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The Influence of Surfactant Concentration and Surfactant Type on the Interfacial Tension of Heavy Crude Oil/Brine/Surfactant System

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#### Abstract

The interfacial tension that exists amid crude oil and brine can be lowered by chemical surfactant flooding as a result of the mobilization of trapped oil. The influence of surfactants on the interfacial tension (IFT) that exists in a heavy crude oil/ brine system was examined experimentally. The influence of surfactant concentration was observed. The laboratory experiments were performed at ambient and reservoir temperatures. Five different surfactants were made use of; two industrial surfactants (Alpha Olefin Sulfonate and Methyl Ester Sulfonate) and three formulated surfactants from vegetable oils (surfactants from Jatropha, Castor, and Palm kernel oils). The heavy crude oil was acquired from a field X in the Niger Delta, and the brine used was prepared in the laboratory. IFT between brine and heavy crude oil was measured by means of the Du NOUY ring. From the results, it was found that the Castor oil derived surfactant performs best at both ambient and reservoir temperatures.

Keywords: Concentration; Enhanced oil recovery; Interfacial tension; Surfactant.

#### 1. Introduction

Naturally, petroleum crude is a limited reserve. Be that as it may, the amount of crude oil existing needs to meet global requests. At intervals, oil production has been deliberately lessened, and this has caused genuine oil crises supplemented by a general increment in the cost of oil. The petroleum industry is presently being faced with persistent challenges to increase well throughput as demand for oil is accumulating daily, particularly in the developed and developing countries. This, in turn, has constrained the oil industry to recover oil from more complex zones, where the oil is less accessible, meaning that recovery strategies are cease-lessly progressed. This has contributed to the progress of strategies for enhanced oil recovery (EOR), which, whereas utilized nowadays, also always experience further development.

For the growing global demand for energy to be satisfied, an additional representative response to fulfil this requirement exists in maintaining the production of petroleum from active fields for numerous purposes <sup>[1]</sup>. One scheme that has gained a lot of consideration and thorough research recently is the application of surfactant in chemical flooding. Surfactant flooding majorly recovers oil typically based on the reduction in IFT and alteration in the reservoir rocks' wettability <sup>[2]</sup>. For the production of residual oil, a thorough knowledge of the contact between water, crude oil, and the rock's surface is essential; The inter-phase chemistry has a very significant part to play in improving oil recovery; an influential factor is the interaction of viscous, capillary and gravity forces.

Capillary number ( $N_{ca}$ ) conveys the viscous drag forces in a system to the surface tension forces, as depicted by Equation (1), and it is dimensionless. The viscous force helps to gather crude oil, while the capillary forces favours trapping crude oil <sup>[3]</sup>.

$$N_{ca} = \frac{\mu v}{\sigma}$$

(1)

where:  $N_{ca}$  defines the capillary number;  $\mu$  stands for the Liquid dynamic viscosity; V represents the liquid velocity;  $\sigma$  is the IFT between two immiscible liquids.

If viscous forces dominate when the capillary number is higher, and the influence of IFT between fluids in the pores of rock is abridged, thus supplementing recovery. The capillary number for characteristic reservoir conditions ranges from  $10^{-8}$  to  $10^{-2}$ . Lowering the IFT is one of the most systematic ways of increasing the capillary number.

Due to its capability to minimize IFT between fluids that are immiscible, surfactant flooding has gained a lot of consideration in its use in EOR, thus augmenting the capillary number is needed to activate the leftover petroleum in the reservoir. This involves the introduction of liquid chemicals and surface-active (surfactants) into an oil reservoir. This introduction of chemicals successfully dominates the phase behaviour properties in the reservoir, thereby mobilizing the stuck crude oil by lowering the IFT of the injected liquid/crude oil immiscible liquids system.

Surfactants are chemicals like short-chain fatty acids, are also known as amphiphiles, i.e., they have one part that has an attraction for non-ionic media (hydrophobic) and one part that has an attraction for ionic media (hydrophilic) <sup>[4]</sup>. The hydrophilic properties of a surfactant are defined by the head and tail structure, for example, the number of branches in its hydrocarbon chain, The hydrocarbon chain's length, and the functional groups <sup>[5-6]</sup>.

The use of surfactant additives to improve enhanced oil recovery methods' efficiency has been studied comprehensively over the decades, and the use of biodiesel or FAMEs as a surfactant addictive has shown to improve the efficiency of these processes <sup>[7]</sup>.

