

Does the Solvent in a Dispersant Impact the Efficiency of Crude-Oil Dispersion?

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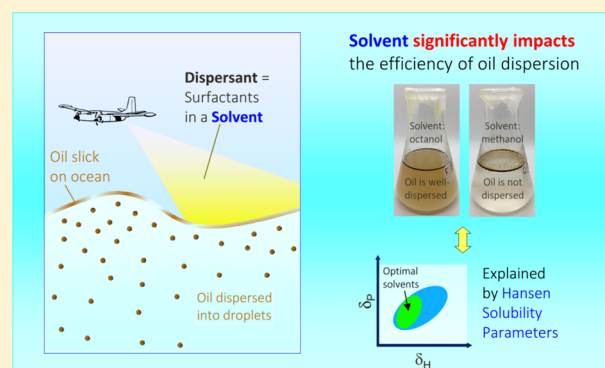
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Supporting Information

ABSTRACT: 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 blends of the food-grade surfactants, soy lecithin (L) and Tween 80 (T), in a solvent. We have shown that these “L/T 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. However, with regard to the dispersion efficiency of crude oil, the solvent is considered to play a negligible role. In this paper, we re-examine the role of solvent in the L/T system and show that it can actually have a significant impact on the dispersion efficiency. That is, the dispersion efficiency can be altered from poor to excellent simply by varying the solvent while keeping the same blend of surfactants. We devise a systematic procedure for selecting the optimal solvents by utilizing Hansen solubility parameters. The optimal solvents are shown to have a high affinity for crude oil and limited hydrophilicity. Our analysis further enables us to identify solvents that combine high dispersion efficiency, good solubility of the L/T surfactants, a low toxicity profile, and a high flash point.



INTRODUCTION

The spilling of crude oil onto bodies of water (oceans, seas, rivers, and lakes) adversely affects the local environment as well as the larger ecosystem in so many ways. Large oil spills have occurred in the last 30 years, including the Exxon Valdez event in 1989, which spilled over 11 million gallons of oil into Prince William Sound, Alaska, and the Deepwater Horizon spill in 2010 which polluted the Gulf of Mexico with over 210 million gallons of oil.^{1–4} The most used method to clear an oil spill is by the introduction of dispersants such as the industry-standard called Corexit.^{4–6} During the Deepwater Horizon event, more than 2 million gallons of Corexit were sprayed onto the oil using aircraft and ships.^{3,4} Although the components of Corexit are generally deemed to be nontoxic, recent studies have continued to attribute negative environmental and health effects to Corexit.^{7–10} This has motivated work in our labs to develop a new generation of effective, yet nontoxic, dispersants.^{11,12}

The function of a dispersant is illustrated in Figure 1a.^{5,6} 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, and this process is greatly enhanced by the agitation provided by waves. The oil droplets, which are stabilized by adsorbed surfactant molecules, are then carried below the water surface, where the oil in them is subsequently degraded by various micro-organisms present in the water.^{1,2} The fraction of the oil film that is dispersed as droplets into the water column is termed the dispersion efficiency. Dispersants like Corexit exhibit dispersion efficiencies above 90% for low dispersant/oil ratios (DOR) (~1:20), indicating that they are highly effective at dispersing the oil slick into droplets.

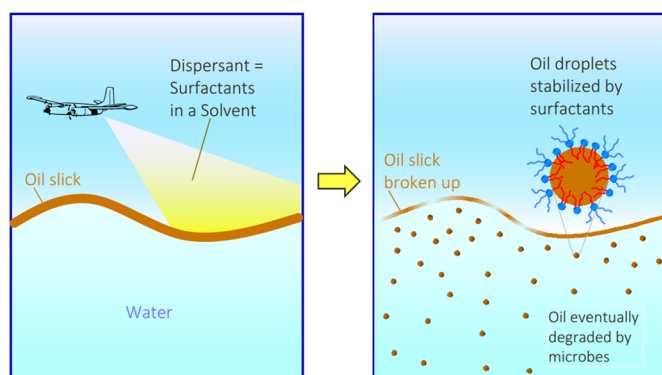
In our lab, we have created a completely food-grade dispersant that is equally as effective as Corexit.^{11,12} The surfactants in this dispersant (Figure 1b) are lecithin (L), a phospholipid extracted from soybeans, and Tween 80 (T), a nonionic surfactant that is used in ice creams and other food products.¹¹ The two above surfactants are dissolved in a

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(a) How dispersants work



(b) Composition of ‘food-grade’ dispersant in this study

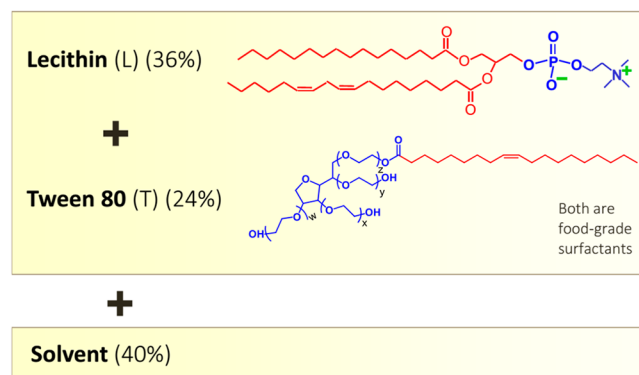


Figure 1. (a) Mechanism by which dispersants mitigate an oil spill. An oil slick is shown on the surface of a body of water. Dispersants, that is, mixtures of surfactants in a solvent, are sprayed onto the oil slick from aircraft or ships. This serves to break up the oil slick into microscale oil droplets, which are carried below the water surface. The oil is eventually degraded by microbes in the water. Each oil droplet is stabilized and prevented from coalescing because of the surfactant molecules that cover its surface: note that the hydrophobic tails of the surfactant molecules (in red) insert into the oil while the hydrophilic heads (in blue) are oriented toward the water (surfactants not drawn to scale with respect to the droplet). (b) Composition of dispersant used in this study. Two food-grade surfactants, lecithin (L) and Tween 80 (T), are combined in a 60:40 weight ratio. The total surfactant concentration in the dispersant is 60% by weight. The remaining 40% is a solvent, which is the focus of the present study.

