaded onto Halloysite Nanotubes (HNT)

The dispersion effectiveness of the ternary mixtures of surfactants loaded onto HNT at SOR of 12.5 mg/g are shown in Figures B.4, B5 and B.6.

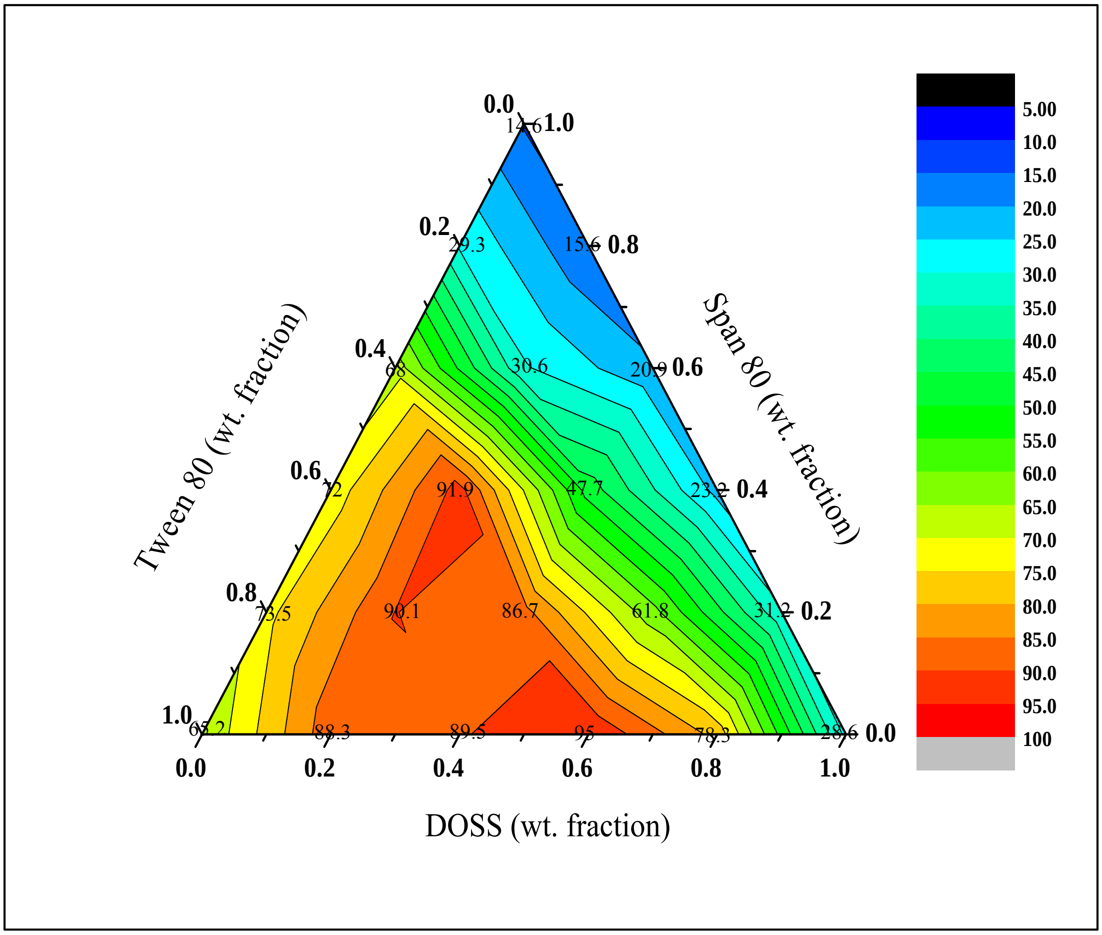

Figure B.4 Ternary contour plot for HNT loaded with DOSS, Tween 80 and Span 80 (SOR=12.5 mg/g)

The dispersion effectiveness of the ternary mixtures of DOSS, Tween 80 and Span 80 loaded onto HNT was higher than that of HNT loaded with 100 wt.% DOSS, Span 80 and Tween 80. The maximum dispersion effectiveness attained was between 90-95 vol.% at a lower SOR of 12.5 mg/g.

