Efficient dispersion of crude oil by blends of food-grade surfactants: Toward greener oil-spill treatments

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A B S T R A C T

Effectiveness of oil spill dispersants containing lecithin/Tween 80 (L/T) blends in ethanol was measured as a function of L:T ratio, surfactant:solvent ratio, solvent composition, and dispersant:oil ratio (DOR) using baffled flask dispersion effectiveness tests. Optimal L:T ratios are between 60:40 and 80:20 (w/w); at higher L:T ratios, effectiveness is limited by high interfacial tension, while at lower L:T ratios, insufficient lecithin is present to form a well-packed monolayer at an oil–water interface. These optimal L:T ratios retain high effectiveness at low DOR: 80:20 (w/w) L:T dispersant is 89% effective at 1:25 DOR (v/v) and 77% effective at 1:100 DOR (v/v). Increasing surfactant:solvent ratio increases dispersant effectiveness even when DOR is proportionally reduced to keep total surfactant concentration dosed into the oil constant. Replacing some of the ethanol with octane or octanol also increases dispersant effectiveness, suggesting that ethanol's hydrophilicity lowers dispersant–oil miscibility, and that more hydrophobic solvents would increase effectiveness.

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1. Introduction

Oil dispersants are an important tool for the remediation of marine oil spills (Committee on Effectiveness of Oil Spill Dispersants (National Research Council Marine Board), 1989), but their deployment in the marine environment continues to be a subject of controversy. Many authors (Committee on Effectiveness of Oil Spill Dispersants (National Research Council Marine Board), 1989; Buist et al., 2008; European Maritime Safety Agency, 2009; Committee on Understanding Oil Spill Dispersants: Efficacy and Effects (National Research Council), 2005) assert that modern dispersants' toxicity is of no concern when deciding whether to apply them to an oil spill, as numerous studies (Committee on Understanding Oil Spill Dispersants: Efficacy and Effects (National Research Council), 2005; Almeda et al., 2014; Rico-Martinez et al., 2013; Hemmer et al., 2011; Wetzel and Van Fleet, 2001) have found modern oil dispersants to be considerably less toxic than dispersed crude oil and such dispersants are applied to spills at relatively low dispersant:oil ratios (typically 1:20 to 1:100 v/v) (European Maritime Safety Agency, 2009). Others, (Almeda et al., 2014; Rico-Martinez et al., 2013; Wise et al., 2014) however, express concern at introducing into the environment any oil dispersant which is not completely nontoxic. In order to secure broader acceptance of dispersant use, therefore, it is useful to investigate alternative dispersant formulations made of nontoxic compounds.

Recently, Athas et al. (Athas et al., 2014) reported qualitatively that crude oil treated with mixtures of lecithin (L) and Tween 80 (T) in ethanol readily emulsifies into seawater. They attribute the effectiveness of these L/T blends as oil-in-water emulsifiers both to the complementary shapes of Tween 80 (hydrophilic) and lecithin (hydrophobic), which enable a densely-packed surfactant monolayer to form at the oil–water interface (see Fig. 1), and to the steric hindrance of oil droplet coalescence by Tween 80's large polyoxyethylene chains. Since lecithin and Tween 80 are nontoxic surfactants (Carlsson et al., 2006; Fiume, 2001), the prospect of an oil dispersant based on lecithin-Tween 80 blends warrants further study (Nyankson et al., 2015).

In this work, agitation protocols based on the US EPA's "baffled flask" dispersant effectiveness test (developed by Venosa et al. (Venosa et al., 2002)) have been used to measure the dispersion effectiveness of L/T-based oil dispersants as a function of L:T ratio, surfactant:solvent ratio, dispersant:oil dosage ratio (DOR), and dispersant solvent composition. These dispersion effectiveness data improve upon the observations of emulsification reported in Athas et al. in several respects. First and foremost, the BFT is a widely used protocol which quantitatively measures the fraction of an oil slick dispersed into seawater, so BFT effectiveness data may be used to directly compare the performance of lecithin:Tween 80 dispersants to that of other, more established

