ABSTRACT

Title of Thesis: **Dispersing Crude Oils of Varying Viscosities Using a Food-Grade Dispersant**

Futoon Osama Aljirafi, Master of Science, 2020

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The mitigation of crude oil spills in the ocean is generally done using chemical dispersants, which convert the oil slick into small droplets. These dispersants are mixtures of surface-active molecules (surfactants) dissolved in a solvent. Questions regarding the toxicity of current commercial dispersants have prompted our lab to develop an eco-friendly alternative based on the food-grade surfactants, soy lecithin (L) and Tween 80 (T). In previous studies, the roles played by L/T and the solvent in a typical dispersant have been studied, but all those studies were done with a light crude oil, i.e., one with a low viscosity. In this thesis, we examine if our food-grade dispersant remains effective at dispersing heavier crude oils, i.e., crudes of higher viscosity. We study a light, a medium, and a heavy crude and compare their dispersion into seawater using a fixed L/T blend in various solvents. As expected, we find that the efficiency of dispersion is lower when the crude is more viscous. Moreover, in line with our previous findings, simply varying the solvent can alter the dispersion efficiency from poor to good. The solvents that promote dispersion can be identified systematically by using a plot of Hansen Solubility Parameters (HSPs). However, there do exist several key differences between the solvents most effective for the three crudes. Our analysis suggests that crude oil composition must be taken into account when optimizing the formulation of a dispersant.

Dispersing Crude Oils of Varying Viscosities Using a Food-Grade Dispersant

By

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Thesis submitted to the Faculty of the Graduate School of the
University of Maryland, College Park, in partial fulfillment
of the requirements for the degree of
Master of Science
2020

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Dedication

I dedicate this thesis to my family, for without you, I would not be where I am today.

To my mother and father: Thank you for your constant encouragement, guidance, and Love. Your support, knowledge, and foresight has helped me reach the stars, and for that I will be forever grateful. Without your sacrifices, wisdom, and sage advice, I would not be in the same position I am in today. Regardless of the circumstances I faced, you always supported me and gave the strength I needed to persevere. So again, I say thank you. No words can ever amount to the level of gratitude I feel for all that you have done for me.

To Layali: Thank you for your continuous support and great advice. Your "glass half full" outlook on life has been a great source of positivity.

To Abdullah: Thank you for always being there. Your jokes never ceased to make me laugh; and in times of great stress, I greatly appreciated that.

And to Khalid: Thank you for always putting a smile on my face.

Acknowledgements

First and foremost, I would like to acknowledge and sincerely thank my advisor, Dr. Srinivasa Raghavan. I would not only like to thank him for giving me the opportunity to work in his lab, but to work in a lab with such intelligent, open-minded, and curious people. His passion for research and the work we do in the lab is infectious. It motivated me to work harder in the lab and learn more than I ever thought I would. The knowledge he imparted on me is priceless, and I will forever be grateful for all the sage advice and support he has given me throughout the years; for because of him I have not only become a better researcher, but a better person. So, again, thank you very much Dr. Raghavan for all that you have done for me.

Second, I would like to thank my committee members: Dr. Mikhail Anisimov and Dr. Amy Karlsson. Their continuous support and guidance have made me a better student and researcher. I am extremely thankful for all their advice throughout the years and the time that they have taken to sit on my thesis committee.

In addition, I would like to acknowledge and sincerely thank my wonderful current and past lab members: So Hyun Ahn, Leah Borden, Hema Choudhary, Nikhil Subraveti, Faraz Burni, Sairam Ganesh, Medha Rath, Wenhao Xu, Dr. Niti Agrawal, Dr. Ben Thompson, and Jay Fernandes. If it were not for their intellect, understanding, and selflessness, I would not be where I am today. I would like to give a special thanks to Dr. Niti Agrawal, for her feedback, collaboration, and support in the lab; your help was invaluable. Thank you all for the great lab atmosphere and continuous support. You all made the lab such a great place to work.

Last, but not least, thank you to my family and to my friends. Your support throughout the years has meant the world. Without you, I would not be where I am today.

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Chapter 1: INTRODUCTION & OVERVIEW

The 2010 Deepwater Horizon oil spill was the biggest oil spill in the history of the United States. Approximately 60,000 barrels of oil/day were continuously pumped into the ocean over an 87 day period.[1,2] This amounted to ~ 5 million barrels (~ 210 million gallons) of Sweet Louisiana crude oil being released into the Gulf of Mexico.[1,3] Although this was the biggest oil spill to plague the Gulf, it was not the first. The Gulf has had to endure numerous large oil spills, such as the 1979 Ixtoc-I spill, in which over 3 million barrels of oil were spilled into the ocean.[4] Oil spills not only torment the shores of the United States, but other nations as well. Examples include the 1983 Castillo de Bellver oil spill off the coast of Cape Town, South Africa (over 50 million gallons of crude oil spilled) and the 2002 Prestige oil spill off the coast of Galicia, Spain (over 17 million gallons of oil released).[5,6]

In most of the aforementioned oil spills, chemical dispersants were used as the main method for oil-spill remediation, because they can be applied over large areas.[3,7,8] Although other remediation methods exist, such as in-situ oil burning (at the water surface) and mechanical recovery methods (e.g. using skimmers); they can be grossly inefficient, expensive, and impractical.[3,9,10] This is especially true when there is a very large area of spilled oil; hence the use of dispersants. In the Deepwater Horizon oil spill, over 2 million gallons of dispersants were sprayed over the Gulf of Mexico; with the two most extensively used dispersants being Corexit 9500A and Corexit 9527.[2,8] Dispersants are composed of surfactants (amphiphilic, surface-active agents) that are dissolved in a solvent (or a mixture

of solvents).[11] They are used for oil spill remediation due to the fact that they decrease the interfacial tension between sea water and crude oil, facilitating the breaking up of oil slicks into droplets and the dispersion of oil droplets into bodies of water (Figure 1.1).[12,11]

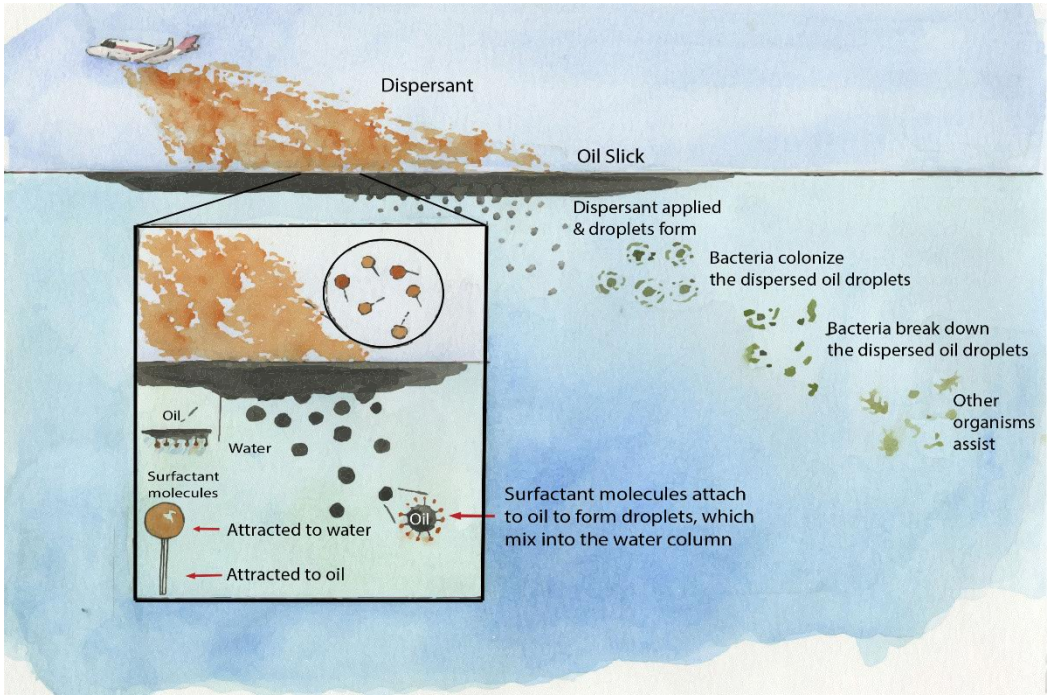

Figure 1.1. Airplanes and vessels are used to spray dispersants over large oil slicks. This causes the breakup of the oil slick into droplets, which are stabilized by the surfactant molecules in the dispersant. The oil droplets get dispersed through the water column (preventing the oil from coalescing back onto the surface). These oil droplets are then broken down by microorganisms in the water. From Ref. 3.

In recent years, the toxicity of dispersants like the Corexits to marine life has come into question.[13-15] The anionic surfactant, dioctyl sodium sulfosuccinate (DOSS), in Corexit has been one of the main causes of concern regarding toxicity.[16] This has motivated our group to formulate a new class of eco-friendly dispersants as an alternative to the Corexits. Our dispersant is composed of a *food-grade* surfactant blend, i.e., a mixture of

lecithin (L), a phospholipid extracted from soybeans that is used as an emulsifier in foods like chocolate, and Tween 80 (T), a non-ionic surfactant commonly used as an additive in ice cream (Figure 1.2).[17,18] Dispersants are usually compared for their effectiveness at dispersing crude oil into seawater under lab-scale conditions. In this regard, our L/T dispersant has been shown to be equally as effective as Corexit.[13,17,19]