Seethepalli *et al.* research on the contact crude oil on carbonate rock surfaces has with dilute basic anionic surfactant mixtures. Anionic surfactants capable of altering the wettability of the reservoir rock surface to the water-wet condition and also the surfactant DTAB with crude oil from West Texas and reducing the IFT with crude oil to very small values (<0.01 dynes/cm) were also identified <sup>[8]</sup>.

Babu *et al.* synthesized a novel castor oil-based surfactant, for EOR methods in oil and gas production. The behaviour of SMES was investigated by evaluating the IFT by including and excluding NaCl and its stability at reservoir temperature. The new surfactant showed excellent surface action, lowering the IFT of surfactant solution up to 38.4 dynes/cm and 27.6 dynes/cm, not including and including NaCl, correspondingly <sup>[9]</sup>.

Saxena *et al.* presented a study on the synthesis of surfactant from natural soap-nut oil possessing outstanding characteristics for use in Enhanced Oil Recovery schemes. The surfactant produced from soap-nut oil exhibited the auspicious properties of reducing IFT, emulsification, alteration of reservoir rock wettability, that are needed for its use in EOR. At critical micelle concentration (CMC), an extremely low tension value of 0.02123 dynes/cm was achieved for surfactant/ crude oil solution, which was significantly reduced to 0.002037 dynes/cm at the ideal salinity <sup>[11]</sup>.

Many of the industrial surfactants employed in the oil and gas industry are expensive, globally dangerous, and essentially non-biodegradable <sup>[11]</sup>. Synthesized biodegradable surfactants from natural resources can replace non-biodegradable surfactants that are applied in chemical EOR <sup>[12]</sup>. Consequently, the need for surfactants to be extracted from natural oils is growing. <sup>[13-14]</sup>. An extensive range of surfactants is produced from vegetable oils like Jatropha oil, Castor oil, Palm Kernel oil, which displayed potential for lowering the IFT at the interface between water and crude oil and changed the rock's wettability to water wet from oil-wet <sup>[9,15-16]</sup>.

In this paper, the IFT at the interface between the solutions of brine, heavy crude oil, and surfactant was experimentally studied using Du NOUY ring method. All tests were carried out at room and reservoir temperatures. Five surfactants were employed: two industrial surfactants (Alpha Olefin Sulfonate and Methyl Ester Sulfonate) and three formulated surfactants from vegetable oils (surfactants from Jatropha, Castor and Palm kernel oils). The heavy crude oil was extracted in the Niger Delta from a field X, and the brine used was formulated in the laboratory.

The interaction between salinity and surfactants was also studied. Lastly, the influence of different surfactants on IFT has been measured, and the best surfactant for crude oil has been selected based on the results.

### 2. Materials and methods

## 2.1. Materials

Five different surfactants were used; two industrial surfactants (alpha olefin sulfonate and methyl ester sulfonate) provided by Deriks Ventures and three formulated surfactants from vegetable oils (surfactants from Jatropha, Castor and Palm kernel oils procured from National Research Institute for Chemical Technology (NARICT, Zaria)). Lab grade sodium chloride with 99% purity (EMSURE) was used to prepare the brine, toluene (Fisher Scientific UK, HPLC grade) was used to clean the core samples. The vegetable oils were sulfonated using 18M fuming tetraoxosulphate (vi) acid (Fisher Scientific UK, HPLC grade). Glycerol (Fisher Scientific UK) was used to produce glycerine sulphuric acid. 99% purity sodium hydroxide (EMSURE) was used for the neutralization process. The heavy crude oil employed in IFT measurement tests was obtained from a field X in the Niger Delta (Nigeria), the brine used was formulated by dissolving sodium chloride in distilled water at different concentrations. This solution was stirred for 45 minutes using a magnetic stirrer and filtered using a filter paper. Table 1 displays the crude oil's properties.

Table 1. Crude oil properties

Crude oil properties	Value
Density (g/cm <sup>3</sup> ) @ 25°C	0.92
Total acid number (mg of KOH/g)	0.72
API gravity	22.3

# 2.2. Methods

## i. Formation of glycerol-sulphuric acid

420g of H<sub>2</sub>SO<sub>4</sub> was reacted with 70g of glycerol to form acrolein (glycerol-sulphuric acid).



## ii. Sulfonation of vegetable oils

100g of vegetable oils (Castor/Jatropha/Palm kernel oil) was reacted with 100g of glycerolsulphuric acid while stirring at 50-55°C for two hours.