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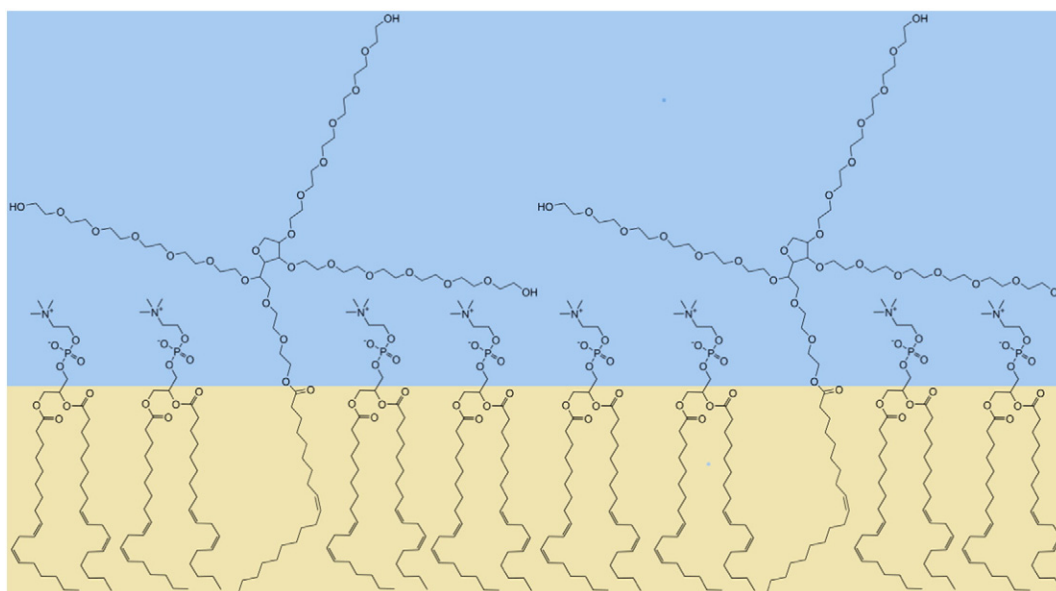
Fig. 1. Schematic of Tween 80 and lecithin packed in a monolayer at the oil–water interface (oil = lower phase; water = upper phase) at a mixture composition of 80:20 lecithin: Tween 80 (w/w).

dispersants (Venosa et al., 2002). Additionally, oil–water dispersions generated by the BFT are more realistic approximations to real dispersant-treated spills on the ocean, as the BFT imparts a known mixing energy to the oil–water mixture which produces turbulence similar to that observed within breaking waves at sea (Kaku et al., 2006), and employs a much higher seawater:oil ratio (1200:1 v/v) than Athas et al. used (10:1 v/v) so that oil droplets are dilute in the dispersion, as they would be at sea. Finally, Athas et al. only reported dispersant performance at a single, unusually high (European Maritime Safety Agency, 2009) DOR (1:10 v/v); a single solvent composition (100% ethanol) and surfactant:solvent ratio (60:40 w/w) despite the wide variety of solvents and solvent:surfactant ratios currently employed in dispersants (European Maritime Safety Agency, 2009); and three different dispersant L:T ratios (100:0, 0:100, and 60:40), which does not permit identification of the optimum L:T ratio. In this work, the effects of each of these variables on dispersant performance are explored thoroughly. The results of these tests not only confirm the prediction by Athas et al. that L/T blends are effective marine oil dispersants, but shed further light on the fundamental mechanisms of L/T dispersant action and indicate promising directions for future investigations.

2. Experimental

2.1. Materials

Tween 80 (Sigma-Aldrich), ethanol (AAPER), and lecithin (95% L-α-phosphatidylcholine, soy) were used as received. Synthetic seawater (SSW) was prepared by adding 427 mM NaCl, 55 mM MgCl$_2$, and 27 mM Na$_2$SO$_4$ to distilled water—a simplified version of the SSW formulation reported by Kester et al. (Kester et al., 1967). South Louisiana Macondo surrogate crude, a light sweet crude with a viscosity of 12 cSt @ 20 °C provided courtesy of BP through the Gulf of Mexico Research Initiative, was received on ice, stored at −5 °C, and used as received.