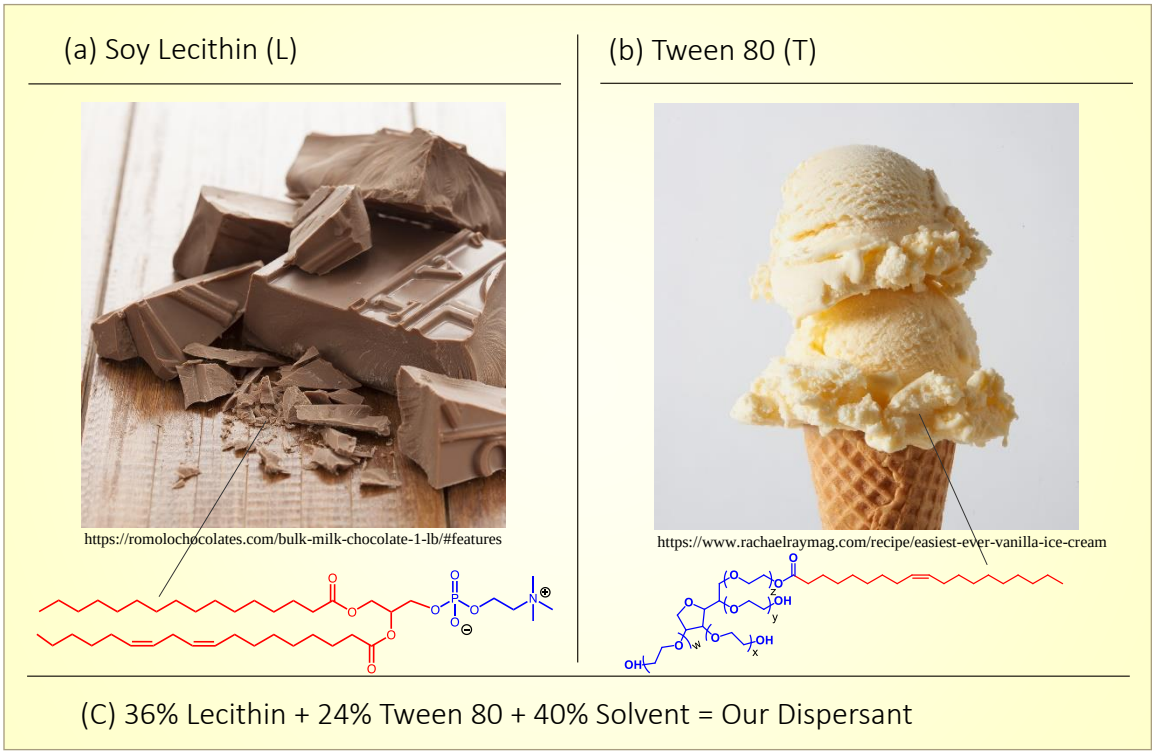

Figure 1.2. (a) Structure of soy lecithin and a photo of chocolate, in which soy lecithin is used as an emulsifier. (b) Structure of Tween 80 and a photo of ice-cream, in which Tween 80 is used as a stabilizer. (c) Recipe for the "food-grade" dispersant developed by our lab. The dispersant is composed of 36 wt% lecithin, 24 wt% Tween 80, and 40 wt% of a non-toxic solvent (such as ethanol). Thus, the overall composition of the dispersant is 60 wt% surfactant and 40 wt% solvent.

Initial studies on the L/T dispersant performed in our lab (Athas *et al.*[17]) focused on the synergistic interactions between L and T in regard to dispersion. Specifically, a

60/40 ratio of L/T was determined to be optimal for crude-oil dispersion. All tests were done with a 'Sweet Louisiana Crude' (SLC), which is a crude-oil of low viscosity obtained from the Macondo oil well in the Gulf of Mexico. Also, the solvent was fixed to be ethanol, a relatively non-toxic, "food-grade" solvent. Note that a dispersant must be a flowable liquid formulation so that it can be sprayed onto oil spills. We dissolved 60 wt% surfactant in ethanol — thus, the solvent was still a considerable portion (40 wt%) of the formulation (Figure 1.2). As mentioned, with the above composition of our L/T dispersant, it was highly effective at dispersing the SLC crude oil into seawater.[13,17,19]

Could the solvent itself have an effect on oil dispersion? This possibility had been largely ignored in all of the literature, but we conducted a follow-up study (Fernandes *et al*.[19]) to test for solvent effects (while keeping the 60/40 L/T blend as the surfactant in all cases). To our surprise, we found that the *solvent had an equally large effect as the surfactants in affecting oil dispersion*. With some solvents (e.g., propylene glycol), oil dispersion was very poor, whereas with other solvents (e.g., octanol and some glycol ethers), oil dispersion was excellent. To explain these results, we introduced an analysis based on Hansen Solubility Parameters (HSPs), which are measures of the intermolecular bonding in various solvents. On an HSP plot, the 'good solvents' (i.e., the ones that promoted good dispersion) clustered in one region of the plot. The insight from this analysis was that the solvent properties had to closely resemble the crude oil itself, while still allowing for solubilization of the surfactants.

This study begins where the previous studies left off. Previous studies were all done with the SLC, which is a 'light' crude oil. Crude oils are classified into *light*, *medium*, and *heavy*, based on their density (this is discussed further in Chapter 2). A light crude will not only have a low density but also a low viscosity; for example, the SLC is a thin, light brown liquid. In comparison, the medium and heavy crudes tend to be brown to dark brown in color and can have the consistency of syrup. Some of the questions that motivate the studies in this thesis are:

(1) What differences arise when dispersing crudes of different density/viscosity?

(2) Will L/T dispersants be effective at dispersing light, medium, and heavy crudes?

(3) Will the solvent effects seen in previous studies with the light crude (SLC) continue to exist when dispersing medium and heavy crudes?

To study the above aspects, we select three different crude oils: SLC (light), Harmony (medium), and IFO 380 (heavy).[20] We then make dispersants using the same L/T blend in 18 different solvents and use these to disperse these crudes into seawater. As might be expected from intuition, we find that it is harder to disperse the viscous crudes (i.e., the dispersion efficiency decreases in the order light > medium > heavy), but the L/T blend still shows promising results. With regard to solvent effects, our results corroborate those from our earlier study (Fernandes *et al*.) in that the solvent on its own greatly impacts the efficiency of dispersion. The HSP analysis to find the optimal solvents shows largely similar results for all three crudes. However, there were outliers in each set, which we attribute to differences in the chemical composition of the crudes. Together, our results

show that the dispersants chosen to combat an oil spill should take into consideration the composition and viscosity of the crude oil spilled.

Chapter 2: BACKGROUND

2.1 Crude Oil Properties

Crude oils are sourced from different places around the world. They vary in composition and physical properties. Some crudes are characterized as sweet (which means they have < 0.5% sulfur content), while others are characterized as sour (> 0.5% sulfur).[21] The composition of crude oil is quite complex; thus, an analysis scheme is required to analyze the crude in a systematic manner. The most utilized scheme breaks crude oil components into four categories: saturates, aromatics, resins, and asphaltenes (SARA).[22,23] The 'saturates' category consists of saturated hydrocarbons (linear, branched, and cyclic). Waxes commonly found in crude oils, such as n-paraffin wax, are classified as saturates. Aromatics are compounds that have aromatic rings. Both resins and asphaltenes are larger molecules that also have polar substituents. Resins consist of naphthenic aromatic hydrocarbons, and are miscible in heptane (or pentane).[24] Asphaltenes are the heaviest and most polar of all the components in crude oil. Unlike resins, they are not soluble in an excess of heptane (or pentane).[22] Moreover, asphaltenes have a substantive effect on crude oil viscosity and may also induce oil in water (o/w) or water in oil (w/o) emulsions.[25,26]

In classifying crudes, and petroleum products in general, many physical properties are taken into account. These properties include composition, viscosity, and density.[27] Light crude oils are mainly composed of saturates (more than 90%), with a small quantity of aromatics, and a negligible amount of resins (~1%) and asphaltenes.[26,28] Medium crudes are also mainly composed of saturates; however, they contain more of aromatics and resins

(with a very small amount of asphaltenes). Heavy crudes contain a smaller fraction of saturates, with the majority being aromatics, resins and asphaltenes.[28] The composition of these crudes has a direct effect on properties such as density and viscosity. The higher the asphaltene content, the higher the density and viscosity, and the heavier the crude oil.[29] This is due to the fact that in heavy crude oils (asphaltene content >10%), the asphaltenes self-associate and form nanoaggregates, which induce a higher viscosity (Figure 2.1). [26,30] While asphaltenes induce a high viscosity, they do not cause non-Newtonian behavior.[29,30] It is the wax (i.e. higher molecular weight paraffins) in the crudes that can lead to non-Newtonian behavior, i.e., to a viscosity that decreases with increasing shear-rate (termed 'shear-thinning'). This arises because, at low temperatures, waxes crystallize and flocculate, forming a wax crystal network.[31,32] With increasing shear, this network is disrupted, and when shear is stopped, the network is re-formed.

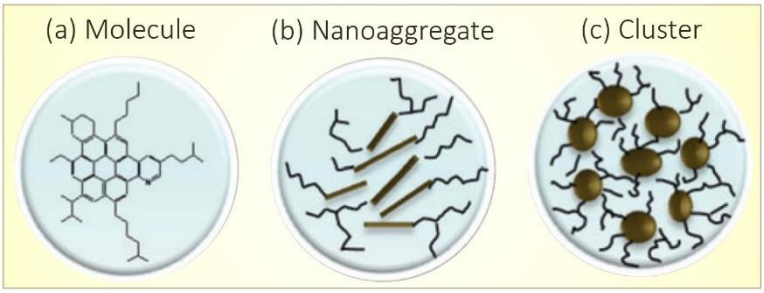

Figure 2.1. (a) Molecular structure of a typical asphaltene molecule. These molecules are ~1.5 nm in size and consist of a single fused aromatic ring with peripheral alkanes that may contain polar substituents (e.g., groups that contains Oxygen, Sulfur, or Nitrogen). (b) Asphaltenes can stack and form nanoaggregates that are ~ 2 nm in size. (c) Nanoaggregates can then form clusters that are ~5 nm in size. Adapted from Ref. 26.

In this study, three different crude oils: Sweet Louisiana (SLC), Harmony (HAR), and IFO 380 (IFO) were examined. Table 2.1 shows literature values for some important

physical properties of these crudes.[20] The selected crudes correspond to a light (SLC), a medium (HAR), and a heavy (IFO) crude. Additional physical properties of these crudes are discussed in Chapter 3.

Table 2.1. Literature values for crude oil physical properties. Data from Ref. 20.

Crude	Viscosity (mPa-s)	Density (g/cm^3)	Type
Sweet Louisiana	7	0.84	Light
Harmony	3588	0.942	Medium
IFO 380	10,490	0.966	Heavy

2.2 Dispersion of Crude Oil into Seawater Using a Chemical Dispersant

In the event of an oil spill, oil slicks tend to form on the surface of the water. From these slicks, small quantities of crude oil naturally disperse through the water column, due to the mechanical energy provided by waves or rough winds. Dispersants are used to facilitate and increase this dispersion (see Figure 1.1 in Chapter 1).[33] The active agents in dispersants are surfactants which migrate to the surface of the oil droplets (i.e., to the oil/water interface) due to their amphiphilic nature. This helps to stabilize the oil droplets and prevents them from re-coalescing to the surface of the water (i.e. preventing the oil slick from re-forming).[34,35] The surfactants also lower the oil/water interfacial tension, which helps facilitate the break up of the oil slick into droplets.[36] In addition to the effect of the surfactants, the mixing energy from the wind, waves, and ocean currents, helps to further break apart the oil slick (facilitating oil droplet formation).[34] After the oil droplets

form, they are carried under the surface of the water, where they disperse, and eventually get degraded by microorganisms present in the body of water. [33,35]

2.3 Emulsification vs. Dispersion

Dispersion and emulsification are two terms that are used quite interchangeably in this field of study.[37] When oil droplets are induced in the water column, they are said to be dispersed. In a similar vein, when oil and water are mixed in the presence of a surfactant, a stable suspension of oil droplets can be obtained, which is called an emulsion or more precisely an oil-in-water (O/W) emulsion. In both a dispersion and an emulsion, the oil droplets will be coated with the surfactant. Despite these similarities, we will draw a fine distinction between these two terms.

