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Wettability of Freon hydrates in crude oil/brine emulsions

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Abstract

The surface energy of petroleum hydrates is believed to be a key parameter with regard to hydrate morphology and plugging tendency in petroleum production. As of today, the surface energy of natural gas hydrates is unknown, but will depend on the fluids in which they grow. In this work, the wettability of Freon hydrates is evaluated from their behavior in crude oil emulsions. For emulsions stabilized by colloidal particles, the particle wettability is a governing parameter for the emulsion behavior. The transition between continuous and dispersed phases as a function of brine volume in crude oil–brine emulsions containing Freon hydrates has been determined for 12 crude oils. Silica particles are used for comparison. The results show that phase inversion is highly dependent on crude oil properties. Based on the measured points of phase inversion, the wettability of the Freon hydrates generated in each system is evaluated as being oil-wet, intermediate-wet, or water-wet. Generation of oil-wet hydrates correlates with low hydrate plugging tendency. The formation of oil-wet hydrates will prevent agglomeration into large hydrate aggregates and plugs. Hence, it is believed that the method is applicable for differentiating oils with regard to hydrate morphology.

Keywords: Hydrates; Crude oil emulsions; Phase inversion; Wettability

1. Introduction

In an emulsion containing colloidal solid particles, one of the liquids is likely to wet the solid more than the other liquid, with the more poorly wetting liquid becoming the dispersed phase [1]. Hence, the type and stability of emulsions stabilized by colloidal particles are governed by the wettability of the solid. The effect of particle wettability upon emulsion behavior has previously been the subject of several review papers [2–6]. It is generally found that for equal volumes of oil and water, oil-wet particles, i.e., particles with contact angles larger than 90° measured through the aqueous phase, tend to stabilize water-in-oil emulsions, whereas hydrophilic or water-wet particles tend to stabilize oil-in-water emulsions. Strongly water-wet and strongly oil-wet particles remain dispersed in the bulk phase (either water or oil) and are unable to stabilize emulsions, whereas intermediate-wet particles are able to form very stable emulsions (oil-continuous or water-continuous, depending on whether they are weakly oil-wet or weakly water-wet). A schematic illustration of spherical particles at a planar oil–water interface is given in Fig. 1. The inversion between oil-continuous and water-continuous emulsions occurs when the contact angle is equal to 90°.

Several authors, e.g., Binks and Lumsdon [7,8], have demonstrated that inversion of emulsions stabilized by solid particles, i.e., the shift from water-continuous to oil-continuous emulsions or vice versa, can be induced by altering the volume ratio of the two liquid phases. The volume fraction of dispersed phase necessary for inverting the emulsion is governed by the wettability of the particles. Generally it has been found that as the hydrophilic character of the particles increases, the volume fraction of water (φ_w) needed for the inversion to occur decreases. Hydrophobic

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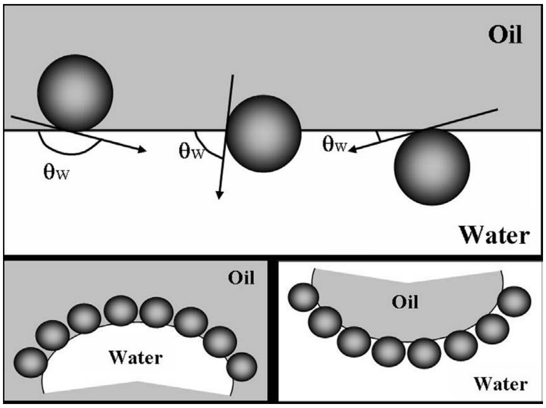

Fig. 1. Spherical particles at planar oil/water interface. Oil-wet particles (contact angle $> 90^\circ$) will reside mainly in the oil phase (right) and tend to stabilize water-in-oil emulsions. Water-wet particles (contact angle $< 90^\circ$) reside mainly in the water phase (left) and tend to stabilize oil-in-water emulsions. (Adapted from Binks [3].)

particles cause inversion at high volume fractions of water. As an example, Binks and Lumsdon [7] reported inversion at approximately $\varphi_\text{W} = 0.3$ for hydrophilic particles and at $\varphi_\text{W} = 0.9$ for hydrophobic particles in model systems consisting of toluene, water, and modified silica particles. In other words, weakly oil-wet particles are able to stabilize oil-continuous emulsions at higher volume fractions of water than weakly water-wet particles.