2.2. Baffled Flask Test (BFT)

Tests exploring the effects of lecithin:Tween 80 ratio and dispersant:oil ratio on dispersant effectiveness employed a slightly modified version of the high-mixing-energy Baffled Flask Test

procedure developed by Venosa et al. (Sorial et al., 2004a, 2004b) Dispersants were composed of 80 wt.% total surfactant (i.e., various mixtures of lecithin and Tween 80) and 20 wt.% ethanol as solvent. A 120 mL baffled Wheaton trypsinizing flask with a stopcock added at its base (Fig. 2, left) was filled with 120 mL of synthetic seawater, taking care to introduce an air bubble into the stopcock so oil would not accumulate there during the test. A wire containment ring 1.5 cm in diameter was then suspended 1–2 mm above the surface of the water so that it pulled up a meniscus of seawater, and 100 μL of oil was deposited within that meniscus using a Rainin positive displacement pipette, forming a confined slick. 1–4 μL of dispersant (depending on the desired volumetric dispersant:oil ratio) was then deposited onto the slick using a 25 μL fixed-needle syringe, after which the containment ring was removed and the flask agitated for 10 min at 200 rpm on an orbital shaker with an orbital diameter of ~2 cm. After the agitation period, the oil–water dispersion was allowed to settle for 10 min, and then the stopcock at the base of the flask was purged by releasing 2–3 mL of dispersion into the waste. A 30 mL sample of the dispersion was then taken through the stopcock, and the crude oil was extracted from that sample in a separatory flask using 3 × 3.5 mL aliquots of dichloromethane (DCM). Finally, DCM was added to the extract to bring it up to a final

Fig. 2. Standard-size baffled flask (left) and scaled-down/low-energy baffled flask (right) employed in effectiveness tests, each filled with 120 mL synthetic seawater as they are during testing.

volume of 10.5 mL (since some DCM would evaporate during the extraction).

The absorbance of this crude oil–DCM extract was measured between 200 and 600 nm at 0.2 nm intervals using a Thermo Scientific Evolution 60S UV–Vis spectrophotometer. A 100%-dispersion-standard oil–DCM mixture, containing 10 μL of oil-dispersant mixture in 2.8 mL of DCM, was also prepared after every extraction, and its absorbance was measured at the same wavelengths. (30 mL/120 mL = 25% of the oil–water dispersion was sampled, so 100% dispersion would have put 25% of the original slick, or $(100 \mu L \times 0.25 \times (2.8/10.5)) = 10 \mu L$, into a 2.8 mL oil–DCM extract.) Prior work by Riehm and McCormick (Riehm and McCormick, 2014) demonstrated that the absorbance of these crude oil–DCM mixtures within the wavelength range 360–400 nm varies linearly with crude oil concentration. Thus, the ratios of the absorbance of each sample's extract to the absorbance of the 100% oil–DCM standard at corresponding wavelengths were averaged between 360 and 400 nm to yield each sample's effectiveness value. If the range of all measured effectiveness values between 360 and 400 nm spanned more than one percentage point of measured effectiveness, typically due to scattering from emulsified seawater or another contaminant in the oil–DCM extract, the data from that sample were discarded.

2.3. Oil–water dispersion imaging

Oil–water dispersions from the post-settling dispersion sample generated by this test procedure were imaged in a 1×0.2 cm glass cuvette using a Hirox KH-7700 Digital Microscope System. Images were converted to greyscale using ImageJ and particle sizes were measured manually.

2.4. Oil–water interfacial tension

The interfacial tension between crude oil–dispersant mixtures and synthetic seawater was measured using a spinning drop tensiometer originally designed by D. Joseph. (Joseph et al., 1992) A 1–5 uL droplet of crude oil/dispersant mixture containing 2 wt.% surfactant (10–20 mM, depending on dispersant composition) was injected into a glass tube containing ~25 mL of synthetic seawater, which was sufficient to dilute any lecithin or Tween 80 leaching from the droplet to well below reported critical micelle concentrations for either surfactant (Martínez-Landeira et al., 2002; le Maire et al., 2000). The tube was then spun horizontally at a predetermined speed so that centrifugal forces centered and deformed the droplet along the tube's horizontal axis, and the droplet's interfacial tension was calculated from its shape according to the method of Princen et al. (Princen et al., 1967).