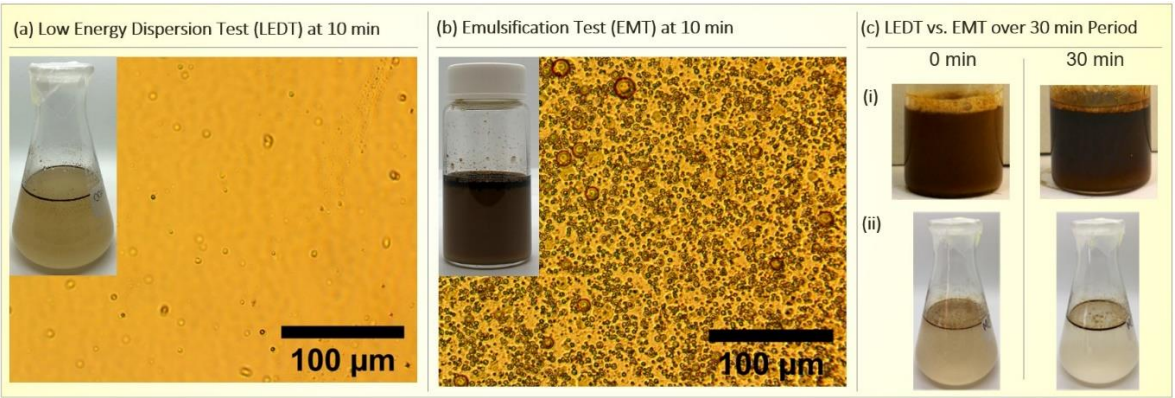

Figure 2.2. Result of a Low Energy Dispersion Test (LEDT) and an Emulsification Test (EMT) applied to oil/water (O/W) mixtures using the same dispersant (L/T in octanol). (a) In the LEDT, the dispersant to oil ratio (DOR) is 1:10 and the O:W ratio is 1:1000 (thin layer of oil). The flask is gently agitated by an orbital shaker. 10 min after agitation is stopped, the water column looks homogeneous and brown, and oil droplets are seen in the micrograph. (b) In this EMT, the O:W ratio is 1:10 (i.e., there is much more oil), and the DOR is 1:1 (i.e., there is much more surfactant). The sample is vigorously mixed. 10 min after agitation is stopped, the vial looks homogeneous and brown and the micrograph shows numerous oil droplets. (c) (i) Over a 30 min period the emulsion created in the EMT remains stable. (ii) Over a 30 min period the dispersion created in the LEDT is shown to be unstable. Many of the oil droplets aggregate and rise to the surface of the water after the 30 min period.

The distinction is brought out by two tests used in our lab: the Low Energy Dispersion Test (LEDT) and the Emulsification Test (EMT).[17,19] The key differences between the tests are in the oil (O) to water (W) ratio, the dispersant to oil ratio (DOR), and the extent of agitation. In the LEDT, a 1:1000 O:W ratio is used, which simulates a thin oil slick over a vast body of water. The dispersant is added at a DOR of 1:10. The sample is then exposed to mild agitation, similar to wave action in the ocean (by placing it on an orbital shaker at 250 rpm for 10 min). In the EMT, the O:W ratio is 1:10 (i.e., there is much more oil), and the DOR is 1:1 (i.e., there is much more dispersant). The sample is then vigorously agitated using a vortex mixer or sonicator. Figure 2.2 (a) and 2.2 (b) show an example of these two tests using the same dispersant (L/T in 1-octanol) and the same oil (SLC). In both cases, 10 min after agitation, the water column looks homogeneous and contains oil droplets. But the concentration of oil droplets is very low in the LEDT (because very little oil is used), whereas it is much higher in the EMT. This is reinforced by Figure 2.2 (c) where an EMT and a LEDT are performed and left to rest for a 30 min period. We clearly see that after the EMT, the water column remains a dark brown homogenous solution (stable emulsion) for the duration of the period (30 min). However, in the LEDT most of the oil droplets aggregate and rise to the surface after the 30 min period, showing the instability of the dispersion in comparison to the emulsion. In this thesis, the LEDT will be used to test dispersion of crude oil, because the conditions simulated in this test emulate the at-sea conditions in a more accurate manner.[19,20]

2.4 Dispersant Composition: Surfactant Selection

Dispersants are chemicals used during oil-spill cleanup to help break apart large oil slicks. They are composed of a surfactant blend dissolved in a solvent (or mixture of solvents).[12,36] The first step in formulating an effective dispersant is the selection of the surfactant(s). Surfactants are amphiphilic molecules with both hydrophilic and lipophilic parts.[34,35] Because of their amphiphilic nature, surfactant molecules reach their lowest free energy when they are positioned at the O/W interface.[36,38] Once at the interface, the surfactants decrease the O/W interfacial tension, thereby decreasing the energy required to form oil droplets.[11,12,35,36]

The hydrophilic-lipophilic balance (HLB) is a commonly used parameter that characterizes surfactant solubility in water and oil.[12,17,35,36] It ranges from 0 to 20, with low values denoting a surfactant that preferentially dissolves in the oil phase, while high values denote surfactants that predominantly dissolve in the aqueous phase.[36,38] The HLB has been used as an initial measure in selecting surfactants for use in a chemical dispersant, and values of the HLB between 9-11 are believed to be optimal in this regard.[12,17,36] When calculating the overall HLB of a surfactant blend, a weighted average of the HLB values of the individual surfactants is used.

The dispersant formulated in our lab is a blend of lecithin (L) and Tween 80 (T), as discussed earlier in Chapter 1 (see structures of L and T in Figure 2.3).[17] L is a zwitterionic phospholipid with two long tails (one *cis*-unsaturated) and a zwitterionic head, and has an HLB of 8. T is a more hydrophilic surfactant and has a higher HLB of 15. It is a non-ionic

surfactant with a large head containing oxyethylene groups and one *cis*-unsaturated tail. It is a non-ionic surfactant with a large head containing oxyethylene groups and one *cis*-unsaturated tail.[12,17] A 60:40 weight ratio of L:T was found to be ideal for dispersing oil in water, and the HLB of this blend was calculated to be 10.8 (within the 9-11 range).[17] At this weight ratio, L and T work synergistically to stabilize oil droplets. L molecules do not desorb from the oil droplets due to their two lipophilic tails, while the long heads of T impart steric repulsions when oil droplets come close.[17]

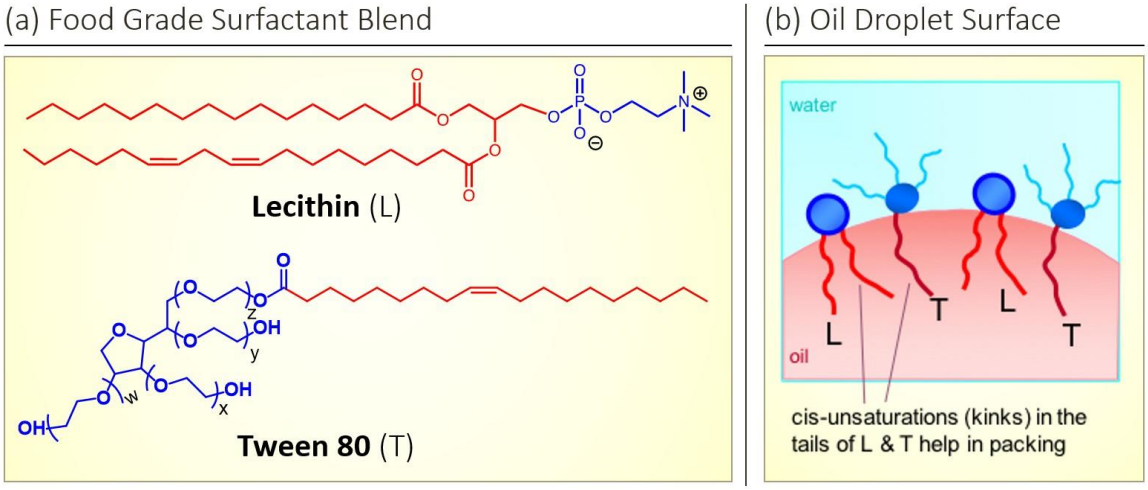

Figure 2.3. (a) Molecular structures of lecithin (L) and Tween 80 (T). The blue parts of the molecules represent the hydrophilic (polar) heads, while the red portions represent the lipophilic tails. (b) L and T are shown at the surface of an oil droplet. Their heads extend toward the water, while the tails are contained in the oil droplet. The two synergistically stabilize the oil droplets in an emulsion or dispersion. Adapted from Ref. 17.

2.5 Dispersant Composition: Solvent Selection

Dispersants are designed to be flowable liquid formulations so that they can be sprayed onto oil spills. It has been commonly believed that the surfactants are the active ingredients that help in dispersion, and the solvent in which the surfactants are dissolved is an inert carrier fluid. Thus, selection of solvent has been usually performed on the basis of

factors like flash point (volatility), viscosity, density, and nontoxicity. Recently, however, we discovered that the solvent could be an active component in the dispersant (not just a carrier for the surfactants), i.e., that it could directly affect oil-dispersion efficiency.[19] Some solvents could promote oil dispersion, while others could hinder it.

We explained our results by analyzing solvents in terms of their solubility parameters. The solubility parameter δ, first introduced by Hildebrand, is defined as[39]

$$\delta = \left(\frac{E}{V}\right)^{\frac{1}{2}} \tag{2.1}$$

where E is the energy of vaporization of the solvent and V is its molar volume. E is the energy required to overcome the intermolecular forces between solvent molecules, thus vaporizing the solvent.[39,40] While the Hildebrand solubility parameter represents the solvent by a single number, a more rigorous set of solvent parameters were developed by Hansen. The Hansen Solubility Parameters (HSPs) are a set of three parameters that together comprise the above δ. That is

$$\delta = (\delta_D^2 + \delta_P^2 + \delta_H^2)^{\frac{1}{2}} \tag{2.2}$$

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 utility of HSPs is that they quantify the intermolecular interactions between solvent molecules. Fluids that have similar HSPs tend to be miscible (i.e., they are chemically similar). We showed that the HSPs of solvents that promoted dispersion were close to the HSPs of the crude oil itself. This insight will be further extended in Chapter 3.

2.6 Dispersant Efficiency and its Determination

The fraction of an oil slick dispersed through the water column upon addition of a dispersant, is termed the dispersion efficiency. The Baffled Flask Test (BFT) has been the standard test to measure this quantity; not only does it yields consistent results, it has also been approved by the Environmental Protection Agency (EPA).[20,41,42] The BFT gets its name due to the fact that a baffled flask is used. Baffled flasks are conical flasks with built-in baffles (deep grooves long the sides) which substantially increase the mixing energy applied to a given sample (Figure 2.4). Samples placed in baffled flasks experience turbulent flow due to the presence of the baffles. To perform this test, 120 mL of synthetic seawater is added to the flask, followed by 100 µL of crude oil to the surface of the water. To the surface of the oil, 4 µL of dispersant is added, resulting in a 1:25 dispersant to oil ratio (DOR).[42] The sample is then placed on an orbital shaker, and agitated for 10 minutes at 250 rpm. The turbulent flow from the baffles ensures that the oil, dispersant, and seawater are thoroughly mixed, facilitating oil droplet formation. Following the agitation period, the sample is removed from the orbital shaker and allowed to rest for 10 min; after this, a 30 mL sample of the solution is withdrawn from the center of the flask and placed in a separatory funnel. Thereafter, an extraction is performed using dichloromethane (DCM), in order to extract the oil from the sample. A small quantity of the final extract is then transferred to a glass cuvette, and the oil concentration is measured by spectrometry.

