Journal of Inventive Engineering and Technology (JIET)
ISSN: 2705-3865
Volume-5, Issue-3, pp-31-39
www.jiengtech.com
Research Paper Open Access

Synthesis and performance of surfactant for enhanced oil recovery application

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ABSTRACT : *Enhanced oil recovery is still very relevant in the oil and gas industry today because of the need to maximise the available reserves as much as possible. In this study, an anionic surfactant was synthesised and characterised for the purpose of enhanced oil recovery applications. The Fourier transform infrared spectroscopy (FT-IR) analysis was used to identify the functional groups in the surfactant and the surface tension method was used to determine its critical micelle concentration. Also, interfacial tension and contact angle measurements were used to investigate the interfacial actives of the surfactant. The results of the study showed that the surfactant has a CMC of 0.1 v/v% and it reduced the surface tension of deionised water from 72.48 mN/m to 30.45 mN/m at this concentration. Furthermore, the surfactant demonstrated high interfacial actives even in saline environments and it achieved a 96.96% crude oil-brine IFT reduction. The surfactant also demonstrated surface wettability alteration potential by modifying solid surfaces towards increased water wetness. Finally, the surfactant increased oil recovery by producing an additional 14% OIIP recovery in tertiary application due to its high surface activity. The results of this study show that the synthesised surfactant has an enhanced oil recovery potential that can be explored.*

KEYWORDS: *surfactant; wettability, salinity, enhanced oil recovery and interfacial tension.*

Date of Submission: 27-05-2024 Date of acceptance:04-06-2024

I. INTRODUCTION

The conventional oil recovery processes are generally classified as primary, secondary, and tertiary phases. During the primary and secondary oil recovery phases, oil production is driven by natural energy drives and injections of fluids such as water and gas that are present in the vicinity of the reservoirs. In tertiary phase however, external components such as surfactants, polymer, heat etc. are introduced into the reservoirs to enhanced oil mobility and production. [1, 2]. On completion of primary and secondary recovery processes, high volume of original-oil-in-place (OOIP) is still trapped in the reservoir awaiting appropriate enhanced oil recovery (EOR) process [3]. The EOR involves a variety of operations such as chemical flooding, gas injection, microbial recovery, and thermal recovery [2]. The different EOR operations ultimately aim to improve the overall oil displacement efficiency. Such improvement is achieved by influencing one or more of the following: oil viscosity [4], rock wettability [5], interfacial tension (IFT) [6, 7] and capillary forces in addition to altering the mobility ratio between the displacing and displaced fluids to more favorable values [8].

Generally, high interfacial tension exists between immiscible fluids such as brine and oil in the pores of the reservoirs. This invariable results in high capillary forces that favour entrapment of oil in the pores and reduction in oil production. One of the widely used EOR methods in the petroleum industry is surfactant flooding. This is due to surfactants' ability to modify the water-oil interface and the properties of the rock surface thereby promoting increased oil recovery. The tendency of a fluid to spread or adhere to the rock surfaces in the presence of an immiscible fluid is commonly referred to as rock wettability. Basically, this type of adhesion occurs due to various forces including van der Waals forces, structural forces, and electrostatic forces, which result in stable distribution of fluids in porous media [8]. In the presence of two liquids, the one that has the strongest adhesion to the surface is referred to as the wetting phase. Reservoir rocks exhibit different wettability, but sandstones are majorly water-wet or intermediate-wet in nature.

Surfactants are long-chain molecules that contain both hydrophilic and hydrophobic moieties. This property enables surfactants to adsorb at the interfaces of immiscible phases thereby promoting interfacial interactions. Surfactants are extensively used in many applications because of their abilities to alter the properties of surfaces and interfaces [9]. In chemical enhanced oil recovery, surfactant flooding is a well-established method of EOR because it has proven to be successful in increasing oil recovery through a combination of mechanisms. These include interfacial tension (IFT) reduction, wettability alteration, foam generation and emulsification [2, 7]. According to recent research studies, worldwide energy demand is estimated to increase by 30% in 2040 compared to 2010. It is also estimated that by 2040, oil consumption will reach 111.1 million barrels per day. As oil reserves dwindle and energy needs surge due to increase in population and industrial development, it is therefore imperative to enhance oil recovery from depleting reservoirs [2]. Hence, this work aims to synthesise an anionic enhanced oil recovery surfactant and to investigate its potentials to modify oil-brine IFT, alter rock surfaces wettability and enhanced oil recovery.

II. METHODOLOGY

A. SAMPLES PREPARATION

Saline solutions: The saline solutions used in this work were prepared in similar way to the one used by Udoh and Benson [10] using Kolo oilfield brine formation of 32 g/L salinity as case study. The formation brine has compositions of 98.2% sodium chloride, 0.6% calcium chloride, 0.8% magnesium carbonate and 0.2% sodium sulphate. Three types of salinities (100%, 50% and 10% formation brine) were considered during this experiment. Table 1 shows the breakdown of these compositions.

