

An Effective Dispersant for Oil Spills Based on Food-Grade Amphiphiles

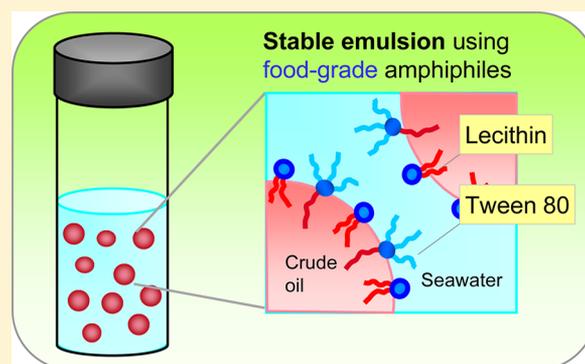
Jasmin C. Athas,[†] Kelly Jun,[‡] Caitlyn McCafferty,[†] Olasehinde Owoseni,[§] Vijay T. John,[§] and Srinivasa R. Raghavan^{*,†,‡}

[†]Department of Chemistry & Biochemistry and [‡]Department of Chemical & Biomolecular Engineering, University of Maryland, College Park, Maryland 20742, United States

[§]Department of Chemical & Biomolecular Engineering, Tulane University, New Orleans, Louisiana 70118, United States

S Supporting Information

ABSTRACT: Synthetic dispersants such as Corexit 9500A were used in large quantities (~2 million gallons) to disperse the oil spilled in the ocean during the recent Deepwater Horizon event. These dispersant formulations contain a blend of surfactants in a base of organic solvent. Some concerns have been raised regarding the aquatic toxicity and environmental impact of these formulations. In an effort to create a safer dispersant, we have examined the ability of food-grade amphiphiles to disperse (emulsify) crude oil in seawater. Our studies show that an effective emulsifier is obtained by combining two such amphiphiles: lecithin (L), a phospholipid extracted from soybeans, and Tween 80 (T), a surfactant used in many food products including ice cream. Interestingly, we find that L/T blends show a synergistic effect, i.e., their combination is an effective emulsifier, but neither L or T is effective on its own. This synergy is maximized at a 60/40 weight ratio of L/T and is attributed to the following reasons: (i) L and T pack closely at the oil–water interface; (ii) L has a low tendency to desorb, which fortifies the interfacial film; and (iii) the large headgroup of T provides steric repulsions between the oil droplets and prevents their coalescence. A comparison of L/T with Corexit 9500A shows that the former leads to smaller oil droplets that remain stable to coalescence for a much longer time. The smaller size and stability of crude oil droplets are believed to be important to their dispersion and eventual microbial degradation in the ocean. Our findings suggest that L/T blends could potentially be a viable alternative for the dispersion of oil spills.



INTRODUCTION

Dispersants are commonly employed for the remediation of oil slicks floating on an expanse of water.^{1–4} In the case of a large oil spill such as the Deepwater Horizon event in the Gulf of Mexico in 2010, over 2 million gallons of dispersants needed to be used.⁵ Typical dispersants used on oil spills are blends of different surfactants dissolved in a solvent.^{3,4} The overall liquid dispersant is sprayed onto the oil slick using a combination of aircraft and ships. In the presence of the added dispersant, wave action serves to disperse the crude oil slick into discrete droplets, each of which is stabilized by adsorbed surfactant molecules.^{1,2} The stabilized droplets get transported beneath the water surface, and with time much of the oil is degraded by microbes in the ocean.^{6,7}

The dispersion of an oil slick in water is essentially a process of emulsification.^{3,4} Thus, an effective dispersant must be a good emulsifier of crude oil in seawater, i.e., it must convert the oil slick into discrete droplets that remain stable to coalescence. Typically, the smaller the droplets, the more efficient the extent of dispersion.^{4,6} This is because small droplets are more likely to be transported away by wave action and currents.^{6,7} Moreover, smaller droplets will be less buoyant and therefore

less likely to revert to the water surface and coalesce into a slick. On the molecular level, the requisite characteristics of dispersants and emulsifiers are identical: (1) the molecules must reduce the interfacial tension between oil and water; (2) the molecules should remain bound to the surface of the oil droplets, i.e., at the oil–water interface; and (3) the presence of bound molecules at the interface should inhibit the coalescence of the droplets.³

Dispersants currently used in oil-spill treatment are usually a blend of nonionic and anionic surfactants.^{1,2} The most used formulations in this regard are the Corexits, specifically, Corexit 9500A.^{5,8} This formulation contains the nonionic surfactants Tween 80, Span 80, and Tween 85 and the anionic surfactant dioctyl sodium sulfosuccinate (also known as Aerosol OT or AOT or DOSS),^{9,10} although the exact mass fraction of each component in the formulation is not known. A solvent that is commonly used in the formulation to dissolve these surfactants is 1-(2-butoxy-1-methylethoxy) propanol.⁹ While the Corexits

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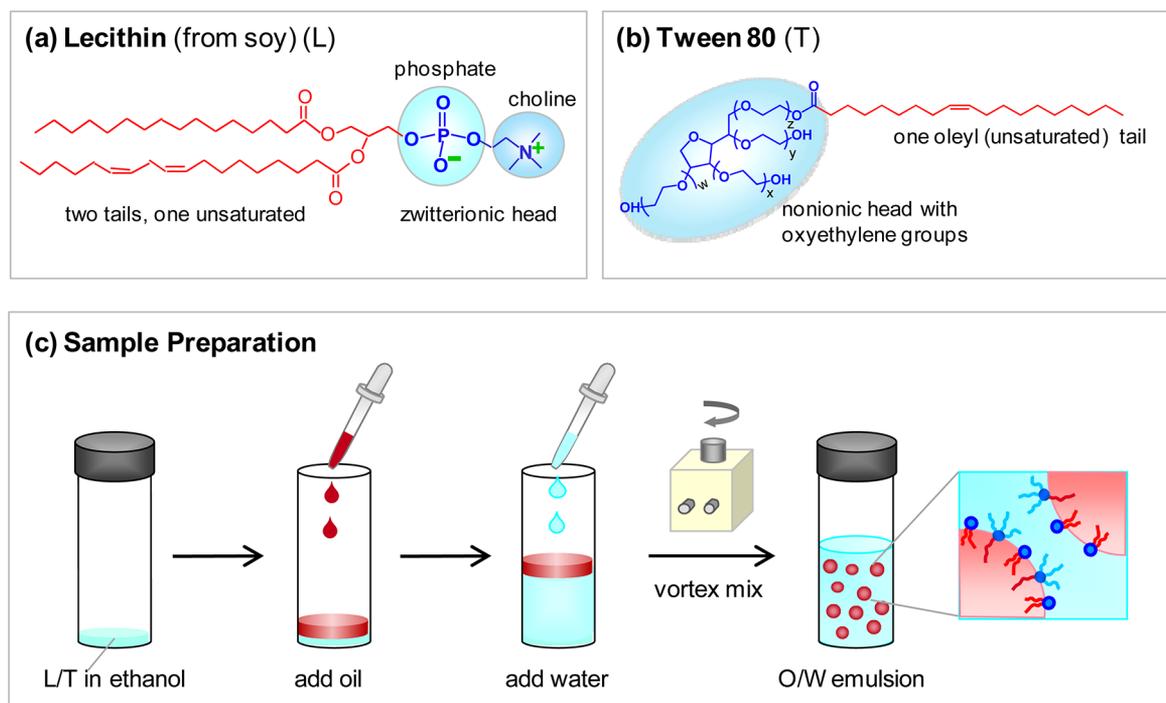


Figure 1. Emulsification of crude oil in seawater using mixtures of lecithin and Tween 80. The molecular structure of soy lecithin (L) is shown in (a) and that of Tween 80 (T) is shown in (b) (hydrophobic tails in red; hydrophilic head in blue). The procedure for preparing emulsions is illustrated schematically in (c). First, the L/T mixture is dissolved in ethanol (60% total surfactant) to create the dispersant, and this is mixed with the oil of interest (e.g., crude oil). Typically, the dispersant/oil weight ratio is maintained at 1:10. Thereafter, water of the desired composition (e.g., synthetic seawater) is added; typically the oil/water ratio is fixed at 1:10 by weight. The sample is then mixed using a vortex mixer at 3000 rpm for 30 s to create the oil/water (O/W) emulsion. A cartoon of the emulsion (inset) shows the surfactant molecules adsorbed on the oil droplets with their hydrophilic portions (blue) oriented toward the water and their hydrophobic portions (red) anchored in the oil.