Figure 2.4. Photograph of a 250 mL baffled flask that is used in the Baffled Flask Test (BFT) for determining the efficiency of oil-dispersion.

Chapter 3: Dispersing Viscous Crudes Using Lecithin/Tween 80 Blends in Various Solvents

3.1 Introduction

The overarching goal for all the work that has been done by our lab in this field, is to develop a "food-grade" dispersant that can improve upon the already existing dispersants that are used for oil spill remediation (i.e., Corexit). Our dispersant should be able to effectively promote the break-up of an oil slick into small, stable, oil droplets in the water column. As discussed in Chapter 1, the toxicity of dispersants has come into question by some scientists and the public on many occasions, especially after the Deep Water Horizon oil spill. So, our dispersant must be non-toxic to both humans (who would be helping to clean-up the oil spill as the dispersant is sprayed), in addition to marine animals (e.g., fish, plankton). Thus, we seek to develop a completely food-grade, nontoxic, environmentally benign dispersant as an ideal candidate for replacing the industry standard dispersants.

As previously discussed, we have developed a dispersant based on a *food-grade* surfactant blend, i.e., a mixture of lecithin (L) and Tween 80 (T) (see Figures 1.2 and 2.3), which are collectively dissolved in a solvent.[17] This L/T dispersant has been shown to be equally as effective as the industry-standard (i.e., Corexit) at dispersing crude-oil into seawater.[13,17,19] Previous studies have focused on the L/T ratio for optimal dispersion and also on the effect of the solvent itself. Not only is surfactant selection important for high dispersion efficiency, but solvent selection is important as well.[17,19] However, all studies thus far have been conducted with a light crude oil, viz. a Sweet Louisiana Crude (SLC).

The term ‘light’ as applied to crudes implies that the oil has a low density and viscosity (see Section 2.1). Indeed, the SLC is a thin, light brown liquid. In this Chapter, we will study the effectiveness of the L/T dispersant at dispersing medium and heavy crudes, which have higher density and viscosity. These crudes tend to be brown to dark brown in color and can have the consistency of syrup. We will thus compare results for three different crude oils: SLC (light), Harmony (medium), and IFO 380 (heavy).[20] Dispersants using the same L/T blend in 18 different solvents will be used to disperse these crudes into seawater. We will thus attempt to learn whether L/T dispersants are equally effective at dispersing all these crudes, or if there are significant differences when dispersing crudes of different density/viscosity? A second key question is whether the solvent effects seen in previous studies on L/T dispersants with the light crude (SLC) continue to exist when dispersing medium and heavy crudes?

With regard to previous studies that have examined dispersion of different crudes, a notable one is that of Holder *et al.*, in which the dispersion effectiveness of Corexit 9500 was reported for 23 different crude oils (varying in both density and viscosity).[20] The focus of that study was on the testing protocols used to determine dispersion efficiency.[20] Both crude oil viscosity and paraffin content had an effect on this efficiency, but the authors only tested one dispersant (Corexit 9500), and neither varied the surfactants nor the solvent in the dispersant. We know from previous work that both these components critically influence the effectiveness of the dispersant. Thus, many of the questions noted above have not been studied in the literature, and therefore, our study represents a novel contribution to the field of oil-spill mitigation.

3.2 Experimental

Materials. Soybean lecithin (95%) was purchased from Avanti Polar Lipids while the Tween 80 surfactant, i.e., poly(oxyethylene sorbitan monooleate), was from Sigma-Aldrich. The following solvents were purchased and studied: 1-propanol and isobutanol from J. T. Baker; 2-ethyl-1-hexanol and dipropylene glycol from TCI America; acetic acid and petroleum ether from Fisher Scientific; ethanol from Pharmco-Aaper; and isopropanol from VWR. All remaining solvents, including 1-butanol, 1-octanol, 3-octanol, 1,3-butanediol, acetone, diethylene glycol, diethylene glycol ethyl ether, diethylene glycol butyl ether, ethylene glycol butyl ether, methanol, propylene glycol, and undecanol were obtained from Sigma-Aldrich. Sweet Louisiana crude oil, Harmony crude oil, and IFO 380 crude oil were obtained through the Gulf of Mexico Research Initiative (GoMRI) program. Deionized (DI) water, purified by a reverse osmosis system, was used in our experiments. 32 g of sea salt (Instant Ocean from Spectrum Brands) was dissolved in 1 L of DI water to make synthetic seawater.

Dispersant Preparation. The dispersants were prepared in 1 dr (3.70 mL) vials, in which the total weight of the dispersant was 1 g. All the dispersants were composed of a 60:40 w/w surfactant:solvent ratio. The surfactant component (60% by weight) of the dispersant was comprised of a 60:40 w/w L/T ratio. Thus, the dispersant was always composed of 0.36 g L, 0.24 g T, and 0.4 g solvent. 18 dispersants were prepared using 18 distinct solvents. To accelerate the dissolution of the dispersant components, the vials were placed in an ultrasonic bath (i.e., sonicator) until a homogeneous solution was obtained. A Branson Bransonic 1510R-MT Ultrasonic Cleaner was used to create the ultrasonic bath.

Rheology. To perform the rheological experiments, an AR2000 stress-controlled rheometer (TA Instruments) was used. All the steady-shear experiments were conducted using a cone-and-plate geometry (2° cone). All the rheological experiments were conducted at constant temperature of 25 °C.

Sample Preparation and Shear Test. To observe the mechanism of dispersion, the three crude oils were tested without the addition of any dispersant. A series of mixing tests were conducted in which the samples were prepared as follows. First, 10 mL of synthetic seawater was added to a 20 mL vial. Thereafter, 1 g of crude oil was added on top of the sea water. Thus, the ratio of oil:seawater was 1:10 for all tests. The sample was then vortex mixed for 30 seconds at 3200 rpm. The vortex mixer used was a Vortex Genie-2 (Scientific Industries). The shear test was then performed as described in the next section.

Sample Preparation and Waxy Crystal Extraction from Crude Oil. To determine the total amount of wax and polar materials (e.g. asphaltenes) in a crude oil sample, the procedure proposed by Burger et al. was followed.[43-45] The only modifications made were to the filter paper used, a 0.1 µm Millipore filters; in addition, the experiment was scaled down. First, a 9.5 dr (35.12 mL) vial, with a stir rod, was weighed and tared. To this vial, 1 g of crude oil was added. The crude oil was dissolved using 7 g of petroleum ether and stirred for 30 mins. Following the dissolution of the crude, 22 mL of acetone was added to the vial. Thereafter, the vial was placed in a freezer, to cool to -20 °C for 24 hours. In addition to preparing the oil sample, an anti-solvent consisting of 3 parts acetone to 1 part

petroleum ether was also prepared and pre-cooled to -20 °C. A Buchner porcelain filtering funnel, blank glass fiber filters, and a vacuum flask were pre-cooled to -20 °C as well. To perform the experiment, the prepared oil sample was removed from the freezer, and allowed to come to room temperature for 2 hours. Thereafter, any solids found in the sample were extracted using the Buchner funnel and the 0.1 µm Millipore filter. The precipitate was then redissolved in Toluene and poured into a 100x15 mm glass petri dish to dry the solvent. The total amount of precipitate was weighed after the solvent fully evaporated.

Sample Preparation and Low-Energy Dispersion Test. The Low-energy dispersion test (LEDT) was used to qualitatively assess dispersion. To prepare the sample, the following steps were performed. First, 100 mL of synthetic seawater was added to a 125 mL conical flask. Second, 100 µL of crude oil (Sweet Louisiana, Harmony, or IFO 380) was pipetted on top of the seawater. Lastly, 10 µL of dispersant was pipetted on top of the oil. Therefore, the oil:seawater (O:W) ratio was 1:1000 and the dispersant:oil ratio (DOR) was 1:10 for all tests. The LEDT was then conducted as described in the next section. The Innova 4000 incubator shaker was the orbital shaker used for this set of experiments.

Dispersion Efficiency Measurement. To quantitatively assess dispersion efficiency, the EPA-approved baffled flask test (BFT) procedure was followed.[20,41,42] This experiment requires the use of a 150 mL conical baffled (trypsinizing) flask. This type of flask contains four extra deep baffles which are designed to provide superior agitation and mixing of solutions in comparison to non-baffled conical flasks.[46] The flasks used were purchased

from DWK Life Sciences Wheaton. The procedure for performing the experiment is as follows. First, 120 mL of synthetic sea water was added to the baffled flask. Subsequently, 100 µL of crude oil was pipetted onto the surface of sea water; at a 1:1200 oil:seawater ratio. Then, 4 µL of dispersant was pipetted on top of the oil at a 1:25 DOR. Two other DORs, 1:10 and 1:50, were also tested. The prepared sample is then mixed for 10 minutes on the Innova 4000 incubator (orbital shaker) at 250 rpm. Thereafter, the sample is removed from the shaker and left to rest for 10 minutes. Following this rest period, 30 mL of the sample was extracted from the middle of the water column into a 50 mL graduated cylinder. The extract was then deposited into a separatory funnel where dichloromethane (DCM) was used to extract the oil from the water. Lastly, a Varian Cary 50 UV-vis spectrophotometer was used to measure the amount of oil present in the DCM solution (in the 340-400 nm range).

3.3 Results and Discussion

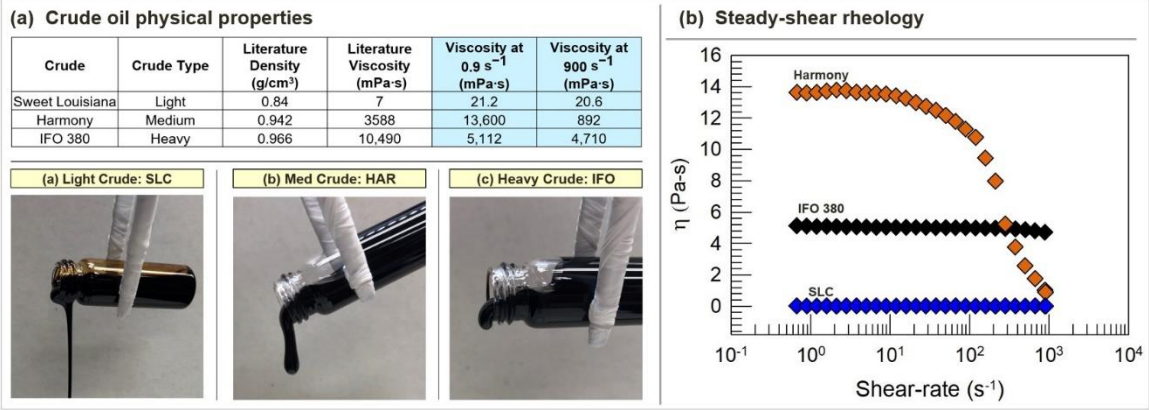

Figure 3.1. Physical Properties of the Crude Oils Studied. (a) Table showing the viscosity, density, and crude type. All literature values are from Holder *et al*. The viscosities at 0.9 and 900 s^{-1}, highlighted in the blue columns, are experimental data from (b). Photos of the three crudes are also shown. (b) Data from steady shear rheology for viscosity (η) vs. shear-rate at 25 °C. SLC and IFO show Newtonian behavior, while HAR exhibits shear-thinning behavior.

