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## Modified Brine Salinity and Nanoparticles Size-Dependent Emulsion Formation in Enhanced Oil Recovery

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### Summary

The effect of modified brine salinity and varying size of CaCO<sub>3</sub> nanoparticles on emulsion formation was investigated for different brine-oil-nanoparticles systems. Emulsion formation experiments were performed by employing a commercially available sonication equipment, Branson Sonifier® SFX250. The brine salinity showed a significant effect on emulsion formation in decane-brine-nanoparticles (50 nm CaCO<sub>3</sub>) systems i.e., a decrease in brine salinity showed an increase in emulsion formation and correspondingly smaller size of emulsion droplets. Similarly, decane-brine (deionized water) sonicated with different size of CaCO<sub>3</sub> nanoparticles (15-40, 50, and 90 nm) showed that emulsion formation is inversely related to the size of nanoparticles i.e., increases with a decrease in size of nanoparticles and correspondingly smaller size of emulsion droplets. Emulsion results will be presented for different model and crude oils sonicated with brines of different salinity (North Sea water, deionised water, and formation water) in the presence of three different sizes of CaCO<sub>3</sub> nanoparticles (15-40, 50, and 90 nm). Emulsion characterization of brine-oil-CaCO<sub>3</sub> nanoparticles systems presented in this work will help in understating the interaction of CaCO<sub>3</sub> nanoparticles with brine-oil in the chalk reservoirs and its potential application in enhanced oil recovery.

## Introduction

Due to depleting oil and gas resources worldwide, it is essential to develop novel enhanced oil recovery (EOR) technologies for additional oil recovery from the existing petroleum reservoirs. Smart water flooding is one of those advanced EOR techniques in which the salinity and ionic composition of the injection brine is fine-tuned, which can result in mobilizing the trapped oil and may improve the oil recovery (Yousef et al., 2012). Wettability alteration has been reported as the key mechanism to explain the additional oil recovery in smart water flooding (Yousef et al., 2011). Low salinity water flooding has also been reported widely in the literature for improved oil recovery. Sheng, 2014, reported that seventeen mechanisms of low salinity water flooding have been proposed in the literature. However, most of these mechanisms are related to each other and wettability alteration is probably the most plausible working mechanism.

In addition to wettability alteration mechanism, formation of water-soluble oil emulsion in the presence of fines has also been suggested as a potential working mechanism to mobilize the trapped oil and increase the sweep efficiency (Zahid et al., 2011; Chakravarty et al., 2015). Formation of emulsions was demonstrated in the laboratory experiments (Zahid et al., 2011; Chakravarty et al., 2015). These fines may either be the available particles in the rock pores or they may formed in situ under the reservoir conditions. The formation of water-soluble oil emulsions may take place on interaction of insoluble fines with brine-oil system in the reservoir. However, the interaction mechanism is not yet clearly understood. It may be possible that the available migrating fines, on interaction with brine-oil, reduces the interfacial tension between the two liquids to form Pickering emulsion (Pickering, 1907). These migrating fines may act as emulsifier similar to that of surfactants.

Recently, nanotechnology and application of nanoparticles has shown significant potential in the oil and gas industry including nanoparticle based EOR applications. Nanoparticles in the injection brine can easily flow through the reservoir pores without clogging them due to their small size. Nanoparticles based water flooding can promote emulsion formation and stabilization, wettability alteration of the rock, and reduction in interfacial tension (Bennetzen and Mogensen, 2014). Emulsion formation and stabilization with nanoparticles can be affected by the particle size, shape, concentration, and wettability (Binks, 2002). The nanoparticles can also be tailor-made with different materials to meet the desired physical and chemical properties. These attributes make nanoparticles based EOR applications an attractive choice. For intended use of nanoparticles based EOR technology, it is essential to understand the interaction of brine-oil-nanoparticles system. This work presents emulsion formation and characterization of different brine-oil- $\text{CaCO}_3$  nanoparticles systems in relation to modified brine salinity and varying size of nanoparticles.