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 dispersion efficiency.^{11,12} However, thus far, we have not focused on the solvent used in the dispersant. Our original solvent was ethanol, which is a relatively nontoxic, food-grade material, but it is unsuitable for use in the field because of its low flash point. Generally, the solvent is treated as an inert component that has negligible effect on dispersion efficiency; its role is then deemed to be merely to convey the surfactants into the oil slick.^{13,14} Selection of the solvent is commonly made based on factors like toxicity, volatility, or viscosity of the overall mixture.¹⁴

The purpose of this paper is to re-examine the role of the solvent in a dispersant. Can the solvent actually be an active component, that is, can it significantly impact the efficiency of crude oil dispersion? To test solvent effects, we have used the blend of food-grade surfactants from our previous work, that is, L/T in a weight ratio of 60/40. With this surfactant composition kept constant, we examine 26 different solvents. Mixtures of L/T and the solvent are tested for their ability to disperse one type of crude oil (a sweet Louisiana crude obtained from the Macondo well in the Gulf of Mexico) into simulated seawater. Our results show a clear hierarchy among the solvents—some give rise to poor dispersion and others to excellent dispersion. To explain these differences, we have conducted an analysis based on the Hansen solubility parameters (HSPs)^{15,16} of the solvents. Our analysis shows that the optimal solvents fall in a cluster on a “Hansen plot”. Together with the molecular structure of the solvents, our study provides new insights into the role of the 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.

EXPERIMENTAL SECTION

Materials. Soybean lecithin (95%) was purchased from Avanti Polar Lipids while the Tween 80 surfactant, that is, poly(oxyethylene

sorbitan monooleate), was purchased 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 dimethyl sulfoxide from Fisher Scientific; *N*-methyl-2-pyrrolidone from Fluke Analytica; ethanol and methanol from Pharmco-Aaper; and isopropanol and *N,N*-dimethylformamide from VWR. All remaining solvents, including 1-butanol, 1-octanol, 3-octanol, 1,3-butanediol, acetone, diethylene glycol, diethylene glycol (dEG) ethyl ether, dEG butyl ether, ethylene glycol butyl ether, glycerol, methanol, *n*-dodecane, *n*-octane, propylene glycol (PG), and undecanol, were obtained from Sigma-Aldrich. 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 4 mL vials. All the dispersants contained the same surfactant/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 the different solvents. To expedite dissolution, vials were placed in a heat bath at 50 °C and then sonicated until a homogeneous solution was obtained. If the surfactants were insoluble after this period, this was also noted.

Sample Preparation and Low-Energy Dispersion Test. For testing dispersion, each sample was prepared as follows. First, 100 mL of synthetic seawater was added to a 125 mL conical flask. Next, 100 μ L of sweet Louisiana crude oil was pipetted on top of the seawater. Finally, 10 μ L of dispersant was pipetted on top of the oil. Thus, the ratio of oil/seawater ratio was 1:1000, and the DOR was 1:10 for all tests. The low-energy dispersion test (LEDT) was then conducted as described in the next section. The orbital shaker used was an Innova 4000 incubator shaker.

Efficiency Measurement. To measure dispersion efficiency, we followed the EPA-approved baffled flask test (BFT) procedure.^{17,18} The procedure requires baffled flasks of 150 mL capacity. These are conical flasks with four extra-deep baffles and were purchased from Wheaton. The same amounts of seawater, crude oil, and dispersant as above were added to the above flask. The sample was mixed for 10 min on the Innova 4000 incubator shaker at 250 rpm and then removed and allowed to rest for 10 min. Thereafter, a 30 mL sample