In this study, three different crude oils are tested: Sweet Louisiana Crude (SLC), Harmony (HAR), and IFO 380 (IFO). We classify SLC as a light crude, HAR as a medium crude, and IFO as a heavy crude.[20] This is evident from the viscosities reported for the three (Figure 3.1a): the viscosity η of HAR is 500× that of SLC and the η of IFO is 3× that of HAR. To verify these differences, a rheological study was performed to measure η as a function of shear-rate for the three crudes. Figure 3.1b shows this data, and a key finding is that HAR is a shear-thinning oil (i.e., its η decreases with shear-rate) whereas IFO and SLC exhibit Newtonian rheology (i.e., their η is constant across the range of shear-rates).

From the data, we note that it is HAR that has the highest η if we are comparing zero-shear viscosities (i.e., the η in the Newtonian plateau). On the other hand, at high shear

rates (e.g. 900 s^{-1}), IFO has an η that is 5× that of HAR, which itself is 44× that of SLC. Thus, the data indicate why HAR and IFO are classified as medium and heavy crudes, respectively, but they also indicate an important difference between the two (i.e., the shear-thinning nature of HAR) that is not captured from a single value of the viscosity. Photos of the three oils being poured out of vials are included in Figure 3.1. We note that the SLC is a thin fluid that is easily pourable. The HAR indeed flows more easily out of the vial than the IFO. The pourability of HAR reflects that its viscosity decreases under flow. In contrast, IFO has the consistency of thick syrup or molten tar and flows slowly out of the vial.

The question becomes, *why is HAR shear-thinning?* What components present in HAR give it this property? The rheology of crudes depend on many factors such as temperature[47] and composition.[29,48] A high Newtonian viscosity is generally linked to asphaltenes, which are large molecules with a fused aromatic ring and peripheral alkanes that branch off this ring.[29] Asphaltenes self-associate and form nanoaggregates, which impart a higher viscosity to the sample.[27,31] On the other hand, non-Newtonian (shear-thinning) behavior in crudes is generally linked to the presence of waxes.[29,48] The waxes generally have "platelet" structures that overlap and interlock to create networks. Shear-thinning arises because these wax networks are broken into smaller structures by shear, which results in a decrease in viscosity.[32] When shear is stopped, the wax network is re-formed and the viscosity is regained. Thus, based on the rheological results, we conclude that the HAR crude contains a substantial fraction of wax whereas the IFO crude contains a large proportion of asphaltenes.

Crude	% Organic Precipitate	Type
Sweet Louisiana	2.5	Light
Harmony	21.1	Medium
IFO 380	20.2	Heavy

Figure 3.2. Results of extraction experiments to determine the total precipitates (which include waxes and asphaltenes) in the three crudes. The precipitate % in each crude is shown in the table. Photos of samples in the Petri dishes before drying in (i) and after drying in (ii). Note that, after drying, the precipitates are solid and stuck to the Petri dishes in all cases.

To verify the presence of waxes/asphaltenes, we used a protocol developed by Burger *et al*. on all three crudes to determine the total fraction of organic precipitates in them.[43,45] These precipitates are the total solids left behind that cannot be solubilized or volatilized during the specified extraction procedure (see details in the Experimental Section), and are expected to include both waxes and asphaltenes. Figure 3.2 shows, as expected, that there are negligible precipitates (2.5%) in the SLC, but much more in the HAR (21%) and IFO (20%). It is likely that the precipitates in HAR are waxes, while those in IFO are asphaltenes, consistent with the results of Figure 3.1.

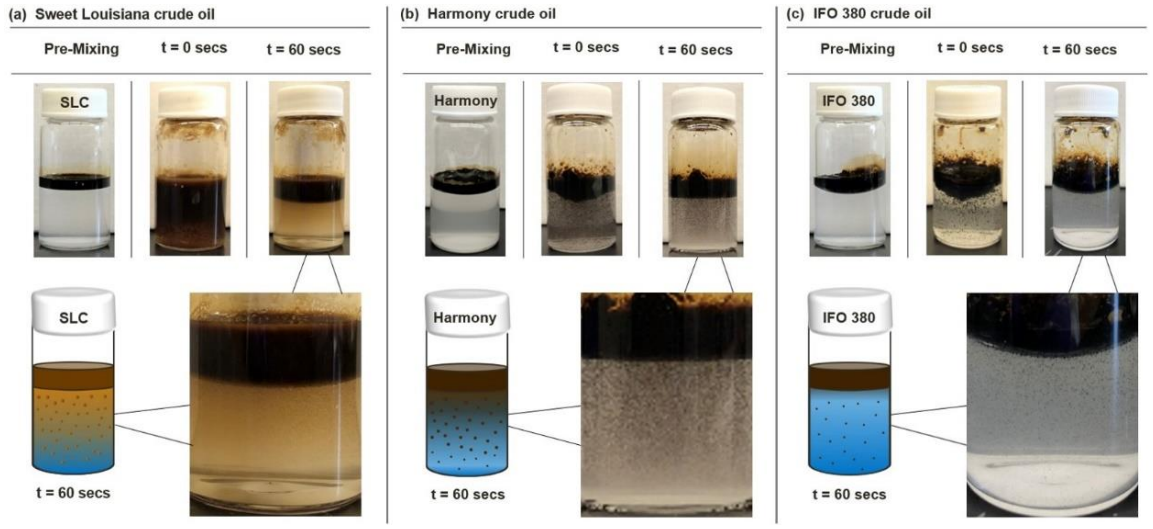

Figure 3.3. Dispersion of three crude oils in seawater using no dispersant. (a) SLC; (b) HAR; (c) IFO. Prior to vortex mixing, the oil forms a distinct layer over the seawater. Photos are then shown as soon as mixing is stopped (t = 0), and at t = 60 s afterwards. A close-up of the latter and a schematic are also included. (a) With the SLC, numerous small oil droplets are present in the water, both at t = 0 and 60 s. (b) With the HAR, there are fewer oil droplets in the water and the droplets are mostly large. (c) With the IFO, there are very few oil droplets in the water, as most of the oil has returned to the surface.

Before studying the dispersion of crude oils by our food-grade dispersant, we first examine the dispersion of these oils into seawater in the *absence* of any dispersant. For this, 1 g of the oil was added to 10 mL of seawater, with the oil initially forming a distinct layer over the water. Then the vial was vortex-mixed for 30 seconds. Once mixing was stopped at t = 0, photos of the vial were then taken at regular intervals. The results (Figure 3.3) show that dispersing the medium and heavy crudes is much more challenging than dispersing the light one. The challenges arise from the fluid mechanics of the problem, i.e., when the oil is of higher viscosity, more energy is required to break the liquid into small droplets.

In the case of the light oil (SLC) (Figure 3.3a), numerous oil droplets are found in the water at $t = 0$, with the entire vial appearing brown. Even at $t = 60$ s, the water appears brown and individual droplets are difficult to resolve by eye, indicating that they are small. These droplets will still coalesce and rise to the surface within minutes in the absence of a dispersant. In the case of the medium oil (HAR) (Figure 3.3b), the vial at $t = 0$ contains significant black specks of oil within the water, and such specks can also be seen at $t = 60$ s. The heavy oil (IFO) is the hardest to disperse: even at $t = 0$, there is hardly any oil in the water, and there is even less at $t = 60$ s. Note that the dispersion of HAR is better than that of the IFO, even though the zero-shear viscosity is twice as high for the former. The improved dispersion with HAR is probably because of its shear-thinning nature. The applied shear (vigorous agitation) decreased the viscosity of the HAR, thus facilitating its break-up into small oil droplets. Overall, Figure 3.3 highlights the difficulty from a fluid-mechanics perspective of dispersing the oil.

We proceed to test dispersion of the crude oils into seawater in the presence of the dispersant. For this, the dispersant contained soy lecithin (L) and Tween 80 (T) in a 60:40 weight ratio. 18 different solvents, that are known to solubilize both L and T were selected, and thus 18 different dispersants were made. The same surfactant:solvent ratio of 60:40 w/w was maintained in all cases. The test used to discriminate regarding the quality of dispersion was the low-energy dispersion test (LEDT), which was introduced in our previous work.[19] The LEDT is a simple and rapid test, and it has been shown to correlate well with the industry-standard baffled flask test (BFT), which is more tedious, time-consuming, and labor-intensive.[19]

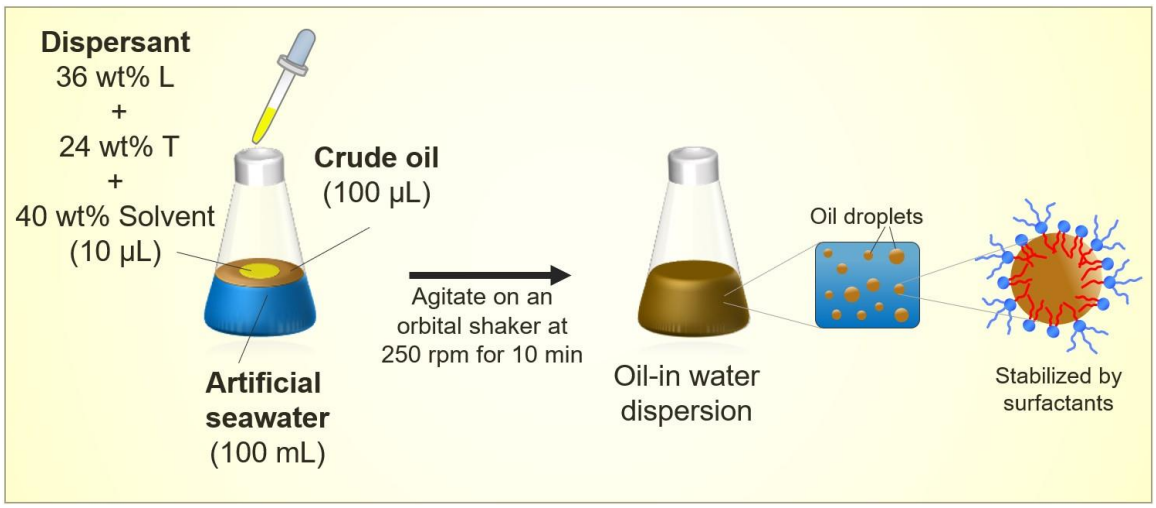

Figure 3.4. Schematic of the low energy dispersion test (LEDT). Crude oil is added to sea water at a ratio of 1:1000, then the dispersant is added at a dispersant:oil ratio (DOR) of 1:10. The sample is then placed in an orbital shaker at 250 rpm for 10 min, then removed and allowed to rest for 30 min, before a photo is captured. The schematic shows oil droplets stabilized in the water column by the surfactants in the dispersant. The hydrophilic parts of the surfactants (in blue) are pointing to the water side while the hydrophobic parts (in red) are directed into the oil side.

