ABSTRACT

Title of Thesis: **THE IMPACT OF THE SOLVENT BASE FOR A DISPERSANT ON THE EFFICIENCY OF CRUDE OIL DISPERSION**

Jay Clifton Fernandes III, Master of Science, 2018

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Dispersants used in the mitigation of oil spills are mixtures of amphiphilic molecules (surfactants) dissolved in a solvent. The recent large-scale use of dispersants has raised environmental concerns regarding the safety of these materials. In response to these concerns, our lab has developed a class of eco-friendly dispersants based on mixtures of the food-grade surfactants soy lecithin (L) and Tween 80 (T) in a solvent. We have shown that these "LT dispersants" are very efficient at dispersing crude oil into seawater. The solvent for dispersants is usually selected based on factors like toxicity, volatility or viscosity of the overall mixture. But with regard to dispersion efficiency of crude oil, the solvent is considered to play a negligible role. In this thesis, we re-examine the role of solvent and show that it can actually have a significant impact on the dispersion efficiency. That is, the dispersion efficiency can be altered from good to poor simply by varying the solvent while keeping the same amounts of surfactants. We devise a systematic procedure for selecting the optimal solvent by utilizing Hansen Solubility Parameters (HSPs). Our analysis enables us to identify solvents that combine high dispersion efficiency, good solubility of the LT surfactants, a low toxicity profile, and a high flash point.

THE IMPACT OF THE SOLVENT BASE OF A DISPERSANT ON THE EFFICIENCY OF CRUDE OIL DISPERSION

By

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Dedication

I dedicate this thesis to my family.

To my father: Thank you for always emphasizing the importance of academics. Without your constant guidance, knowledge, and foresight, I would not have the opportunities that I am presented with today.

To my mother: Thank you for always providing me with love, support, and encouragement. No matter the circumstance, you always give me the strength and courage to persevere.

To my wife: Thank you for motivating me to write this thesis.

And to Libbie: Thank you for always being there.

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Thank you to my committee members: Dr. Mikhail Anisimov and Dr. Taylor Woehl. They are extremely busy professors. For them to take time out of their schedules to sit on my committee is humbling.

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Thank you to my family and friends. It takes a village and without your support I wouldn't be the person who I am today.

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tails anchored to the oil and the hydrophilic heads oriented toward water. If the dispersion is efficient, the dispersion in the flask will have a brown color for a considerable time, which will then be reflected in the photo of the sample taken after 30 min (see Figure 3.2)19

The spilling of crude oil onto bodies of water (oceans, seas, rivers, lakes) is well-known to adversely affect the local environment and the larger ecosystem in so many ways. Pelagic and avian species are susceptible to the immediate effects of spilled oil. Seabirds in the marine environment become coated in oil, and in turn, their feathers become matted. Additionally, the oil mixes with and strips away the seabirds' natural insulating oils. Thus, seabirds become less buoyant and their stability in water is compromised.[1] Furthermore, their skin is unprotected from the environmental conditions, which may cause hypothermia and lead to death.[2] Fish and other aquatic creatures are also susceptible to components found in crude oil, such as mercury.[3] Additionally, oil spills have devastating effects on beaches and shorelines if the oil reaches the coast. As the oil reaches subtidal and marsh areas, there is a spike in mortality of marine flora and fauna.[4] For example, the 1969 *Florida* barge catastrophe (when 175,000 gallons of oil spilled off the coast of Massachusetts) caused 95% of the sea floor-dwelling creatures near the coastline to be killed.[4] Larger oil spills have subsequently occurred, such as the *Exxon Valdez* event in 1989, which spilled over 11 million gallons of oil into Prince William Sound, Alaska[4] and the more recent Deepwater Horizon spill in 2010 which polluted the Gulf of Mexico with over 210 million gallons of oil.[5] These events cause irreparable damage to the environment and must be avoided by any means necessary.

After an oil spill is reported, one course of action is containment and control using oil booms and skimmers.[2,6] However, typically, the oil spreads so quickly and over such a large area that containment is difficult. Moreover, containment and recovery can lead to

exorbitant costs.[6-9] It has been estimated that mechanical containment methods cost $44 per gallon of spilled oil.[10,11] The combination of low recovery efficiencies and high costs mean that mechanical containment is generally impractical and can only be used under very limited conditions. As a result, the most used method to remediate an oil spill is by the introduction of *dispersants*.

Dispersants are currently used to clean-up more than 90% of typical oil spills at a relatively low cost (estimated to be $7 per gallon of spilled oil).[10,11] Early formulations of dispersions were limited by their toxicity. In 1967, the supertanker *Torrey Canyon* ran aground off the coast of Great Britain, and this is regarded as the first major marine pollution event.[4] The British government responded by using over 2.5 M gallons of dispersants to clean up the oil spill.[4] Unfortunately, the chemicals within the dispersants were more toxic to the environment than the spilled oil itself.[4,7,12] More recently, during Deepwater Horizon in 2010, the U.S. employed over 2 M gallons of newer dispersants in an attempt to clear the oil spill.[13] The current industry-standard dispersant is called Corexit, and it is less toxic than previous versions. However, recent studies have continued to attribute negative health effects to Corexit.[14-17] This has motivated work in our lab to develop a new generation of non-toxic dispersants.

The function of a dispersant is shown in Figure 1.1a (see further discussion in Chapter 2). The dispersant contains amphiphilic molecules ("surfactants") in a solvent base. The surfactants break up the oil slick into discrete droplets with sizes in the microscale. These droplets are then carried below the surface of the water layer, where they

can subsequently be degraded by various micro-organisms present in the water. The fraction of the oil slick that is dispersed as droplets into the water column is termed the dispersion efficiency. Dispersants like Corexit are highly effective at converting the oil slick into droplets, i.e., their dispersion efficiency is > 90% for low amounts of dispersant.

<div align="center">

(a) (b)

</div>
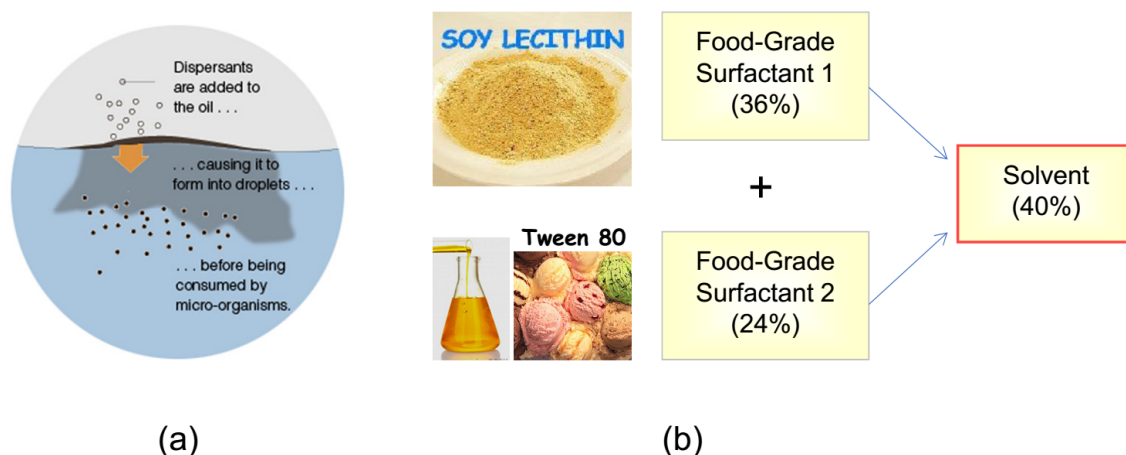
Figure 1.1 (a) Action of dispersants on an oil spill. The dispersants break the oil layer on the water surface into microscale droplets, which are carried below the water surface, where they can be degraded by micro-organisms. Figure credit: New York Times, 2010 (http://www.nytimes.com/interactive/2010/04/28/us/20100428-spill-map.html) (b) Food-grade dispersants developed by our lab at UMD. These dispersants combine two non-toxic, food-grade surfactants, soy lecithin and Tween 80, in a non-toxic solvent. The focus of this thesis is on the role of solvent with regard to the efficiency of the dispersion. Figure credit: EC21, 2018 (https://www.ec21.com/product-details/Soy-Lecithin-Powder-Soyabean-Powder--10088120.html) Tidesmark, 2018 (http://tidesmark.com/product/polysorbate-80/)

In our lab, we have created a completely food-grade dispersant that is equally as effective as Corexit.[18-20] The surfactants in this dispersant (Figure 1.1b) are lecithin (L), a phospholipid extracted from soybeans, and Tween 80 (T), a nonionic surfactant that is used in ice creams and other food products. The two above surfactants are dissolved in a solvent to create the dispersant. In previous studies, we have explored different ratios of L and T

and found that a weight ratio around 60:40 L:T maximized the efficiency of the dispersion.[18-20] However, thus far, we have not paid much attention to the solvent used in the dispersant. Our original solvent was ethanol, which is relatively non-toxic and is a food-grade material, but it is unsuitable for use in the field because ethanol has a low flash point.[9,21,22] Furthermore, the role and effect of the solvent within a dispersant system has not been comprehensively studied. Most researchers treat the solvent as a component that has a negligible effect on dispersion efficiency. Selection of the solvent is therefore made based on factors like toxicity, volatility or viscosity of the overall mixture. The purpose of this thesis is to re-examine the role of the solvent in a dispersant. Can the solvent have a big impact on the efficiency of crude oil dispersion, and if so, why? These are the questions that motivate our studies.