## Materials and Method

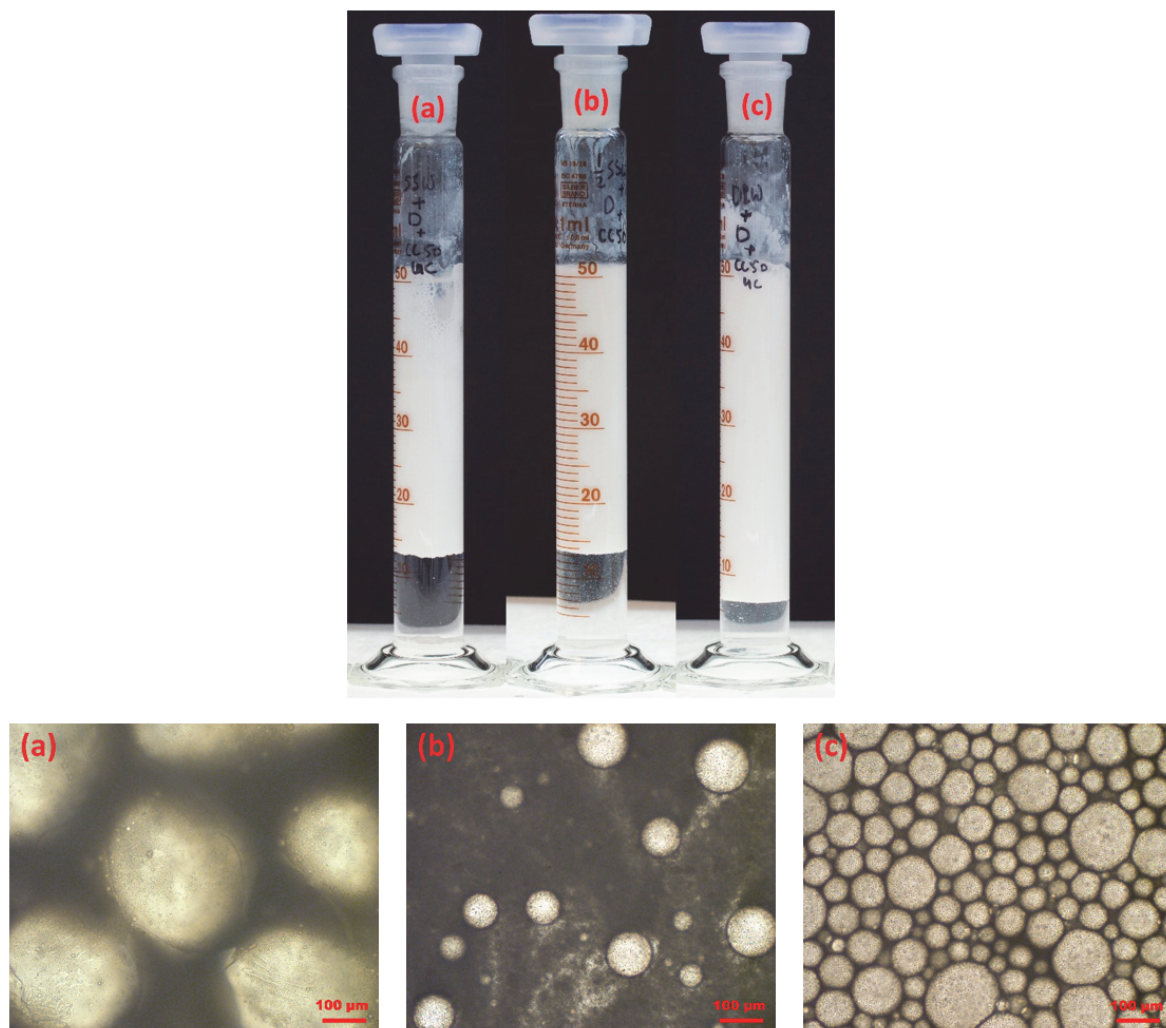
Decane (D) and a mixture of 1:1 (v/v) hexane-hexadecane (HH) were used as model oils. A crude oil sample from North Sea reservoir was also employed. Different brines were used with a wide range of brine salinity e.g., synthetic seawater (SSW) with a brine salinity of North Sea water to deionized water (DIW) with zero salinity. Two brines were also used that mimicked the composition of formation water obtained from different production wells in the Halfdan Field. Calcium carbonate ( $\text{CaCO}_3$ ) nanoparticles of three different sizes (15-40, 50, and 90 nm) were used as emulsifying particles. Characterization of  $\text{CaCO}_3$  nanoparticles was performed with Transmission Electron Microscopy (TEM).

Branson Sonifier® SFX250, a commercially available sonication equipment, was employed for emulsion formation in brine-oil-nanoparticles systems. To test the emulsion formation, 25 ml of each brine and oil samples were taken into a 50 ml graduated glass cylinder together with 2 g of  $\text{CaCO}_3$  nanoparticles. The prepared samples were sonicated for 5 minutes by using a 6.5 mm tapered microtip (sonication probe) with an output power of 30 W (Arshad et al., 2017). All the experiments were performed at room temperature for the same experimental conditions. Emulsion characterization (emulsion droplet size) was performed with an optical microscope (Axio Scope.A1).