Figure 3.4 shows a schematic of the LEDT. In brief, the procedure involves making a sample of (seawater+oil+dispersant) in a conical flask, which is then placed on an orbital shaker for 10 min at 250 rpm (which simulates agitation of an oil slick by gentle wave motion). The sample is then removed and allowed to rest for 30 min, before a photo is captured. A qualitative (visual) assessment is made regarding the dispersion of the crude oil in the water column. The results from LEDTs performed using the medium crude (HAR) and the heavy crude (IFO) are shown in Figure 3.5. The results for the light crude (SLC), which were published in our earlier study, can be found in Figure B.1 in the appendix.

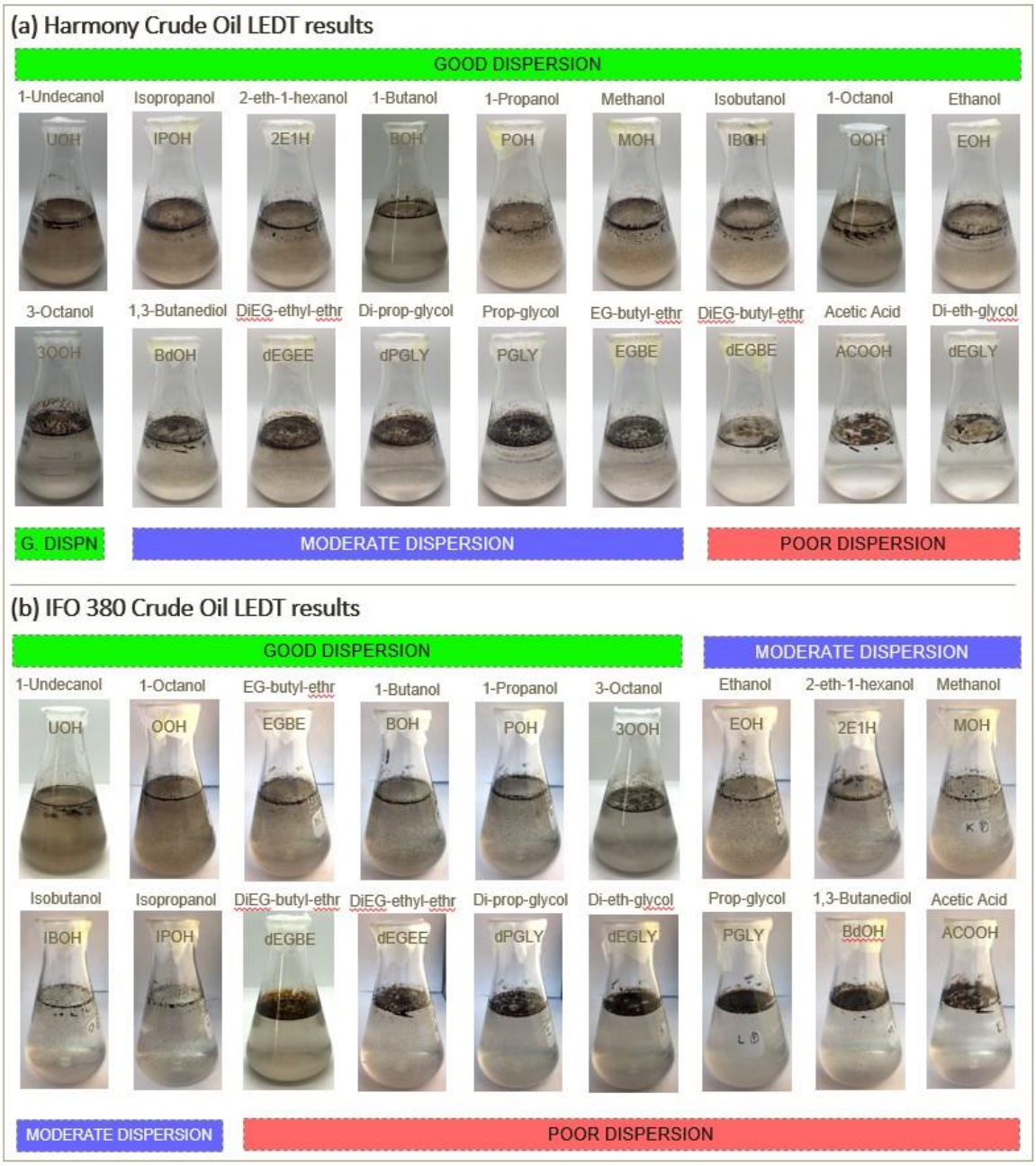

Figure 3.5. LEDT results showing the dispersion of two crude oils, (a) HAR and (b) IFO, in seawater using L/T dispersants. All the dispersants were made using the same L/T blend, but varying the solvent. Photos for each sample are labeled with both the full name and the abbreviation for the solvent. The results are arranged in order from left to right (top row, then bottom row) from best to worst dispersion. Three categories are used to classify the results: good, moderate, and poor. A 'good' dispersion corresponds to a brown/black water column, implying numerous oil droplets in it. A 'poor' dispersion yields a colorless water column, with much of the oil droplets having coalesced and risen above the water.

Figure 3.5 shows wide differences in dispersion quality among the solvents. Thus, the choice of solvent makes a huge difference to the quality of dispersion in the cases of both HAR and IFO. In this regard, we corroborate the findings from our earlier study with SLC,[19] where we had first reported the large effect of solvents on dispersion efficiency (see Figure B.1). We conclude that solvent effects arise regardless of whether the crude oil is light, medium, or heavy. Clearly, solvents do more than simply carry the surfactants to the oil slick. Solvents act synergistically with the surfactants to help disperse and stabilize oil droplets in the water column. It is important to note, however, that a solvent on its own cannot disperse crude oil. It is only in the presence of surfactants (L/T in this case) that solvent effects are seen.

We have arranged the samples in Figure 3.5 in order from best to worst extent of dispersion. Moreover, three categories ("*good*", "*moderate*", and "*poor*" dispersion) are used to classify the results, as in our previous study.[19] The categorization was done as follows. The "*good*" category was allocated to samples that had a brown/black water-column, indicating a high concentration of oil droplets dispersed through the water. As these photos were taken 30 min after agitation was stopped, the oil droplets are stable and being deterred from coalescence for at least 30 min. On the opposite end of the spectrum, the "*poor"* category is assigned to samples with a clear (i.e., colorless) water column, which means there are negligible oil droplets in it. In addition, the surface of the water is covered with oil (resembling the sample before agitation), which shows that most of the oil has coalesced and reformed the oil slick. This is in stark contrast to the "good" samples, in which oil is mostly absent from the surface of the water. Samples categorized as

"*moderate*" dispersion fall between "good" and "poor" dispersion. While placement of samples in this category is more subjective, it is still a necessary category to have, because not all characteristics needed to be labelled as "good" or "poor" are present. In the case of the experiments performed with the HAR oil, all flasks which had some oil in the water column but had no coalescence of oil at the surface of the water were placed in the moderate category.

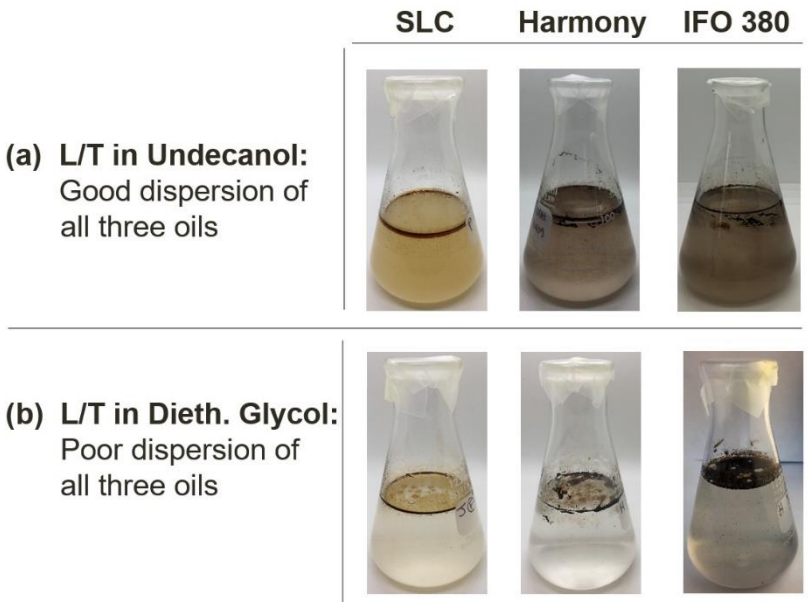

Figure 3.6. Examples of LEDT flasks showing the same categorization results for the same solvent. (a) Using *undecanol* as a solvent resulted in "good" dispersion for all three crude oils. (b) Using *diethylene glycol* as a solvent resulted in "poor" dispersion for all three crude oils.

In comparing the LEDTs for the three crudes (SLC, HAR, IFO) several conclusions can be reached. First, we find that there are some solvents like *undecanol* and *octanol* that result in "*good*" dispersion for all three crudes. Photos of undecanol samples with all three crudes are shown in Figure 3.6a. We rated undecanol as the best solvent for HAR and IFO while octanol was slightly better for SLC. Interestingly, both these are long-chain alcohols,

but a further discussion as to why these are the best solvents is given under Figure 3.9. Conversely, other solvents like *diethylene glycol* and *acetic acid* resulted in "*poor*" dispersion for all three crudes. Results for the former are shown in Figure 3.6b Those two solvents impaired the dispersant's ability to perform well, regardless of the crude. The stark contrast between the photos in Figure 3.6a and 3.6b show the importance of choosing the solvent judiciously.

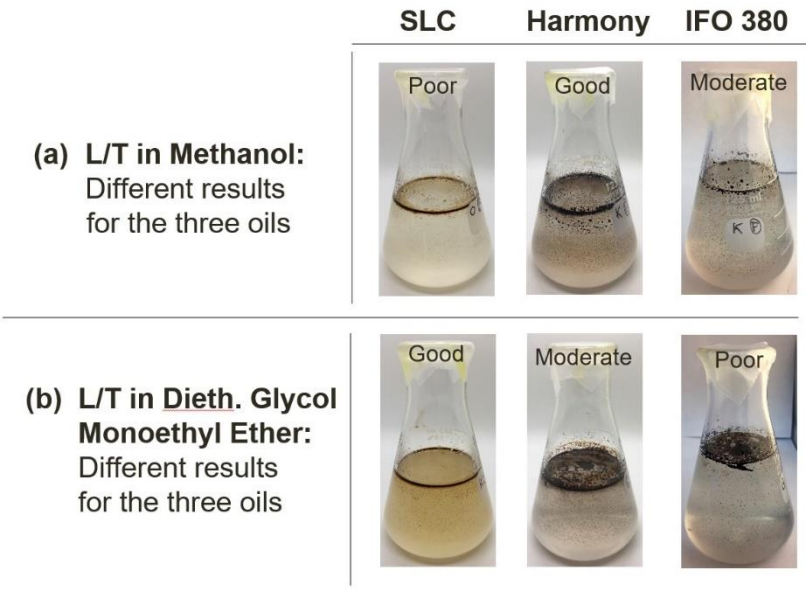

Figure 3.7. Examples of LEDT flasks showing different categorization results for the same solvent. (a) Methanol; and (b) Diethylene glycol monoethyl ether.