2.1 Crude Oil Properties

Crude oils are complex mixtures with many components.[23] They can be classified based on their saturates, aromatics, resins, and asphaltenes (SARA).[23,24] Three oil types can be distinguished by SARA: light, medium, and heavy crude oils. Light crude oils have mainly (> 90%) saturates (saturated alkane chains), some aromatics, a tiny fraction (< 1%) of resins, and no asphaltenes.[24] Medium crude oils have a smaller fraction of saturates and greater fractions of aromatics, resins, and asphaltenes.[24] Heavy crude oils contain the least saturates and the highest fraction of asphaltenes. The oil composition influences other properties such as density and viscosity.[23,24] Light crude oils have lower densities and viscosities compared to heavy crude oils. In this study, only one crude oil was examined, which is called "sweet Louisiana crude". Sweet Louisiana crude is a light crude oil with a viscosity of 7 mPa·s and a density of 840 kg/cm^3.[25] It is the oil released from the Macondo well during the Deepwater Horizon event.

2.2 Chemical Dispersion

Oil dispersion is a process where chemical dispersants are applied over an oil slick (Figure 2.1a).[7-9,21,22,26] The surfactant in the dispersant reduce the oil-water interfacial tension (Figure 2.1b).[7-9,12,21,26] When the oil slick is subjected to mixing energy, it breaks apart into stable, fine droplets that become suspended in the water column (Figure 2.1c).[27] These oil droplets are consumed and degraded naturally by marine bacteria.[28] Dispersant application can be from aircraft or vessels.[7,22] Mixing energy to break the slick into droplets

comes from wind, waves, and ocean currents; also, additional mixing can be induced by a vessel's wake or other mechanical action.[7,22]
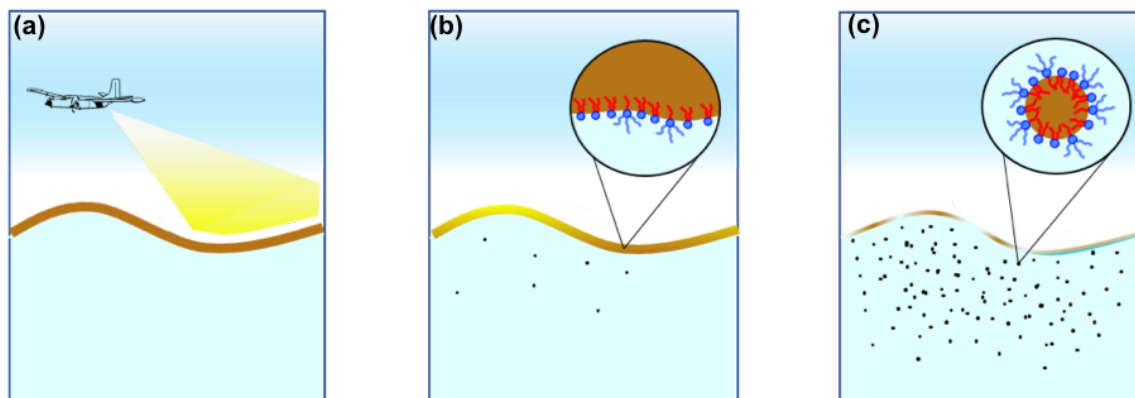
Figure 2.1 Chemical dispersion process by which an oil slick (brown) is broken into droplets within the water. (a) Dispersants are generally applied as a spray from aircraft or vessels. (b) The dispersant diffuses to the interface. The surfactants within the dispersant orient themselves with their hydrophilic heads in the water and their hydrophobic tails in the oil, which reduces the interfacial tension. (c) Energy in the form of waves breaks the film into fine droplets which become suspended in the water column.

2.3 Emulsification vs Dispersion

When the oil droplets are suspended in water, the result is an oil-in-water (O/W) emulsion. Emulsions of oil-in-water are created routinely in the lab or in industry, and the process is termed emulsification. Is dispersion, as shown above by Figure 2.1, the same as emulsification? For the purpose of our study, there are key differences between the two, and these are shown by the schematics in Figure 2.2. In the case of emulsification (Figure 2.2a), a relatively large fraction of oil (at least 5-10%) is combined with water using a high concentration of surfactants. The surfactant content can be represented by the dispersant:oil ratio (DOR), and the DOR (on a weight basis) for forming emulsions can be 1:1 or higher. Moreover, emulsification requires a large amount of mixing energy, which can be provided

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by vortex mixing, sonication, or rotor-stator mixing for sufficient time. Under these conditions, the emulsion formed has a high-volume fraction of oil droplets suspended in water. Because of the high DOR, these droplets are stabilized against coalescence, and therefore emulsions can be colloidally stable for long times. The photos in Figure 2.2a show that a crude oil-in-seawater emulsion is stable (no separation of oil and water phases) at a time of 30 minutes after the mixing is stopped.
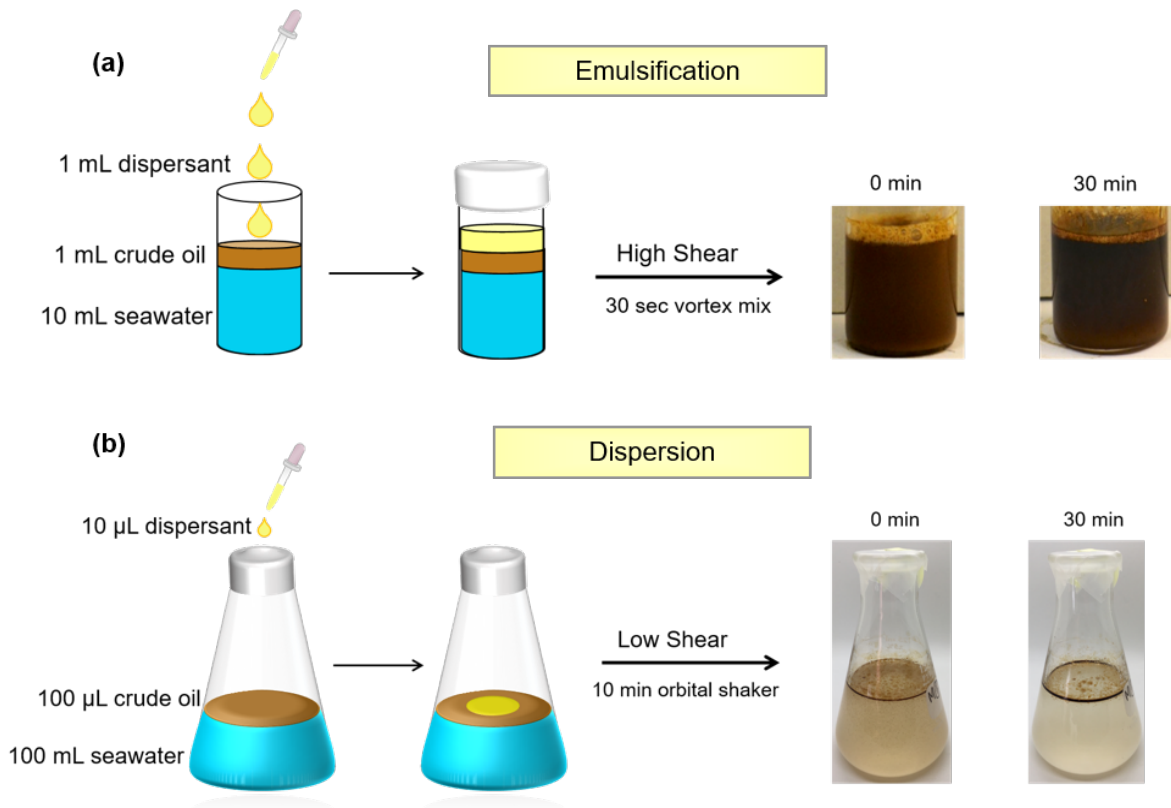
Figure 2.2 Emulsification versus dispersion. (a) In the former case, the oil:water (O:W) ratio is 1:10 and the dispersant:oil ratio (DOR) is 1:1. Intense mixing energy is used to form the emulsion. The photos show that the emulsion is stable over 30 min. (b) In the case of dispersion, the O:W ratio is 1:1000 and the dispersant:oil ratio (DOR) is 1:10. That is, a thin oil film on a large body of water is emulsified with as little dispersant as possible. Also, much lower mixing energy is used to form the dispersion. Under these conditions, most of the oil is dispersed into the water column, which thus appears brown. However, within 30 min, the droplets aggregate and rise to the surface, indicating the instability of the dispersion; thereby the water appears considerably lighter in color.