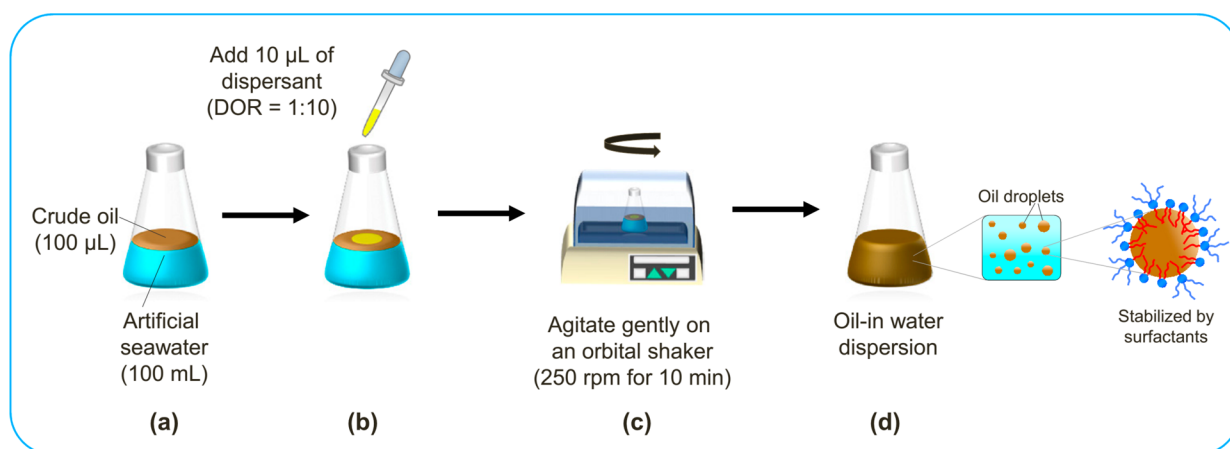


Figure 2. Schematic of the Low-Energy Dispersion Test (LEDT). (a) Crude oil is added to artificial seawater at a ratio of 1:1000 and it forms an immiscible layer on the surface. (b) The dispersant is added on top of the oil at a DOR of 1:10. (c) The sample is then placed on an orbital shaker and agitated gently at 250 rpm for 10 min. (d) If the dispersant is efficient, the result will be an oil-in water dispersion having a brown color due to the presence of suspended oil droplets in the water. The schematic shows the oil droplets, which are each coated with surfactants: note that the hydrophobic tails of the surfactant molecules (in red) insert into the oil while the hydrophilic heads (in blue) are oriented toward the water. The layer of surfactants prevents the droplets from coalescing and thereby stabilizes the dispersion.

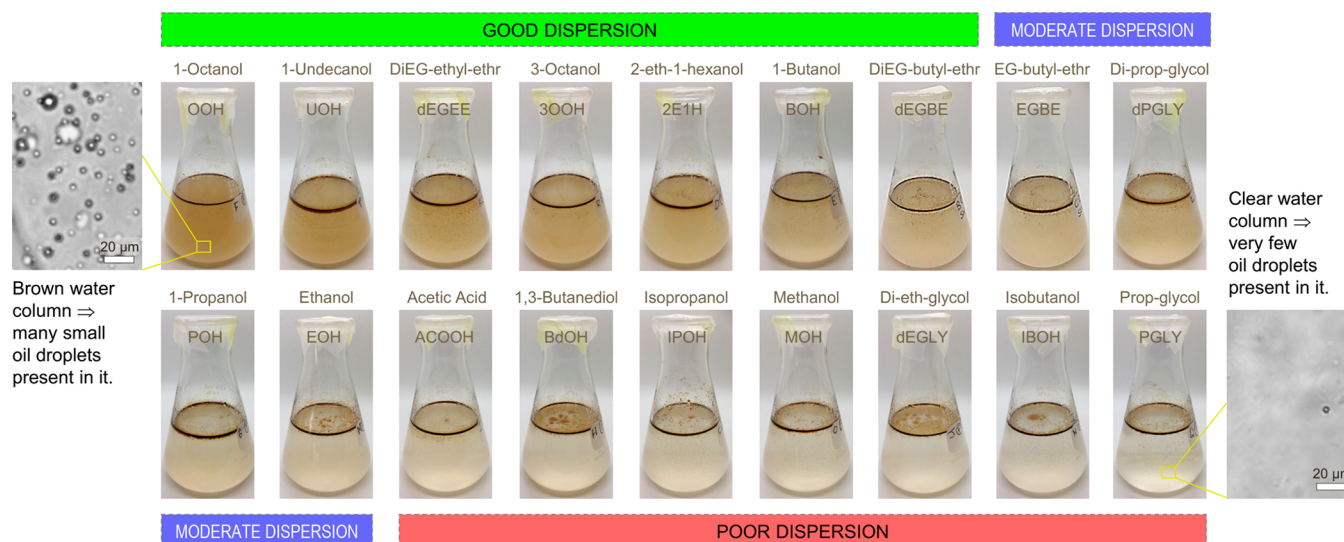


Figure 3. Results from the LEDT on dispersing crude oil in seawater using dispersants made with 18 different solvents. All dispersants have the same surfactant blend (L/T = 60:40) and total surfactant concentration (60 wt %). All photos were taken 30 min after stopping the low-energy agitation (see Figure 2). On each photo, the solvent name and abbreviation are indicated. 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 dispersion. A “good” dispersion yields a brown water column, indicating a high concentration of relatively stable oil droplets. This is indicated by the optical micrograph on the top left. A “poor” dispersion yields a colorless water column, with much of the oil droplets having coalesced and risen above the water. This is indicated by the optical micrograph on the bottom right.

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.

RESULTS

A dispersant contains surfactants dissolved in a solvent. In order to study the effect of solvent, we used the same surfactant blend and varied the solvent alone. The surfactant blend chosen was a mixture of soy lecithin (L) and Tween 80 (T) in a 60:40 weight ratio.^{11,12} This blend of “food-grade” surfactants has been shown to be highly effective at dispersing crude oil in seawater.¹² The similarities in surfactant

composition between the L/T system and the commercial Corexits have been noted before: both have a twin-tailed surfactant and a nonionic surfactant from the Tween series.¹¹ The hydrophilic–lipophilic balance (HLB) of the blend is 10.2.¹¹ As such, the L/T blend is a prototype for surfactant blends that have proved successful in oil dispersion, and it is therefore a good choice for the present study. As in our previous studies, a surfactant/solvent ratio of 60:40 by weight was used in preparing the dispersants here. Using the above composition, we prepared 26 different dispersants, each with a different solvent. A table of all the solvents used in this study and their abbreviated notation in the figures below is provided in Table S1 in the Supporting Information section.