On the other hand, as can be seen in Figure 3.7, there are solvents such as *methanol* and *diethylene glycol monoethyl ether*, which yielded different results for each of the three crudes. This is not simply an effect of viscosity, as can be seen from the methanol case, where the more viscous HAR gives a better result than the SLC. Previously, we had discussed that HAR and IFO may contain substantial amounts of waxes and asphaltenes. One observation with HAR is that all the alcohols, regardless of chain length (from

methanol to undecanol) performed well. We therefore surmise that there are polar components in HAR that are alcohol-soluble or have a strong affinity to alcohols. This may explain why methanol is an outlier for HAR.

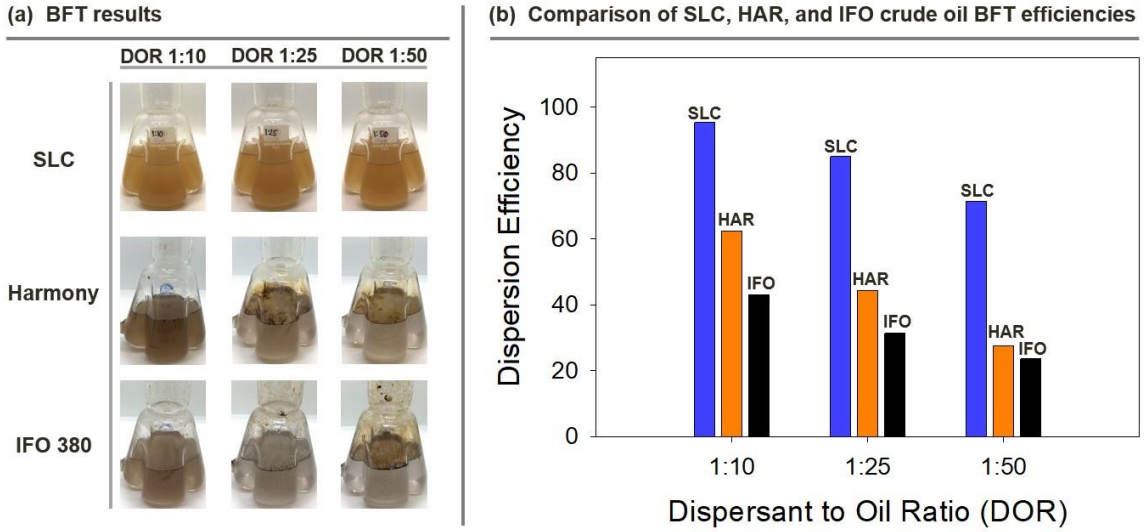

Figure 3.8. Comparison of Baffled Flask Test (BFT) results on samples made with different crudes and different dispersant-to-oil ratios (DORs). (a) Photos of baffled flasks with dispersed oil at different DORs. In all cases, the same L/T ratio and total surfactant concentration are used; the solvent is octanol for SLC and undecanol for HAR and IFO. (b) BFT efficiencies corresponding to the samples in (a).

We now turn to the Baffled Flask Test (BFT) to validate the LEDT results for the three oils. For this, we made L/T dispersants in the best solvents for the three oils as judged by the LEDTs (undecanol for HAR and IFO, octanol for SLC) and performed the BFTs at three different DORs (1:10, 1:25, 1:50). The results (Figure 3.8b) confirm that the more viscous oils are harder to disperse, i.e., the BFT efficiencies follow the trend of SLC > HAR > IFO, or light > medium > heavy crude. These trends are corroborated by the photos of the baffled flasks in Figure 3.8a as well as of the regular flasks in Figure 3.6a.

The water columns for the light crude (SLC) have the highest concentration of oil droplets, which is reflected by the uniform color of the water. The oil droplets are likely to be small (microscale) in the case of SLC. In the case of HAR and IFO, the water column seems to be stratified (layered) in some flasks, indicating that droplets have begun to coalesce and rise to the surface. Also, oil droplets can be resolved by the eye in some flasks, which means they are quite large (millimeter scale). The results at different DORs also show, as expected, that as the DOR decreases (less dispersant is used), the concentration of oil in the water column decreases and the BFT efficiency goes down.

Note that the BFT efficiencies, on the whole, are excellent for SLC (ranging from 95% at 1:10 down to 71% at 1:50). For the viscous oils, the BFT efficiencies are moderate for HAR (from 62% at 1:10 to 28% at 1:50) and quite low for IFO (43% at 1:10 to 24% at 1:50). These efficiency values are comparable to the values reported by Holder et al. for the SLC but are better than the reported values for the two heavy crude oils, when using Corexit (86% for SLC, 20% for HAR, 27% for IFO, all at 1:25 DOR). Our experimental efficiency values, at 1:25 DOR, are 85% for SLC, 44% for HAR, 31% for IFO. Thus, a broad conclusion is that the L/T dispersant is very efficient at dispersing crude oils, provided the solvent is chosen wisely.

Why are undecanol and octanol the best solvents for L/T dispersants? Conversely, why is diethylene glycol a bad solvent? Is there a rational explanation for these findings? Indeed, the results can be broadly explained based on Hansen Solubility Parameters (HSPs), which was a key insight from our previous study.[19] As discussed in Section 2.5,

there are three HSPs to characterize a solvent.[39] These parameters quantify the following three types of intermolecular interactions between solvent molecules: dispersion (D) interactions (δ_D), polar (P) interactions (δ_P), and hydrogen-bonding (H) interactions (δ_H).

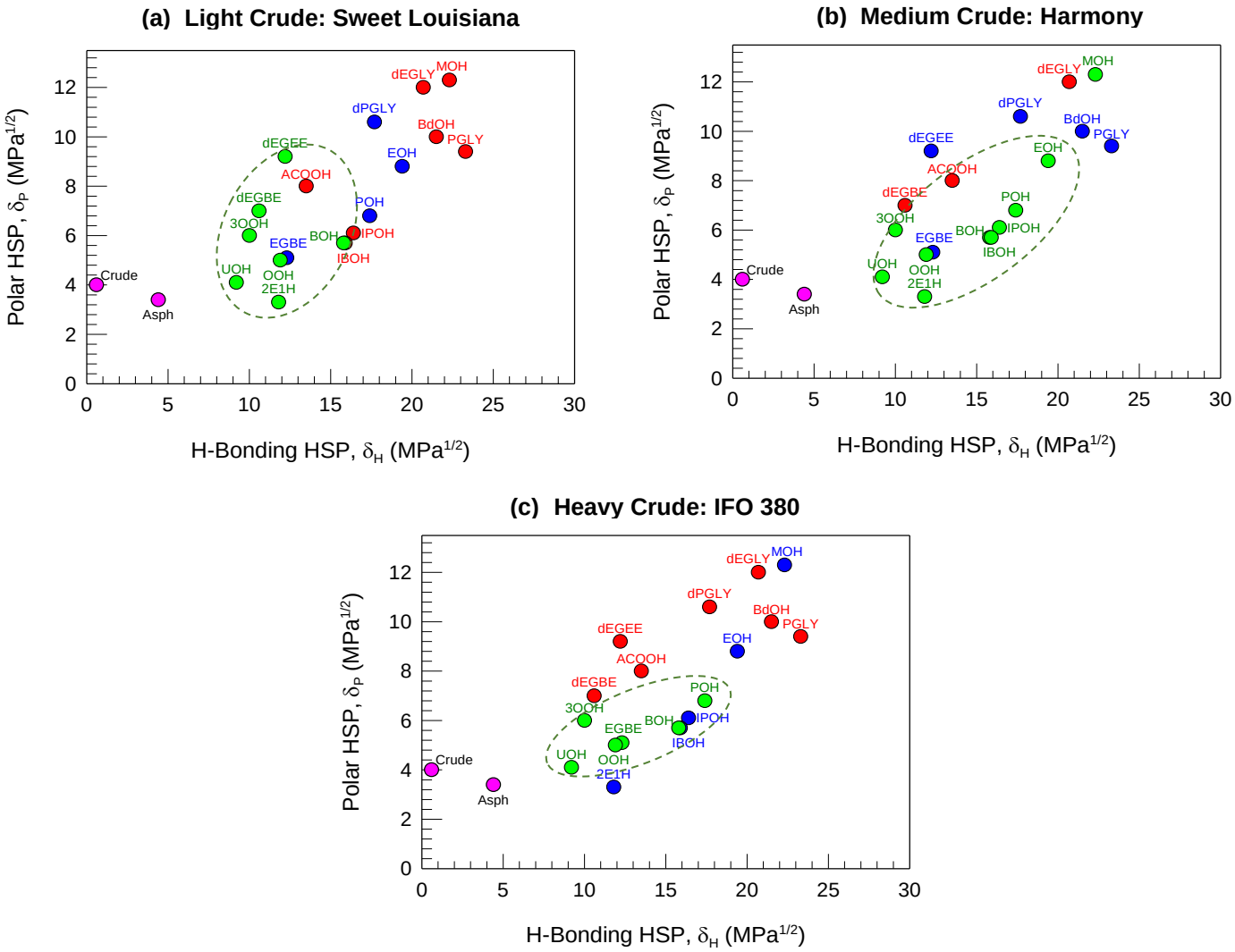

Figure 3.9. 2-D Hansen Solubility Parameter plots denoting LEDT results for all three crude oils. 18 solvents, that are proven to solubilize the L/T surfactant blend, are plotted as individual points on the above Hansen plots. The x-axis is the Hansen Solubility Parameter (HSP) for H-bonding interactions δ_H and the y-axis is the HSP for polar interactions δ_P. The points are color coded based off the results obtained from the LEDT sets performed for each of the three crude oils ((a) SLC, (b) HAR, (c) IFO). Green denotes "good" dispersion, blue is "moderate" dispersion, and red is "poor" dispersion. All the "good" results are encircled by a dashed green oval.

The sum of the squares of the three HSPs gives the square of the Hildebrand (total) solubility parameter.[39] Here, HSPs will be used to deduce the relationship between the solvents used in our dispersants and the efficiency of dispersion. This will be done using the plots shown in Figure 3.9 for the three crude oils studied.