For comparison, in the case of dispersion (Figure 2.2b), a small quantity of oil is combined with water using a low dispersant amount. The oil is basically a thin film on the water and the oil:water ratio is 1:1000. The dispersant used is also at a low amount (the DOR is ~ 1:10). Moreover, the mixing energy used is also generally much less – this is typically in an attempt to simulate the waves that an oil slick on the ocean would experience. Despite the lower DOR and mixing energy, most of the oil does get dispersed into the water column, as shown by the brown color of the flask in Figure 2.2b. However, this dispersion is unstable, likely because the droplets are not completely covered by a layer of surfactant. Thus, within 30 min, the droplets aggregate and rise to the water surface in the flask. The water column thereby has a considerably lighter color. Our focus in this thesis will be on dispersion because it is more closely related to sea conditions.[22,25]

2.4 Dispersant Composition

A typical dispersant is a blend of surfactants dissolved in a solvent. As noted previously in Chapter 1, our lab has created a food-grade dispersant consisting of two surfactants, soy lecithin (L) and Tween 80 (T), dissolved in ethanol.[18] Lecithin is a phospholipid that can be derived from soybean, eggs, sunflower seeds, and rapeseeds.[29] The lecithin used in our studies was derived from soybeans. It is a phospholipid with two hydrocarbon tails, one saturated and the other unsaturated, and a zwitterionic phospho-choline headgroup (Figure 2.3a). L is commonly used in the food industry as an emulsifier and in the pharmaceutical industry to prepare liposomes for drug delivery.[18,29] Polysorbate 80, commonly known as Tween 80, is a non-ionic, single-tailed surfactant (Figure 2.3b)

and is used as an emulsifier in food and pharmaceutical applications.[18] Studies show that Americans consume between 12 and 111 mg/day of T from foods, specifically ice cream.[18]
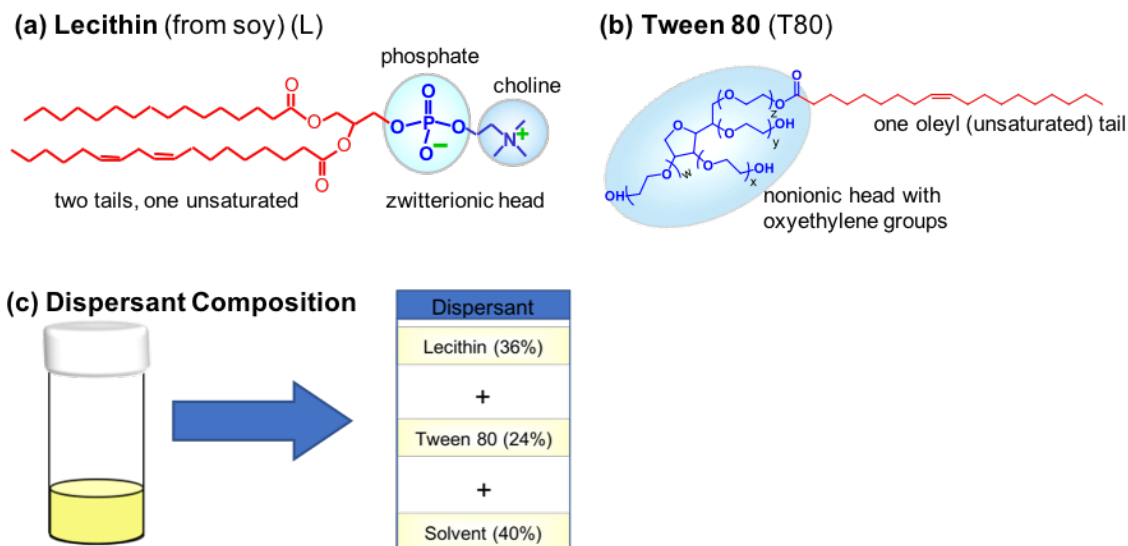
Figure 2.3 Composition of a food-grade dispersant prepared in our lab. The dispersant consists of soy lecithin (L) and Tween 80 (T), the structures of which are shown in (a) and (b) (hydrophobic tails in red; hydrophilic head in blue). These are dissolved in a solvent, with a final composition of 36% lecithin, 24% Tween 80, and 40% solvent w/w. The solvent used previously was ethanol.

The remaining component in the dispersant is a solvent, which in the case of our previous work was ethanol. The following characteristics are usually taken into account when selecting the solvent for a dispersant.[21,22] The solvent should:

1. Fully solubilize the surfactants.

2. Have low toxicity.

3. Have a flash point $> 60°C$, and thus a low vapor pressure at room temperature.

4. Have a lower density than seawater to prevent sinking of dispersant.

5. Have a low viscosity to enable spray application.

The importance of these solvent characteristics will be emphasized in Chapter 3.

2.5 Selection of Surfactants in a Dispersant

When formulating a dispersant, the primary step is selecting appropriate surfactants. A useful tool in this regard is the hydrophilic lipophilic balance (HLB).[22,27,30] HLB is a scale ranging from 0-20 and various surfactants are assigned a value based on their hydrophilic and lipophilic properties.[27,30] Surfactants with a low HLB are predominantly soluble in oil while those with a high HLB are predominantly soluble in water. The HLB value for a surfactant blend is the weighted average of the individual surfactant HLB values:[18,30]

$$\left(HLB\right)_{blend} = \sum HLB_i \cdot w_i \qquad (2.1)$$

where w_i is the weight fraction of the ith surfactant with a value HLB_i.

Oil dispersion is a process in which O/W emulsions are formed (Figure 2.2). By the HLB scale, an O/W emulsion is formed by surfactants or their blends with HLBs within the range of 8-18.[27,30] The HLB concept is useful in the initial selection of surfactants to form an emulsion, but is not useful in predicting the long-term stability of the resulting emulsions.[30] In the case of L and T, their HLB values are 8 and 15 respectively. While both these values fall within the above range for O/W emulsification, neither L nor T are good emulsifiers when used on their own.[18] However, L/T blends, specifically at weight ratios around 60:40 L:T (HLB = 10.8) were found to be much better emulsifiers than the pure components.[18-20] This suggests a synergy between L and T molecules when it comes to the formation and stability of O/W emulsions.

A mechanism for the L/T synergy in emulsification is shown in Figure 2.4.[18] There are three aspects worth highlighting. First, L and T can pack tightly at the oil-water interface (Figure 2.4a). Note that L has two tails (length ~ C_{16}), one of which has two *cis*-unsaturations. T has one C_{16} tail with one *cis* unsaturation. The *cis*-unsaturations act as kinks in the tail, enabling them to be flexible at room temperature. The flexibility and kinks of L and T allow the molecules to pack closely. A second aspect (Figure 2.4b) is that L is oil-soluble, but not water-soluble. As a result, it is unfavorable for L to desorb from the oil-droplet. Lastly, T has a strong affinity for water as a result of the oxyethylene chains in its headgroup. When T is adsorbed on the oil droplet, the oxyethylene chains extend into the water phase. When two oil droplets approach each other, the oxyethylene chains provide steric repulsions (Figure 2.4c). Taken together, the presence of L and T together is responsible for ensuring the stability of the O/W emulsion.

(a) Lecithin & Tween pack tightly on the droplet

cis-unsaturations (kinks) in the tails of L & T help in packing

(b) Lecithin persists on the droplet surface

L does not desorb due to its low solubility in water (low HLB)

(c) Tween stabilizes droplets by steric repulsions

oxyethylene groups in the heads of T favor water
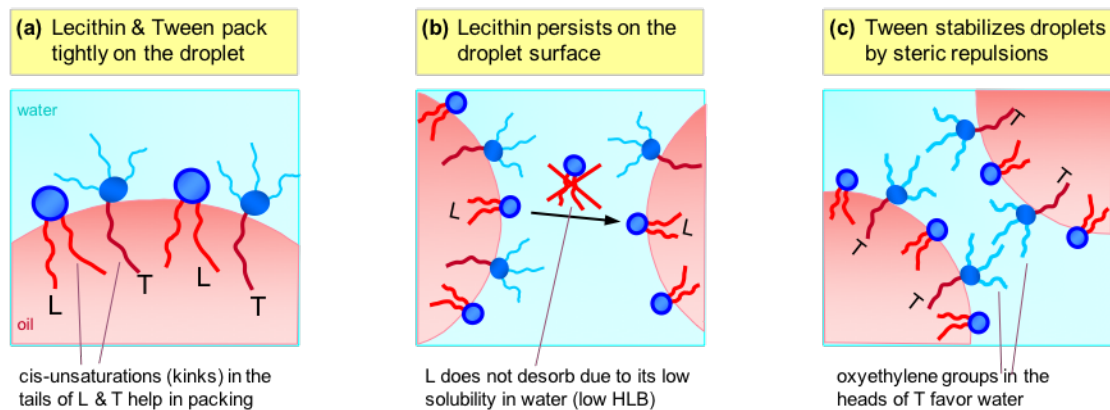
Figure 2.4 Mechanism for synergistic emulsification by lecithin (L) and Tween 80 (T). (a) L and T pack tightly on the oil droplet surface because of their structures. (b) L does not desorb from the interface due to its hydrophobic nature. (c) The oxyethylene side chains from T impart steric stabilization to the oil droplets.

2.6 Solvent Selection: Hansen Solubility Parameters

In Chapter 3, our focus will be on selecting the solvent to be used in dispersants. In this regard, we will make use of solubility parameters, which are extensively used for selecting solvents to be used to dissolve specific polymers (e.g., in the coatings industry).[23,31] The solubility parameter δ was first introduced in 1950 by Hildebrand and is defined as:[23]

$$\delta = \left(\frac{E}{V} \right)^{1/2} \tag{2.2}$$

Here, E is the energy of vaporization of the solvent and V is its molar volume. E is the energy required to transform a substance from liquid to vapor, which is a measure of the intermolecular interactions within the solvent.[23] The units for δ are MPa$^{1/2}$. While the Hildebrand solubility parameter represents the solvent by a single number, this was refined and extended by Hansen. The Hansen Solubility Parameters (HSPs) are a set of three parameters that together comprise the above δ. That is:

$$\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \tag{2.3}$$

where δ_D is the contribution from intermolecular dispersion (D) interactions, δ_P that from polar (P) interactions, and δ_H that from hydrogen-bonding (H) interactions.

The three HSPs have been compiled for many solvents. In the case of a species to be dissolved, like a polymer, the HSPs can be calculated from group-contribution methods. The general principle for solubility is that "like dissolves like". That is, a good solvent for a polymer would be one whose HSPs are very close to that of the polymer. Note that if a polymer and a solvent have similar HSPs, it implies that the two are chemically similar and

that there will be favorable intermolecular interactions between the two. Similarly, liquids with similar HSPs are expected to be miscible. We will use HSPs in an analogous manner in Chapter 3.