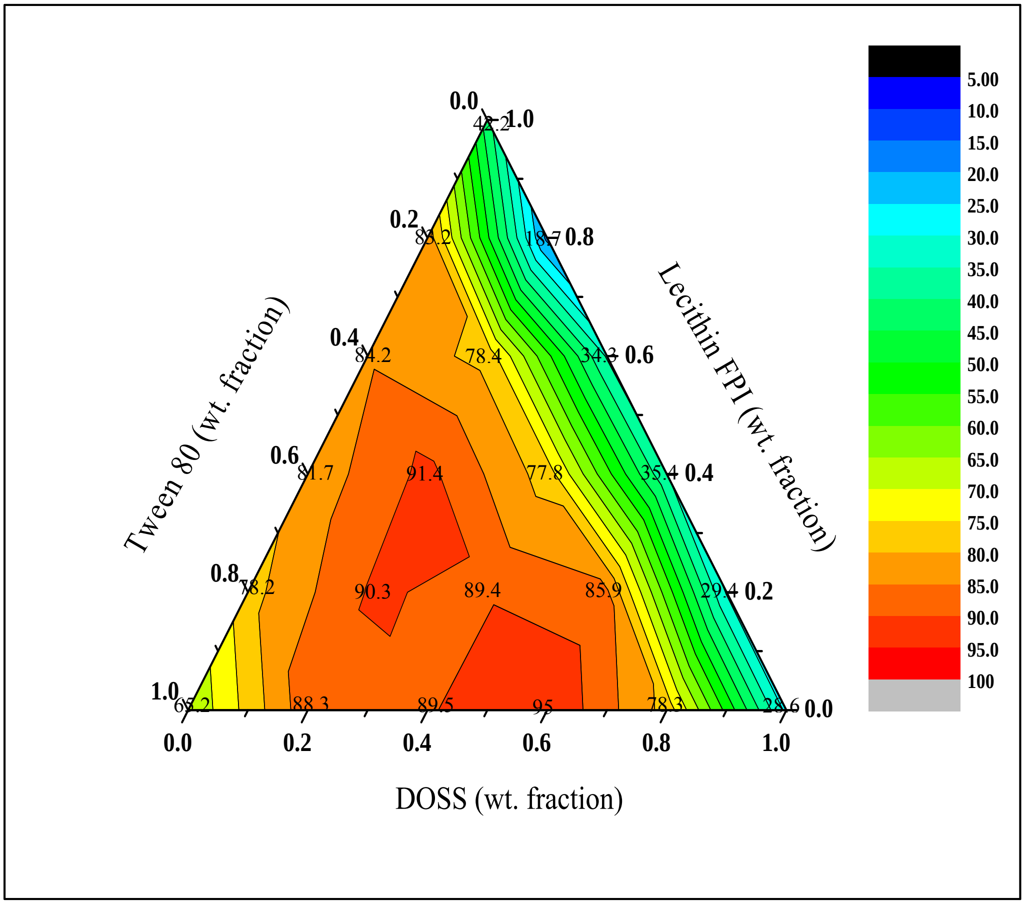

Figure B.5: Ternary contour plot for HNT loaded with DOSS, Tween 80 and Lecithin FPI (SOR=12.5 mg/g)

The synergy of DOSS-Tween 80 and Tween 80-Lecithin FPI mixtures in forming emulsion is visible in Figure B.5. The maximum dispersion effectiveness observed was between 90-95 vol.%. The region occupied by the 90-95 vol.% dispersion effectiveness of HNT-Tween 80-DOSS-Lecithin FPI formulation was bigger than that of DOSS-Tween 80-Span 80 formulation.