are considered to be effective at crude-oil dispersion, there have been mixed reports regarding their toxicity.^{11–15} It is worth noting that the anionic surfactant AOT in the Corexits is not approved as a food-grade component worldwide and is considered an irritant of the eyes and skin.¹⁶ AOT has been reported to slow down the rate of bacterial oxidation of crude oil.¹¹ Moreover, AOT itself does not degrade easily and persists in the ocean longer than the other components of Corexit.⁸

Recently, we embarked on a study to identify dispersants that are safe, nontoxic, and environmentally benign while also having good dispersing ability against oil spills. Toward this end, we focused on food-grade amphiphiles that are commercially available. To identify effective dispersants, we studied the emulsification of one type of crude oil (a Louisiana crude obtained from the Macondo well in the Gulf of Mexico) against simulated seawater (i.e., water with added salts). Our studies revealed one promising candidate, which is the subject of this paper: a dispersant formed by blending lecithin and Tween 80. Lecithin (L) is a phospholipid derived from soybeans, and it has two hydrocarbon tails and a zwitterionic phosphocholine headgroup (Figure 1a). It is commonly used as an emulsifier in the food industry, and it is also used to prepare liposomes for drug delivery.¹⁷ Tween 80 (T), also called polysorbate 80, is a nonionic, single-tailed surfactant (Figure 1b) that is commonly used as an emulsifier in foods and pharmaceutical products; it is believed that people in America consume between 12 and 111 mg/day of T in various foods, notably ice cream.¹⁸ Note that T is also present in Corexit 9500A.

Our studies show that neither L nor T is an effective emulsifier of crude oil (or other oils) on its own. However, L/T

blends, especially at a weight ratio of 60/40 L/T, are effective at forming stable emulsions that resist coalescence or creaming for long periods of time. This suggests that the two amphiphiles act synergistically in terms of emulsification. The focus of this paper is in demonstrating this synergistic effect between L and T. To our knowledge, this is the first systematic study on the same, although there do appear to be anecdotal or semi-quantitative reports in this regard among some scientists and food enthusiasts.^{19,20} To mimic the scenario used with oil spills, we dissolve concentrated L and T in a solvent, ethanol. This solution is then combined with oil and water, followed by vortex mixing, to create oil/water (O/W) emulsions (Figure 1c). We use visual observations, optical microscopy, and interfacial tensiometry to study these emulsions.

EXPERIMENTAL SECTION

Chemicals. Soybean lecithin (95%) was purchased from Avanti Polar Lipids while the Tween 80 surfactant (poly(oxyethylene sorbitan monooleate)) was obtained from Sigma-Aldrich. Span 20, dioctyl sodium sulfosuccinate (98%), 2-butoxyethanol (reagent grade), hexadecane (reagent grade), paraffin oil, and mineral oil were purchased from Sigma-Aldrich. Ethanol (reagent grade) was purchased from Fisher Scientific. Corexit 9500A was obtained as a gift from Nalco Energy Services. Louisiana sweet crude oil was obtained from British Petroleum's Macondo prospect through the Gulf of Mexico Research Initiative (GOMRI) program.⁹ Deionized water (DI water) from a Thermo Barnstead Genpure water purification system was used in all experiments. Sea salt (32 g, Instant Ocean from Spectrum Brands) was dissolved in 1 L of DI water to make a synthetic version of seawater.

Preparation of Emulsions. The procedure for preparing O/W emulsions using crude oil and synthetic seawater is shown in Figure 1.

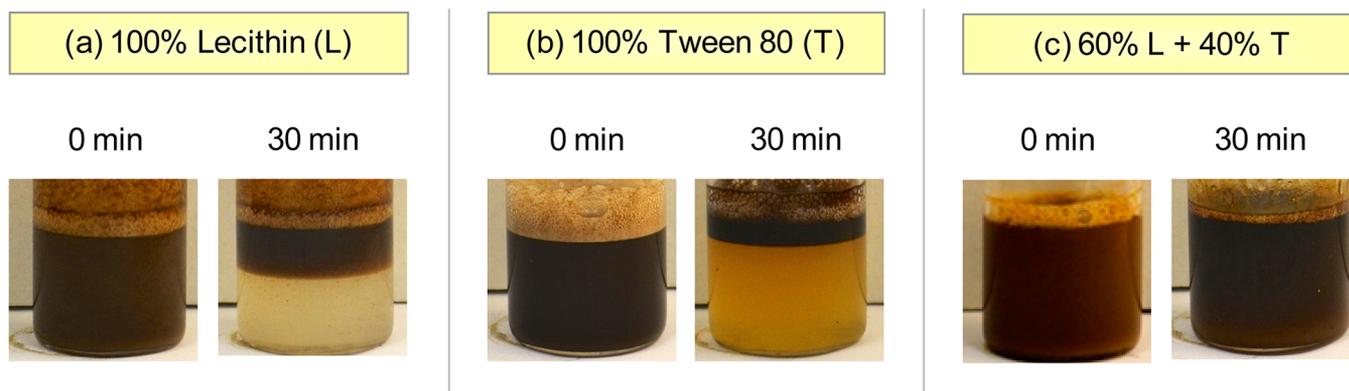


Figure 2. Synergistic emulsification by mixtures of lecithin (L) and Tween 80 (T). Samples of crude oil and seawater (1:10) are emulsified using either L alone (a), T alone (b), or a 60/40 mixture of L/T (c). The dispersant/oil ratio is fixed at 1:1, i.e., the total surfactant content in each sample is 5 wt %. Photographs are shown in each case for the sample immediately after preparation by vortex mixing and 30 min after the cessation of vortex mixing. Note that in (a) and (b) the emulsion destabilizes and rapidly separates into an oil-rich phase (darker liquid at the top) and a water-rich phase (lighter-colored liquid at the bottom). However, in the case of (c), the emulsion remains stable and no such separation is seen after 30 min.

First, surfactants L and T were dissolved at the desired ratio in ethanol, with the total surfactant concentration being 60 wt %. This solution was our overall dispersant. The dispersant was combined in a 20 mL vial with the oil, followed by the addition of the water. The sample was then placed on a vortex mixer (Fisher Vortex Genie 2) for 30 s at 3000 rpm. The overall dispersant was typically added at 10% (w/w) of the oil content, i.e., the dispersant/oil weight ratio was 1:10 (unless otherwise noted). The oil/water weight ratio was also typically maintained at 1:10. This implies that for a typical O/W emulsion, the total surfactant content in the sample was 0.54 wt %. Similar O/W emulsions were made with the Corexit 9500A dispersant using the same dispersant/oil weight ratio of 1:10. Although the exact composition of this dispersant is not known (see Table 1 later), it is likely that the solvent in this case is 1-(2-butoxy-1-methylethoxy) propanol and that the total surfactant content in the dispersant is around 83 wt %.^{9,10} In addition to emulsions with crude oil, emulsions were also prepared with mineral oil, hexadecane, and paraffin oil and by using DI water as the continuous phase. Following preparation, vials containing the emulsions were sealed with parafilm and placed on the benchtop for visual observation at room temperature. Photographs were taken at periodic intervals to assess the stability.

Optical Microscopy. A Zeiss Axiovert 125 TV inverted microscope equipped with the Motic Image Plus imaging system was used to obtain bright-field images of the samples. A drop of freshly prepared sample (immediately after vortex mixing) was placed on a microscope slide and covered with a coverslip. Images were collected at regular time intervals. ImageJ (NIH) was used to analyze the images and to obtain droplet size distributions.

Interfacial Tensiometry. Interfacial tension was measured using a spinning drop tensiometer (Grace Instruments M6500). The instrument has a capillary tube of 2 mm inner diameter with a total volume of 0.292 cm³. First, a mixture of dispersant and crude oil was created, and ~0.001 cm³ of this mixture was introduced into the capillary containing seawater using a microsyringe to create a small droplet. The capillary was then sealed and rotated at a speed in the range of 5000–6000 rpm around its longitudinal axis. The temperature of the capillary was maintained at 25 °C by circulating water at ambient temperature around the tube. The droplet radii were then measured using an optical microscope connected to a digital display. The interfacial tension was calculated using the following expression²¹

$$\gamma = \frac{\Delta\rho\omega^2R^3}{4} \quad (1)$$

where γ (mN/m) is the interfacial tension, $\Delta\rho$ (g/cm³) is the difference in density between the droplet and the surrounding fluid, ω (rad/s) is the angular velocity, and R (cm) is the droplet radius.