2.7 Solvent Selection: Toxicity Parameters

An important consideration in selecting the right solvent for a dispersant is that it should be non-toxic. For various solvents, values of their lethal doses (LD_{50}) are available. The LD_{50} is the minimum dosage in mg/kg (mg of substance per kg of body weight) where half the test population dies. Two LD_{50} values were found for each solvent, one the oral LD_{50} from experiments with rats, and the other the dermal LD50 obtained from experiments with rabbits. The LD_{50} values were categorized using the criteria outlined by the International Labor Organization (ILO), as shown in Table 1 below.[32]

Table 2.1 Toxicity exposure categories for LD_{50} (mg/kg).

Exposure	Category 1	Category 2	Category 3	Category 4	Category 5
Oral	5	50	300	2000	5000
Dermal	50	200	1000	2000	5000

The descriptions for each category are: [32]

- Categories 1 and 2 are considered fatal if swallowed/in contact with skin.

- Category 3 is toxic if swallowed/in contact with skin.

- Category 4 is harmful if swallowed/in contact with skin.

- Category 5 may be harmful if swallowed/in contact with skin.

2.8 Dispersant Efficiency and its Determination

The dispersion efficiency refers to the fraction of the oil slick that gets dispersed into the water column upon adding the dispersant. This is usually determined by a test called the Baffled Flask Test (BFT), the protocol for which has been approved by the Environmental Protection Agency (EPA).[33] The BFT uses a baffled flask, which is a conical flask with built-in baffles (protrusions along the walls at the bottom of the flask). In this flask, seawater (~ 100 mL) is first added, and then ~ 100 μL of crude oil is introduced as a film on the seawater surface. Then, the dispersant is added at a fixed DOR (typically between 1:5 and 1:20). The sample is mixed for 10 min on an orbital shaker at 250 rpm, then removed and allowed to rest for 10 min. Thereafter, a 30 mL sample is withdrawn from the center of the water column and placed in a separatory funnel where the oil is extracted using dichloromethane (DCM). The oil concentration in the DCM solution is then measured using UV-Vis spectroscopy in the range of 340 to 400 nm. This concentration is used to calculate the dispersion efficiency.

During the BFT, the baffles in the flask introduce turbulent flow into the sample and thereby ensure substantial mixing of the oil film with the water (i.e., formation of oil droplets). If an identical sample is placed in a regular conical flask (without baffles) and mixed for the same time on an orbital shaker, the mixing energy would be much less. However, in Chapter 3, we have done precisely the latter because it provides us with a way of visually distinguishing between efficient and inefficient dispersants. We term our protocol the "Low-Energy Dispersion Test" (LEDT), and this is discussed further in Chapter 3.

3.1 Introduction

The broader goal of our work is to improve the design of dispersants used to remediate crude oil spills. The ideal dispersant should be very efficient at converting the oil slick on the surface of the water into small (microscale), stable droplets. At the same time, the dispersant should be non-toxic to aquatic life and also to human responders at the scene. In this regard, our focus has been on developing food-grade dispersants based entirely on non-toxic and food-grade components. As mentioned in Chapters 1 and 2, a dispersant is a mixture of active components, i.e., the surfactants, solubilized in an inert liquid, the solvent.

Much attention has been paid to the surfactants. For a dispersant to be effective, the surfactants must arrange at the interface between the crude oil and seawater and thereby reduce the interfacial tension.[27,30] This facilitates the formation and dispersion of oil droplets in the water column. Moreover, the surfactants should ensure the stability of the droplets to coalescence. Selecting the wrong surfactants will guarantee poor dispersion, but what about the solvent? The solvent is believed to aid in the transport of surfactants through the oil slick, but the conventional wisdom is that it plays no major role in promoting (or hindering) dispersion.

The goal of this thesis is to examine whether solvents exert an independent effect on dispersant efficiency. We reiterate that an efficient dispersant is one that converts a large fraction of the oil slick into droplets for as small an amount of dispersant as possible. For

example, the industry standard Corexit, as well as our food-grade alternative have been shown to convert more than 80% of the oil into droplets for a dispersant:oil ratio (DOR) of 1:20. The question is whether these efficiencies would be altered significantly if the same surfactants were used but the solvent alone was changed. Our results show that this is indeed the case. We have used the food-grade surfactants from our previous work, i.e., soy lecithin (L) and Tween 80 (T) in a weight ratio of 60:40 (see Sections 2.3 and 2.4 and Figure 2.3). With this surfactant composition kept constant, we have examined 28 different solvents. Our results show a clear hierarchy among the solvents, with some giving rise to significantly higher dispersion efficiencies than others. To explain this hierarchy, we have conducted an analysis based on Hansen Solubility Parameters (HSPs), which were introduced previously in Section 2.6. Together with the molecular structure of the solvents, our study provides new insights into the role of solvent in oil dispersion. Finally, we combine the above results with data on the toxicity profiles and flash points of the solvents to identify a small number of "optimal" solvents for use with L/T dispersants.

3.2 Experimental

Materials. Soybean lecithin (95%) was purchased from Avanti Polar Lipids while the Tween 80 surfactant (poly(oxyethylene sorbitan monooleate)) was obtained from Sigma-Aldrich. The solvents 1-butanol, 1-octanol, 3-octanol, 1,3-butanediol, acetone, diethylene glycol, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, dipropylene glycol n-butyl ether (98.5% isomers), ethylene glycol butyl ether, glycerol, methanol, n-dodecane, n-octane (reagent grade, 98%), propylene glycol, and undecanol were obtained from Sigma-Aldrich. 1-propanol and isobutanol were obtained from J. T. Baker. 2-ethyl-

1-hexanol and dipropylene glycol were obtained from TCI America. Acetic acid and dimethyl sulfoxide were obtained from Fisher Scientific. N-methyl-2-pyrrolidone was obtained from Fluke Analytica. Ethanol and methanol were obtained from Pharmco-Aaper. Isopropanol and N,N-dimethylformamide were obtained from VWR. Isopar-M, an industrial hydrocarbon solvent comprised of mainly normal alkanes and isoalkanes (C_{11}–C_{16}), was gifted from Seacole Specialty Chemical. Sweet Louisiana crude oil was obtained from British Petroleum's Macondo prospect through the Gulf of Mexico Research Initiative (GoMRI) program. Deionized (DI) water, purified by a reverse osmosis system, was used in our experiments. Sea salt (32 g, Instant Ocean from Spectrum Brands) was dissolved in 1 L of DI water to make synthetic seawater.

Dispersant Preparation. The dispersants were prepared in 20 mL vials. All the dispersants contained the same surfactant-to-solvent ratio of 60:40 w/w. The surfactant component (60% by weight) consisted of 60:40 L:T w/w. Typically, the total weight of dispersant was 1 g (0.36 g L, 0.24 g T, and 0.4 g solvent). Different dispersants were prepared using 28 different solvents. To expedite dissolution, vials were placed in a heat bath at 50°C then sonicated until the surfactants and solvent formed a homogeneous solution. If the surfactants were insoluble after this period, this was also noted.

Sample Preparation and Low-Energy Dispersion Test. Each dispersion test sample was prepared as follows. First, 100 mL of artificial seawater was added to a 125 mL conical flask. Next, 100 μL of sweet Louisiana crude oil was pipetted on top of the seawater. Finally, 10 μL of dispersant was pipetted on top of the oil. Thus, the ratio of oil:seawater

ratio was 1:1000 and the dispersant:oil ratio (DOR) was 1:10 for all tests. The low-energy dispersion test (LEDT) was then conducted as described in the next section. The shaker used was an Innova 4000 incubator shaker.

Efficiency Measurement. To measure dispersion efficiency, we followed the EPA-approved baffled flask test (BFT) procedure, as discussed in Section 2.7.[33] The procedure calls for a 150 mL trypsinizing baffled flask. Trypsinizing baffled flasks, which are conical flasks with four extra-deep baffles commonly used in biological research and clinical testing, were purchased from Wheaton. The same amounts of seawater, crude oil, and dispersant as above were added to the flask. The sample was mixed for 10 minutes on an Innova 4000 incubator shaker at 250 rpm, then removed and allowed to rest for 10 minutes. Thereafter, a 30 mL sample was withdrawn from the center of the water column and placed in a separatory funnel where the oil was extracted using dichloromethane (DCM). The oil concentration in the DCM solution was then measured using UV-Vis spectroscopy on a Varian Cary 50 spectrophotometer.

