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Characterization of water-in-crude oil emulsions in oil spill response

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Abstract: The formation of water-in-crude oil emulsions occurs when crude oils are spilled into sea. The water-in-crude oil emulsions significantly change the properties of the spilled crude oils and in turn influence the choices made relating to oil spill countermeasures. The water-in-crude oil emulsions were characterized using various techniques in this study. The environmental scanning electron microscopy observation of water droplets in the emulsions is also presented. It is a powerful tool in emulsion observations.

Keywords: oil spill; water-in-oil emulsions; oil spill response; DSC; ESEM

Introduction

Oil is the major source of energy in our modern industrial world. It fuels the machines and lubricates the wheels of the world's production. But when this vital resource is out of control, it can destroy life and devastate the environment and economy.

As long as oil is explored, transported, stored and used there will be the risk of oil spills with the potential to cause significant environmental damages. When oil is spilled into a marine environment, it is subject to several processes called weathering (Daling, 1999). The three dominant processes that cause changes in oil characteristics over time are spreading, evaporation and emulsification if oil spills at sea. Spreading reduces oil thickness, and evaporation increases density and viscosity. The emulsification process significantly increases the viscosity of spilled oil and its density (Sebastião, 1995). All these in turn influence choices made relating to oil spill countermeasures.

Crude oil is a mixture of aliphatic, aromatic hydrocarbons and oxygen, nitrogen and sulphur containing compounds such as resins and asphaltenes. Once the crude oil is spilled, it will spread over the surface of the water and a thin layer of oil film form. As the volatile constituents evaporate quickly and thus the less volatile substances will concentrate over time. The spilled crude oil will undergo mixing with seawater under the influence of wind and waves through the ingress of seawater and the ingress of oil drops into the water. This process is promoted, under the action of waves, through the repeated expanding and shrinking of the layer on the sea surface and through the forced sinking and floating by the action of high rolling waves. As time passes, the spilled oil becomes heavier and heavier as the volatile constituents evaporate. A water-in-crude oil emulsion begins to be formed. In a water-in-crude oil emulsion, crude oil forms a continuous phase and seawater is dispersed in this phase. Some emulsifying substances that surround water particles and prevent the latter from coalescing are required for a stable emulsion to be formed. As discussed in the literature (Fingas, 1995), asphaltene, resin, and wax as non-volatile constituents in crude oils serve as emulsifying agents. Asphaltene tends to form micelles in crude oils. When water is added to the crude oil, asphaltene is adsorbed by electrostatic attraction on the water particles to form a mechanically protecting layer, which prevents the water particles from coalescing. Resin prevents the coalescence of water particles as well and also maintains the space between each of the adsorbed asphaltene particles through weak surface activity and its own viscosity.

The water-in-crude oil emulsification is the most important weathering process that makes crude oils persistent on the water surface. The water-in-crude emulsification therefore has a great influence on oil response operations. Therefore it is of important interest to academic and industrial societies to better understand the characteristics of the water-in-crude oil emulsions. For oil spill responses, the following are

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important characteristics: density; viscosity; water content; droplet sizes.

1 Experimental

1.1 Preparation of water-in-crude oil emulsions

The water-in-oil emulsions were formulated by blending a 50% evaporated (weathered) crude oil with seawater using 500 r/min speed agitator for 10, 30 and 120 minutes respectively at 20℃ in a cylindrical Pyrex vessel of 100 mm in diameter and 180 mm in height. The volumetric ratio of oil phase to internal aqueous phase is 1:7. After mixing the prepared emulsions were kept for one week in order to get stable emulsions.

1.2 Density

Density is defined as the mass per unit volume of a substance. It is most often reported for oils in units of g/ml or g/cm^3. Density is temperature-dependent. The emulsion will float on water if the density of an emulsion is less than that of the water. The emulsion density was measured using a digital density meter. The measurements were run in triplicate and the mean value was reported.

1.3 Viscosity

Viscosity of a liquid is a measure of the internal friction in that liquid, that is, the resistance to shear, agitation or flow. The greater the resistance to flow, the higher will be its viscosity. Like density, viscosity is affected by temperature. As temperature decreases, viscosity increases. The SI unit of viscosity is the millipascal-second(mPa.s). This is equivalent to the former unit of centipoise(cP). The viscosity was obtained using dynamic viscosity meter. The measurements were run in triplicate and the mean value was reported.

1.4 Water content

Once the water and crude have been intimately mixed due to turbulent flow or shearing action, an emulsion is formed. When tiny droplets of water are stabilized in a continuous external oil phase, it is called emulsified water. The water content of an emulsion affects the density, viscosity and other properties of the emulsion. Water contents were determined using DSC (Charoenrein, 1989) technique at cooling rate of -5℃ per minutes.

The emulsified water content in an W/O emulsion can be calculated based on the following formula:

$$C_w = \frac{H/h}{m} \times 100\% , \quad (1)$$

where, C_w represents water content in an emulsion (%); H is the total enthalpy of sea water (mJ); h is the enthalpy of seawater (mJ/g); m is the emulsion sample weight (g).