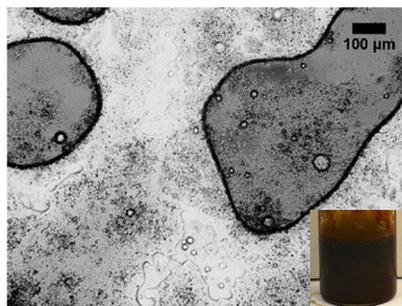
RESULTS AND DISCUSSION

We prepared O/W emulsions of crude oil in seawater as shown in Figure 1. Our dispersant contained the two surfactants L and T dissolved in ethanol (60 wt % surfactant, 40 wt % ethanol). The oil/water ratio was generally maintained at 1:10 by weight. At this relatively low fraction of oil, a stable emulsion is expected to contain discrete oil droplets in an aqueous continuous phase. The shear exerted during mixing is through a vortex mixer, and this is employed only for a short amount of time (30 s). Thus, the extent of shear is modest, and it should lead to microscale droplets. More vigorous mixing, e.g., via rotor-stator mixers or sonication, was not considered in this study. The above conditions were chosen so as to permit a rudimentary comparison between emulsification and dispersion of oil (i.e., in the context of oil spills).^{3,4} Note that in the case of an oil spill a thin layer of oil floats on a large body of water, implying that the oil/water ratio is very low. Moreover, mixing of the dispersant with the oil and water occurs only through wave action, which is not very vigorous and thus is expected to yield relatively large (microscale) oil droplets.^{6,7}

Initial observations indicated a synergy between L and T in forming stable O/W emulsions. This is illustrated through photographs in Figure 2. For the samples shown here, we have chosen a relatively large amount of surfactant, i.e., a 1:1 ratio of dispersant/oil by weight. Since the dispersant contains 60% surfactant, the total L + T is 5 wt % in each sample. We kept this amount constant and varied the ratio of L/T. (Thus, each vial contains 1 g of oil, 10 g of water, 0.6 g of L + T, and 0.4 g of ethanol). Results are shown in Figure 2 for three cases: L alone, T alone, and a 60/40 ratio of L/T. For the cases of L or T alone, a homogeneous brown-colored emulsion is formed initially (right after vortex mixing). Within a few minutes, though, the oil droplets coalesce and rise to the top of the vial. The photographs taken 30 min after vortex mixing show a distinct layer of oil above the aqueous phase. Note that the aqueous phase is much lighter in color, indicating that much of the oil has been removed from it. In other words, both these emulsions are unstable, which implies that L and T alone are not effective as emulsifiers. In contrast, the sample prepared with a 60/40 L/T blend behaves differently. In this case, the initial emulsion and the same sample after 30 min are both nearly identical: both are homogeneous, dark-brown liquids, and there is no indication of the oil separating out of the

100% Lecithin

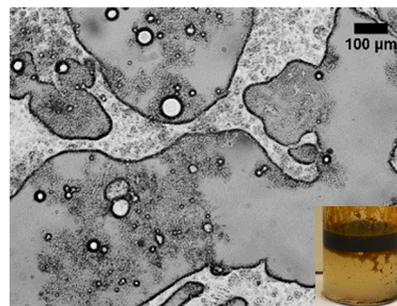
(a) 0 min



(b) 15 min

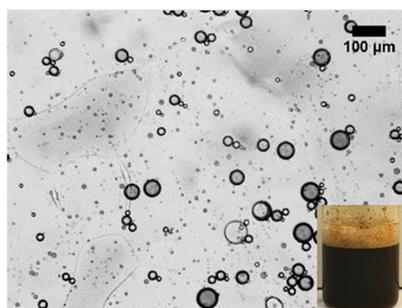


(c) 30 min



100% Tween 80

(d) 0 min



(e) 15 min



(f) 30 min

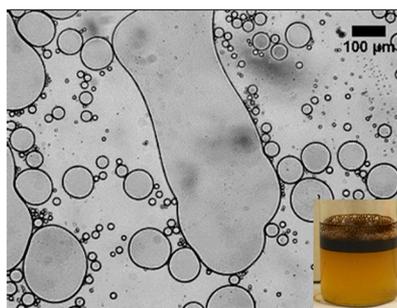


Figure 3. Instability of O/W emulsions formed using lecithin (L) or Tween 80 (T) alone. Crude oil and seawater (1:10) are emulsified using a dispersant/oil ratio of 1:10, i.e., the samples contain 0.54 wt % surfactant. Optical micrographs and photographs of the sample vial (insets) are shown at three different time points for the case of L alone in (a–c) and T alone in (d–f). In both cases, the initial oil droplets rapidly coalesce into larger droplets and blobs, which rise to the surface and form an oil-rich layer.

aqueous phase. We can thereby infer from visual observations that the L/T blend is a much better emulsifier than either component alone.

We then further studied L/T blends as emulsifiers for a variety of cases. First, we varied the ratio of L/T from 100/0 to 0/100 in regular increments. From visual observations, the 60/40 ratio of L/T was found to give the most stable emulsions, and this ratio was fixed for subsequent studies. We then confirmed that stable emulsions of crude oil could be obtained with deionized water instead of seawater (i.e., in the absence of salts in the aqueous phase). We also emulsified other kinds of oils using the 60/40 L/T blend. Results for the case of mineral oil emulsified with deionized water (30:70 ratio by weight of oil/water) are shown via photographs in Figure S1 (Supporting Information). Here again, we see that the L/T blend outperforms the individual components and gives rise to a considerably more stable emulsion. We also verified that the emulsification was independent of the use of ethanol as a solvent for the two amphiphiles. Stable O/W emulsions could be prepared either by introducing L and T as neat components or by presolubilizing L/T using a different solvent such as 2-butoxyethanol. Thus synergistic emulsification by L/T is a robust effect that holds for various cases, regardless of the type of oil, water, or solvent.

Dispersants for oil spills are used in relatively low amounts relative to the oil. We therefore reduced the total concentration

of L + T to 1/10th the value used for the samples in Figure 2. We again used crude oil/seawater at a 1:10 ratio and added the dispersant (60/40 L/T in ethanol) at a dispersant/oil ratio of 1:10. This corresponds to about 0.54 wt % L + T in the overall sample. Even at this low concentration of amphiphile, the emulsions made with the L/T blend are relatively stable. The photographs in Figures 3 and 4 show a small extent of creaming (i.e., oil rising to the top of the emulsion with time) in the case of the L/T blend, whereas there is substantial creaming in samples containing L or T alone. The differences are especially clear when we examine the microstructures of these samples using optical microscopy. For this, a drop of freshly prepared sample was placed on a microscope slide and enclosed with a coverslip at $t = 0$. Images of the sample were then taken over the course of 30 min, and these are shown in Figure 3.

First, consider the case of L alone (Figure 3a–c). At $t = 0$, we see large oily “blobs” of arbitrary shape ($>100 \mu\text{m}$ in size) coexisting with small spherical droplets of oil in the aqueous continuous phase. Moreover, considerable coalescence of the oil droplets occurs, resulting in larger droplets that become noticeable in the images at 15 and 30 min. The images therefore confirm the instability of the emulsion when L alone is used. A similar instability is also observed for the case of T alone (Figure 3d–f). Here, large blobs are absent at $t = 0$, but the coalescence of small droplets occurs frequently and rapidly at this stage. In turn, we see many larger droplets at 15 min, and