3.3 Results and Discussion

We started by preparing 28 different dispersants, with the same surfactants and a varying solvent. Each dispersant, as noted above, contained the same surfactant:solvent ratio of 60:40 w/w. The surfactants were soy lecithin (L) and Tween 80 (T) in a 60:40 weight ratio. We wanted to devise a simple and rapid test that could distinguish between good and poor dispersion.[25,33-36] In this regard, the BFT was found to be unsuitable because the baffles induce significant mixing of the oil and water, which promotes dispersion. Also,

the BFT is a tedious and time-consuming test. For these reasons, we have modified the standard BFT procedure and come up with a low-energy dispersion test (LEDT), which is shown schematically in Figure 3.1.
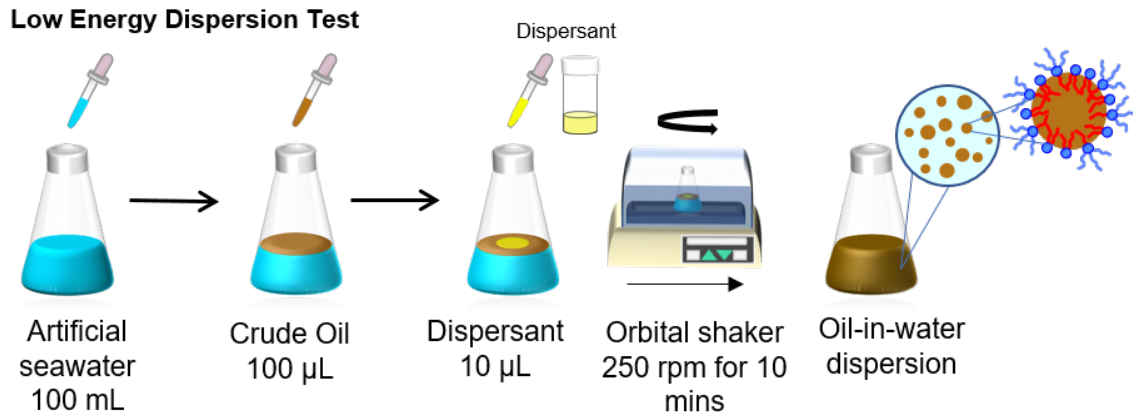
Figure 3.1 Schematic of the low-energy dispersion test (LEDT). Crude oil is added to sea water at a ratio of 1:1000. The dispersant is added on top of the oil at a dispersant:oil ratio (DOR) of 1:10. The sample is then placed on an orbital shaker at 250 rpm for 10 min. A cartoon of the dispersion shows oil droplets coated with surfactants, with the hydrophobic tails anchored to the oil and the hydrophilic heads oriented toward water. If the dispersion is efficient, the dispersion in the flask will have a brown color for a considerable time, which will then be reflected in the photo of the sample taken after 30 min (see Figure 3.2).

The LEDT uses a conical flask instead of a baffled flask. Once the sample (seawater+oil+dispersant) is in the flask, it is placed on a shaker for 10 min at 250 rpm. After shaking, the sample is immediately removed and placed in a photo box. After 30 minutes of rest, photos of the sample are taken, and are visually assessed (see below). Note that the DOR used in the LEDT is relatively high (1:10). We have experimented with higher and lower DORs (see Figure 3.4 below) and settled on a DOR at which substantial differences can be seen visually. Regarding the level of mixing or shear imparted in the LEDT, the orbital shaking is akin to swirling the sample in the flask using one's hands at

moderate speed. Thus, it is rather moderate shear, and is much less than that imparted by

vortex mixing or sonication. In practical terms, the LEDT might correspond to gentle wave

action on an oil slick, e.g., when the sea is calm.

Figure 3.2 Results from the low-energy dispersion test (LEDT) on dispersing crude oil in
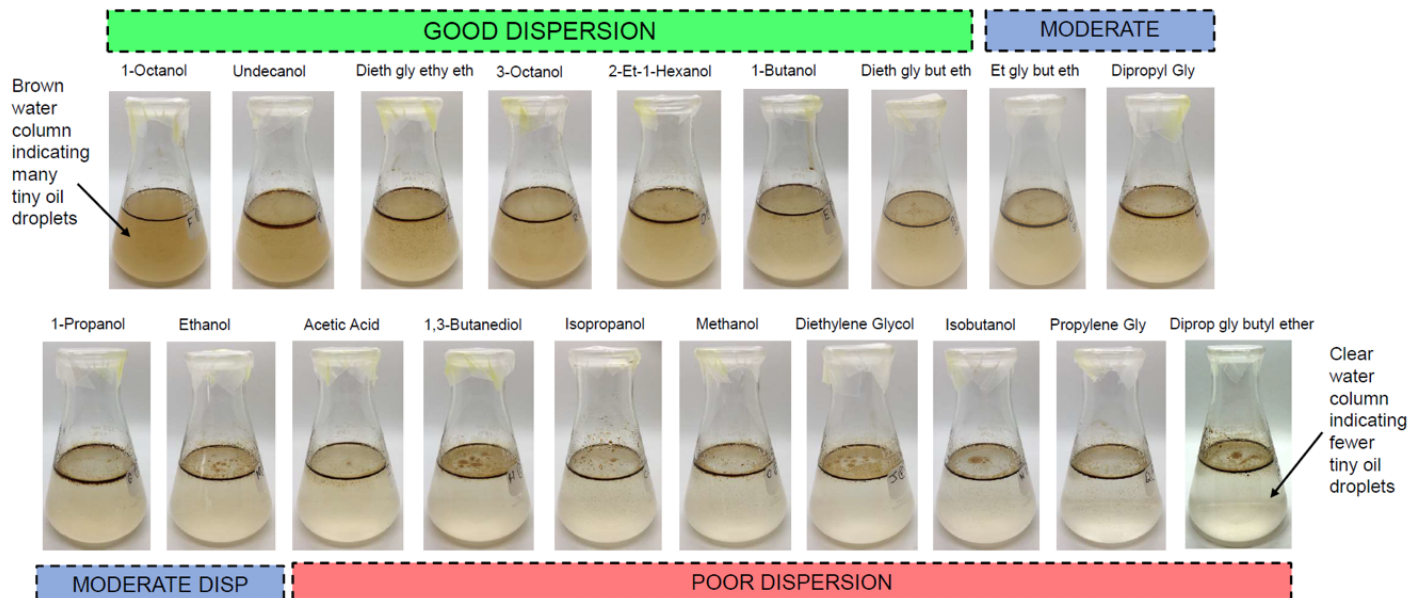
seawater using the same surfactant blend (L:T = 60:40) and concentration, but varying
solvent. Photos are shown for each sample with the solvent name above. The results are
arranged in order from left to right (top row, then bottom row) from best to worst extent of
dispersion. Furthermore, the results are categorized into three bins: good, moderate, and
poor. A "good" dispersion yields a brown water column, indicating a high concentration
of relatively stable oil droplets. A "poor" dispersion yields a colorless water column, with
much of the oil droplets having coalesced and risen above the water.

Of the 28 different solvents, we found that 9 of the solvents did not solubilize one

or both of the surfactants (L and T). These mixtures were not tested further as they did not

meet the definition of a dispersant.[21,22] The remaining 19 solvents solubilized the

surfactants and were tested using the LEDT. The results are shown in Figure 3.2. From

visual inspection of the flasks, it is clear that there are wide differences in dispersion

performance among the 19 solvents. We have arranged the flasks in Figure 3.2 in order from best to worst extent of dispersion. Moreover, we have categorized the results into three bins: good, moderate, and poor dispersion. The categorization was done as follows.

In the case of a "good" dispersion, the water column has a light to dark brown color. Since the crude oil is a dark brown, the brown color of the water indicates a high concentration of these oil droplets suspended in the water. Also, note that the photos in Figure 3.2 are taken 30 minutes after the mixing is stopped. So, a brown water column at 30 minutes indicates both that there are numerous oil droplets and also that the droplets are stable to coalescence or aggregation for at least that period of time. Correspondingly, note that the water surface is clear of coalesced oil, although a brown ring of oil does remain. In contrast to the above, in the case of a "poor" dispersion, the water column is colorless at the 30 min mark. This suggests that most of the oil droplets have coalesced and risen to the surface due to their lower density. Indeed, brown splotches can be seen on the water surface in the flasks marked "poor", whereas these are mostly absent in the flasks marked "good".

Figure 3.2 immediately shows that the solvent exerts a huge impact on dispersion. This can be mystifying at the outset. The solvent constitutes 40% of the dispersant, but it is only meant to carry the surfactants (remaining 60%) to mix with the oil layer. One immediate question or concern then would be whether the solvent is having surfactant-like properties. That is, does the solvent act as an emulsifier. To clarify this point, we conducted dispersion tests with the solvent alone (i.e., completely omitting the surfactants). We chose

the best performing solvent by our LEDT (top left sample in Figure 3.2), which is 1-octanol, and one of the worst performing solvent (bottom right sample in Figure 3.2), propylene glycol. Results from the LEDT with these two solvents are shown in Figure 3.3 along with a test run with no dispersant at all. In all cases, there is negligible dispersion. We repeated the tests with considerably higher amounts of solvent (10 µL of pure solvent), but the results were unchanged. These results confirm that surfactants are the primary driving force for dispersion. If the solvent has an effect, it must be in concert with the surfactants.
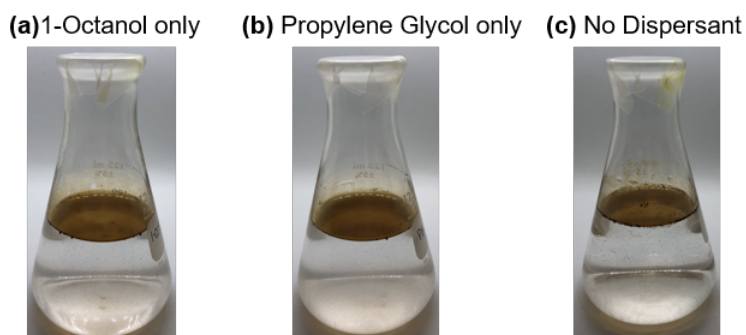
Figure 3.3. Results from the low-energy dispersion test (LEDT) on dispersing crude oil in seawater using no surfactants. In (a) and (b), a solvent alone is used. In (a), the solvent is 1-octanol, and in (b) it is propylene glycol. In (c), neither surfactant nor solvent are used. It is clear that there is negligible dispersion of the oil in all three samples.

Our goal in developing the LEDT was to use it as a tool for screening "good" dispersants. The LEDT is simple and quick compared to the BFT, as it relies on visual inspection. But are the LEDT results reliable and valid in relation to the BFT? Figure 3.4 presents a comparison of the two. The L/T dispersant with 1-octanol as a solvent was used in all cases, and the tests were done for different amounts of dispersant, i.e., for varying

DORs, from 1:10 (highest dispersant) to 1:100 (lowest dispersant). The BFT results are presented as dispersion efficiencies on the plot, and the corresponding flasks are shown in Figure 3.4c. In the case of the LEDTs, the flasks are shown in Figure 3.4b, and in addition, we quantified the color of the flask in terms of the transmittance T (%) through a sample withdrawn from the center of the water column (measured by UV-vis spectroscopy at a wavelength of 370 nm). That is, if the flask is brown, its transmittance will be low whereas if the flask is clear, its transmittance will be high.

