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# The role of dispersants' dynamic interfacial tension in effective crude oil spill dispersion

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## ABSTRACT

The dispersion effectiveness of dispersants containing Tween 80, Span 80, and dioctyl sodium sulfosuccinate (DOSS) was characterized using a modified Swirling Flask test, and was correlated with both initial and dynamic interfacial tension produced by those dispersants at an oil–water interface. Compositional trends in effectiveness were shown to be governed by: (1) initial oil–water interfacial tension observed upon dispersant–oil–saltwater contact; (2) rate of increase (or decrease) from the initial interfacial tension as DOSS was rapidly lost to the aqueous phase; and (3) gradually slowing kinetics of dispersant adsorption to the oil–water interface as Span 80 concentration was increased, which ultimately diminished dispersion effectiveness considerably even as dynamic interfacial tension remained  $<10^{-3}$  mN/m. It is proposed that this third phenomenon results not only from the hydrophobicity of Span 80, but also from the dependence of mixed Tween–Span–DOSS reverse micelles' stability in crude oil on dispersant composition.

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## 1. Introduction

Oil dispersants have been employed as a component of marine oil spill responses around the world for decades (Committee on Effectiveness of Oil Spill Dispersants, 1989). In spite of their widespread use, though, the published literature exploring the fundamental interfacial science of dispersants' formulation and action remains underdeveloped. Much of the published body of work (Committee on Effectiveness of Oil Spill Dispersants, 1989; Committee on Understanding Oil Spill Dispersants: Efficacy and Effects, 2005; European Maritime Safety Agency, 2009; Resby et al., 2007; Proceedings of the International Oil Spill Conference, 2011; Proceedings of the European Oil Spill Conference (Interspill), 2012) on dispersants has focused on empirical characterizations of dispersants, such as “dispersion effectiveness,” which is the percentage of an oil slick treated with a given dispersant that is dispersed into artificial seawater under a stated set of mixing conditions (Clayton et al., 1993), and/or on the study of proprietary dispersant formulations, of unknown composition. A few authors (Rewick et al., 1984; Brochu et al., 1986/1987) have directly measured the initial interfacial tension upon application of various dispersants to a crude oil–salt water interface and attempted to

correlate these values with the results of effectiveness tests on those dispersants, but have met with limited success. Of particular note is a paper by Brochu et al. (1986/1987) who measured both initial oil–water interfacial tension and dispersion effectiveness for 49 different surfactant mixtures at a crude oil–salt water interface. Their data showed some correlation between these properties, but also contained a great deal of unexplained variation in dispersion effectiveness. Thus, it seems natural to propose that other, more dynamic interfacial phenomena also control the breakup of oil slicks into seawater by dispersants.

The aim of this work is to elucidate the relative influences of initial interfacial tension and of dynamic changes in interfacial tension on the dispersion effectiveness of mixtures of sorbitan monooleate (Span 80), (PEO)<sub>20</sub> sorbitan monooleate (Tween 80), and dioctyl sodium sulfosuccinate (DOSS) (Fig. 1). These three surfactants have been widely used for decades as primary surface active agents in oil dispersants around the world (Committee on Effectiveness of Oil Spill Dispersants, 1989; Canevari et al., 1974; European Maritime Safety Agency, 2009), and exhibit high dispersion effectiveness when mixed (Brochu et al., 1986/1987; Brandvik and Daling, 1998). Additionally, Tween 80 (EC<sub>50</sub> > 100 mg/L, *Daphnia magna* (96 h)) (Carlsson et al., 2006) and Span 80 (LC<sub>50</sub> > water solubility limit, *Salmo gairdneri* (96 h)) (Aliphatic Esters Panel, American Chemistry Council, 2013) are desirable in environmental applications for their exceptionally low toxicity. While DOSS is less non-toxic (Maggi and Cossa (1973) found

Abbreviation: DOSS, dioctyl sodium sulfosuccinate.

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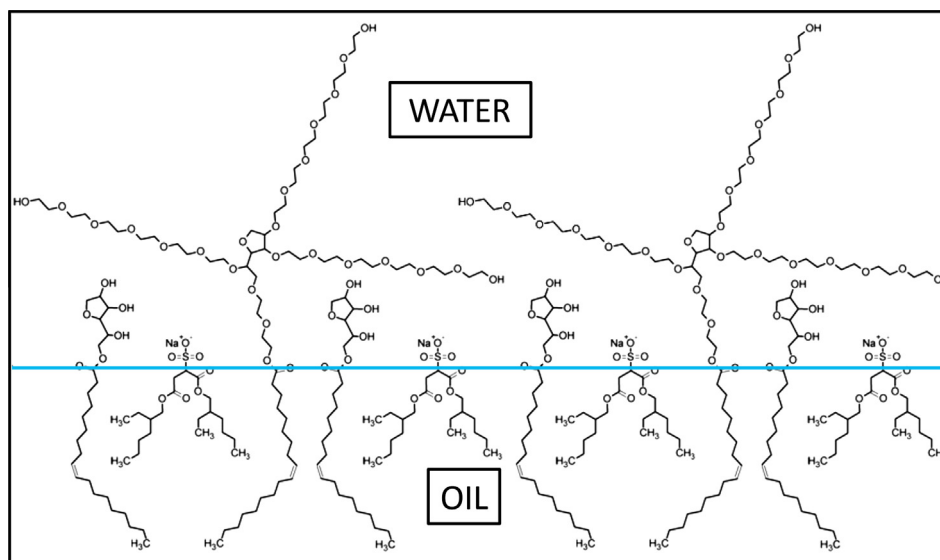