## Brine Salinity

A series of experiments were performed to evaluate the effect of brine salinity on emulsion formation for a given constant size of  $\text{CaCO}_3$  nanoparticles in different brine-oil-nanoparticles systems. Figure 1 illustrates such an example of decane (D) sonicated with brines of three different salinities of SSW, 0.5SSW, and DIW in the presence of 50 nm  $\text{CaCO}_3$  nanoparticles. The results show that the amount of emulsion formation is directly affected by the brine salinity for a given constant nanoparticles size (50 nm) i.e., a decrease in brine salinity favours the emulsion formation. It can also be noticed that the emulsion droplet size decreases with a decrease in brine salinity from SSW to DIW. Decane sonicated with SSW in the presence of 50 nm  $\text{CaCO}_3$  nanoparticles produces emulsion droplets of large sizes, indicating an emulsion of poor quality (image “a” in Figure 1). Although a decrease in brine salinity to 0.5SSW decreases the emulsion droplet size, the emulsion droplets are far apart from each other and still indicate a poor emulsion quality (image “b” in Figure 1). DIW sonicated with decane and 50 nm nanoparticles produces the smallest and most compact emulsion droplets for this brine-oil system (image “c” in Figure 1) that is an indication of good quality and better stability of emulsion. HH-brine (SSW, 0.5SSW, and DIW) system sonicated with 50 nm  $\text{CaCO}_3$  nanoparticles shows similar results as that of decane-brine-50 nm nanoparticles. Similar experiments were performed for D/ HH sonicated with different brine salinities (SSW, 0.5SSW, and DIW) in the presence of a given constant  $\text{CaCO}_3$  nanoparticles size of 15-40 and 90 nm.

D + 2 g 50 nm  $\text{CaCO}_3$  (a) SSW; (b) 0.5SSW; (c) DIW



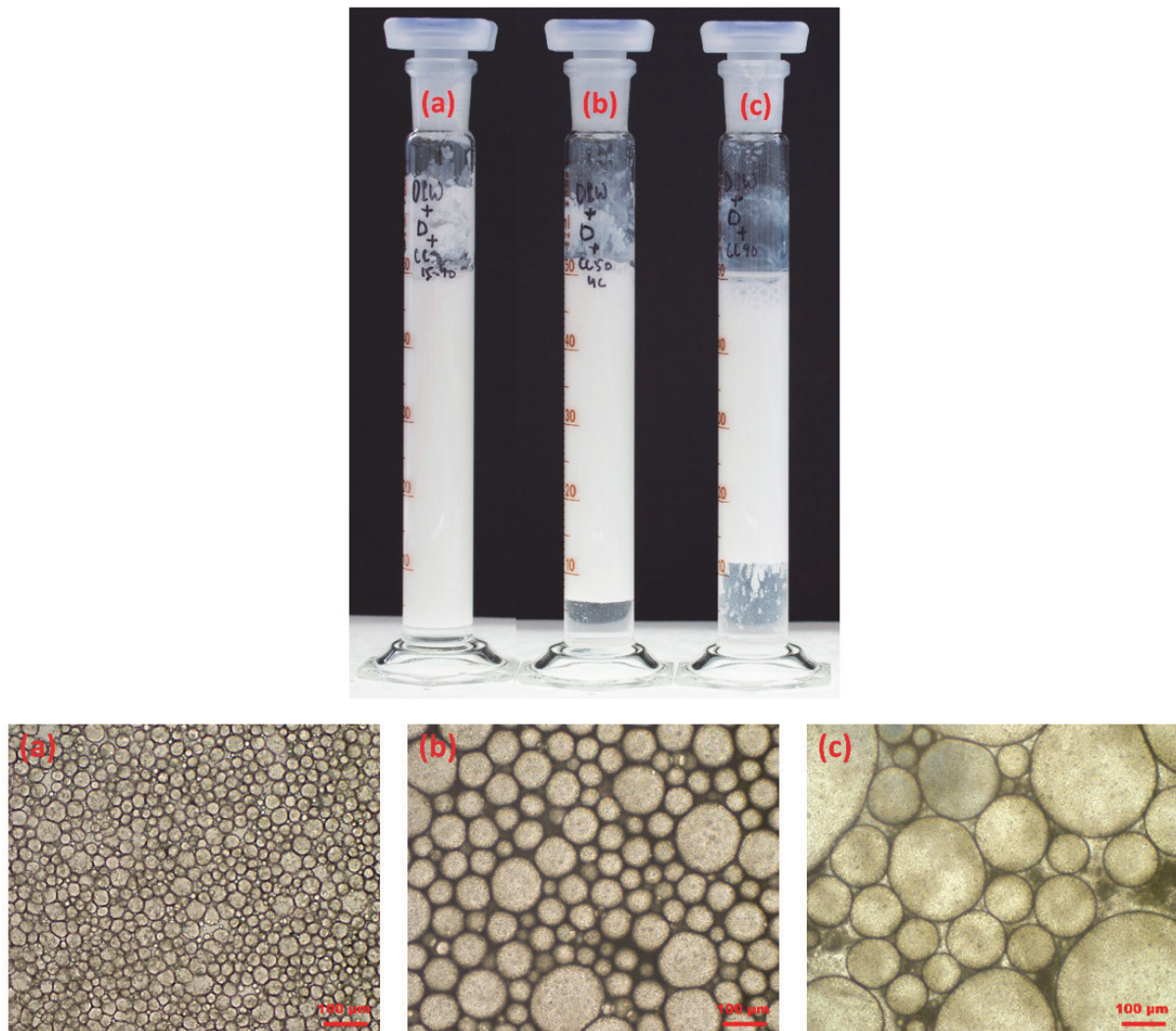
**Figure 1** Emulsion formation and microscopic results of decane (D) with brines of different salinity in the presence of 50 nm  $\text{CaCO}_3$  nanoparticles. SSW and DIW stands for synthetic seawater and deionised water, respectively.