(a)

(b) **LEDT Results**

DOR 1:10   DOR 1:25   DOR 1:50   DOR 1:75   DOR 1:100

(c) **BFT Results**
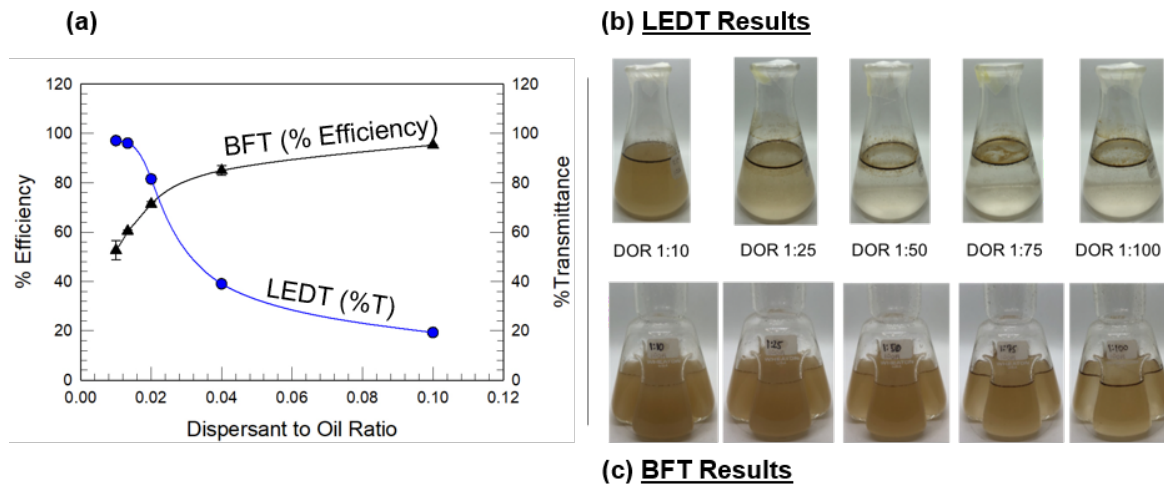
Figure 3.4 Comparing results from LEDTs and BFTs on the same samples. Results are for dispersing crude oil in seawater using the same surfactant blend (L:T = 60:40) solubilized in 1-octanol. The dispersant:oil ratio (DOR) is varied from 1:10 to 1:100. (a) Plot of the BFT efficiency (left axis) and the sample transmittance from the LEDT (right axis) vs. the DOR. (b) Photos of the flasks from the LEDTs. (c) Photos of the flasks from the BFTs.

Figure 3.4a shows that there is a systematic correlation between the LEDT and BFT results. A high BFT efficiency E corresponds to a low transmittance T and vice versa. For example, with a DOR of 1:10, the water column is a deep brown ($T = 19$%) and the BFT efficiency corresponding to this is 95%. At the other extreme, for a DOR of 1:100, the

sample is colorless and nearly transparent ($T = 99\%$), and the BFT efficiency E is around 50%. The trends with decreasing DOR are as expected. With lower dispersant, the oil dispersion efficiency should decrease, which is revealed by both techniques. But what is most striking is the sensitivity of the LEDT compared to the BFT. Across the range of DORs, the BFT efficiency E varies over a relatively small range: from 50 to 95%. Visual inspection of the baffled flasks in Figure 3.4c also reveals a brown water column in all cases; thus, it is difficult to discern from the photos if there are substantial variations in the dispersion efficiency. However, the LEDT shows a brown water column with $T < 40\%$ only for DORs of 1:10 and 1:25 (with the corresponding BFT efficiencies being > 80%). For the lower DOR of 1:50, the LEDT reveals the water to be practically clear with $T \sim$ 80%, which would be classified as "poor" dispersion as per Figure 3.2. Even for this case, the BFT efficiency is $\sim 60\%$, which is reasonably good. This shows that the LEDT is more sensitive than the BFT. Put differently, a good LEDT result is guaranteed to be a good BFT result ($E > 80\%$) because the BFT puts more shear on the sample. A mediocre LEDT result, however, may still give good BFT efficiencies. On the whole, the results from Figure 3.4 validate the LEDT as a quick and reliable way to screen dispersant performance.

Next, in an attempt to gain insight into the differences between solvents, we turn to Hansen Solubility Parameters (HSPs). As explained in Section 2.6, the HSPs quantify the different intermolecular interactions between solvent molecules: δ_D corresponds to dispersion (D) interactions, δ_P to polar (P) interactions, and δ_H to hydrogen-bonding (H) interactions. In the case of the solvents studied here, the δ_D values were very similar and is therefore omitted from our discussion. We therefore focus on a 2-D Hansen plot with δ_P

on the y-axis and δ_H on the x-axis. Figure 3.5 plots all 28 solvents on this 2-D plot (each solvent is a point).
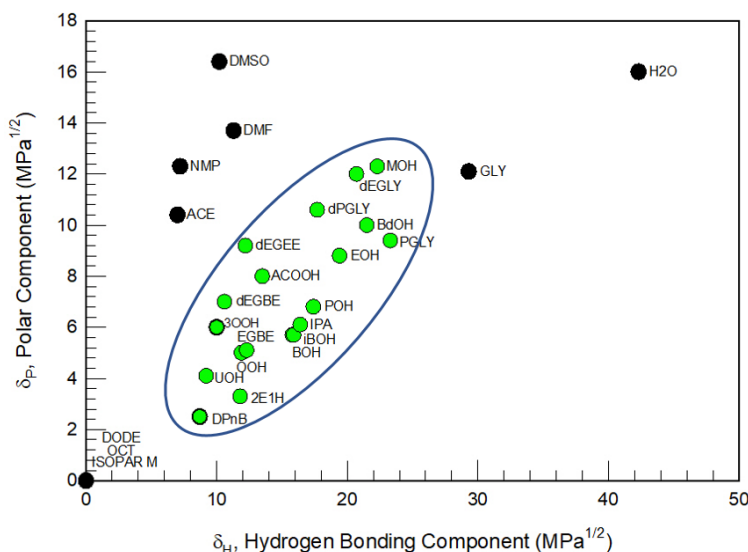
Figure 3.5 Solubility of L and T surfactants represented on a 2-D Hansen plot (the polar HSP δ_P vs. the HSP for H-bonding δ_H). Solvents that solubilized the surfactants are shown in green whereas solvents that did not are shown in black. The soluble points form a region enclosed with a blue ellipsoid.

As noted earlier, nine of the solvents did not solubilize the surfactants while the remaining 19 solvents did. Figure 3.5 shows that the solvents fall in two distinct clusters: a soluble region, with solvent points in green and enclosed with a blue ellipsoid, and an array of insoluble solvents, marked with black points. (See Table A.1 in the Appendix for all the solvent abbreviations.) The above Hansen plot reveals a clear pattern for the solubility results in the case of L and T mixtures. L is hydrophobic and does not dissolve in water. T is hydrophilic and therefore insoluble in hydrophobic solvents such as octane but is still moderately soluble in hydrophobic solvents. The center of the ellipsoid represents the ideal solvent for L/T mixtures, and such a solvent would be rather

hydrophobic in nature. Note also that the origin (0,0) of this plot corresponds to pure n-alkanes (oils). Thus, the axis of the ellipsoid seems to lie along a straight line between oil on one end and water on the other.
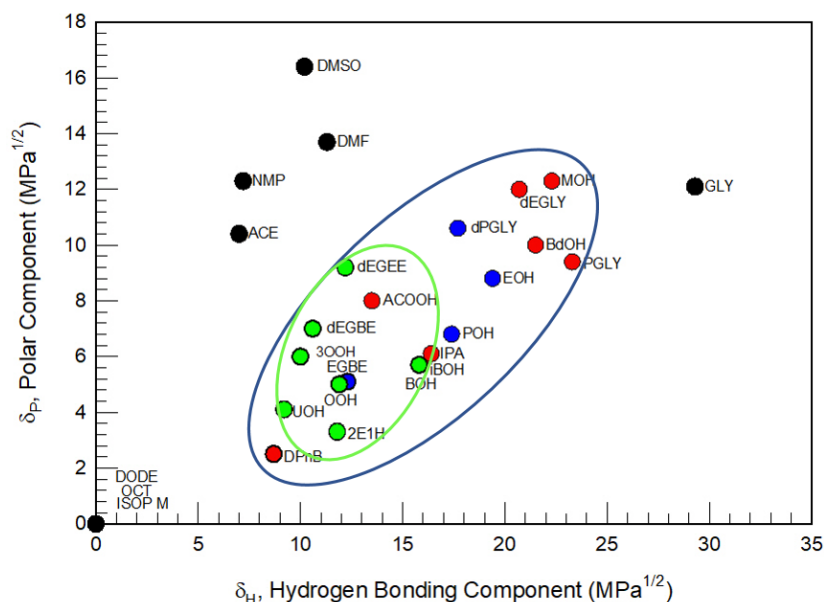
Figure 3.6 Performance of dispersants based on L and T surfactants and various solvents. The results from Figure 3.2 are shown on a 2-D Hansen plot (δ_P vs. δ_H). Solvents that yielded "good" dispersion are shown as green points, "moderate" dispersion as blue points, and "poor" dispersion as red points. Solvents that did not solubilize the surfactants are shown as black points. The blue ellipsoid encloses all the soluble points (same as in Figure 3.5). Within this, the green oval encloses all the "good" solvents.

