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

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ABSTRACT

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.

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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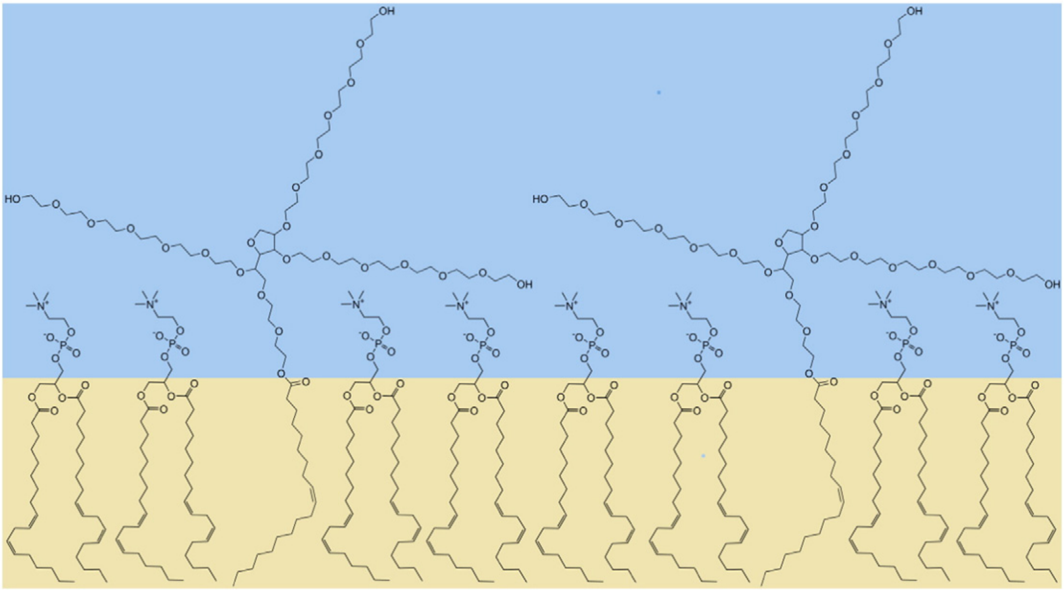

Fig. 1. Schematic of Tween 80 and lecithin packed in a monolayer at the oil–water interface (oil = lower phase; water = upper phase) at a mixture composition of 80:20 lecithin: Tween 80 (*w/w*).

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_2SO_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.