60% Lecithin + 40% Tween 80

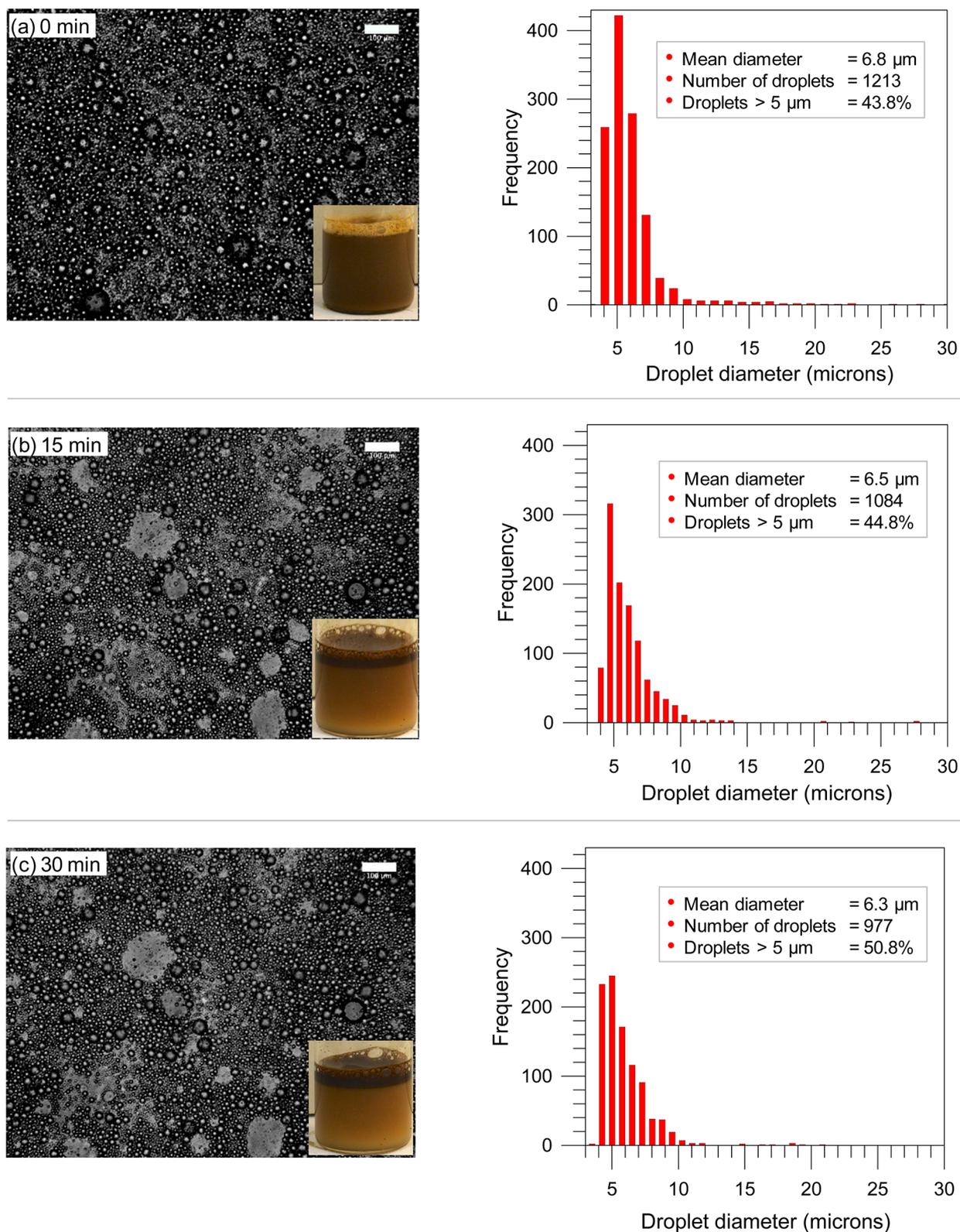


Figure 4. Relative stability of O/W emulsions when using a 60/40 mixture of lecithin (L) and Tween 80 (T). Crude oil and seawater (1:10) are emulsified using a dispersant/oil ratio of 1:10, i.e., the samples contain 0.54 wt % L/T in a 60/40 ratio. Optical micrographs and photographs of the sample vial (insets) are shown at three different time points in (a–c). Scale bars in the images represent 100 μm . In each case, a droplet size distribution (DSD) is extracted from the micrograph and is plotted alongside. Small but systematic changes are seen in the DSD as time progresses. However, most droplets remain stable to coalescence, and the mean droplet diameter stays relatively constant.

these further coalesce into blobs at 30 min. In contrast, consider the results for 60/40 L/T (Figure 4a–c). In this case, the images at the three time points all look similar and show a large number of discrete, spherical droplets. The droplets are considerably smaller than in the previous cases, with most droplets being $\sim 5 \mu\text{m}$ in diameter. Also, we saw negligible coalescence events in the microscopic field of view.

To quantify the images in Figure 4a–c, we used the ImageJ software to extract droplet size distributions, which are shown as histograms next to each image. (The images correspond to the same microscopic field of view at three distinct times.) In creating these histograms, we counted all spherical droplets and omitted any irregular bloblike regions. We find that the average droplet diameter from the histograms varies negligibly (it is $6.8 \mu\text{m}$ at $t = 0$, $6.5 \mu\text{m}$ at 15 min, and $6.3 \mu\text{m}$ at 30 min). However, there is a slow but distinct shift in the entire droplet distribution to larger sizes with time, which is indicative of Ostwald ripening.^{21,22} That is, smaller droplets tend to coalesce into larger structures, which in turn tend to rise to the top of the vial (inset photographs). This is why the total number of droplets counted for the histograms decreases from 1213 at $t = 0$ to 977 at the 30 min mark. Correspondingly, the fraction of droplets that are larger than $5 \mu\text{m}$ in diameter increases from 44% at $t = 0$ to 51% at the 30 min mark. Overall, we conclude that 60/40 L/T gives a relatively stable emulsion (only weak coalescence), especially when compared to L or T alone.

We also tested the emulsifying ability of the 60/40 L/T blend at lower concentrations of oil and surfactant, and the results are shown in the Supporting Information. Figure S3 presents results on samples at oil/water ratios of 1:15 and 1:25, with the dispersant/oil ratio fixed at 1:10. Figure S4 shows results on samples at an oil/water ratio of 1:20, with the dispersant/oil ratio lowered to 1:15 and 1:25. In all cases, images similar to those in Figure 4 are shown at the 0 and 30 min marks, and photographs of the samples at these time points are also provided. The results are qualitatively similar to those in Figure 4. Generally, the mean droplet size at $t = 0$ is larger when less dispersant is used, and there is more coalescence, reflected as a change in droplet size and a reduction in the total number of spherical droplets in the field of view. Nevertheless, these emulsions are also relatively stable over 30 min. Also, at each composition tested, the emulsion stability with 60/40 L/T was significantly better than that with L or T alone.

Why is the L/T blend an efficient emulsifier, and why is the 60/40 ratio important? To address these issues, we first turn to tensiometry. Specifically, we measured the interfacial tension γ between crude oil and seawater for varying ratios of L/T with the total concentration of L + T constant at 0.54 wt %. Figure 5 reports the interfacial tension as a function of composition. We find that the samples with L or T alone have higher interfacial tensions than their mixtures. Thus, L and T indeed do act synergistically to lower the O/W interfacial tension. However, we are unable to detect significant differences in γ over L/T ratios ranging from 10/90 to 90/10. This means that the effect of L/T on interfacial tension is one piece of the puzzle but cannot be the only aspect of importance.

Another consideration is the hydrophilic–lipophilic balance (HLB) of the surfactant blend compared to those of the individual surfactants.^{4,21} The HLB scale extends from 1 to 20, and a value below 10 indicates lipophilic behavior whereas a value above 10 indicates hydrophilic behavior.²¹ The HLB of soy lecithin (L) is around 8, and it is indeed oil-soluble but not water-soluble.^{23,24} In comparison, the HLB of Tween 80 (T) is

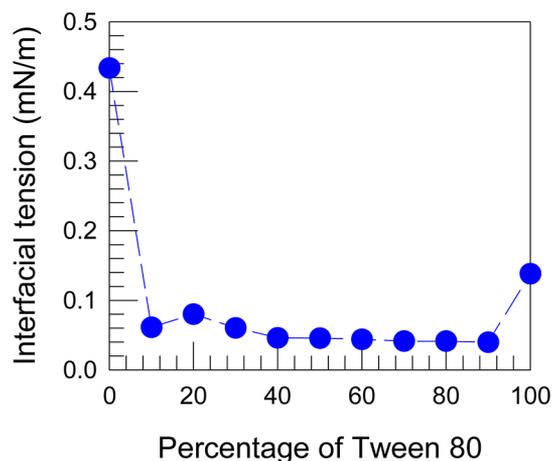


Figure 5. Interfacial function vs L/T ratio. The interfacial tension between crude oil and seawater is measured for a constant L + T concentration of 0.54 wt % and for different L/T ratios. The data are shown as a function of the %T in the mixture.