Figure 3.6 shows most of the data as that in Figure 3.5, but now the focus is not on the solubility of the surfactants (L and T) in each solvent but on the dispersion efficiency of that surfactant-solvent mixture. That is, we have taken the LEDT results for dispersant performance from Figure 3.2 and color-coded the solvent points within the soluble region accordingly. The solvents that gave rise to "good" dispersion are shown as green points, and these mostly lie in one cluster within the soluble region (i.e., within the blue ellipsoid).

This cluster of "good" solvents is outlined by a green oval, again indicating an underlying pattern to the dispersion results.
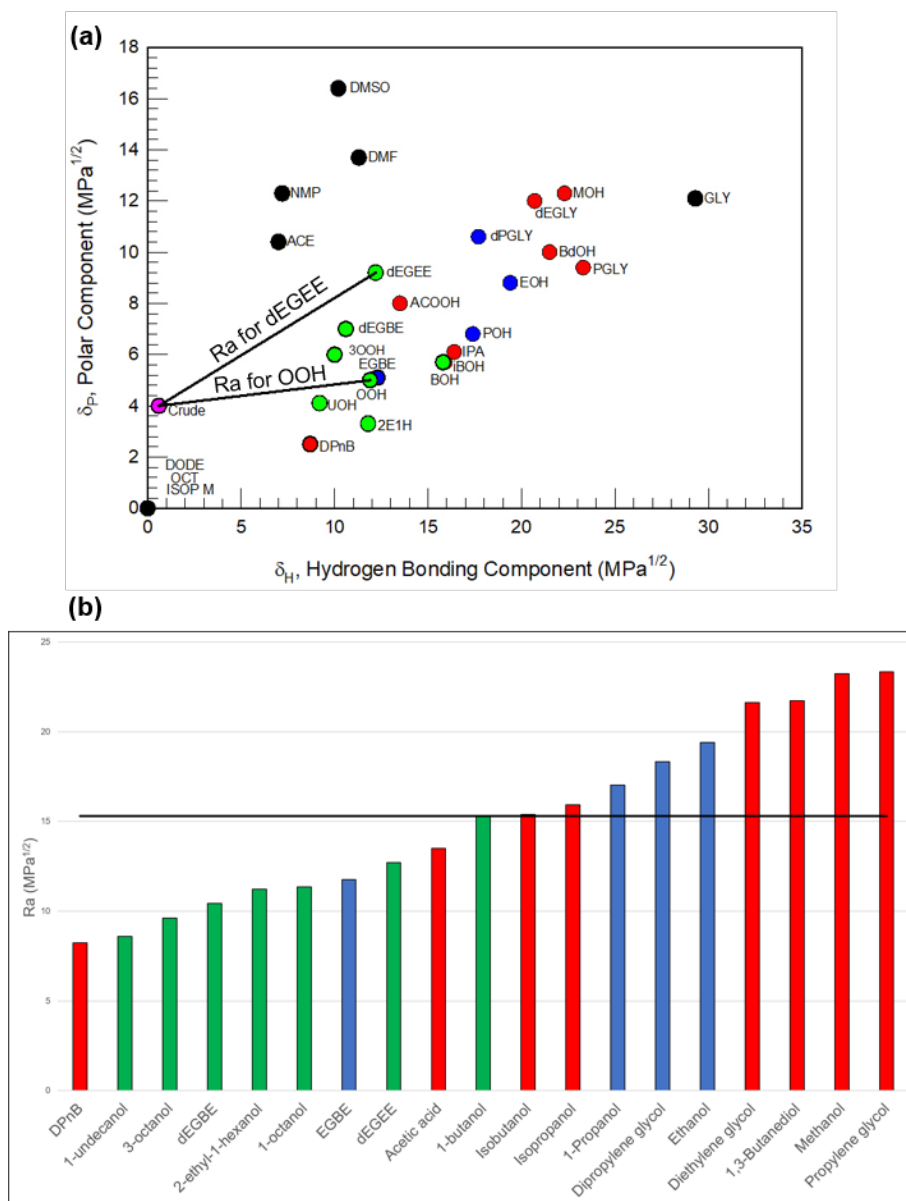
Figure 3.7 Quantifying the performance of crude-oil dispersants based on L and T in various solvents. (a) On the same 2-D Hansen plot (δ_P vs. δ_H) as in Figure 3.6, a pink point is marked for light crude oil. From this point, lines are drawn to each of the soluble solvent points, and the lengths of these lines = Ra are computed. (b). A bar graph of the Ra values for various solvents is shown in increasing order. The bars are color-coded as in Figure 3.2 ("good" dispersion in green, "moderate" in blue and "poor" in red). The horizontal line indicates an Ra of 15.3 MPa$^{1/2}$; no solvent with a higher Ra than this value yielded good dispersion results from the LEDT.

Next, we look to find further meaning to the pattern uncovered in Figure 3.6. That is, why are the "good" solvents clustered in one region. In this regard, we hypothesized that the role of solvent in promoting dispersion may be tied to its affinity with crude oil. Values can be found in the literature for the HSPs of light crude oils (similar to the sweet Louisiana crude studied here).[37] This allows us to place the crude oil on the HSP plot, as shown in Figure 3.7a. Note that the crude oil point is not too far from the origin, indicating that its composition is mostly hydrocarbons with a slight polar component, possibly coming from aromatics. Next we measured the distance from the crude oil point to each of the solvent points on the Hansen plot. This distance, which is termed Ra can be calculated from the underlying HSPs by:

$$Ra = \sqrt{\left(\delta_P^{solvent} - \delta_P^{crude}\right)^2 + \left(\delta_H^{solvent} - \delta_H^{crude}\right)^2}$$ (3.1)

Figure 3.7b shows solvent-crude oil Ra values in increasing order, color-coded to consistently match that of the solvent performance from Figures 3.2 and 3.6. The plot shows that most of the "good" solvents correspond to low Ra and most of the "poor" solvents correspond to high Ra. Moreover, no solvents with $Ra > 15.3$ MPa$^{1/2}$ exhibited good dispersion by the LEDT. A small Ra means that the HSPs of the crude oil and the solvent are similar, which means a strong affinity between the two materials. Thus, the insight from this plot is that good dispersion is facilitated when the solvent has strong affinity for the crude oil rather than for water. The one outlier on this plot is dipropylene glycol n-butyl ether, which has the lowest Ra and yet did not yield good dispersion. However, in the case of DPnB which is a commercial solvent created by Dow Chemical,

we are unsure whether the L and T dissolved completely. Barring DPnB, the next five

solvents all have low *Ra* values and yielded good dispersions.
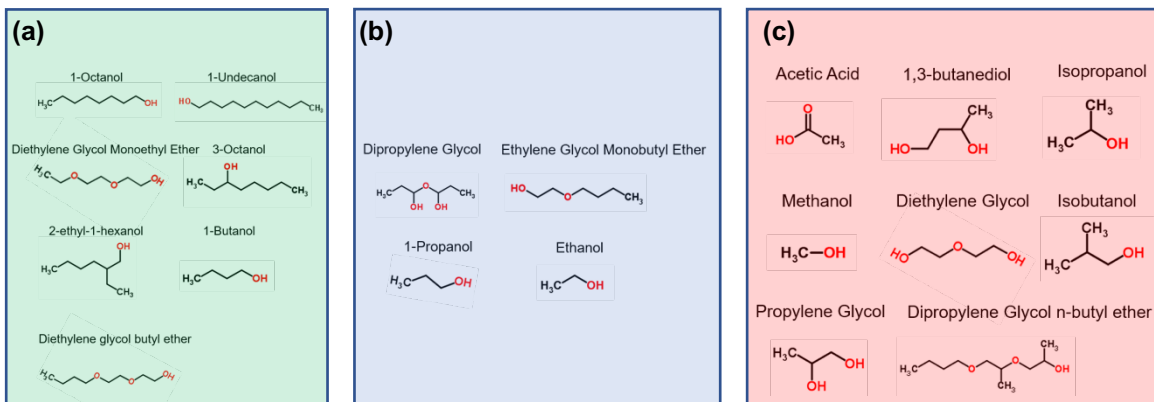
Figure 3.8 Molecular structures of the solvents categorized as those that yield (a) "good" dispersion; (b) "moderate" dispersion; and (c) "poor" dispersion. In the "good" category, nearly all solvents have at least a four-carbon tail with minimal branching.

It is also interesting to examine the molecular structure of the 19 solvents studied.

These are shown in Figure 3.8a, categorized by their ability to yield "good", "moderate",

or "poor" dispersion. Some trends jump out of this figure. First, consider the series of

n-alcohols. The shortest chain alcohol, i.e., methanol is in the "poor" category, while

ethanol and 1-propanol are in the "moderate" category, and the even longer alcohols like

1-butanol, 1-octanol, and 1-undecanol are in the "good" category. Thus, in this series of

solvents, longer chain lengths, indicating more hydrophobicity, leads to a better dispersant.

Note also that 1-butanol is soluble in water, while 1-octanol is not; yet, both give good

dispersion. Another case to note is that diethylene glycol is in the "poor" category, but

variations of this compound with a monoethyl ether or monobutyl ether portion instead of

one –OH end-group are both in the "good" category. Overall, as a rule of thumb, it appears

that the ideal solvent for a dispersion should have limited hydrophilicity. If the solvent was

completely hydrophobic, such as an n-alkane, it would be unable to solubilize the T surfactant.