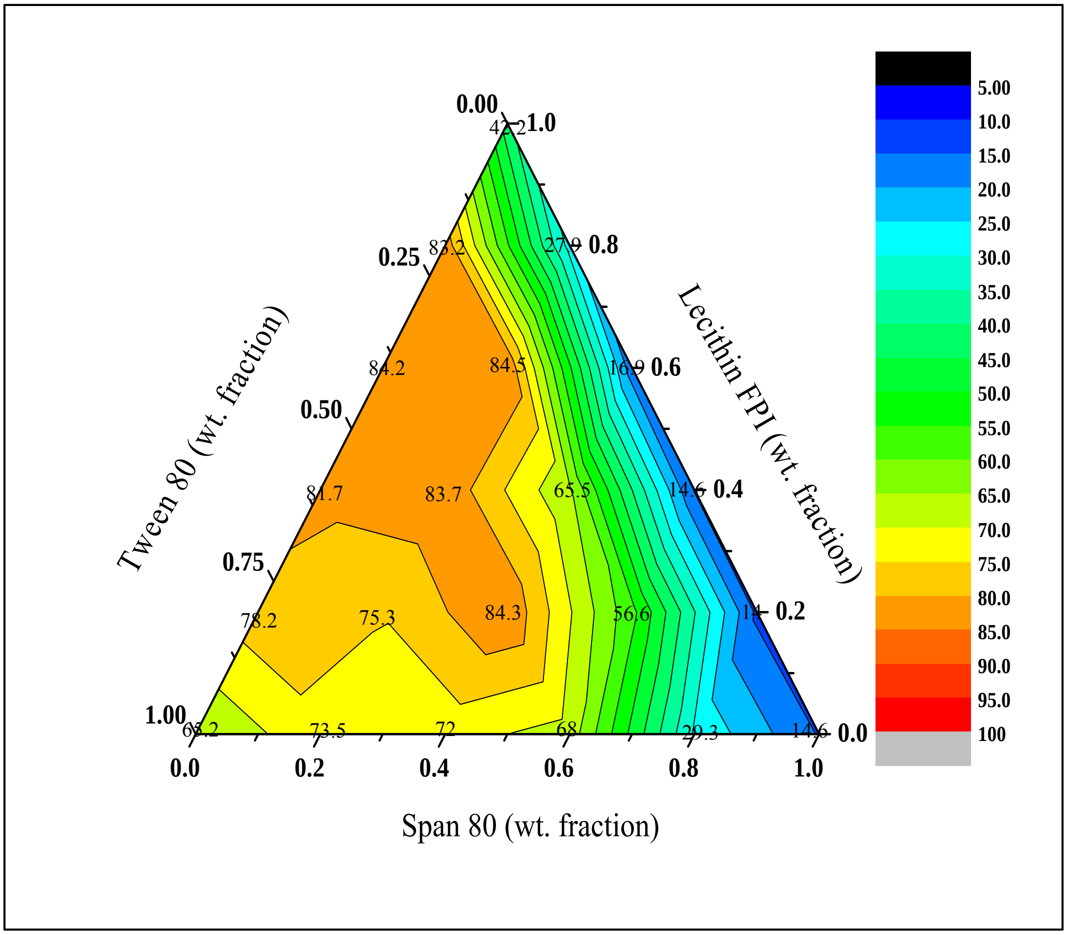

Figure B.6 Ternary contour plot for HNT loaded with Span 80, Tween 80 and Lecithin FPI (SOR=12.5 mg/g)

The synergy of Tween 80 and Lecithin FPI in forming emulsions is seen in Figure B.6. The dispersion effectiveness of the ternary mixtures of Tween 80, Lecithin FPI and Span 80 loaded onto HNT was higher than that of HNT loaded with 100 wt.% Tween 80, 100 wt.% Span 80 and 100 wt,% Lecithin FPI. The maximum dispersion effectiveness for this formulation was between 80-85 wt.%. HNT-Tween 80-Span 80-Lecithin FPI formulation therefore works better at higher SORs.