2.5. Low-energy Baffled Flask Test

Tests exploring the effects of dispersant solvent composition and surfactant:solvent ratio on dispersant effectiveness employed a scaled-down version of the Baffled Flask Test which imparted lower mixing energy (Venosa et al., 2002) to the dispersion, as well as a slightly different set of materials.

2.6. Materials

Tween 80 (Sigma Aldrich), ethanol (Fisher Scientific), and lecithin (>40% L-α-phosphatidylcholine, egg yolk) were used as received. Synthetic seawater (SSW) was prepared using "Sea Salt" (Lake Products Company, Inc., Maryland Heights, MO), a synthetic sea salt blend based on ASTM standard D1141-98. Pennsylvania crude, a light sweet crude with a viscosity of 5 cSt @ 20 °C, was used as received from Baar Products and stored at room temperature (as received).

2.7. Procedure

Tests exploring the effects of dispersant solvent composition and surfactant:ethanol ratio employed a scaled-down version of the Baffled Flask Test which imparted lower mixing energy to the dispersion. A 125 mL Erlenmeyer flask with three baffles in its base (Fig. 2, right) was filled with 120 mL of synthetic seawater, and then 100 μL of oil was deposited onto the seawater surface. Dispersant was immediately added to achieve the desired ratio of surfactant to oil (ca. 2 to 42 μL) and the flasks were sealed and placed on a shake table with an orbital diameter of 1.9 cm at 200 rpm for 10 min. After mixing, the flasks were removed from the rotator and allowed to sit for 10 min at which point 30 mL of aqueous phase was extracted from the center of the flask using a syringe. The extracted oil–water dispersion was placed into a separatory funnel and the crude oil was extracted using 3×5 mL aliquots of dichloromethane. The concentration of dispersed oil in the oil–dichloromethane extract was determined by UV–vis spectroscopy based on the method by Venosa et al. (Venosa et al., 2002), using a calibration curve generated for each dispersant formulation. It was necessary to generate a different calibration curve for each dispersant.

3. Results

3.1. Lecithin:Tween 80 (L:T) ratio

Fig. 3, which shows dispersant effectiveness as a function of L:T (w/w) ratio, indicates that the most effective L/T-based dispersants have a L:T ratio between 60:40 and 80:20; there is not a statistically significant difference in measured effectiveness for dispersants in this compositional range. This result is consistent with the excellent emulsification reported by Athas et al. (Athas et al., 2014) for 60:40 L:T blends. The high mixing energy (Kaku et al., 2006) which is employed in this Baffled Flask Test procedure, pushing maximum observed dispersion effectiveness above 80%, makes it difficult to optimize dispersant composition more precisely than this. Other, commercial dispersants tend to exhibit similarly high values (80–90% effectiveness) under this test protocol when a comparable DOR, temperature, and crude oil is employed (Venosa et al., 2002; Venosa and Holder, 2011; Srinivasan et al., 2007).