Low-Energy Dispersion Test. To analyze solvent effects, we needed to devise a simple and rapid test to distinguish between good and poor dispersion. In previous work, the Baffled Flask Test (BFT) has been used extensively.^{17,18} However, we found the BFT to be unsuitable for our purpose. This was first because the baffles greatly enhanced the mixing of oil and water, thereby promoting dispersion. Ideally, we wanted our test results to be independent of the mixing energy, and for this reason, a test that employed a low extent of mixing was desirable. A second issue with the BFT was that it was time-consuming and tedious. We wanted a test that could be performed quickly while still revealing useful insights. For these reasons, we have modified the standard BFT procedure and come up with a LEDT, as shown schematically in Figure 2.

The LEDT uses a conical flask instead of a baffled flask. Into this flask, 100 mL of seawater is first introduced (Figure 2a). Thereafter, 100 μ L of the crude oil is pipetted on to the water surface, where the oil forms a thin layer (oil slick). Next, 10 μ L of the dispersant is pipetted on the oil (Figure 2b). Under these conditions, the ratio of oil/seawater is 1:1000, and the DOR is 1:10. The flask is then placed on an orbital shaker for 10 min at 250 rpm (Figure 2c). After shaking, the sample is removed and placed in a photo box. After 30 min of rest, photos of the sample are taken, and from these, the extent of dispersion is visually assessed (see below). 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, for example, when the sea is calm.

Of the 26 different solvents studied, we found that 8 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. The remaining 18 solvents solubilized the surfactants and were tested using the LEDT. The results are shown in Figure 3. From visual inspection of the flasks, it is clear that there are wide differences in dispersion performance among the solvents. We have arranged the flasks in Figure 3 in order from best to worst dispersion. Moreover, we have categorized them 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. Because the crude oil is a dark brown, the brown color of the water indicates a high concentration of oil droplets suspended in the water. Also, note that the photos in Figure 3 are taken 30 min after the mixing is stopped. Therefore, a brown water column indicates both that there are numerous oil droplets and also that the droplets are stable to coalescence for at least 30 min. In this case, note also that the water surface is clear of coalesced oil. At the other extreme, 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 because of their lower density. Indeed, brown splotches can be seen on the water surface in the flasks marked "poor", whereas those are mostly absent in the "good" cases. The classification of "moderate" dispersion falls between the extremes of "good" and "poor", and it is admittedly subjective as to where the demarcations are made. Nevertheless, this classification will prove useful for the rest of this paper. It is also worth pointing out that optical microscopy images of samples withdrawn from the water

column in the above samples corroborate this classification. That is, in the case of "good" dispersions, there are numerous oil droplets, as shown by the image on the top-left in Figure 3; in the case of moderate dispersions, there are fewer droplets, and in "poor" dispersions, there are hardly any droplets, as shown by the image on the bottom-right in Figure 3.

Figure 3 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 would be whether the solvent on its own could act as a surfactant. 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), which is 1-octanol (OOH), and the worst performing solvent (bottom right sample in Figure 3), which is propylene glycol (PG). Results from the LEDT with these two solvents are shown in Figure 4 along with a test run with no dispersant at

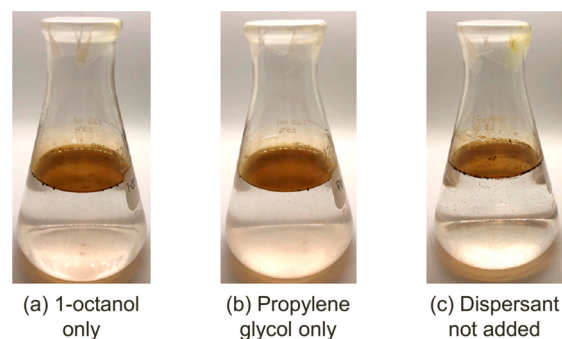
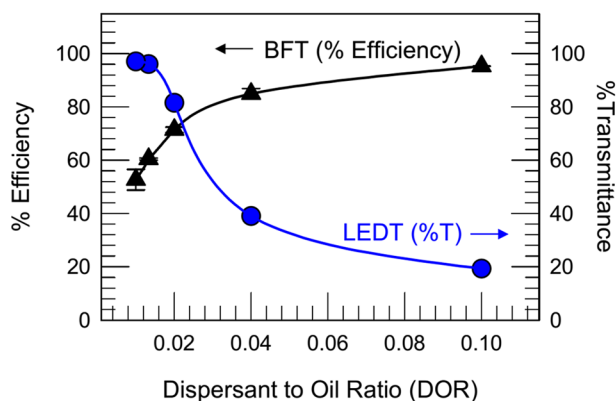


Figure 4. Results from the LEDT on dispersing crude oil in seawater using no surfactants. In (a,b), a solvent alone is used. In (a), the solvent is 1-octanol (best solvent from Figure 3), and in (b) it is PG (worst solvent from Figure 3). In (c), neither surfactant nor solvent is used. Negligible dispersion of the oil is observed in all three samples.

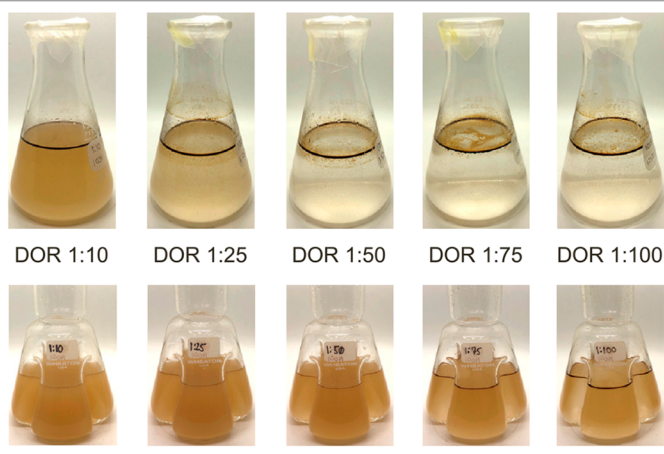
all. In all cases, the photos of the flasks show that there is negligible dispersion. We repeated the tests with considerably higher amounts of solvent (10 μ L of pure solvent), but the results were unchanged. These results confirm that surfactants are the primary driving force for dispersion. If the solvent has an effect, it must be in concert with the surfactants.