The plots in Figure 3.9 are two-dimensional HSP plots in which δ_H is along the x-axis and δ_P along the y-axis. Because the solvents all have similar δ_D values, this third HSP is omitted from the analysis.[19] Each solvent corresponds to a point on the plot, and the results are color-coded based on the results from the LEDTs (Figures 3.5 and B1). The 18 solvents on these plots all solubilize the L/T surfactant blend; that is, they are hydrophilic enough to solubilize the T and hydrophobic enough to solubilize the L.[17,19] On the plots, we have also marked two points (shown in pink) corresponding to crude oil and its asphaltene component. The HSPs for crude oil (denoted as 'Crude' on the plot, with δ_H = 0.6 and δ_P = 4) are those for a light crude-oil (North sea crude).[19,49] For asphaltene (denoted as Asph, with δ_H = 4.4 and δ_P = 3.4), the HSP values are for the asphaltenes extracted from a Venezuelan bitumen.[49] Note that the higher δ_H for asphaltene implies stronger hydrogen-bonding interactions than for the crude oil. For comparison, a completely non-polar solvent like dodecane would fall at the origin of these plots (0, 0), while water (δ_H = 42.3, δ_P = 16.0) would fall at the diametrically opposite far-end from the origin (outside of the scales shown).[19,39]

The color-coding of the points in the HSP plots follows the same scheme as for the LEDT results in Figure 3.5, i.e., green denotes "*good*" dispersion, blue is "*moderate*"

dispersion, and red denotes "*poor*" dispersion. For the three crudes, the HSP plots show that the solvents corresponding to "*good*" dispersion remain the same, for the most part. In each plot, the "good" dispersion points are clustered near each other and are encircled by a dashed green oval. These ovals are situated in the same area of each plot (near the bottom corner). Thus, the pattern noted in Fernandes *et al*. for the SLC is seen for the HAR and the IFO as well.[19] The one major outlier is methanol (MOH), which gives good dispersion for the HAR even though it lies far from the green oval. The reasons for this were discussed under Figure 3.7.

What sets apart the best solvents for L/T dispersants from the rest of the solvents? That is, why are solvents like undecanol (UOH) and octanol (OOH) "good" solvents for all three crudes? From Figure 3.9, we note that these solvents lie close to the points for the crude-oil (Crude) and asphaltene (Asph). This finding implies that solvents like UOH and OOH have a strong chemical affinity to the crude oil and its components. Indeed, the vector distance between any two points on an HSP plot is a measure of the chemical affinity between the two — that is, the smaller this distance, the higher the affinity.[39] Conversely, solvents like diethylene glycol (dEGLY) are very far from the Crude/Asph points, indicating that they are chemically very dissimilar and therefore have weak affinity. The relation between solvent affinity for the crude and oil dispersion was hypothesized in our previous study. Such a solvent is more likely to persist in the oil slick, allowing the dispersant to be more effective rather than being carried away into the water column.[19]

Overall, our results suggest the following thumb rule or heuristic: *when it comes to selecting a solvent for L/T or other dispersants, the solvent should be as chemically similar*

to the crude as possible, while also solubilizing the surfactants. In short, "like seeks like" is the heuristic. Note that we cannot simply choose a nonpolar oil as the solvent because it would be unable to solubilize the surfactant blend; so that is why the caveat regarding solubility is added at the end of the heuristic. Another heuristic, based on Figure 3.9, is that if the crude oil of interest has a higher fraction of polar components, it could be beneficial to choose a solvent that has some polar components (hydrophilicity) itself. This point underscores the need to know the composition of the crude itself. By knowing the crude composition, dispersants can be optimized for that crude.

3.4 Conclusions

The work discussed in this chapter shows that both crude oil viscosity and composition influence the dispersion efficiency of a dispersant. We corroborated the conclusions made in previous work, that the solvent has an active role in the dispersion efficiency of a dispersant. We began our discussion by analyzing the results obtained from our "waxy crystal extraction" experiments, which highlighted the fact that the Harmony and IFO 380 crudes contain relatively large amounts of wax and polar material (e.g., asphaltenes); two components that can affect dispersion and emulsion stability. Following those set of experiments, we discussed a set of shear tests which highlighted the difficulty of dispersing crude oil from a fluid-mechanics perspective. We then discussed the results obtained from all three sets of LEDTs. The results from this systematic study showed that, overall, the solvents that yielded "good" dispersion remained for the most part unchanged across all three crude oils. However, it did highlight the fact that crude oil viscosity and composition had influenced the dispersion, since the three sets of LEDT

results were not identical. The results from two of our best solvents were then quantified by BFTs performed at three different dispersant-to-oil ratios (DORs), to deduce whether a trend existed between crude oil viscosity and dispersion efficiency (and to validate the LEDT). The results showed that there was an inverse relationship between crude oil viscosity and dispersion efficiency (the higher the crude viscosity, the lower the efficiency). Finally, HSPs were used to reinforce the principle that the solvent chosen must have an affinity for the crude oil.

Overall, although some solvents yield good dispersion regardless of the crude oil being studied, crude oil viscosity and composition remain important factors that must be considered when choosing a dispersant for oil spill remediation. If the oil that is spilled is known to have a higher number of polar components, it may be wise to use a dispersant formulated with a solvent that is a bit more hydrophilic. Having one size-fit-all dispersant may not be the best solution, since crude compositions can be quite different.

Chapter 4: CONCLUSIONS & RECOMMENDATIONS

4.1 Conclusions

The motivation for this work was to gain insight into the effects of using crude oils of varying viscosity on dispersion efficiency. Moreover, we wanted to deduce whether the use of heavier crude oils caused a change in the solvent effects determined in our previous work for the light crude oil (SLC). In this work, we studied the physical properties and compositions of the crude oils on hand, to gain insight into the effects they may have on dispersion efficiency. Following those studies, we investigated the mechanism of dispersion from a fluid-mechanics perspective, showing the difficulty of dispersing crude oil. We proceeded by systematically testing different dispersants (each containing a different solvent), via the LEDT, to determine whether solvent behavior changed from one crude to another. The LEDT was used because it allowed for the quick, and accurate screening of dispersant performance. The results obtained from the LEDTs were further analyzed using HSPs. The HSP analysis revealed the fact that the cluster of "good" solvents found for the SLC, remained for the most part the same for all three crude oils (with the presence of some outliers). This showed that there is a relatively universal "good" solvent region, when it comes to choosing solvents for a dispersant. Thus, our final recommendation would be to formulate dispersants with consideration for the type of crude oil spilled; since crude oils have unique compositions and viscosities, and in turn will react to dispersants differently. Considering the aforementioned conclusions, further investigation into the mechanism of crude oil dispersion is described below.

4.2 Future Directions

Different types of crude oils. Although this study investigated the effect of crude oil viscosity on dispersant effectiveness, it would be insightful to perform a similar study on a larger set of crude oils. Before the solvent effects are analyzed it would be crucial to analyze the physical properties and composition of the crude oils being tested, for that would uncover whether there is a strong relationship between certain crude components and components in the dispersant (e.g., solvent). This would be an important investigation to perform since heavier crudes are being extracted from oil reservoirs, and if an oil spill happens to occur during the transportation of these crudes, it is important to use a dispersant that is effective at dispersing heavy crude oils.

Emulsification vs. Dispersion. On a more fundamental basis, it would be interesting to investigate the distinctions between oil-in-water emulsification and oil-in-water dispersion, at a deeper level. These two terms are used interchangeably in the literature found in this field, however, as seen in section 2.3 there is a distinction between samples that have been emulsified, and samples that have been dispersed.

Interfacial Tension Measurements. Interfacial tension tests on the oil-water interface could yield useful information regarding the components that are decreasing the interfacial tension at the specified interface. These tests would be performed at the oil-water interface of different crudes (light, medium, heavy), then they would be performed on those same crudes but with the addition of solvent only. Following those studies, we would test the interfacial tension of those same set of crude oils with the addition of a dispersant. In doing

these tests, we would gain insight into the components that are helping to stabilize the oil droplets in the water column, which can in turn help us better formulate our dispersants.

APPENDIX I: SOLVENT ABBREVIATION TABLE

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

Solvent	Abbreviation	Solvent	Abbreviation
Methanol	MOH	3-Octanol	3OOH
Ethanol	EOH	1-Undecanol	UOH
1-Propanol	POH	Ethylene Glycol Monobutyl Ether	EGBE
Isopropanol	IPOH	Diethylene Glycol	dEGLY
1-Butanol	BOH	Diethylene Glycol Monoethyl Ether	dEGEE
Isobutanol	IBOH	Diethylene Glycol Monobutyl Ether	dEGBE
1,3-Butanediol	BdOH	Propylene Glycol	PGLY
2-Ethyl-1-Hexanol	2E1H	Dipropylene Glycol	dPGLY
1-Octanol	OOH	Acetic Acid	ACOOH

APPENDIX II: SUPPLEMENTARY FIGURES

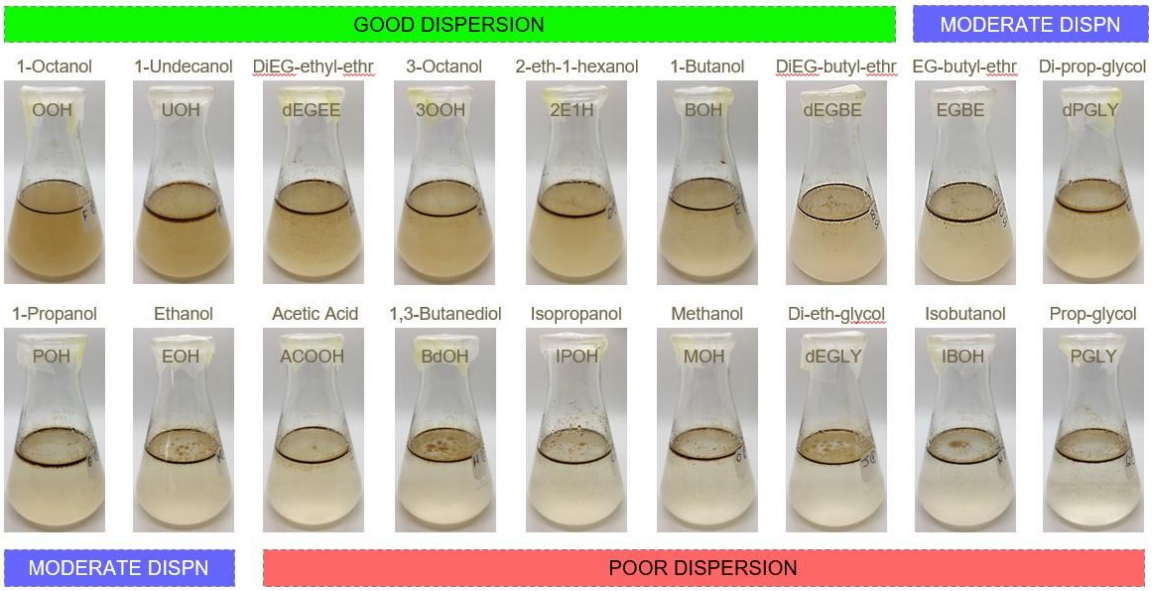

Figure B.1. Low Energy Dispersion Test result for the Sweet Louisiana Crude (SLC) oil. Data from Reference. 19.

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