At L:T ratios higher than 80:20 (i.e., when Tween 80 is eliminated from the formulation), dispersant effectiveness is likely constrained by high interfacial tensions. Measurements of interfacial tension (IFT)
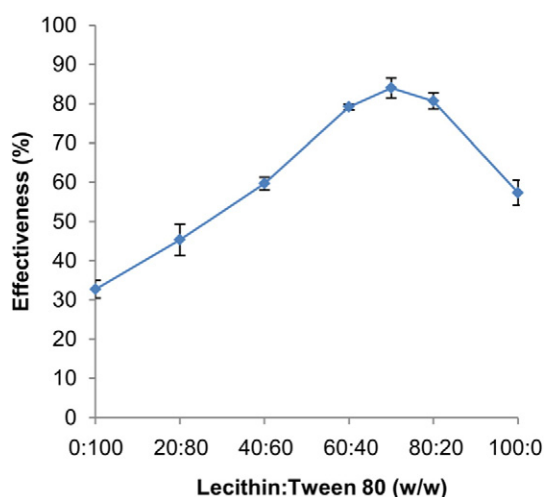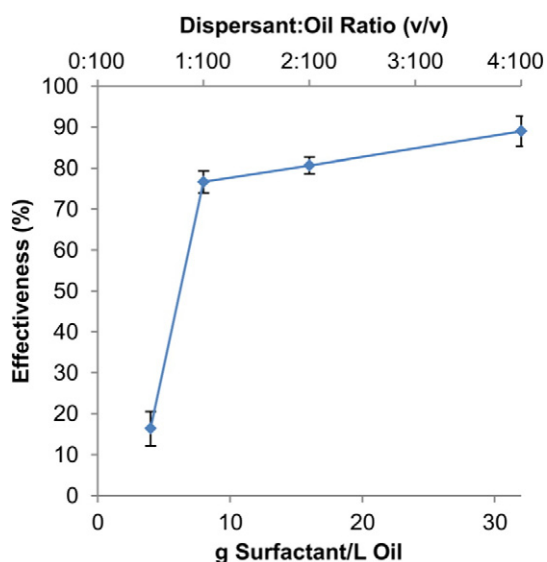

Fig. 3. Effectiveness of dispersants containing various blends of lecithin and Tween 80, as measured using the "high-energy" Baffled Flask Test with a volumetric dispersant:oil dosage ratio (DOR) of 1:50. Effectiveness was measured in triplicate at each composition, and error bars show the standard error of the measurements at each composition.

between seawater and dispersant-treated crude oil (DOR 1:50 (*v/v*)) reveal that, while the IFT at an L:T ratio of 60:40 is 0.08 mN/m, the IFT produced by a L:T ratio of 100:0 is considerably higher, at 0.65 mN/m. Athas et al. (Athas et al., 2014) also conducted measurements of IFTs between seawater and a similar crude oil treated with L/T/ethanol dispersants (though at a DOR of 1:10 rather than 1:50), and observed a dramatic increase in IFT over this same range of dispersant compositions. This sharp rise in interfacial tension when Tween 80 is eliminated from the dispersant explains the corresponding sharp dropoff in effectiveness.

For L:T ratios below 60:40, however, something beyond interfacial tension must account for the decline in dispersant effectiveness. Interfacial tension (IFT) between seawater and dispersant-treated crude oil (DOR 1:50) for L:T ratios of 40:60 and 20:80 was found to remain low (0.02 mN/m and 0.16 mN/m, respectively) despite the fact that the effectiveness of these dispersant compositions was considerably lower than that of 60:40 to 80:20 L:T dispersants. Athas et al. (Athas et al., 2014), too, found that IFT at the dispersant-treated crude oil/seawater interface (1:10 *v/v* DOR) remains consistently low (~0.05 mN/m) for dispersant L:T ratios as low as 10:90 (*w/w*). Riehm and McCormick (Riehm and McCormick, 2014) observed low effectivenesses at low interfacial tensions ($<10^{-4}$ mN/m) for certain oil dispersant blends of Tween 80, Span 80, and DOSS, and attributed this to much longer dynamic interfacial tension transients (and, thus, slower interfacial adsorption of surfactants) at low-effectiveness dispersant compositions than were observed for high-effectiveness dispersant compositions. For lecithin/Tween 80 blends, however, we do not observe such a compositional trend in the length of dynamic interfacial tension transients, so another mechanism must be operative here. Another possible explanation for lower effectiveness at lower L:T ratios despite low IFTs is that the geometries of the surfactants as they pack at the oil–water interface (see Fig. 1) are able to form a dense monolayer, or perhaps even a multilayered lamellar structure, at a L:T ratio of 80:20 (*w/w*), and are less able to do so at a L:T ratio of 20:80 (*w/w*). A careful investigation of this hypothesis, via cryogenic electron microscopy, dilatational interfacial viscoelasticity measurements, etc., will be conducted using a model crude oil (in order to prevent interfacially-active components of crude oil from confounding study of the dispersant's interfacial assembly) in future work.