Our goal in developing the LEDT was to use it as a tool for screening 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 5 presents a comparison of the two. The L/T dispersant with OOH as a solvent was used in all cases, and the tests were done for different amounts of dispersant, that is, for varying DORs, from 1:10 (highest dispersant) to 1:100 (lowest dispersant). Results from the BFT are presented as dispersion efficiencies on the plot, and the corresponding flasks are shown in Figure 5c. In the case of the LEDTs, the flasks are shown in Figure 5b, and in addition, we quantified the color of the liquid in 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 liquid in the flask is brown and opaque, the transmittance will be low, whereas if the liquid is colorless and clear, the transmittance will be high.

(a) Comparison of LEDT and BFT Results



(b) LEDT Results



(c) BFT Results

Figure 5. Comparison of results from the Low-Energy Dispersion Test (LEDT) and the Baffled Flask Test (BFT) 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 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 5a 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 decreases and this is revealed by both techniques. However, what is 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 4c also reveals a dark-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 (the corresponding BFT efficiencies are $>80\%$). For the lower DOR of 1:50, the LEDT reveals the water to be practically clear with $T \approx 80\%$, which would be classified as “poor” dispersion as per Figure 3. Even for this case, the BFT efficiency is $\sim 60\%$, which is reasonably high. This shows that the LEDT is more sensitive than the BFT. Put differently, a “good” LEDT result is guaranteed to give a good BFT result ($E > 80\%$) because the BFT puts more shear on the sample. A “poor” LEDT result, however, may still give good BFT efficiencies. On the whole, the results from Figure 5 validate the LEDT as a quick, reliable, and sensitive way to screen the dispersant performance.

To reiterate our results, we have shown that the solvent can have a huge “active” role in oil dispersion. Combining the data from Figures 3 and 5, a couple of examples can be instructive. Take the case of the same L/T blend in a solvent like PG—in this case, the solvent hinders dispersion, and the system is classified as “poor” in Figure 3. Based on Figure 5, this corresponds to BFT efficiencies around 50%. Just by changing the solvent to OOH, the quality of dispersion dramatically improves and the BFT efficiency increases to 95%. In other

words, 1-octanol works synergistically with the L/T surfactants, and the overall dispersant performs extremely well. In stark contrast, PG seems to work antagonistically to the surfactants and impairs the performance of the overall dispersant. Interestingly, in our earlier work, we stuck with ethanol (EOH) as the solvent, and from Figure 3, this only gives a “moderate” dispersion—indicating that our previous results could have been much improved by choosing a better solvent. Another way to emphasize the practical utility of this result is to note that, simply by changing the solvent, the same extent of oil dispersion could be achieved with a 5 \times lower amount of dispersant (DOR of 1:10 vs 1:50). For a large oil spill, this could translate to requiring several million gallons less of the dispersant.

Analysis of Results Using HSPs. Next, in an attempt to gain insight into the differences between solvents, we turn to Hansen Solubility Parameters (HSPs). The HSPs are a set of three values (δ_D , δ_P , δ_H) that characterize a solvent.^{15,16} They quantify various 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. The HSPs are components of the overall solubility parameter δ , which is related to the cohesive energy density of the solvent. Traditionally, HSPs have been used to correlate and predict the solubility of a polymer: solubility is optimized when the HSPs of the polymer and solvent are close to each other. Here, we will apply HSPs to our dispersants, which are a very different type of system. In the case of the solvents studied here, their δ_D values were quite similar, and this parameter is therefore omitted from our discussion. We thereby focus on “2-D Hansen plots” with δ_P on the y -axis and δ_H on the x -axis. Figure 6 plots all 26 solvents on this 2-D plot (each solvent is a point).

As noted earlier, eight of the solvents did not solubilize the surfactant blend while the remaining 18 solvents did. Figure 6 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 S1 in the Supporting Information for all the