Our finding is that the best solvents are those with strong affinity for the oil, as measured by their *Ra* values in Figure 3.7. Such solvents are likely to persist within the crude oil slick rather than entering the water column. We believe this is beneficial as it would ensure that the surfactants also remain within the oil slick. If the solvent was too hydrophilic, it might carry some of the surfactants with it (especially the T in our case) as it moves into the water.

A second effect that may occur is co-surfactancy, since several of the "good" solvents have some amphiphilic character, meaning a clear separation of the polar and non-polar parts of the molecule. This is particularly so for 1-octanol and 1-undecanol, which both have an –OH group on one end and then an alkyl tail, and are known to be effective co-surfactants in the formation of micelles. Although OOH does not disperse oil on its own (Figure 3.3), OOH molecules could still participate in the stabilization of oil droplets. That is, the interface of droplets would not only have L and T, but also some OOH molecules. While co-surfactancy could be a factor, the results suggest that it is not the most important one. This is because other solvents on our "good" list do not have as clear of an amphiphilic tendency, including 3-octanol and 2-ethyl-1-hexanol, which are branched versions of OOH, and diethylene glycol monoethyl ether.

Table 3.1 Toxicities of the solvents in Figure 3.8. The reported LD_{50} values are shown in each case. The categories for toxicity (see Table 2.1) are: Categories 1 and 2 = fatal, Category 3 = toxic, Category 4 = harmful, Category 5 = may be harmful.

Solvent	LD50 (dermal; rabbit)	LD50 (oral; rat)	Dermal Category	Oral Category
1,3-butanediol	N/A	22800 mg/kg	5	5
3-octanol	>5000 mg/kg	> 5000 mg/kg	5	5
Diethylene glycol	11890 mg/kg	12565 mg/kg	5	5
Diethylene glycol monoethyl ether	8500 mg/kg	7500 mg/kg	5	5
Dipropylene glycol	>5010 mg/kg	>5000 mg/kg	5	5
Ethanol	20000 mg/kg	7060 mg/kg	5	5
Methanol	15800 mg/kg	5628 mg/kg	5	5
Propylene glycol	20800 mg/kg	20000 mg/kg	5	5
Dipropylene glycol n-butyl ether	5340 mg/kg	1475 mg/kg	5	4
Isopropanol	12800 mg/kg	5000 mg/kg	5	4
1-undecanol	5000 mg/kg	3000 mg/kg	5	4
Diethylene glycol monobutyl ether	2700 mg/kg	4500 mg/kg	4	4
Isobutanol	2000 mg/kg	3100 mg/kg	4	4
1-octanol	>1000 mg/kg	>3200 mg/kg	3	4
2-ethyl-1-hexanol	1970 mg/kg	3730 mg/kg	3	4
Acetic acid	1112 mg/kg	3310 mg/kg	3	4
1-butanol	3400 mg/kg	790 mg/kg	4	3
1-Propanol	4049 mg/kg	1870 mg/kg	4	3
Ethylene glycol monobutyl ether	220 mg/kg	470 mg/kg	2	2

Finally, we conclude this Chapter with a discussion on solvent selection that includes aspects unrelated to dispersion efficiency. As discussed in Chapter 2, toxicity is a most important aspect, and Table 3.1 contains toxicity data on the 19 solvents corresponding to Figure 3.8, as documented in their respective safety data sheets. Note that the LD_{50} is the lethal dose required to kill half the test subjects. Ideally, the solvent should be classified as being in Category 5 for both dermal and oral exposure, which means it is harmful only if ingested or contacted in very large amounts. Table 3.1 shows that about half the solvents on this list are indeed in Category 5.

Another important factor is the solvent flash point. Solvents with a flash point lower than 60°C cannot be used for dispersants because a low flash point implies a high vapor pressure at room temperature. The solvent vapor would pose a risk of igniting during storage and application. Other considerations include the solvent viscosity, which should be low enough to enable the dispersant to be applied as a spray, and the solvent density, which should also be low to ensure that the dispersant remains at the interface instead of sinking into the water column. The viscosity and density were both sufficiently low for all the solvents in Table 3.1.

To sum up the most relevant characteristics, the ideal solvent should:

(1) solubilize the L and T surfactants,

(2) yield a good dispersion by the LEDT (i.e., high efficiency as per the BFT)

(3) have a low toxicity profile, as per Table 3.1, and

(4) have a flash point > 60°C.

Based on these criteria, the optimal solvents from our studies are listed in Table 3.2. Only two solvents, dEGEE and 3OOH, satisfied all four criteria. UOH is another potential solvent that satisfies three of the criteria, but has a slightly worse toxicity profile. Between dEGEE and 3OOH, the former has a higher flash point of 96°C, and therefore, would be our top candidate for use in L/T dispersants.

Table 3.2 Optimal solvents for use in dispersants (based on L and T surfactants). The top three solvents based on toxicity, flash point, and dispersant performance (Figure 3.2).

Solvent	Oral Category	Dermal Category	Flash Point °C	Performance	Optimal Choice
Diethylene glycol monoethyl ether	5	5	96	GOOD	1
3-octanol	5	5	66	GOOD	2
1-undecanol	4	5	121	GOOD	3

3.4 Conclusions

This work shows that the solvent base selection for a dispersant affects dispersion performance and efficiency. Furthermore, we demonstrated by systematic trends why certain solvents behave differently than others. First, through the use of HSPs, the solvent should have similar properties to that of the crude oil. Solvents with similar cohesive energies to the crude oil are more likely to produce good dispersion than if the solvent had very different cohesive energies. Secondly, the molecular structure of the solvent provides additional insight into the solvent behavior. We conclude that the ideal solvent for a dispersant should have limited hydrophilicity.

Dispersant formulation is a function of trade-offs. The ideal dispersant is not necessarily the optimal dispersant. Regulations are constantly changing as we are moving toward "greener", safer, and less toxic chemical dispersants. As a result, a dispersant's efficiency is not the sole factor for formulating a dispersant. However, we have shown through systematic approaches that it is possible to achieve both high dispersion efficiency and low toxicity. We recommend future dispersant formulators to seriously consider selecting those solvents.

4.1 Conclusions

The motivation for this work was to develop a dispersant made entirely of food-grade, non-toxic components. In this work, we used systematic approaches to further elucidate solvent behavior. The LEDT can be a valuable tool when formulating and testing future dispersants. The test is a quick and efficient way to screen dispersant performance saving valuable time compared to the BFT. With the help of HSPs, we found that solvents which exhibited good dispersion behavior formed a cluster suggesting that the solvent should have similar energies to the crude oil. After examining molecular structure, we believe that the ideal solvent for a dispersant should have limited hydrophilicity. Lastly, taking into account toxicity and other solvent parameters, optimal solvents for dispersant formulation exist. Finally, we recommend that careful consideration should be taken when selecting the solvent base for future dispersants. In light of these conclusions, we describe additional experiments to further investigate the solvent's mechanism in crude oil dispersion below.

4.2 Future Directions

Different types of crude oils. Crude oils are very complex mixtures. Investigating the solvent effect on other crude oils, specifically heavier oils can provide additional valuable insight. We believe that similar systematic trends we discussed above will exist with the other crude oil types. This is important because crude oil will continue to be a primary source of energy for many more years. The crude oil that is currently being extracted is becoming heavier, therefore, necessitating the need for a new generation of dispersant.

Time based observations. While performing the dispersant experiments explained throughout this thesis, we noticed very slight delays in the reduction of the interfacial tension and subsequent Marangoni effect. An interesting direction would be to further examine this phenomenon as it can provide insight into the mechanism and transport process of the solvent. Furthermore, it may provide predictive behavior and trends in determining dispersant efficiency.

Interfacial Tension Measurements. Interfacial tension tests on the oil-water interface using only a solvent may help further elucidate the emulsion stability of the dispersed oil droplet. Solvents with longer alkane chains are strongly anchored to the oil droplet[38] compared to solvents with short alkane chain tails. Having the solvent anchored to the oil droplet longer will help reduce the interfacial tension as well as improve emulsion stability.

Table A.1 Solvent abbreviation table. Alphabetical listing of all solvents used, and their respective abbreviations found throughout this manuscript.

Solvent	Abbrv.	Solvent	Abbrv.
1-Butanol	BOH	Ethanol	EOH
1-Octanol	OOH	Ethylene Glycol Monobutyl Ether	EGBE
1-Propanol	POH	Glycerol	GLY
1,3-Butanediol	BdOH	Isobutanol	iBOH
2-Ethyl-1-Hexanol	2E1H	Isopar M	ISOP M
3-Octanol	3OOH	Isopropanol	IPA
Acetic Acid	ACOOH	Methanol	MOH
Acetone	ACE	n-Dodecane	DODE
Diethylene Glycol	dEGLY	N-Methyl-2-pyrrolidone	NMP
Diethylene Glycol Monobutyl Ether	dEGBE	n-Octane	OCT
Diethylene Glycol Monoethyl Ether	dEGEE	N,N-dimethylformamide	DMF
Dimethylsulfoxide	DMSO	Propylene Glycol	PGLY
Dipropylene Glycol	dPGLY	1-undecanol	UOH
Dipropylene Glycol n-Butyl Ether	DPnB	Water	H2O

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Publication that is planning to be submitted after defense:

1. Fernandes, J. and Raghavan, S.R. The Impact of the Solvent Base for a Dispersant on the Efficiency of Crude Oil Dispersion. *Manuscript in preparation*

Conference presentation delivered prior to defense:

1. Fernandes, J., Agrawal, N. Omarova, M., John,V., and Raghavan, S.R., The Impact of the Solvent Base for a Dispersant on the Efficiency of Crude Oil Dispersion. Gulf of Mexico Oil Spill & Ecosystem Science Conference. February 7, 2018.