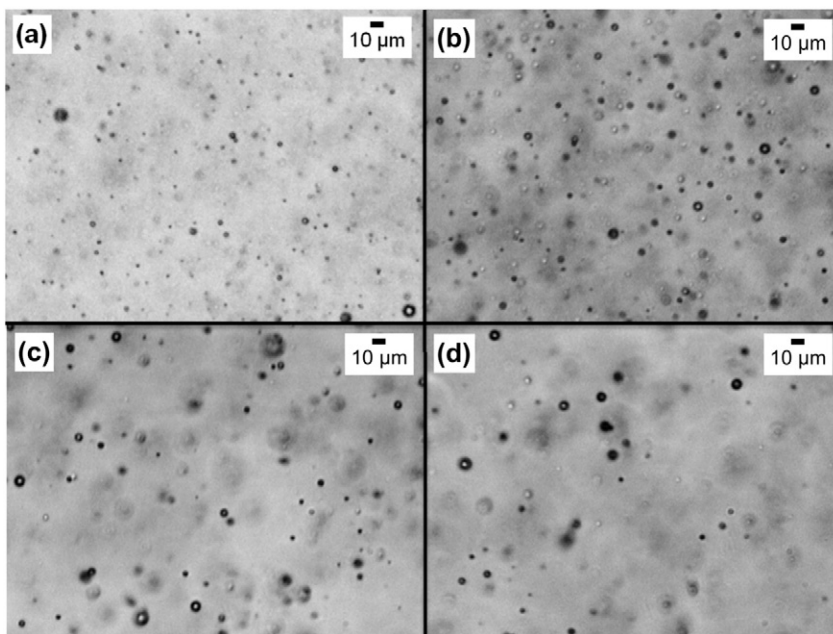### 3.2. Dispersant:oil ratio

In Fig. 4, the effectiveness of dispersant containing 80:20 L:T (*w/w*), one of the most effective L:T ratios, is shown over a range of DORs. Remarkably, decreasing the DOR from 1:25 *v/v* to 1:100 *v/v* only reduces effectiveness a small amount, from 89% to 77%. This dispersant is therefore not only highly effective, but also highly efficient (Srinivasan et al., 2007), since it nearly reaches its maximum effectiveness at such a low DOR. The sharp dropoff in dispersant effectiveness between DORs of 1:100 and 1:200 is consistent with abrupt declines in effectiveness observed for other dispersants below a particular dispersant:oil ratio (Srinivasan et al., 2007; Khelifa et al., 2007), and it has been proposed that this critical DOR may correspond to a critical micelle concentration for such dispersants in the crude oil. The critical micelle concentrations for lecithin in various nonpolar solvents have been found by others to range from 0.05–0.5 mM (Walde et al., 1990), which is 1–2 orders of magnitude lower than the ~5 mM lecithin concentration in the crude oil treated with 80:20 L:T (*w/w*) dispersant at a DOR of 1:200 which is characterized in Fig. 4. However, solutions of lecithin in oil which are exposed to water have been reported to form an "organogel" phase, consisting of entangled rod-like water-in-oil micelles, at minimum lecithin concentrations of 5–10 mM (Shchipunov, 1997; Shchipunov, 2001), which is the approximate concentration of lecithin at which we have observed the abrupt dropoff in effectiveness. (Tween 80 is insoluble in oil on its own, but is readily incorporated into water-in-oil microstructures formed by a variety of hydrophobic surfactants (Paul and Mitra, 2005; Davies et al., 1987)). Thus, further investigation of the role (if any) of this "organogel" in effective oil dispersion by L/T mixtures is warranted, via studies of interfacial tension, dilatational viscoelasticity, and any water-in-oil microstructures which are formed by L/T mixtures within (model) crude oil or at the oil–water interface.

