



A surface tension based method for measuring oil dispersant concentration in seawater



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ABSTRACT

This work developed a new method to determine concentration of Corexit EC9500A, and likely other oil dispersants, in seawater. Based on the principle that oil dispersants decrease surface tension, a linear correlation was established between the dispersant concentration and surface tension. Thus, the dispersant concentration can be determined by measuring surface tension. The method can accurately analyze Corexit EC9500A in the concentration range of 0.5–23.5 mg/L. Minor changes in solution salinity (<0.3%), pH (7.9–9.0), and dissolved organic matter (<2.0 mg/L as TOC) had negligible effects on the measurements. Moreover, effects of extracts from marine sediments were negligible, and thus, the method may be directly applied to seawater–sediment systems. The method accuracy was confirmed by comparing with direct TOC analysis. This simple, fast, economical method offers a convenient analytical tool for quantifying complex oil dispersants in water/seawater, which has been desired by the oil spill research community and industries.

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1. Introduction

Oil dispersants have been widely employed to mitigate environmental impacts of spilled oil (Fu et al., 2014; Gong et al., 2014a; Zhao et al., 2015). The application of modern dispersants began in the *Torrey Canyon* oil spill in 1967, where 1000 tons of dispersants (primarily BP1002) were applied to treat the spilled Kuwait crude oil (Southward and Southward, 1978). Since then, application of dispersants has evolved to be a common countermeasure for mitigating oil spill, while the search for more effective and less toxic oil dispersants remains active (Lessard and Demarco, 2000). In 1996, 12 tons of Corexit EC9500A was applied during the *Sea Empress* spill in the UK, representing the first filed application of this popular oil dispersant. In 1997, 10 tons of Corexit EC9500A was used in the *Captain Spill* in the *North Sea* to disperse 650 tons of spilled crude oil. In 1998, ~11.5 tons of Corexit EC9527A were sprayed in the offshore pipeline spill in Texas (Lessard and Demarco, 2000). During the Deepwater Horizon (DwH) oil spill in the *Gulf of Mexico* in 2010, BP applied approximately 2.1 million gallons (or ~8.0 million liters) of Corexit EC9500A and EC9527A (Kujawinski et al., 2011), representing the single largest application of oil dispersants in the history.

When applied, oil dispersants embed themselves at the interfaces between oil and water due to the amphiphilic nature of the surfactant molecules, which lowers the interfacial tension and facilitates the formation and entrainment of small (<100 μm) oil-surfactant droplets into the water column, thus enhancing biodegradation of spilled oil (Clayton et al., 1993; Singer et al., 1996).

Corexit EC9500A is a mixture of nonionic and anionic surfactants as well as organic solvents (Place et al., 2010). The major nonionic surfactants include ethoxylated sorbitan mono- and trioleates and sorbitan monooleate (commercially known as Tween 80, Tween 85, and Span 80), and the major anionic surfactant is sodium dioctylsulfosuccinate (DOSS). Table S1 of the Supporting information (SI) gives detailed information on the compositions of Corexit EC9500A. The solvents are a mixture of *n*-alkanes ranging from nonane to hexadecane, including di(propylene glycol) butyl ether (DPnB), propylene glycol, and 2-butoxyethanol. (Place et al., 2010; Sciencecorps, 2010). The wide application of the dispersant, especially since the 2010 DwH oil spill, has triggered extensive investigations into its effectiveness, toxicity, and environmental fate and transport (Anderson, 2011; Goodbody-Gringley et al., 2013; Moles et al., 2002).

Yet, it has been challenging to quantitatively analyze oil dispersants conveniently and economically. This is not only due to the complex nature of the mixture of a variety of dispersants and solvents, but also proprietary and incomplete information on the type and quantity of the dispersant components. For instance, the most common practice for

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analyzing Corexit EC9500A in water has been to analyze one or some of the key dispersant components that can be quantified following the standard methods (Kujawinski et al., 2011). According to the EPA methods for detecting dispersants in water (USEPA, 2010), DOSS and DPnB are analyzed by LC/MS/MS (liquid chromatography with tandem-mass spectrometry) (detection limits = 20 and 125 $\mu\text{g/L}$, respectively); and the other solvent components, such as propylene glycol and 2-ethylhexanol, are solvent-extracted and then determined by GC/MS (Gas chromatography–mass spectrometry) (detection limits = 10 and 500 $\mu\text{g/L}$, respectively). Researchers have also reported methods for the analysis of nonionic surfactants. For instance, Tween 80 can be analyzed by using HPLC-MS (detection limit = 0.01 $\mu\text{g/L}$) (Christiansen et al., 2011; Im et al., 2008). Scelfo and Tjeerdema (1991) developed a method to monitor the anionic surfactant (ethoxylated sorbitan esters) of Corexit EC9527A by incorporating ion-pair formation with bis(ethylenediamine) copper (II), then extracting and analyzing the complex by flame atomic absorption spectroscopy. Similarly, Kasahara et al. (1995) developed a spectrophotometric method by using a trifluoromethyl derivative as a counter ion for extraction and quantification of anionic surfactants in seawater. However, these methods bear the following drawbacks: 1) they are quite costly, and/or time- and labor-consuming, especially for the LC/MS/MS method, 2) the results for individual components may not reflect the integrity of the dispersant as a whole, and 3) the undisclosed components in a dispersant are neglected.

To quantify the concentration of Corexit EC9527A and Corexit EC9500A in aqueous solutions, Mitchell and Holdway (2000) applied a UV–Vis spectroscopic method, where the concentration is measured at a wavelength of 230 nm. The mean concentration ranged from 0 to 280 mg/L for Corexit EC9527A and 0 to 450 mg/L for Corexit EC9500A. However, the effects of water chemistry and environmental conditions on the viability of the methods were not addressed, though such factors are known to alter the UV–Vis spectra. Consequently, more rapid and economical analytical methods have been desired by the oil spill research community and relevant industries.