15, and it is water-soluble but not oil-soluble.⁴ The HLB of an L/T blend can thus be calculated by

$$(\text{HLB})_{\text{blend}} = 8w_L + 15w_T \quad (2)$$

where w_L and w_T are the weight fractions of L and T in the blend. Brochu et al. have noted that an HLB in the range of 9–11 may be optimal for creating stable emulsions of crude oil in seawater.⁴ If this is correct, then it can account for why L or T alone is not an effective emulsifier as each one's HLB falls below or above this range.²³ It further explains why L/T blends may be better since HLBs of between 9 and 11 can be achieved by blending L/T at ratios between 86/14 and 57/43. Our finding that the 60/40 blend (HLB = 10.8) gives the most stable emulsion seems broadly consistent with this picture. In short, L is too hydrophobic to be a good emulsifier on its own, whereas T is too hydrophilic. A 60/40 L/T blend seems to present a good compromise between the two extremes.

To test whether the HLB is a decisive factor, we created several combinations of surfactants with an HLB of about 10.8. We examined these for their ability to form stable emulsions of crude oil in seawater using visual observations and optical microscopy. Typical results are shown in Figure S5 (Supporting Information). For example an HLB of 10.8 can be obtained by mixing nonionic surfactant Span 20 (HLB = 8.6) with Tween 80 at a weight ratio of 66/34. We also considered AOT, the anionic double-tailed surfactant used in many of the Corexits, which has an HLB of 10.9 on its own. Mixtures of AOT with Tween 80 were also tested. However, as shown in Figure S5, emulsions formed by these alternative surfactant mixtures were not as stable as those with the 60/40 L/T blend. Thus, the emulsification of crude oil is not a simple matter of identifying a “magic” value for the HLB of a surfactant blend. Instead, the roles of each constituent in the blend must be examined in the context of emulsion stability.

We now provide a molecular-level discussion of the synergy between L and T using the schematics in Figure 6. Here, lecithin (L) is depicted with its zwitterionic head in blue and its two alkyl tails in red. Tween 80 (T) is shown with its head in dark blue and its one alkyl tail in dark red. Note that the head of T also has three hydrophilic oxyethylene chains (shown in light blue) extending into the water, consistent with the structure shown in Figure 1. The L and T molecules are

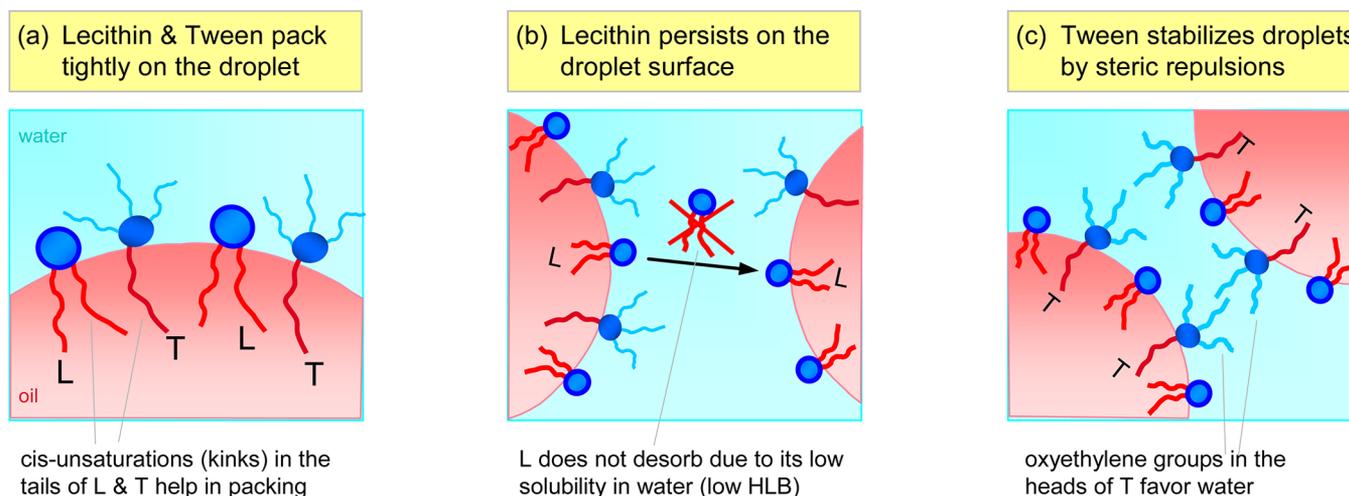


Figure 6. Mechanism for synergistic emulsification by lecithin (L) and Tween 80 (T). Three distinct aspects are highlighted by the schematics. In all cases, L and T are shown with blue heads and red tails. The oxyethylene side chains in the head of T are indicated in light blue. (a) L and T are shown to pack tightly at the surface of the oil droplet. This is aided by the fact that both L and T possess a tail with cis unsaturations, due to which the respective tails have a kink, as shown. (b) L molecules stay anchored to the droplet surface. This is because L is a double-tailed surfactant and thus has a low aqueous solubility (and a low HLB), which makes it unfavorable for the molecules to diffuse through water from one droplet to another. (c) Tween imparts steric stabilization to the droplets. This is due to its oxyethylene side chains, which are highly soluble in water and thus prefer to be surrounded by the solvent rather than undergo interpenetration when droplets meet.

arranged at the O/W interface in such a way that the alkyl tails orient toward the oil and the heads orient toward the water. We believe that three factors are at play in dictating the behavior of L and T at droplet interfaces, and these are discussed in order below.

First, we expect L and T to pack closely at the O/W interface (Figure 6a). The close packing may be aided by favorable interactions between both the tails and the headgroups. Note that L has two tails, which are C_{16} – C_{18} in length, and one of the tails has two cis unsaturations²⁴ whereas T has one oleyl tail, which is C_{18} with one cis unsaturation (Figure 1). The cis unsaturations represent kinks in the tails, and their presence ensures that the tails remain flexible and liquidlike at room temperature (i.e., the corresponding surfactants have low Krafft or melting points).^{21,22} Conversely, saturated C_{18} tails tend to be rigid or “frozen” at room temperature. We hypothesize that the flexible, bent tails of L and T aid in the packing of these molecules close to each other. Note that the interactions between hydrocarbon tails are expected to be via van der Waals or dispersion forces, which are expected to become much higher if the tails can approach in close proximity.²⁵ In addition to the interactions between the tails, the primary hydroxyls on the head of T may also undergo hydrogen bonding with the phosphate groups on the head of L, thus serving to bind the adjacent head groups.²⁶ Due to these interactions, L and T will remain anchored at the interface and thereby create a stable interfacial film. We believe this helps to explain the reduction in interfacial tension for L/T mixtures over L or T alone.

A second aspect is the nature of L. Because this molecule has two C_{16} – C_{18} tails, it is quite hydrophobic (low HLB) and it is oil-soluble but not water-soluble. Thus, once L reaches the interface, it will have a low tendency to desorb into the aqueous continuous phase (although if its interfacial activity is weak, it may tend to partition from the interface into the bulk of the oil phase).²⁴ Note that when droplet interfaces become bare, i.e., free of surfactant, they can coalesce.^{21,27} This is often an issue because surfactants exist in dynamic equilibrium between the O/W interface and the continuous (W) and disperse (O)

phases. Surfactant with relatively high water solubility can desorb from one droplet, diffuse through the aqueous phase, and adsorb onto a different droplet.²⁷ In comparison, double-tailed surfactants such as L are much less likely to do the same because their aqueous solubility is lowered by the extra tail (Figure 6b). To sum up this point, we hypothesize that the double-tailed, hydrophobic nature of L is important to the stability of O/W emulsions.

The third aspect is the nature of T. Unlike L, this molecule is largely hydrophilic and water-soluble.^{25,28} It readily forms spherical micelles in water at low concentrations (CMC of 0.012 mM). Its affinity for water is due to the three oxyethylene oligomers present on its headgroup. We hypothesize that the same oxyethylene “hairs” are also important for providing steric stabilization to oil droplets and preventing their coalescence.^{4,28} For short hairy chains on droplet surfaces, steric stabilization of the droplets is expected to be an enthalpic effect, dictated by the affinity between the hairs and the solvent.^{21,22} If the hairs are highly soluble in the solvent, as is the case for oxyethylene in water, then they would prefer to be surrounded by solvent molecules rather than by each other.²⁵ As a result, when droplets approach each other, a short-range repulsion (steric barrier) arises due to the hairs (Figure 6c).^{21,22} However, this effect is compromised if the T molecules desorb from the droplet into the aqueous phase, leaving bare uncovered regions at the interface. Uncovered droplets could then undergo flocculation or coalescence.