3.3. Oil–water dispersion imaging

Images were taken of dispersions of crude oil treated with 80:20 L:T (*w/w*) dispersant at DORs of 1:25, 1:50 and 1:100 (*v/v*) and with 100:0 L:T (*w/w*) dispersant at a DOR of 1:50 (*v/v*) (Fig. 5). The median particle diameters in these dispersions were all 3–4.5 μm, smaller than the 6–7 μm median particle diameters of the oil-in-water emulsions made by Athas et al. at similar dispersant compositions and a higher DOR (1:10 *v/v*). This is likely due to the fact that the emulsions made by Athas et al. had a much higher oil:water ratio (1:10 *v/v*) than the dispersions generated using the high-energy Baffled Flask Test (1:1200 *v/v*), so that droplets collided and coalesced much more readily in the emulsions than they did in the high-energy BFT dispersions.

3.4. Surfactant:solvent ratio and solvent composition

In order to explore the effects of surfactant:solvent ratio and solvent composition on dispersant effectiveness, a different baffled flask with smaller baffles (Fig. 1, right) was employed which imparted lower mixing energy to the oil–water dispersion. This "low-energy" dispersant effectiveness was found to be more sensitive to surfactant:solvent ratio and solvent composition than effectiveness measured using the standard baffled flask (Fig. 1, left). Fig. 6 shows the dispersion effectiveness of a 60:40 L:T dispersant as a function of surfactant:solvent ratio (*w/w*) and of total surfactant dosage in the crude oil (g/L), using ethanol as the dispersant solvent. Dispersion effectiveness increased with total surfactant mass per volume of oil and with increasing surfactant:ethanol ratio in the dispersant. The latter result is likely due to ethanol's immiscibility with crude oil; at the lowest surfactant:solvent ratio tested, 30:70 *w/w*, a significant fraction of the dispersant dosed onto a test oil slick ran off into the water rather than penetrating the slick. Such dispersant runoff was not observed at higher surfactant:solvent ratios, but it seems likely that the hydrophilicity of the dispersant solvent continued to have a

Fig. 4. Effectiveness of dispersant containing an 80:20 L:T (*w/w*) surfactant blend at various dispersant:oil dosage ratios, as measured using the high-energy Baffled Flask Test. Effectiveness was measured in triplicate at each composition, and error bars show the standard error of the measurements at each composition.

Fig. 5. Optical micrographs of dispersions of crude oil in seawater produced using the high-energy Baffled Flask Test (the dispersions were imaged immediately following the 10 min settling period). The dispersions were produced using the following DORs and dispersant L:T ratios: (a) 1:25 DOR (v/v), 80:20 L:T (w/w); (b) 1:50 DOR (v/v), 80:20 L:T (w/w); (c) 1:100 DOR (v/v), 80:20 L:T (w/w); (d) 1:50 DOR (v/v), 100:0 L:T (w/w).

deleterious effect on the ability of the dispersant to fully permeate and disperse the oil slick.

In order to try to improve dispersant–oil miscibility, therefore, another set of low-energy Baffled Flask Tests was completed using dispersants with a 60:40 L:T (w/w) ratio and a 30:55:15 surfactant:ethanol:cosolvent ($w/w/w$) ratio in which the cosolvent was either octane or octanol. Miscibility of octane and octanol with the dispersants and with crude oil was confirmed visually. Fig. 7 shows that both adding octane to the dispersant and, to a greater extent, adding octanol to the dispersant improves its effectiveness. Future work will focus on the identification of other moderately hydrophobic solvents, like octanol, which improve dispersant–oil miscibility and therefore dispersant effectiveness.