It has been observed that surface tension (γ) is correlated with the concentration of a surfactant (Fu et al., 2015; Menger et al., 2009; Myers, 1999). Specifically, Menger et al. (2009) observed that when γ is plotted against $\ln[\text{surfactant}]$, the curve can be divided into three distinct regions (Fig. 1): Region A: γ slightly decreases with increasing surfactant concentration; Region B: γ decreases sharply and almost linearly with increasing surfactant concentration; and Region C: the slope abruptly levels off (i.e., γ remains nearly constant) at the surfactant concentration above the CMC value. Conventionally, it is assumed that the surfactant is saturated at the air/water interface throughout Region A (Perez et al., 1998; Vader, 1960), which allows the calculation of the area-per-molecule via the classic Gibbs equation (Menger et al., 2009).

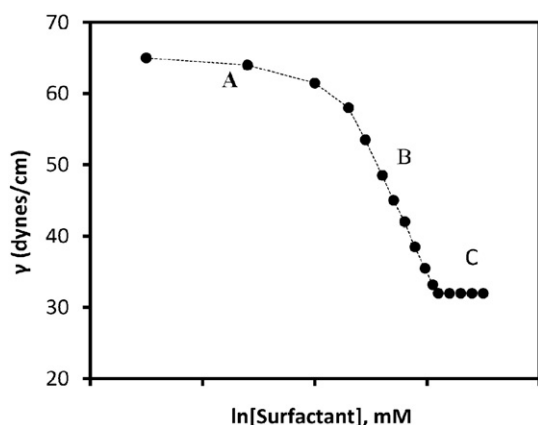


Fig. 1. Three regions of a typical surface tension vs $\ln[\text{surfactant}]$ plot. Reprinted with permission from Menger et al. (2009). Copyright American Chemical Society.

In an effort to determine the CMC value of oil dispersants, Gong et al. (2014b) observed that the Corexit EC9500A concentration is linearly correlated to γ of solution. Hence, the concentration of the dispersant may be measured by indirectly measuring the combined effect of the dispersant components, i.e., by gauging the surface tension of a dispersant solution.

Based on the linear correlation between γ and dispersant concentration, the goal of this study was to develop and validate a new analytical method for simple and rapid quantification of oil dispersants in seawater. To illustrate the concept, Corexit EC9500A was used as the model dispersant and Gulf coast seawater as the prototype solution matrix. The specific objectives were to: 1) establish the linear correlation between γ and $\ln[\text{dispersant concentration}]$, 2) assess the effects of environmental factors, such as salinity, pH, and dissolved organic matter (DOM) on the correlation, and 3) identify the applicable conditions as well as constraints of the method. The new method is expected to provide a convenient and economical analytical tool for researchers and practitioners in the field of oil spill and marine pollution.

2. Experimental methods

2.1. Materials

Seawater samples were collected at the Grand Bay area, AL, USA in the Gulf of Mexico (N30.37873, W88.30679) in November 2012. It was stored in sealed containers at 4 °C and filtered through 0.22 μm membrane to remove suspended solids before use. Marine sediment was collected from the Ocean Springs National Seashore Park, MS, USA (N30.39772, W88.79175). The sediment was classified as loamy sand sediment and the organic matter content is 1.6% (sediment analysis was performed by the Soil Testing Laboratory at Auburn University, more physicochemical characteristics of sediment are shown in Table S2 in SI).

All chemicals used in this study were of analytical or higher grade, and were used as received, including humic acid (Fluka Chemie, Switzerland), sodium hydroxide (NaOH, Fisher Scientific, Fair Lawn, NJ, USA), and hydrochloric acid (HCl, 36.5–38.0%, Mallinckrodt Chemical, St. Louis, MO, USA). Corexit EC9500A was acquired per courtesy of Nalco Company (Naperville, IL, USA). A Corexit EC9500A stock solution was prepared at 1 g/L by mixing Corexit EC9500A and seawater in a glass flask under magnetic stirring for 1 h, and then the desired working solutions (up to 200 mg/L) were obtained by diluting the stock solution with seawater. Serial dilution was avoided to reduce cumulative error (Scelfo and Tjeerdema, 1991).

2.2. Effects of environmental factors

Effects of environmental factors on the viability of the surface-tension based method were assessed at various solution salinities, pH and DOM concentrations. The pH of the seawater was adjusted using HCl (0.5 M) or NaOH (0.5 M) solution from the initial 7.9 to the final value of 6.0, 7.0 or 9.0. Different DOM concentrations were achieved by diluting a DOM stock solution (550 mg/L as TOC), which was obtained by dissolving the standard humic acid into seawater. The salinity effects were tested using artificially prepared seawater at various salinity levels (0, 1%, 2%, and 4% (expressed as wt.% of salt) following the method by Kester et al. (1967). The effects of the environmental factors on the surface tension measurement as well as on the γ – $\ln[C]$ (C is the dispersant concentration) correlations were evaluated by measuring the γ – $\ln[C]$ curves under various pH, salinity and DOM levels.

In marine oil spill studies, mixed sediment–seawater systems are often encountered (Zhao et al., 2015). To determine the effects of possible sediment exudates, surface tension was also measured using sediment amended seawater. The sediment amended seawater was prepared as follows: first, mix seawater with the sediment at a sediment/seawater ratio of 16 g/40 mL on a rotator at 50 rpm for 48 h;

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