Altogether, our analysis helps to explain why L and T must both be present at comparable extents to ensure emulsion stability. If L alone were present or if the L/T ratio was high, then there would be only a weak barrier to the coalescence of droplets. Conversely, if T alone were present or if the L/T ratio was too low, then a steric barrier would initially exist, but the desorption of T into the aqueous phase would expose bare interfacial regions on the droplets, again promoting their coalescence. When L and T are both present, the favorable interactions between L and T, along with the double-tailed nature of L, ensure that the L/T interfacial film on the droplets

is stable and persistent. The persistence of molecules at the interface has been shown to be important for emulsification and dispersion.^{25,27} In addition, the presence of T provides steric stabilization to the droplets. Our mechanism thus explains the origin of synergy between L and T.

Finally, we attempted to compare our results with those for Corexit 9500A, which was one of the key dispersants used against the Deepwater Horizon oil spill in 2010. We introduced Corexit 9500A into a 1:10 mixture of crude oil and seawater using the same procedure as before (Figure 1). The dispersant was added at a 1:10 weight ratio relative to the oil, which is the same as in Figures 3 and 4. Note that the Corexits are a mixture of several surfactants (Table 1) and the overall concentration of

Table 1. Comparison of the Contents in an L/T Blend and in Corexit 9500A

Lecithin-Tween 80	Corexit 9500A
double-tailed surfactant: lecithin (zwitterionic, one unsaturated tail)	double-tailed surfactant: AOT (anionic, both saturated tails)
nonionic surfactant: Tween 80 (one unsaturated tail)	nonionic surfactant: Tween 80, Tween 85, Span 80 (all with one unsaturated tail)
solvent: ethanol	solvent: 1-(2-butoxy-1-methylethoxy) propanol and petroleum distillates.
composition: 60% surfactant, 40% solvent.	composition: 83% total surfactants, 17% total solvents.
viscosity: 21.8 cst.	viscosity: 22.5 cst.

surfactants in Corexit 9500A is ca. 83% by weight.⁹ Thus, the 1:10 ratio corresponds to about 0.8 wt % surfactant in our sample. Photographs of the sample as well as microscopic images are shown in Figure 7. A stable emulsion is formed initially, but the oil droplets coalesce rapidly and form an oil-rich layer above the water within just a few minutes. The microscopic images reveal the presence of both large (~100 μm) oil droplets as well as even larger blobs at $t = 0$. Very rapid coalescence of the droplets could be observed at this stage, and by about 12 s, a huge blob can be seen extending across the image. Thus, Corexit 9500A is not a very good emulsifier of crude oil based on our findings. Similar results were observed even when the Corexit content was increased by a factor of 10, as shown in Figure S2 (Supporting Information).

We should note here that the inability of Corexits to serve as a good emulsifier is not surprising in light of some of the literature.^{9,29} The function of Corexit is to disperse the oil slick, and an open question is whether dispersion is radically different from emulsification.^{4,6} As noted in the Introduction, the dispersant is supposed to break down the oil slick into discrete droplets, which are then expected to be carried away by the waves into the ocean.⁶ Thus, the smaller the droplets and the greater their resistance to coalescence, the better the overall extent of oil dispersion.^{6,9} Our findings in this study show that the L/T blend breaks up the crude oil into small droplets that remain stable and do not coalesce. Thus, at the very least, the L/T blend could be a promising candidate for oil-spill treatment (regardless of considerations regarding toxicity).

It is also worth noting that there are similarities between the L/T blend and Corexit 9500A in terms of composition (Table 1). Both contain a double-tailed surfactant (L in our case, AOT in the case of Corexit), and both contain nonionic surfactant(s).^{9,10} As discussed above, we believe that double-tailed surfactants are important because they persist at the O/W interface. On the other hand, nonionic surfactants such as T

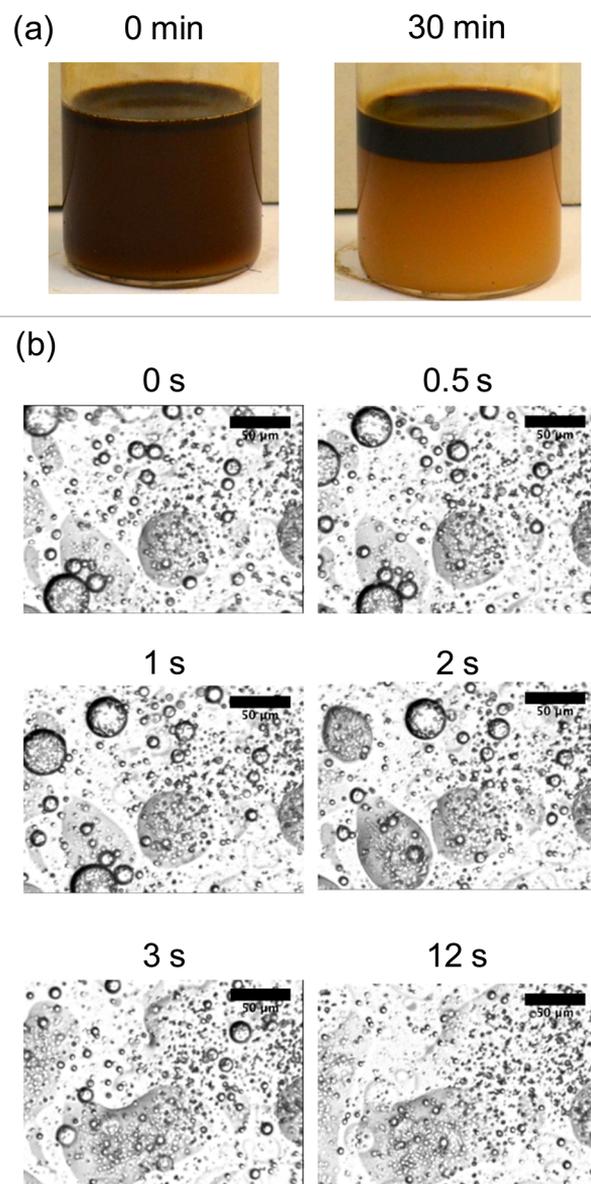


Figure 7. Instability of O/W emulsions formed using Corexit 9500A. Crude oil and seawater (1:10 ratio) are emulsified using a 1:10 ratio of Corexit/oil. (a) Photographs of the vial and (b) time-lapse optical micrographs of the sample after the cessation of vortex mixing (scale bars are 50 μm). The data reveal that the emulsion rapidly destabilizes and separates into oil-rich and water-rich phases.

are able to impart a steric barrier to droplets. Thus, we conjecture that the Corexits are also exploiting the interfacial synergy between the two types of surfactants.

The key difference between the two formulations is the use of L in our case over AOT in the Corexit. Comparing the two, L has longer tails (C_{16} – C_{18} vs C_8) and one of the tails in L is unsaturated whereas both of the C_8 tails in AOT are saturated. Thus, L is much more hydrophobic than AOT, which may allow L to be more persistent at the O/W interface, thus enhancing emulsion stability. We have also speculated above that the unsaturated tail of lecithin helps it to interact synergistically with T, which also has an unsaturated tail. Most importantly, L is a food-grade material with a safe, nontoxic profile whereas AOT may be somewhat toxic to certain organisms.¹⁶

There is also the role of the solvent used to solubilize the surfactants. Our preliminary findings (not shown) suggest that the solvent may be more important for the dispersion of an oil slick than for forming a stable O/W emulsion.³⁰ In our studies here, we have primarily used ethanol as the solvent for our L/T blends. Ethanol was chosen because both L and T are easily solubilized in it and it is a less toxic alternative to other solvents used for lipids such as chloroform and acetone. As noted earlier, our results with respect to the emulsification of crude oil in water remain identical if we substitute ethanol with other solvents such as 2-butoxy-ethanol. The latter is used as the solvent in a different Corexit formulation called Corexit 9527A,³¹ which also has been used against oil spills.