4. Conclusion

The predicted (Athas et al., 2014) effectiveness of lecithin-Tween 80-ethanol blends as marine oil dispersants has been confirmed using baffled flask effectiveness testing. The most effective L:T ratios are 60:40 to 80:20 w/w. At L:T ratios higher than this, effectiveness is limited by high interfacial tension, while at L:T ratios lower than this, insufficient lecithin is present to pack into a dense interfacial monolayer with the Tween 80. The highly effective 80:20 L:T (w/w) dispersant blend (with an 80:20 surfactant:ethanol ratio (w/w)) is also highly efficient, since its decline in effectiveness as DOR is reduced from 1:25 to 1:100 (v/v) is minimal. It is proposed that the sharp dropoff in its effectiveness
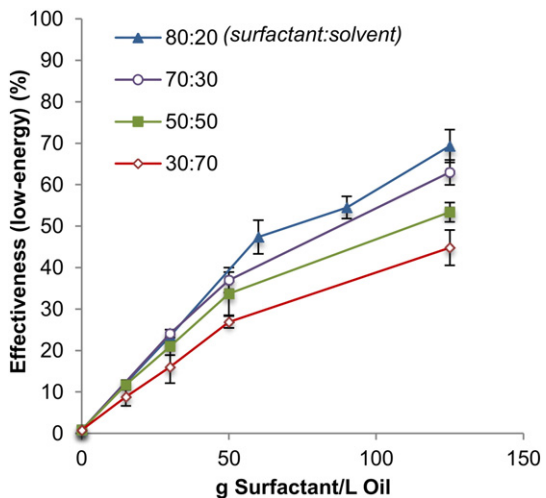
Fig. 6. Effectiveness of dispersants containing a 60:40 L:T (w/w) surfactant blend in an ethanol solvent at various surfactant:solvent w/w ratios (shown in the legend) as a function of total mass of dispersant surfactant added to the crude oil slick, measured using the low-energy Baffled Flask Test. Effectiveness was measured in triplicate at each composition, and error bars show the standard error of the measurements at each composition.
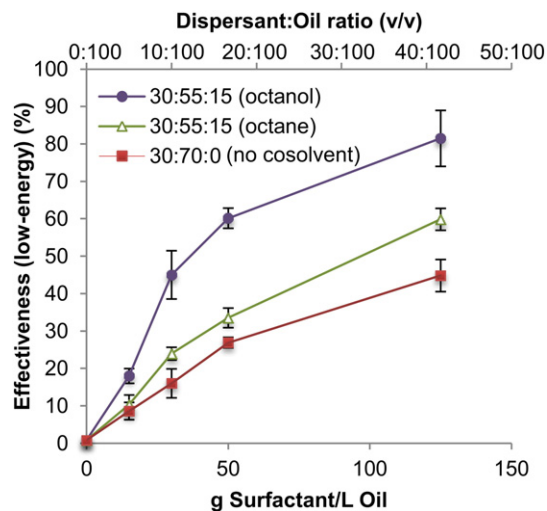
Fig. 7. Effectiveness of dispersants containing a 60:40 L:T (w/w) surfactant blend and various solvents with a surfactant:solvent ratio of 30:70 (w/w) as a function of total mass of dispersant surfactant added to the crude oil slick, measured using the low-energy Baffled Flask Test. The solvents tested were ethanol, 55:15 (w/w) ethanol:octane blend, and 55:15 (w/w) ethanol:octanol blend. Overall dispersant composition is shown in the legend as surfactant:ethanol:co-solvent ($w/w/w$). Effectiveness was measured in duplicate at each composition, and error bars show the standard error of the measurements at each composition.

observed as DOR is reduced from 1:100 to 1:200 (*v/v*) occurs because dispersant surfactant concentration falls below a critical concentration for self-assembly of L:T blends into microstructures in the crude oil and/or at the crude oil/seawater interface.

Increasing surfactant:ethanol ratio in dispersant containing 60:40 *w/w* L:T improves its effectiveness even when total surfactant concentration dosed into the oil is held constant, as does introducing more hydrophobic solvents like octane and octanol to the dispersant. This suggests that, while ethanol plays a key role as a common solvent for lecithin and Tween 80 in these dispersants, its hydrophilicity also limits their effectiveness by diminishing their miscibility with crude oil. Future work will explore the importance of dispersant microstructures both within bulk crude oil and at the oil–water interface in effective crude oil dispersion, likely using a model crude oil, as well as further exploring more oil-miscible solvent formulations for lecithin:Tween 80 dispersants.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Abbreviations

L	lecithin
T	Tween 80
DOR	dispersant:oil ratio
BFT	Baffled Flask Test

Acknowledgments

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