It is a well-known fact that the presence of surfactants in emulsions stabilized by colloidal particles has a significant impact on the stability of the emulsion. The surfactant may adsorb to the particle surface and alter the wettability of the particle, as reported by, e.g., Schulman and Leja [9]. The resulting wettability of the particle will depend on the molecular structure of the surfactant. Hence, different surfactants induce different emulsion behavior.

Petroleum hydrates are crystals formed at given pressure and temperature conditions by low-molecular-weight hydrocarbons confined in a framework of water molecules [10]. The formation of hydrates in petroleum systems is generally regarded as an interface phenomenon, where hydrate nuclei grow at the interface between oil (containing dissolved gas) and water. Hydrates formed in mixtures of oil, gas, and water may either agglomerate and form plugs, or flocculate and form dispersions. Dispersions may be transported, whereas hydrate plugs will eventually block fluid transport completely.

It has been shown that different crude oils have different tendencies to form hydrate pluggs. However, the question of “why?” is yet to be answered. One likely possibility is that some oils contain natural inhibiting components, such as antiagglomerants. This feature has previously been indicated by several authors [11–13]. Antiagglomerating components are surface active components that adsorb to the hydrate surface, resulting in a lyophilic or oil-wet surface. This reduces the possibility of strong attractive hydrogen-bonding between hydrate particles and results in flocculation and dispersions rather than agglomeration and hydrate plugs. The various contents of surface-active species in crude oil, and their ability to change a hydrophilic surface to lyophilic can be investigated by measurements of wettability. However, no convenient method is available today for evaluating the wettability of hydrates, and thus the surface energies of these particles remain to be determined.

In this work, we argue that the adsorption of petroleum components to hydrate surfaces creates colloidal solid particles of varying wettability, depending on crude oil composition, in line with the modified silica particles adapted by Binks and Lumsdon [7]. Hence, by studying the type and stability of crude oil emulsion systems containing hydrate particles, information on the wettability of the hydrate surfaces in each crude oil system may be provided.

An experimental approach to measuring phase inversion of emulsions as a function of volume fraction of brine has been developed and tested. The experiments have been performed using crude oil/brine emulsions, and the influence of colloidal particles has been investigated using both Freon hydrates and silica particles. The measured inversion points are correlated with the wettability of the hydrates generated in each system.

The terminology related to wettability is by tradition quite qualitative, e.g., strongly or weakly oil-wet. For clarifying purposes, the particles referred to in this present work are all in the shape of lenses residing at the oil/brine interfaces, as illustrated by spherical particles in Fig. 1. Strongly oil-wet, with contact angle equal to 180°, or strongly water-wet particles, with angles equal to 0°, are not under consideration. The particles are termed oil-wet (mainly residing in the oil phase), water-wet (mainly residing in the water phase), or intermediate-wet (equal affinity for both water and oil).

2. Materials and methods

2.1. Materials

A sample set of 12 crude oils, 1 Angolan and 11 from the Norwegian continental shelf, have been investigated. The oils span from heavy oils enriched in asphaltenes to light oils and condensates. The crude oils have previously been thoroughly characterized with regard to chemical composition and properties, e.g., acid and base content, biodegradation level, and asphaltene content. Data for some of the crude oils were reported in a previous study [14]. Table 1 summarizes chemical properties for the crude oils in this data set. The TAN and TBN values were determined according to ASTM664-89 [15] and ASTM2896-88 [16] (with modifications by Dubey and Doe [17]), respectively. The asphaltenes were precipitated by refluxing a portion of the oil with a 40 times excess of hexane for 6 h. The biodegradation levels were estimated as described by Peters and Moldowan [18]. The biodegradation levels run from 0 to 10, where 0 corresponds to nonbiodegraded oils and 10 corresponds to ex-