CONCLUSIONS

We have shown that a combination of the double-tailed zwitterionic phospholipid L and the single-tailed nonionic surfactant T acts as an effective O/W emulsifier, especially at a 60/40 weight ratio of L/T. Emulsification has been shown with various oils, in particular, for the case of crude oil in seawater, which is relevant in the context of oil spills. The emulsion contains discrete spherical droplets of oil ($\sim 5 \mu\text{m}$ in diameter), and the coalescence of these droplets occurs very slowly. We hypothesize that the synergy between L and T is due to (i) L and T packing tightly at the O/W interface; (ii) the surfactants persisting at the interface and not undergoing rapid desorption; and (iii) steric stabilization of the droplets by the large hydrophilic headgroups of T. Importantly, from the viewpoint of applications, L and T are cheap, food-grade amphiphiles that are considered to be nontoxic and biodegradable. Thus, the L/T blend could be a more biocompatible candidate for the dispersion of oil spills. Future studies will compare the L/T blend against current dispersants (Corexits) in model systems that simulate the dispersion of a thin layer of oil into seawater. The role of solvent will be a particular point of focus in this context. In addition, future studies will also seek to confirm the nontoxicity of L/T blends on marine organisms.

ASSOCIATED CONTENT

Supporting Information

Additional results regarding emulsification using L/T blends or Corexits. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: sraghava@umd.edu.

Notes

The authors declare no competing financial interest.

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Supporting Information for:
An Effective Dispersant for Oil Spills Based on Food-Grade Amphiphiles

Jasmin C. Athas, Kelly Jun, Caitlyn McCafferty, Olasehinde Owoseni,
Vijay T. John, and Srinivasa R. Raghavan*

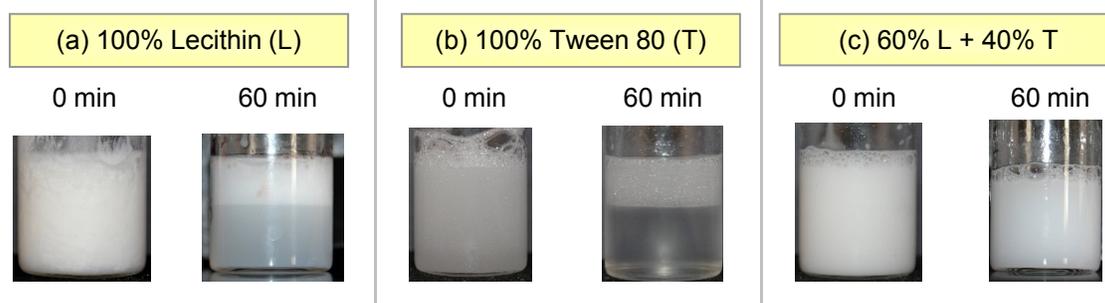


Figure S1. Synergistic emulsification of mineral oil by mixtures of lecithin (L) and Tween 80 (T). Mixtures of mineral oil and deionized (DI) water (3:7 ratio) are emulsified using either L alone (a), T alone (b), or a 60/40 mixture of L/T (c). The total surfactant content in each sample is 5 wt%. Photographs are shown in each case for the sample immediately after preparation by vortex mixing, and 60 min after cessation of vortexing. Note that in (a) and (b), the emulsion destabilizes and rapidly separates into an oil-rich phase (more turbid liquid at the top) and a water-rich phase (more clear liquid at the bottom). However, in the case of (c), the emulsion remains stable and no such separation is seen even after several hours.

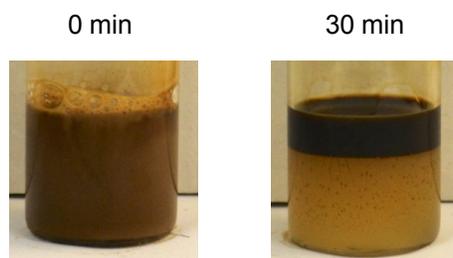
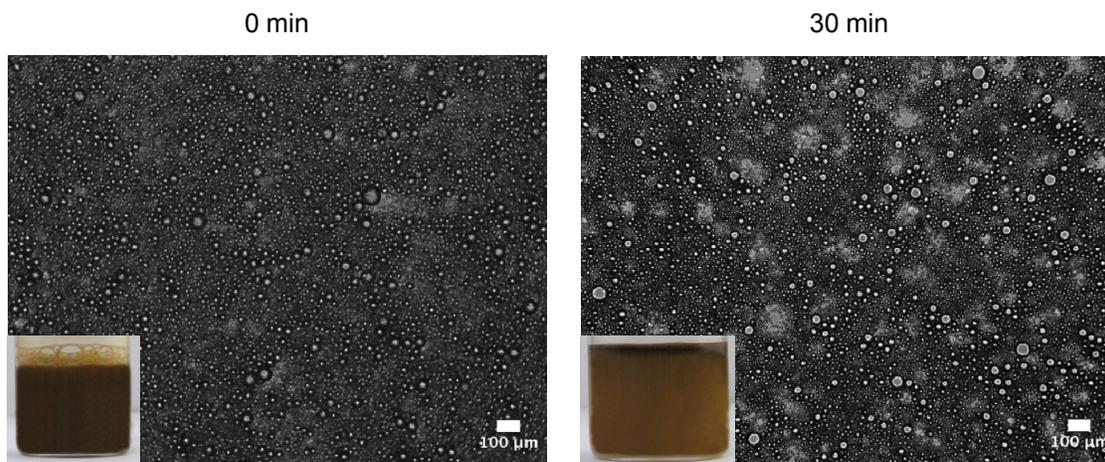


Figure S2. Instability of O/W emulsions formed using Corexit 9500A. Crude oil and seawater (1:10 ratio) are emulsified using a 1:1 ratio of Corexit:oil (i.e., total concentration of dispersant is 10 wt%). Photographs are shown for the sample immediately after preparation by vortex mixing, and 30 min after cessation of vortexing. Note that the emulsion rapidly destabilizes and separates into an oil-rich (dark brown) layer on the top and a water-rich layer at the bottom. Similar data at 1/10th the concentration of Corexit are shown in Figure 7 of the main manuscript.

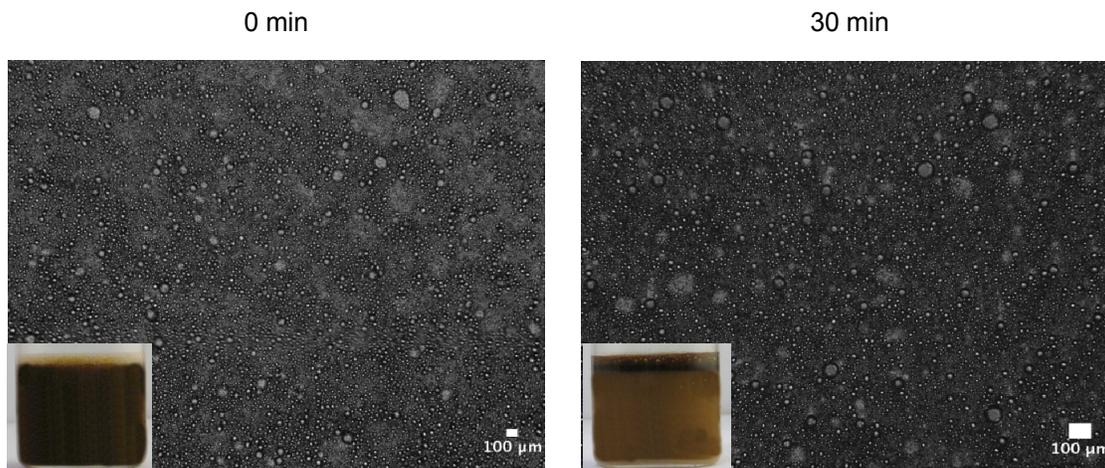
(a) Oil:Water = 1:15



Mean diameter = 8.2 μm

Mean diameter = 7.4 μm

(b) Oil:Water = 1:25



Mean diameter = 8.7 μm

Mean diameter = 6.7 μm

Figure S3. Emulsification using 60/40 L/T: Studies at different oil:water ratios. The results discussed in the main manuscript are for samples at a crude oil:seawater ratio of 1:10 (Figure 4). Here the oil:water ratio is reduced to 1:15 (a) and 1:25 (b). In both cases, the samples are emulsified using a 1:10 ratio of dispersant:oil; thus, the total (L+T) content is 0.37 wt% in (a) and 0.24 wt% in (b). Micrographs and photographs are shown for the sample immediately after preparation by vortex mixing, and 30 min after cessation of vortexing. The emulsions remain relatively stable over this time period, much like the results in Figure 4.