## Size of Nanoparticles

The effect of size of nanoparticles on emulsion formation was studied in different oil-brine (constant salinity) systems by sonicating with  $\text{CaCO}_3$  nanoparticles of varying sizes. Figure 2 presents an example of sonication results of decane and DIW with three different sizes of  $\text{CaCO}_3$  nanoparticles (15-40, 50, and 90 nm). The results clearly show that the amount of emulsion formation is inversely related to the size of nanoparticles i.e., increases with a decrease in size of nanoparticles. Emulsion characterization of these systems shows that the emulsion droplet size increases with an increase in size of nanoparticles i.e., smallest nanoparticles of 15-40 nm form the smallest emulsion droplets (image “a” in Figure 2) followed by 50 nm nanoparticles (image “b” in Figure 2) and 90 nm nanoparticles form the largest droplets (image “c” in Figure 2). DIW-HH system sonicated with three different sizes of  $\text{CaCO}_3$  nanoparticles (15-40, 50, and 90 nm) shows similar results to that of DIW-D, as presented above.

Similar experiments were performed for D/ HH sonicated with different constant brine salinities (SSW and 0.5SSW) in the presence of  $\text{CaCO}_3$  nanoparticles of varying size of 15-40, 50, and 90 nm. All the studied brine-oil systems show an increasing trend in emulsion formation with a decrease in size of nanoparticles and correspondingly smaller sized emulsion droplets.

DIW + D + 2 g  $\text{CaCO}_3$  (a) 15-40 nm; (b) 50 nm; (c) 90 nm



**Figure 2** Emulsion formation and microscopic results of deionised water (DIW) with decane (D) for three different sizes (15-40, 50, and 90 nm) of  $\text{CaCO}_3$  nanoparticles.



## Conclusions

Emulsion characterization was performed for different brine-oil-CaCO<sub>3</sub> nanoparticles systems in relation to modified brine salinity and varying size of nanoparticles. A commercially available sonication equipment, Branson Sonifier® SFX250, was used to perform the emulsion formation experiments. The brine salinity showed a significant effect on emulsion formation when decane is sonicated with three different brines (SSW, 0.5SSW, and DIW) in the presence of 50 nm CaCO<sub>3</sub> nanoparticles i.e., a decrease in brine salinity showed an increase in emulsion formation and correspondingly smaller size of emulsion droplets. Similarly, decane-brine (deionized water) sonicated with different size of CaCO<sub>3</sub> nanoparticles (15-40, 50, and 90 nm) showed that emulsion formation is inversely related to the size of nanoparticles i.e., increases with a decrease in size of nanoparticles and correspondingly smaller size of emulsion droplets. Emulsion characterization of brine-oil-CaCO<sub>3</sub> nanoparticles systems presented in this work will help in understating the interaction of CaCO<sub>3</sub> nanoparticles with brine-oil in the chalk reservoirs and its potential application in enhanced oil recovery.

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