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Dispersibility of crude oil in fresh water

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This study was conducted to advance our understanding of dispersion chemistry in fresh waters.

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ABSTRACT

The effects of surfactant composition on the ability of chemical dispersants to disperse crude oil in fresh water were investigated. The objective of this research was to determine whether effective fresh water dispersants can be designed in case this technology is ever considered for use in fresh water environments. Previous studies on the chemical dispersion of crude oil in fresh water neither identified the dispersants that were investigated nor described the chemistry of the surfactants used. This information is necessary for developing a more fundamental understanding of chemical dispersion of crude oil at low salinity. Therefore, we evaluated the relationship between surfactant chemistry and dispersion effectiveness. We found that dispersants can be designed to drive an oil slick into the freshwater column with the same efficiency as in salt water as long as the hydrophilic–lipophilic balance is optimum.

1. Introduction

The application of chemical dispersants has recently gained popularity as one of the primary oil spill countermeasures for mitigating the overall adverse impact of oil spills on the environment (NRC, 2005), and in recent years dispersant product vendors have developed new formulations that are less toxic and more effective for the treatment of oil spills on water. Use of dispersants on oil slicks minimizes the harmful effects of floating oil on birds and other aquatic wildlife (NRC, 2005). Most dispersants currently on the U.S. Environmental Protection Agency (EPA) National Contingency Plan Product Schedule (NCPPS) have been developed for saltwater environments, and the literature has a paucity of data in the area of freshwater dispersion. In this paper, we will attempt to show that it might be possible to develop effective freshwater dispersants as a response tool, but the decision to use them is a policy decision that will not be addressed.

1.1. Chemical properties of dispersants

One response alternative for crude oil spills in marine environments is chemical dispersion. Dispersion is accomplished by addition of chemicals that interact with the floating oil to reduce the oil–water interfacial tension and facilitate the formation of small oil droplets (NRC, 2005). The individual chemicals are formulated into mixtures that are collectively known as dispersants. The composition of most commercially available dispersants is proprietary, but in general they consist of one or more nonionic surfactants dissolved in a solvent carrier (NRC, 1989). Some dispersants also include one or more anionic surfactants and other additives (*e.g.*, phosphoric acid). The purpose of the solvent is to provide the surfactant mixture with an appropriate viscosity, which ensures that it can be pumped through spray nozzles at environmental temperatures. The solvent may be water miscible (*e.g.*, 2-butoxyethanol) or immiscible (normal alkanes) (NRC, 2005).

Surfactants are the active (*i.e.*, interfacial tension reducing) ingredients in dispersants. Surfactants are compounds that have hydrophobic and hydrophilic components within the same molecule. The amphiphilic character of surfactants causes them to accumulate at interfaces because the hydrophilic part of the molecule interacts strongly with water, but the hydrophobic part is displaced from the aqueous phase because it interferes with more thermodynamically-favorable hydrogen bonding interactions between water molecules (Porter, 1991). Nonionic surfactants are most common in dispersants because they are more effective, are generally less toxic, have a much lower aqueous solubility, and are less affected by electrolyte concentration than are anionic and cationic surfactants (Porter, 1991; Myers, 2006). Their lower water solubility tends to increase the extent to which they partition into the oil phase when the aqueous phase is in great excess, as it is for environmental

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applications. The nonionic surfactants used in commercial surfactants are ethoxylated derivatives of fatty acids, fatty alcohols, and fatty acid esters of sorbitan (NRC, 1989; Fingas et al., 1990; George-Ares and Clark, 2000), in which the hydrophilic portion of the molecule consists of polyethylene glycol chains of varying lengths, and the hydrophobic portion is contributed by the fatty acyl chains, usually ranging between about 12 and 18 carbon atoms in length. Alkyl phenol ethoxylates, which have been linked to endocrine disrupting activity, are nonionic surfactants, but they are no longer used in commercial oil-spill dispersants and were not included in this study.

A typical measure of the relative importance of the hydrophobic and hydrophilic portions of nonionic surfactants is the hydrophile–lipophile balance (HLB), which ranges from zero for completely lipophilic (hydrophobic) molecules to 20 for completely hydrophilic nonionic molecules. Packing arguments suggest that the dominant group, characterized by the ratio of cross-sectional areas, will tend to orient into the continuous phase (NRC, 1989; Porter, 1991). So, surfactants with low HLB tend to stabilize water-in-oil emulsions, whereas those with high HLB stabilize the more desirable oil-in-water emulsions (NRC, 1989; Clayton et al., 1993). Commercial dispersants designed for use in seawater tend to have overall HLBs in the range of 9–11, which is often achieved by combining surfactants with higher and lower HLB.

Although the HLB is the parameter that is most commonly used to describe the characteristics of dispersants, the same HLB can be obtained in many different ways. For example, a single surfactant with the desired HLB can be used, or two or more surfactants can be mixed in proportions that give the same desired HLB. The HLB of surfactant mixtures is given by the mass-weighted average of the individual surfactants (Myers, 2006). Although the industry consensus suggests that combining surfactants with different HLB improves dispersant effectiveness (NRC, 1989; Clayton et al., 1993), not all studies support this conclusion (Fingas et al., 1990). Furthermore, dispersants with different chemical characteristics may have the same HLB but exert different effects on the system (Bruheim et al., 1999; Van Hamme and Ward, 1999; Bruheim and Eimhjellen, 2000). Therefore, the compositions of the dispersant formulations used in this research were varied systematically to produce dispersants with similar HLBs but different chemical compositions.