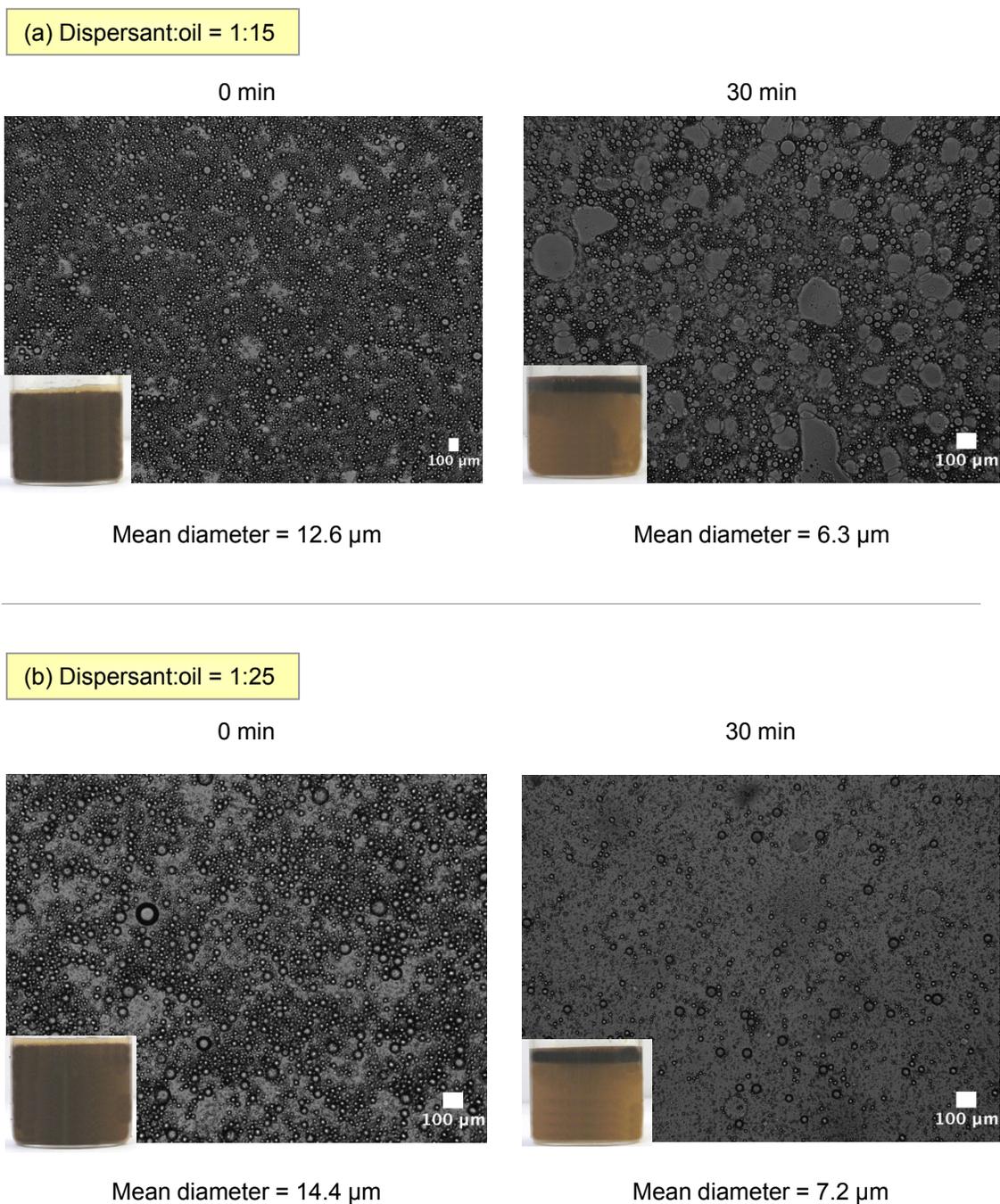
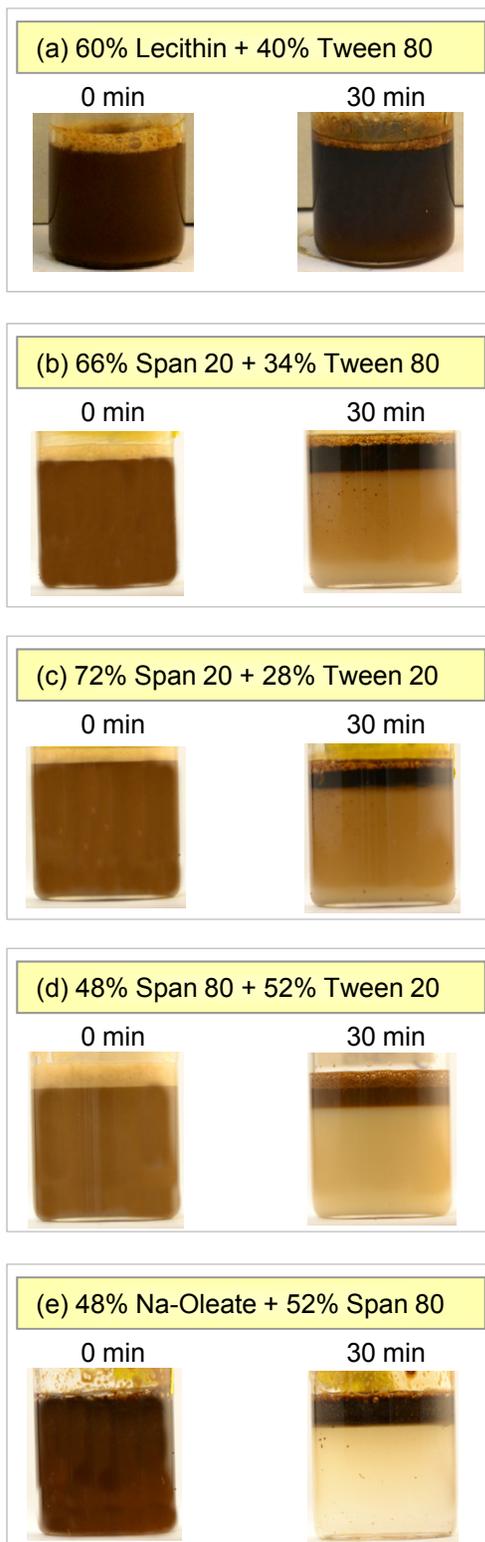


Figure S4. Emulsification using 60/40 L/T: Studies at different dispersant:oil ratios. For the results discussed in the main manuscript, the dispersant:oil ratio was 1:10. Here we show results for lower concentrations of dispersant. The crude oil:seawater ratio for these experiments is 1:20 and the dispersant:oil ratio is 1:15 (a) and 1:25 (b). Thus, the total (L+T) content is 0.37 wt% in (a) and 0.23 wt% in (b). Micrographs and photographs are shown for the sample immediately after preparation by vortex mixing, and 30 min after cessation of vortexing. The emulsions show more coalescence relative to the sample in Figure 4. However, these are still relatively stable compared to samples prepared with L alone or T alone at the same overall concentration.



Surfactant	Chemical name	HLB
Tween 80	Polyoxyethylene (20) sorbitan monooleate	15
Span 20	Sorbitan monolaurate	8.6
Tween 20	Polyoxyethylene (20) sorbitan monolaurate	16.7
Span 80	Sorbitan monooleate	4.3
Sodium oleate	<i>cis</i> -9-Octadecenoic acid sodium salt	18
Lecithin (soy)	L- α -Phosphatidylcholine	8

Figure S5. Emulsification using different surfactant mixtures with the same HLB (10.8). The HLB of 10.8 corresponds to that of 60/40 L/T. The crude oil:seawater ratio for these experiments is 1:10 and the dispersant:oil ratio is 1:1 (i.e., the total surfactant in each sample is 5 wt%). Photographs are shown for the sample immediately after preparation by vortex mixing, and 30 min after cessation of vortexing. At this high amount of surfactant, visual observations give a good indication of emulsion stability. The result for 60/40 L/T is reproduced in (a) and in this case, the sample remains homogeneous after 30 min, indicating a stable emulsion. In comparison, the four other surfactant mixtures all give rise to unstable emulsions, as indicated by the layer of oil (dark) at the top of each sample after 30 min, and the instability is confirmed by optical microscopy. The names and HLBs of the different surfactants are indicated in the table.