1.5 Droplet sizes and distribution

Small droplet sizes also help stable the emulsion by preventing coalescence of water drops. Small droplet sizes also contribute to the physical properties of an emulsion. A Philips XL30 Environmental Scanning Electron Microscopy(ESEM) was used in this study to observe the water-in-crude oil emulsions, and then the images taken in the ESEM were evaluated using image analysis software to analyze the water droplet sizes of the water-in-crude oil emulsions.

ESEM(Nicolopoulos,1998) uses multiple pressure limiting apertures to separate the sample chamber from column. The electron gun and upper parts of the column to be held at high vacuum(10^{-6} – 10^{-7} torr), but the chamber may sustain pressure as high as 50 torr. ESEM also uses an environmental secondary detector(ESD) which can function in non-vacuum environment. ESEM is specifically designed to be able to examine microstructural and ultrastructural details of samples in their natural state or wet state (Létang, 1999). ESEM provides a new approach to the observation of structures of emulsions without any special preparation.

2 Results and discussion

2.1 Density and viscosity

It is shown in Fig.1 that the density of the water-in-crude oil emulsion(30 minutes mixing) is slightly higher than those of crude oil and evaporated crude oil, but still less than the density of seawater. However the viscosity of the water-in-crude oil emulsion is much higher than that of crude oil or evaporated crude oil. That is the reason why the water-in-crude oil emulsion is very viscous and sticky and more difficult to clear up.

2.2 Water content

The typical DSC curve of water-in-crude oil emulsion is shown in Fig.2 and the water content of an emulsion was calculated using formula (1). The calculated water contents of the emulsions are presented in Fig.3. It can be seen that the water content was increased to almost 80% after 30 minutes mixing. The prolonged mixing did not change the water content much. The stable emulsion contains high ratio of water.

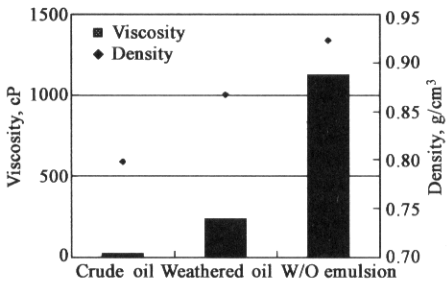

Fig.1 Oil density and viscosity

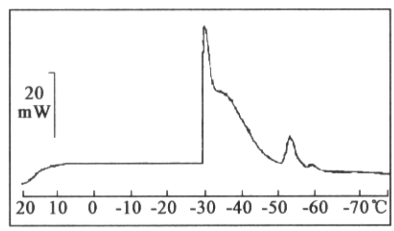

Fig.2 DSC result of W/O emulsion

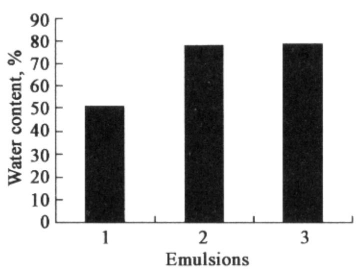

Fig.3 Water content of water-in-crude emulsion

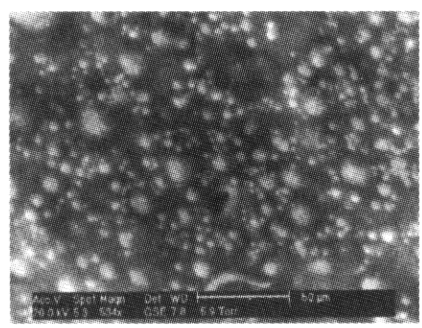

Fig.4 ESEM image of water-in-crude emulsion

2.3 Droplet sizes and distribution

The ESEM images were saved as 8-bit images(Fig.4). The images then were filtered, converted and threshold. Water droplets were counted and numbered using particle size analysis process. The results of ESEM image analysis are shown in Fig. 5. It can be seen that water droplets have a wide range of sizes and droplet sizes generally show the normal distributions. After mixed for 10 minutes, the emulsion contained large droplets and some water droplets coalesced to form larger droplets, but with the increase in mixing time the water droplets became smaller and more stable. It is clearly indicated in Fig. 5 that there is no obvious difference between 30 minutes mixing and 120 minutes mixing. That means the stable emulsion was formed after mixing for 30 minutes. Small droplets sizes help form

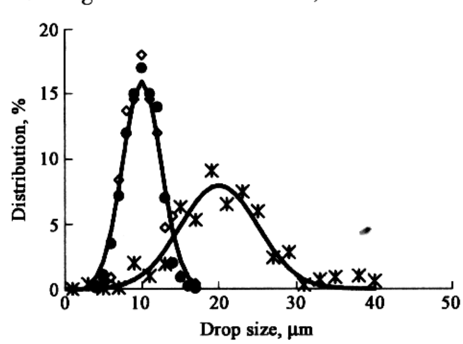

Fig.5 Water droplet size distribution in water-in-crude oil emulsion
* 10 min mixing; ●30 min mixing; ◇ 120 min mixing

stable emulsion by preventing coalescence of water droplets. Small droplet sizes also contribute to the physical properties of an emulsion.

3 Conclusions

Water-in-crude oil emulsions are often formed when crude oil is spilled into sea. The properties change significantly when water-in-crude oil emulsions formed. Better understanding of water-in-crude oil emulsions will help make appropriate choices in oil spill responses. The ESEM provides a new approach to the analysis of water-in-crude oil emulsions. The further work will investigate the emulsions formed at sea after a spill.

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