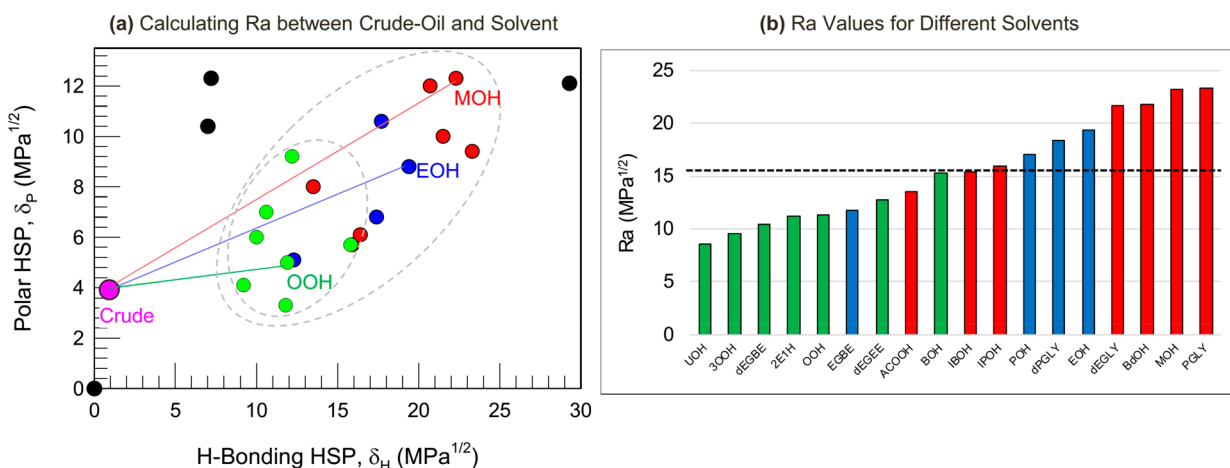


Figure 8. Quantifying the effect of solvent on the efficiency of crude-oil dispersants based on L and T. (a) On the same 2-D Hansen plot (δ_p vs δ_H) as in Figure 7, a pink point is marked for light crude oil. From this point, lines are drawn to each of the soluble solvent points, and the lengths of these lines = R_a are computed. Representative lines are shown for solvents giving “good”, “moderate”, and “poor” dispersion (OOH, EOH, and MOH, respectively). (b). Bar graph of the R_a values for various solvents is shown in increasing order. The bars are color-coded as before (“good” dispersion in green, “moderate” in blue and “poor” in red). The horizontal dashed line indicates an R_a of 15.3 MPa^{1/2}; no solvent with a higher R_a than this value yielded good dispersion.

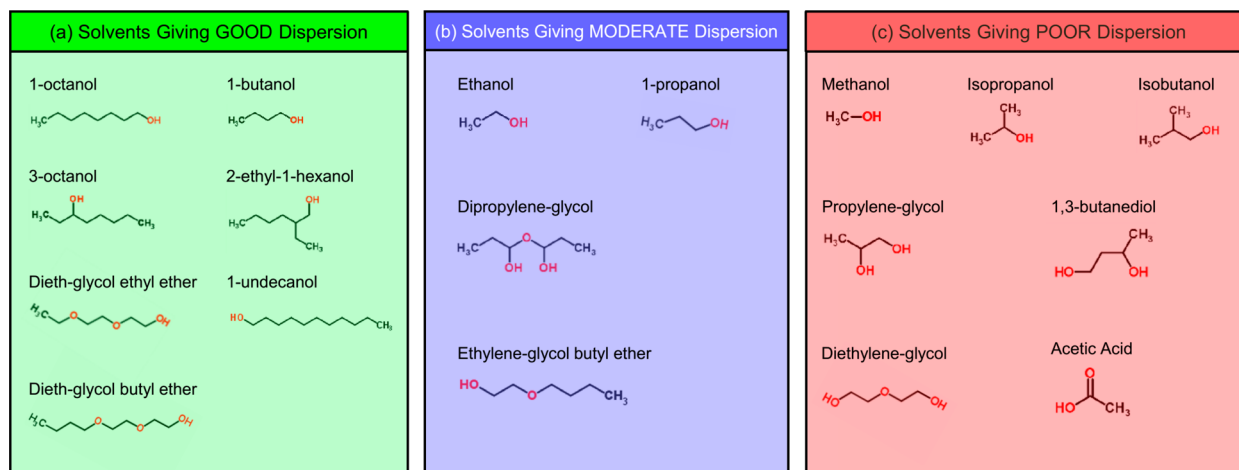


Figure 9. Comparing the molecular structures of the solvents. The solvents are categorized as those that yield (a) “good” dispersion; (b) “moderate” dispersion; and (c) “poor” dispersion. Polar groups in these molecules are highlighted by a red color.

be unable to solubilize the hydrophilic T surfactant in the overall surfactant blend.

To reiterate our key finding from Figure 8, it is that *the best solvents are those with strong affinity for the oil*, as measured by their R_a values. Why is this the case? We hypothesize that such solvents are likely to persist within the crude oil slick rather than leaching off into the water column.^{14,20} This would be beneficial for oil dispersion as it would help ensure that the surfactants (which are the active components) incorporate into and remain within the oil slick. Conversely, if the solvent was too hydrophilic, solvent molecules might carry some of the hydrophilic surfactant (i.e., T in our case) into the water. Such removal of surfactant from the oil/water interface would decrease the efficiency of dispersion.

A second effect that may occur is cosurfactancy because several of the “good” solvents have some amphiphilic character, meaning a clear separation of the polar and nonpolar parts of the molecule.^{14,20} This is particularly so for OOH and UOH, which both have an $-OH$ group at the end of an alkyl tail, and are known to be effective cosurfactants in the formation of

micelles.²⁰ Although OOH does not disperse oil on its own (Figure 4), 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 cosurfactancy 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 (3OOH) and 2 ethyl-1-hexanol (2E1H), which are branched versions of OOH and dEGBE.

Selection of Optimal Solvents. We conclude with a discussion on solvent selection for dispersants that include aspects unrelated to dispersion efficiency.^{13,14} For example, solvent toxicity is a most important aspect, and Table 1 contains toxicity data on the 18 solvents corresponding to Figure 9, as documented in their respective safety data sheets. Here, the LD_{50} is the lethal dose required to kill half the test subjects, and the higher this value, the less toxic the solvent. Based on their LD_{50} values, solvents are classified into categories. The least toxic solvents are those in category 5, which means they are harmful only if ingested or contacted in