## iii. Neutralization

The sulfonated mass cooled to 20°C by pouring the mixture over ice was neutralized with 50% w/v caustic soda (NaOH).



Generally, surfactants are capable of reducing the IFT that exists between the crude oil/water system. The IFT that exists between the fluids (heavy crude oil, surfactants, and prepared sodium salts solutions) was measured using a CSC-DUNOUY tensionmeter, as depicted in Figure 1 for different concentrations at ambient and reservoir temperatures. This allowed the ring to be pulled across the boundary between the higher density liquid (brine), and the lighter liquid (crude oil) that is floating above. The force required for the higher density liguid to break through the surface was recorded as interfacial tension measured in milliNewton/meter (mN/m).

iv. Interfacial tension measurements

Figure 1. CSC-DUNOUY tensiometer

#### 3. Results and discussion

In this study, the IFT between crude oil/brine/surfactant system was investigated experimentally using the Du NOUY ring method. All tests have been carried out at room and reservoir temperatures. Five surfactants were utilized: two industrial surfactants (alpha-olefin sulfonate and methyl ester sulfonate) and three formulated surfactants from vegetable oils (surfactants from Jatropha, Castor and Palm kernel oils). A sample of heavy crude oil was collected from a Niger Delta field, and the brine used was formulated in the laboratory. The best surfactant for crude oil was then selected based on the results.

At the start of the experiment, the measured interfacial tension of crude oil/brine system was 19.8 mN/m and 16.4 mN/m at 20°C and 60°C, respectively, for a brine concentration of 10,000 ppm. Each measurement was carried out at least twice in order to perform quality control.





Figure 2. Interfacial tension versus AOS surfactant concentration under different temperature conditions

Figure 3. Interfacial tension versus Jatropha-oil surfactant concentration under different temperature conditions

The influence of the concentration of AOS surfactant on the tension of the brine/heavy crude oil/ /surfactant system at brine's salinity of 10000 ppm is exhibited in Figure 2. At room temperature, the interfacial tension drops from 16.9 mN/m to 13.6 mN/m as the concentration of the AOS surfactant increases from 10000 ppm to 25000 ppm. At reservoir temperature,

the interfacial tension drops from 14.2 mN/m to 12.9 mN/m as the AOS surfactant concentration increases from 10000 ppm to 25000 ppm. These results show that AOS surfactant is more effective in lowering the IFT at reservoir temperature. As seen in figure 2, the reduction of IFT by the AOS surfactant at room temperature has a similar trend with the AOS surfactant's performance at reservoir temperature.

Figure 3 displays the influence of concentration of the Jatropha-oil surfactant on the IFT of brine/heavy crude oil//surfactant system at brine's salinity of 10000 ppm. At room temperature, the interfacial tension drops from 16.4 mN/m to 13.5 mN/m as the Jatropha-oil surfactant concentration increases from 10000 ppm to 25000 ppm. At reservoir temperature, the IFT drops from 13.80 mN/m to 12.80 mN/m as the Jatropha-oil surfactant concentration increases from 10000 ppm. These results show that Jatropha-oil surfactant is more effective in lowering the IFT at reservoir temperature. As seen in Figure 3, the reduction of IFT by the Jatropha-oil surfactant at room temperature has a similar trend with the Jatropha-oil surfactant's performance at reservoir temperature

Figure 4 shows the influence of the concentration of Palm kernel oil (PKO) surfactant on the IFT of brine/heavy crude oil//surfactant system at brine's salinity of 10000 ppm. At room temperature, the interfacial tension drops from 16.2 mN/m to 13.4 mN/m as the Palm kernel oil surfactant concentration increases from 10000 ppm to 25000 ppm. At reservoir temperature, the interfacial tension drops to 12.5 mN/m from 13.6 mN/m as the concentration of PKO surfactant increases from 10000 ppm to 25000 ppm. These results show that the PKO surfactant is more effective in lowering the IFT at reservoir temperature. As seen in Figure 4, the reduction of IFT by the PKO surfactant at room temperature has a similar trend with the PKO surfactant's performance at reservoir temperature.



