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Interfacial film formation: Influence on oil spreading rates in lab basin tests and dispersant effectiveness testing in a wave tank

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ABSTRACT

Test facilities such as lab basins and wave tanks are essential when evaluating the use of chemical dispersants to treat oil spills at sea. However, these test facilities have boundaries (walls) that provide an ideal environment for surface (interfacial) film formation on seawater. Surface films may form from surfactants naturally present in crude oil as well as dispersant drift/overspray when applied to an oil spill. The objective of this study was to examine the impact of surface film formation on oil spreading rates in a small scale lab basin and on dispersant effectiveness conducted in a large scale wave tank. The process of crude oil spreading on the surface of the basin seawater was influenced in the presence of a surface film as shown using a 1st order kinetic model. In addition, interfacial film formation can greatly influence chemically dispersed crude oil in a large scale dynamic wave tank.

1. Introduction

The recent subsurface oil spill from Deepwater Horizon in the Gulf of Mexico (April, 2010) has highlighted the application of chemical oil dispersants to remediate accidental oil spills at sea. Over the past decade, this interest in using chemical dispersants to treat oil spills has been motivated by constrains encountered by mechanical based spill response options, such as booming and skimming techniques. As a result, a number of new dispersants, such as Corexit 9500, have been developed, which have low toxicity to marine life and are effective at dispersing heavy oils (e.g., Intermediate Fuel Oil 120 and 180) that were believed to be non-dispersible in the past.

The successful application of dispersants to break-up oil slicks has been demonstrated through a multitude of tests in the laboratory, in field mesocosm trials, and application of dispersants on actual spills (Sterling et al., 2004; Venosa et al., 2002; Li et al., 2008). Sea trials would be the ideal scenario; however they are expensive and there is the risk of environmental impacts. Lab-scale tests are not considered to be effective simulation of the real, large-scale problem thus encouraging the development of large-scale sea-model facilities such as wave tanks (Sterling et al., 2004; Venosa et al., 2002). These facilities are capable of simulating natural wave energies to assist in the evaluation of chemical dispersant use on oil spills at sea (Li et al., 2008).

Previous studies have reported that unwanted surface films can form in test facilities (Nedwed and Coolbaugh, 2008). Test facilities, unlike the natural environment, contain boundaries (walls), which are an ideal environment for surface film formation during oil and oil/dispersant application. These bounded or confined systems can restrict the spreading of surfactants on the surface of seawater resulting in surface film formation. However, interfacial films formed in the open ocean are believed to be fragile, since surfactant spreading can continue in an unbounded environment. Crude oil contains organic acids and phenolics that are surface active agents or surfactant molecules, and after addition of the crude oil to water, an interfacial film at the air–water interface may occur. Likewise dispersant drift during application to oil can contribute to surface film formation. If dispersant is accidentally oversprayed, as may happen in the large-scale systems with walls, then surface films are most likely to occur. The studies by Nedwed and Coolbaugh (2008) demonstrated that unwanted surface films affect the thermodynamics of oil spreading on seawater and it was proposed that the presence of these films interferes with the controlled testing of the chemical dispersants. This was only true when dispersing all oils under low energy (non-breaking wave) conditions that do not disrupt interfacial films on the seawater surface (Nedwed and Coolbaugh, 2008). This study raised the issue that the dispersion of oil may not be adequately assessed when interfacial films are present when conducting dispersant tests in large-scale systems.

The formation of unwanted interfacial films on seawater cannot be assessed using current standard protocols (e.g. hydrocarbon

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analysis), which are designed to evaluate dispersant effectiveness in large-scale systems. So, essentially researchers are unaware of the presence of unwanted interfacial films during controlled tests and their impacts on oil dispersion studies conducted in large-scale dynamic systems.

To address this problem, we have designed both lab and wave tank studies. The lab basin studies address interfacial film formation and it effects on the spreading rates of three oil types. The physical and chemical characteristics of the test oils were evaluated prior to testing. A new technique, surface tension measurements, was adapted to detect interfacial films. A 1st order kinetic model was applied to determine the effects interfacial films on oil spreading rates. In theory, thicker oil slicks require greater mixing energy to disperse the oil (Nedwed and Coolbaugh, 2008). Any effects on oil spreading rates could potentially affect oil dispersion.

To address the effects of interfacial films on chemical dispersant effectiveness, large-scale wave tank tests were conducted using one of the three test oils. These studies evaluated the dispersion of oil by natural attenuation and the application of chemical dispersant in the presence and absence of interfacial films. Dispersant effectiveness was evaluated using a combination of hydrocarbon values and interfacial tension measurements. The prolonged effects of interfacial films on dispersant effectiveness in the dynamic state were assessed using a long-time limit adsorption model. The findings of the study will aid in improving our knowledge and understanding of interfacial film formation, provide a reliable method of detecting them, their effects on oil spreading rates and their influence on chemical dispersion of oil in large-scale systems.