1.2. *Effect of salinity on dispersion effectiveness*

The effectiveness of chemical dispersants can be strongly influenced by salinity (*i.e.*, ionic strength), but the relationship between dispersion effectiveness and salinity can vary for different dispersant-oil combinations (Lehtinen and Vesala, 1984; Belk et al., 1989; Fingas et al., 1991; Blondina et al., 1999). Dispersants that were optimized for maximum dispersion effectiveness when used in marine environments [*e.g.*, Corexit 9500 (http://www.epa.gov/emergencies/docs/oil/ncp/schedule.pdf) or Enersperse 700 (no longer on the EPA Product Schedule)] are often ineffective in fresh water (Fingas et al., 1991; Blondina et al., 1999), while those that are optimized for use in fresh water are less sensitive to salinity (Belk et al., 1989). Although most studies vary salinity by diluting natural or artificial seawater, which is dominated by sodium and chloride ions, minor ions such as calcium and magnesium may be more important in determining dispersion effectiveness. One study using the Labofina method of measuring dispersion effectiveness showed very high effectiveness of freshwater and marine dispersants at calcium concentrations that were low relative to seawater concentrations (Belk et al., 1989). The effectiveness of an unidentified marine dispersant increased from 6% in deionized water to 81% in water containing calcium at a concentration of 400 mg/L as $CaCO_3$, which is less than half the concentration found in seawater but still high relative to most fresh water. Another study compared Corexit 9500 with the same dispersant blended with a solution of calcium chloride (concentration unknown), which they labeled Corexit 9500*, for use in fresh water applications such as river water and deionized water (George-Ares et al., 2001). They also compared them to dispersants designed for use in freshwater environments. They found that addition of calcium salt to the Corexit 9500 dispersant increased its effectiveness to that of the other dispersants designed for freshwater use, but statistical analyses were not conducted in the study. Note also that these experiments were conducted in a closed system with a relatively high oil–water ratio (1:250). So, the calcium concentration of the aqueous phase, which was not reported, could have been increased to a level that would be impractical in a real spill scenario where the calcium added with the dispersant could be rapidly diluted to background levels by the large excess of water. In one study, dispersants optimized for fresh water were less sensitive to the calcium concentration than those optimized for marine use (Belk et al., 1989).

1.3. *Objective of research*

The objective of this research was to investigate the relationship between dispersion effectiveness in fresh water and the surfactant composition for weathered crude oil. Although limited research on the chemical dispersion of crude oil and petroleum products in fresh water has been conducted, some previous studies (*e.g.*, Belk et al., 1989) did not identify the dispersants that were investigated, much less describe the chemistry of the surfactants that were used. The absence of information on surfactant composition is a major impediment to the scientific investigation of dispersant effectiveness because this information is necessary for the development of a more fundamental understanding of dispersant effectiveness. Therefore, the relationship between surfactant chemistry and dispersant effectiveness was systematically evaluated. Although commercial dispersants are designed to work over a broad range of oil types and salinities, only one oil type and one water composition were investigated in this study because of the need to first demonstrate the validity of the hypothesis that dispersants can be developed for low salinity waters based on the hydrophile–lipophile balance (HLB).

2. Materials and methods

2.1. *Surfactants*

The surfactants that were used in this research are listed in Table 1. The surfactants were selected from three chemical classes: sorbitan esters, fatty acid ethoxy esters, and fatty alcohol ethoxy ethers. Because many of the surfactants used in this research are widely distributed and used for a variety of purposes, Table 1 provides the trade names in addition to the chemical names of the surfactants that were used. For brevity, the structure of the hydrophilic groups is given as POE(*x*), where "POE" means "polyoxyethylene" and "*x*" is the total number of ethylene oxide units in the POE chains. The size of the hydrophilic groups is also given as "E_x" in some abbreviations. The meaning of the variable '*x*' in E_x is identical to POE(*x*). They both refer to the number of ethoxyl groups. (The sorbitan ester surfactants frequently have several POE chains esterified to different hydroxyl groups of the sorbityl group, but the total number of ethylene oxide monomers is as indicated.).

The chain length and chemical characteristics of the fatty acyl groups are indicated by $C_{y:z}$, where "*y*" is the number of carbon atoms in the fatty acyl chain and "*z*" is the number of carbon–carbon double bonds. The number of carbon–carbon double bonds is important because, for a given chain length, the melting point is a function of the degree of unsaturation. Greater unsaturation (*i.e.*, number of double bonds) is correlated with lower melting point for a given chain length and, therefore, greater tendency to exist as a liquid at ambient temperatures. Several of the surfactants include more than one fatty acyl group in the hydrophobic portion. These are indicated by the use of "di-" (*i.e.*, two fatty acyl groups), "tri-" (*i.e.*, three fatty acyl groups), or "hexa-" (*i.e.*, six fatty acyl groups). The Tergitols (fatty acyl ethers) are composed of mixtures of fatty acyl groups varying from 11 to 15 carbon atoms in chain length.