Table 1. Toxicities of Candidate Solvents for Use in Dispersants^a

| Solvent | LD ₅₀ (dermal; rabbit) | LD ₅₀ (oral; rat) | Dermal Category | Oral Category |
|---------------------------------------|--------------------------------------|---------------------------------|--------------------|------------------|
| 1,3-butanediol (BdOH) | N/A | 22,800 mg/kg | 5 | 5 |
| 3-octanol (3OOH) | >5,000 mg/kg | > 5,000 mg/kg | 5 | 5 |
| Diethylene glycol (dEGLY) | 11,890 mg/kg | 12,570 mg/kg | 5 | 5 |
| Diethylene glycol ethyl ether (dEGEE) | 8,500 mg/kg | 7,500 mg/kg | 5 | 5 |
| Dipropylene glycol (dPGLY) | >5,000 mg/kg | >5,000 mg/kg | 5 | 5 |
| Ethanol (EOH) | 20,000 mg/kg | 7,060 mg/kg | 5 | 5 |
| Methanol (MOH) | 15,800 mg/kg | 5,630 mg/kg | 5 | 5 |
| Propylene glycol (PGLY) | 20,800 mg/kg | 20,000 mg/kg | 5 | 5 |
| Isopropanol (IPOH) | 12,800 mg/kg | 5,000 mg/kg | 5 | 4 |
| 1-undecanol (UOH) | 5,000 mg/kg | 3,000 mg/kg | 5 | 4 |
| Diethylene glycol butyl ether (dEGBE) | 2,700 mg/kg | 4,500 mg/kg | 4 | 4 |
| Isobutanol (IBOH) | 2,000 mg/kg | 3,100 mg/kg | 4 | 4 |
| 1-octanol (OOH) | >1,000 mg/kg | >3,200 mg/kg | 3 | 4 |
| 2-ethyl-1-hexanol (2E1H) | 1,970 mg/kg | 3,730 mg/kg | 3 | 4 |
| Acetic acid (ACOOH) | 1,110 mg/kg | 3,310 mg/kg | 3 | 4 |
| 1-butanol (BOH) | 3,400 mg/kg | 790 mg/kg | 4 | 3 |
| 1-Propanol (POH) | 4,050 mg/kg | 1,870 mg/kg | 4 | 3 |
| Ethylene glycol butyl ether (EGBE) | 220 mg/kg | 470 mg/kg | 2 | 2 |

^aReported values for each solvent (from their Materials Safety Data Sheets) of the median lethal dose (LD₅₀) in cases of dermal and oral administration are shown. The categories for toxicity are: categories 1 and 2 = fatal, category 3 = toxic, category 4 = harmful, category 5 = may be harmful.

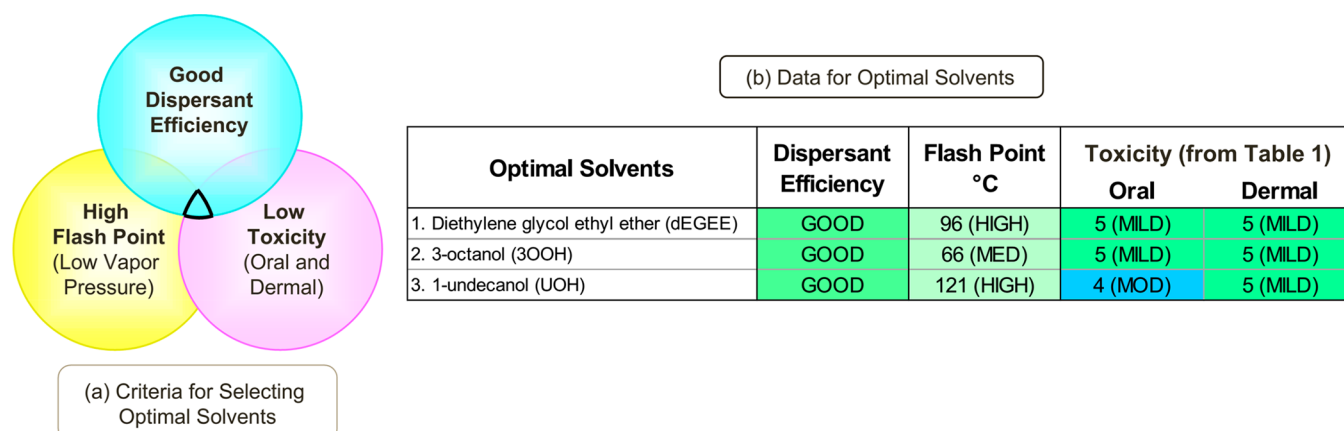


Figure 10. Optimal solvents for use in dispersants based on L/T surfactants. (a) Criteria for selecting the optimal solvents, as shown on a Venn diagram. The optimal solvent should yield good dispersant efficiency (as per Figure 8), have a flash point that is sufficiently high (at least 60 °C), and exhibit low toxicity (as per Table 1). (b) The top 3 solvents, identified by the criteria in (a) are shown, along with their relevant data.

very large amounts. From Table 1, about half the solvents on this list are indeed in category 5 for oral and/or dermal exposure.

Another important factor is the solvent flash point.^{13,14} 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 then pose a risk of igniting during storage and application. Other considerations include the solvent density, which should be low to ensure that the dispersant remains at the interface instead of sinking into the water column.^{13,14} This is indeed the case for all the solvents in Table 1. Also, the dispersant viscosity should be low enough to enable the dispersant to be

applied as a spray. The viscosity of the dispersant is a function of two variables: the viscosity of the solvent itself and the concentration of surfactants dissolved in the solvent. Table S2 in the Supporting Information section shows the viscosities of the various solvents studied here. At the surfactant concentration used here, which is 60 wt % (L + T), the viscosity of the dispersant is about 20 times the solvent viscosity. For instance, the viscosity of the dispersant based on dEGEE is 83 mPa·s and that based on 3OOH is 108 mPa·s. These are sufficiently low to enable application as a spray.