Fig. 1. Sketches of sorbitan monooleate (Span 80), (PEO)<sub>20</sub> sorbitan monooleate (Tween 80), and dioctyl sodium sulfosuccinate (DOSS) at an oil–water interface (horizontal line).

96-h LC<sub>50</sub> values ranging from 3 to >100 mg/L for 13 different marine organisms), it is well-known to be capable of forming reverse micelles without a cosurfactant, above a critical micelle concentration of ~1 mM, in a wide range of hydrophobic solvents (Peri, 1969; Mukherjee and Moulik, 1993; Smith et al., 2013), and has been found to readily incorporate nonionic surfactants, including Tween 80 and Span 80, into its reverse micelles (Paul and Mitra, 2005). In this way, therefore, DOSS is potentially capable of solubilizing a blend of surfactants containing various hydrophilic moieties into a hydrophobic medium, such as a dispersant solvent or a crude oil slick.

Another important dynamic in the effective operation of Tween 80–Span 80–DOSS dispersants is the significant disparity between the rates at which these three surfactants have each been observed to leach out of crude oil slicks, to which dispersant is typically applied, and into surrounding seawater. Knudsen et al. (1997, 1994) found that Tween 80 exhibits a very low leaching rate from crude oil into salt water, more than an order of magnitude lower than that of DOSS, though similar studies (Resby et al., 2007; Hokstad et al., 1996) have failed to confirm this low desorption rate for Tween 80 in part because crude oil components may interfere with Tween 80 quantification. Reichert and Walker (2013) used squalane as a clean oil phase and found that Tween 80 persistently adsorbed from aqueous solution to a squalane–salt water interface and formed an effectively insoluble film, whereas DOSS (also initially adsorbed from the water phase) readily desorbed from the interface into surrounding salt water in subsequent work (Kirby et al., 2014). Span 80 is hydrophobic (HLB = 4.3) and therefore leaches more slowly than either Tween 80 (HLB = 15) or DOSS (Hokstad et al., 1996). Thus, it is expected that over the course of an oil slick's breakup, DOSS partitions from oil into seawater relatively rapidly, while Tween 80 and Span 80 do so much more slowly.

A number of important questions are raised by this observation. For example, is the loss of DOSS from the oil to the aqueous phase during slick breakup rapid enough to limit dispersant effectiveness? To what extent is this counterbalanced by rapid adsorption of DOSS to new interface generated during oil breakup—transiently stabilizing it, and thus promoting effective dispersion? And does slower, more persistent adsorption of Tween 80 and Span 80 to the oil–water interface complement the rapid, transient adsorption

of DOSS? In support of this last hypothesis, Reichert and Walker (2013) found that Tween 80 adsorbing to a squalane–seawater hemispherical interface (70 μm diam.) from a dilute (0.5 μM) aqueous solution forms an insoluble film with a very high dilatational viscoelasticity. This film persisted even after Tween 80 was subsequently purged from the aqueous phase, suggesting that its role (and that of Span 80) may be to stabilize dispersed crude oil/seawater interface in the medium-to-long-term, as water-soluble DOSS cannot.

## 2. Materials and methods

Brochu et al. (1986/1987) reported qualitative, visually-assessed estimates of dispersion effectiveness across the full Tween 80–Span 80–DOSS compositional space (Fig. 2). Their results were used to identify compositional lines in Tween 80–Span 80–DOSS compositional space along which dispersion effectiveness exhibited large, rapid changes. Then, both dispersion effectiveness and interfacial tension were measured as a function of composition along those lines, with the aim of correlating changes in

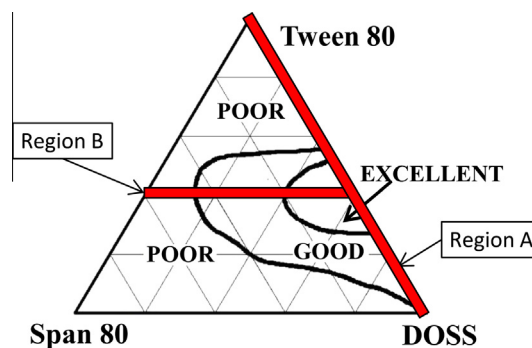


Fig. 2. Dispersion effectiveness of Span 80–Tween 80–DOSS mixtures (in a cyclohexanone solvent) as reported by Brochu et al. (1986/1987). Compositional regions of interest for the experiments discussed herein are highlighted in red. Figure adapted from Brochu et al. (1986/1987). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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