Figure 4. Interfacial tension versus PKO surfactant concentration under different temperature conditions



Figure 5. Interfacial tension versus MES surfactant concentration under different temperature conditions

Figure 5 shows the influence of the concentration of MES surfactant on the IFT of brine/heavy crude oil/surfactant system at brine's salinity of 10000 ppm. At room temperature, the interfacial tension drops from 15.9 mN/m to 13.3 mN/m as the concentration of MES surfactant increases from 10000 ppm to 25000 ppm. At reservoir temperature, the interfacial tension drops to 12.4 mN/m from 13.5 mN/m as the MES surfactant concentration increases from 10000 ppm to 25000 ppm. These results show that MES surfactant is more effective in lowering the IFT at reservoir temperature. As seen in Figure 5, the reduction of IFT by the MES surfactant at room temperature has a similar trend with the MES surfactant's performance at reservoir temperature

Figure 6 shows the influence of the concentration of Castor-oil surfactant on the IFT of brine/heavy crude oil//surfactant system at brine's salinity of 10000 ppm. At room temperature, the interfacial tension drops from 15.7 mN/m to 13.1 mN/m as the Castor-oil surfactant concentration increases from 10000 ppm to 25000 ppm. At reservoir temperature, the interfacial tension drops to 12.2 mN/m from 13.4 mN/m as the Castor-oil surfactant concentration increases from 10000 ppm. These results show that the Castor-oil surfactant is

more effective in lowering the IFT at reservoir temperature. As seen in Figure 6, the reduction of IFT by the Castor-oil surfactant at room temperature has a similar trend with the Castoroil surfactant's performance at reservoir temperature







Figure 7 compares the performance of the five surfactants (AOS, MES, PKO, Jatropha, and Castor surfactants) at room temperature. The salinity of the brine is 10000 ppm. The interfacial tension drops from 16.9 mN /m to 13.6 mN/m using the AOS surfactant, with increasing solution concentration from 10,000 ppm to 25,000 ppm. The interfacial tension drops to 13.5 mN/m from 16.4 mN/m using the Jatropha surfactant with increasing solution concentration from 10000 ppm to 25000 ppm. The interfacial tension drops from 16.2 mN/m to 13.4 mN/m using the PKO surfactant, with increasing solution concentration from 10000 ppm to 25000 ppm. The interfacial tension drops from 15.9 mN/m to 13.3 mN/m using the MES surfactant, with increasing solution concentration from 10000 ppm to 25000 ppm. The interfacial tension drops from 15.7 mN/m to 13.1 mN/m using the Castor surfactant, with increasing solution concentration from 10000 ppm to 25000 ppm. It is therefore concluded that the Castor oilbased surfactant performs best in brine at ambient temperature (as it decreases the interfacial tension that exists in the heavy crude oil/brine system of 19.8 mN/m to 13.1 mN/m when Castor oil-based surfactant of 25000 ppm concentration was introduced to the aqueous solution). Rostami et al. <sup>[17]</sup> reported that IFT decreases as the surfactant concentration rises.



Figure 8. IFT of brine/crude oil/surfactant with different concentrations at reservoir temperature

Figure 8 shows the comparison in the performance of the five surfactants (AOS, MES, PKO, Jatropha, and Castor surfactants) at reservoir temperature. The salinity of the brine is 10000 ppm. The IFT drops from 14.2 mN /m to 12.9 mN/m using the AOS surfactant, with increasing solution concentration from 10,000 ppm to 25,000 ppm. The interfacial tension drops to 12.8 mN/m from 13.8 mN/m using the Jatropha surfactant with increasing solution concentration from 10000 ppm to 25000 ppm. The interfacial tension drops to 12.5 mN/m from 13.6 mN/m using the PKO surfactant, with increasing solution

concentration from 10000 ppm to 25000 ppm. The interfacial tension drops to 12.4 mN/m from 13.5 mN/m using the MES surfactant, with increasing solution concentration from 10000 ppm to 25000 ppm. The interfacial tension drops to 12.2 mN/m from 13.4 mN/m using the Castor surfactant, with increasing solution concentration from 10000 ppm to 25000 ppm.

Similarly, the Castor oil-based surfactant performs best in brine at reservoir temperature (as it lowers the interfacial tension that exists in the heavy crude oil/brine of 16.4 mN/m to

12.2 mN/m when Castor based surfactant of 25000 ppm concentration was introduced to the aqueous solution).

#### 4. Conclusion

The synthesis of surfactants from locally available raw materials using the sulphonation process was investigated. Interfacial tension drops as the surfactant concentration and surfactant temperature increase. The formulated and industrial surfactants were able to lower the IFT in brine/heavy crude oil/surfactant systems.

The castor oil-based surfactant with 25000 ppm concentration performs better in brine (10000 ppm) at both ambient and reservoir temperatures as it lowers the IFT from 19.8 mN/m and 16.4 mN/m to 13.1 mN/m and 12.2 mN/m respectively.

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