To sum up the most relevant characteristics, the ideal solvent in a dispersant should:^{13,14}

(1a) solubilize the surfactants, and

- (1b) yield a good oil dispersion, as per Figure 3 or 7
- (2) have a low toxicity profile, as per Table 1, and
- (3) have a flash point >60 °C.

Figure 10a shows a Venn diagram to illustrate the point above. Based on these three criteria, the optimal solvents for the L/T system from our studies are listed in the table in Figure 10b. Only two solvents, dEGEE and 3OOH, satisfied all three criteria. UOH is another potential solvent that satisfies two of the criteria but has a slightly inferior toxicity profile (Table 1) and also a higher viscosity (Table S2). Between dEGEE and 3OOH, the former has a higher flash point of 96 °C, and therefore it would be our top candidate for use in L/T dispersants.

CONCLUSIONS

This work shows that the solvent in a dispersant can have a huge impact on the efficiency of crude-oil dispersion. While the solvent takes up 20–50% of the volume of a dispersant (the remaining being the surfactants), the typical view is that the solvent is nothing more than a passive carrier of the surfactants into the oil slick. Our study demonstrates instead that the solvent can be an “active” component that works synergistically with the surfactants to promote oil dispersion (conversely, other solvents may hinder dispersion). In our studies, we made dispersants using a food-grade blend of L/T 60/40 and varied the solvent alone. We developed the LEDT as a simple and rapid test to assess how well a given dispersant was able to disperse oil droplets into seawater. By comparisons with the standard BFT, we validated the LEDT and moreover found that the LEDT is a much more sensitive test than BFT.

Having established that some solvents are better than others when it comes to dispersion, we addressed the question as to why this is so. Through the use of HSPs, we showed that the best solvents are those with strong affinity for crude oil, as measured by the similarities in their HSP values. This implies that the solvent should be mostly (but not completely) hydrophobic. To explain this, we hypothesized that such solvents will incorporate into and persist within the oil rather than leaching off into the water. Thereby, the surfactants will also be forced to remain within the oil slick, where they can help to break up the oil into droplets.

Dispersant formulation is a matter of trade-offs. The optimal dispersant is not necessarily the one that has the highest efficiency of oil dispersion. Instead, the formulator has to consider other factors such as the toxicity profiles of the various components as well as their physical properties such as flash point, density, and viscosity. We have shown through this work how to select the optimal solvents that consider several of these factors. By combining the optimal solvent with food-grade L/T surfactants, we can consciously move toward “greener” formulations of chemical dispersants to clear future oil spills.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.langmuir.9b02184>.

Names of all solvents studied here, along with their abbreviations and the viscosities of the solvents studied here (PDF)

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Notes

The authors declare no competing financial interest.

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Supporting Information for:

Does the Solvent in a Dispersant Impact the Efficiency of Crude-Oil Dispersion?

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| Solvent | Abbreviation | Solvent | Abbreviation |
|-------------------|---------------------|-----------------------------------|---------------------|
| Methanol | MOH | Ethylene Glycol Monobutyl Ether | EGBE |
| Ethanol | EOH | Diethylene Glycol | dEGLY |
| 1-Propanol | POH | Diethylene Glycol Monoethyl Ether | dEGEE |
| Isopropanol | IPOH | Diethylene Glycol Monobutyl Ether | dEGBE |
| 1-Butanol | BOH | Propylene Glycol | PGLY |
| Isobutanol | IBOH | Dipropylene Glycol | dPGLY |
| 1,3-Butanediol | BdOH | Glycerol | GLCR |
| 2-Ethyl-1-Hexanol | 2E1H | Acetic Acid | ACOOH |
| 1-Octanol | OOH | Acetone | ACE |
| 3-Octanol | 3OOH | N-Methyl-2-pyrrolidone | NMP |
| 1-Undecanol | UOH | N,N-dimethylformamide | DMF |
| n-Octane | OCT | Dimethylsulfoxide | DMSO |
| n-Dodecane | DODE | Water | H2O |

Table S1. List of solvents investigated in this paper and their abbreviations.

| Solvent | Viscosity at 25°C (mPa.s) |
|---------------------------------------|---------------------------|
| 1,3-butanediol (BdOH) | 90.9 |
| 3-octanol (3OOH) | 6.7 |
| Diethylene glycol (dEGLY) | 0.3 |
| Diethylene glycol ethyl ether (dEGEE) | 3.9 |
| Dipropylene glycol (dPGLY) | 75.0 |
| Ethanol (EOH) | 1.1 |
| Methanol (MOH) | 0.6 |
| Propylene glycol (PGLY) | 48.6 |
| Isopropanol (IPOH) | 2.0 |
| 1-undecanol (UOH) | 17.2 |
| Diethylene glycol butyl ether (dEGBE) | 6.5 |
| Isobutanol (IBOH) | 2.5 |
| 1-octanol (OOH) | 7.3 |
| 2-ethyl-1-hexanol (2E1H) | 9.2 |
| Acetic acid (ACOOH) | 1.1 |
| 1-butanol (BOH) | 2.5 |
| 1-Propanol (POH) | 1.9 |
| Ethylene glycol butyl ether (EGBE) | 3.4 |

Table S2. Viscosities of solvents at 25°C. Data are shown for the solvents in Table 1 of the main paper. The viscosity values were obtained from the literature in most cases. For the cases where values were not available from the literature, the viscosities were measured on an AR 2000 rheometer (TA Instruments) using a cone-and-plate geometry.