2. Experimental

2.1. Oil characterization and dispersant information

The test oils used in the study were Arabian Light Crude (ALC, artificially weathered to remove volatiles by aeration to 93% by volume), Alaskan North Slope Crude Oil (ANS, artificially weathered by aeration to 90% by volume), and Intermediate Fuel Oil 120 (IFO 120). All oils were characterized using thin-layer chromatography followed by scanning flame ionization detection using the IATROSCAN MK6 (Shell, USA) (Maki and Sasaki, 1997). The viscosities of the crude oils were determined using a LV Dial-Reading Viscometer (Brookfield, Canada) and their densities (ρ = mass/volume) calculated by determining the mass of a measured volume of the oil.

Corexit 9500A was selected for this study and information on its ingredients can be found on Nalco's website (2011). The density of Corexit EC9500A is 0.948 g/mL.

2.2. Kinetics of oil spreading (basin tests)

The oil spreading kinetics was determined using the same basin as above. The closed oil containment barrier (as above) was employed, which was suspended by fishing line (3 lb test, Reno, NV USA) controlled by a fishing reel (Quantum, Zebco, OK USA), supported by a 6.4 mm wide by 1.1 m long perforated steel flat bar. This apparatus provided gentle and constant control of the oil containment barrier, which ensured a symmetrical oil lens and that simulated surface films remained intact when releasing the oil. A Canon Digital Rebel T1i (Canon EF 10–22 mm lens) capable of both video (1080 p, 20 fps) and continuous drive modes (8 MP, 3.7 fps) was suspended by a tripod above the lab basin. The video mode was used for experiments where the oil spread rapidly, while the continuous drive mode was used for all other experiments. A scale was created in both vertical and horizontal directions at the bottom of the lab basin. Since acrylic is clear this was achieved by taping a 1 m adhesive backed ruler (ER-S036L-TC; Oregan Rule Co., Oregon USA) to the underside of the basin. A Panasonic laptop (AVC Networks, Taiwan) was used to produce a large display stopwatch and in some cases control the camera.

The oil was quantitatively (15 mL) added to achieve an initial thickness of 2.4 mm at time zero milliseconds (ms) inside the oil containment barrier. The containment barrier was then raised by employing the fishing reel. The oil was released and either video or continuous drive mode recorded the evidence of oil spreading on seawater over time. In order to determine the effect of surface films on the kinetics of oil spreading, a surface film was generated on the seawater surface by placing 1 drop (7.64 ± 0.17 mg or ~0.008 mL/1 m^2) of Corexit 9500A from a calibrated Pipetplus (LTS 20, J02022100, Rainin, USA) set at 19.0 μL. Due to the viscosity of Corexit 9500A, not all the surfactant was dispensed from the pipette; therefore calibration was necessary. This concentration was chosen so that the surface film that was generated was sufficient to affect oil spreading so that it could be studied within a reasonable time (a few hours) and to evaluate its effects on oil spreading rate kinetics.

Two oils, ANS and IFO 120, were tested with/without an interfacial film on seawater. The tests were replicated to ensure accuracy and precision of the measurements. The initial oil thickness was estimated by treating the oil containment barrier as a cylinder. The volume of a cylinder is expressed as (1):

$$V = \pi r^2 h_o \tag{1}$$

where V is the volume of oil, r is the radius (i.d.) of the oil containment barrier, and h_o is the initial oil thickness. The initial volume and radius are known so the equation can be rearranged to calculate the initial oil thickness. Oil thickness (h_t) at each time (t) point was generated using the same concept, since the oil while spreading maintained its original shape. The initial lens measurement was taken from the center to the outer edge of the lens, which was 4.5 cm (45 mm). The pictures generated from the study were analysed and the average radial distance of the oil lens growth in two directions was recorded at various time (s) intervals. All measurements were taken in inches and converted to metric units.

2.3. Wave tank operations (closed system)

This study involved using one oil (ANS), which was dispersed using three different treatments: (A) natural dispersion (no dispersant or surface film); (B) chemical dispersion in the absence of surface film; and (C) chemical dispersion in the presence of surface film. The experimental design was performed in triplicate and random order to reduce the effects of compounding factors, i.e. temperature, salinity and air currents.

Fig. 1 is a schematic diagram of the wave tank facility located at the Bedford Institute of Oceanography (Nova Scotia, Canada) with geometric dimensions of 32 m long, 0.6 m wide, and 2 m high. The water depth was maintained, throughout the studies, at 1.5 m (~29,000 l of seawater). Filtered seawater was pumped (5 HP 230 V, 60 Hz Electric Centrifuge Pump, Leeson, Canada) from the Bedford Basin (NS, Canada) through sock filters (25 μm inside two 5 μm filters; Atlantic Purification Ltd., NS, Canada) into the wave tank. Temperature and salinity were recorded prior to each experimental run with a hand held meter (YSI model #30-1-FT; Yellow Springs, USA). Waves were generated by a computer-controlled flap-type wave maker situated at one end of the tank linked to an adjusted cam that controlled stroke length in order to alter wave-height characteristics (Li et al., 2008). As per Li et al. (2008), plunging breaking waves were produced with a 12 cm stroke and alternating trains of high and low frequency waves