Table 1: Compositional breakdown of saline solutions.

Salts	100% salinity Conc. (g/L)	50% salinity Conc. (g/L)	10% salinity Conc. (g/l)
Sodium-chloride (NaCl)	31.424	15.712	3.1424
Magnesium carbonate ($MgCO_3$)	0.256	0.128	0.0256
Calcium-chloride ($CaCl_2$)	0.192	0.096	0.0192
Sodium-sulphate anhydrate (Na_2SO_4)	0.064	0.032	0.0064
Potassium chloride (KCl)	0.064	0.032	0.0064

Crude oil: The crude oil used in this work is a dead crude oil from the reservoir that was used as case study. The properties of the crude oil measured at 25 ^oC are presented in Table 2.

Table 2: Properties of the crude oil.

Oil properties	Quantity
Density at 25 ^oC (g/cc)	0.9067
Viscosity at 25 ^oC (cp)	15.2206
API at 25 ^oC (^{o})	24.5673

Surfactant synthesis: The anionic surfactant synthesised in this study is a linear alkyl benzene sulfonate surfactant. For the synthesis, 120 ml of commercial grade dodecyl benzene sulfonic acid was reacted with 200 ml of 98% concentrated sodium hydroxide solution. The dodecyl benzene sulfonic acid was measured into a reactor vessel where the neutralisation reaction took place and sodium hydroxide solution was added to it in dropwise manner under continuous stirring condition. The reaction temperature was measured to be about 54°C. The composition of the synthesised surfactant was analysed with the Fourier transform infrared (FTIR) spectrometer.

B. EXPERIMENTAL METHODS

Series of experimental tests were conducted with the synthesised surfactant to investigate its surface activities, interfacial tension reduction capacity, wettability alteration tendency, solubility, and the enhanced oil recovery potential.

CMC determination: The surface activity of the synthesised surfactant was investigated based on its interfacial adsorption using surface tension method. The Du Nouy ring method with the aid of Sigma 703D tensiometer was used. The surface tension measurements of different surfactant solutions were used to determine its critical micelle concentration (CMC) beyond which surface activities of the surfactant do not change much with increase in concentration. Thirteen different surfactant solutions of varied concentrations (0 - 1 v/v%) were prepared and used for the CMC determination. The surface tension of each surfactant solution was measured at ambient temperature of 25 °C.

Surface tension and interfacial tension measurements: The interfacial activity of the synthesised surfactant was investigated based on its ability to adsorb at the interface of air and solutions as well as the interface of crude oil and solutions. The formal is surface tension while the later is interfacial tension. For the surface tension measurements, solutions of different concentrations of surfactant were used, while interfacial tension (IFT) test was conducted on varied saline solutions. The effect of varied brine salinities on oil-brine IFT was investigated with and without surfactant addition. Three brine salinities used for the test are 100% formation brine, 50% formation brine and 10% formation brine. This test verifies how the salinity level of brine influences the surfactant interfacial activity. A fixed concentration of 0.3 v/v% of surfactant based on the CMC was used for all the tests and the tests were conducted at ambient temperature of 25 °C. The Du Nouy ring method with the aid of Sigma 703D tensiometer as used for the IFT and surface tension tests.

Compatibility test: The fluid-fluid interaction of the surfactant in different saline environments was investigated with the three brine salinities (10%, 50% and 100% formation brine) to determine the presence of any non-homogeneity such as phase separation, cloudiness, and precipitation. A fixed concentration of 0.3 v/v% of the surfactant was mixed with different brines and the solutions were subjected to the same condition for a period 24 hour.

Contact angle: The wettability alteration tendency of the synthesised surfactant was investigated in different salinity conditions based on sessile drop method with the aid of Ossila contact angle goniometer. For each measurement, 5 µl droplet of the respective fluid was used for the test. Prior to the test, the glass slides were cleaned thoroughly with ethanol and deionized water, after which they were dried and then aged in crude oil for a minimum of 6 weeks at 100 °C to ensure the surfaces are oil wet. The experiments were carried out in two phases with salinity effect been investigated in the first phase and surfactant effect in different salinity conditions been investigated in the second phase. The three brine salinities (10%, 50% and 100% formation brine) were used with fixed surfactant concentration of 0.3 v/v% for all the tests, and they were conducted at 25 ^{o}C.

Flooding test: The flooding experiment was conducted to determine the enhanced oil recovery potential of the synthesised surfactant. The flooding test was conducted with fluid displacement set up that consist of a cylindrical sand pack cell (10.2 cm in length and 1.3 cm in diameter), a positive displacement pump and graduated bottles for sample collections. The sand pack cell was loaded with dried 4.5 mm sand grains that were cleaned with methanol and deionised water prior usage. The sand pack was initially saturated with formation brine by continuous injection of the brine through the cell. The absolute porosity and pore volume of the sand pack were then measured and calculated with the saturated sand pack. The setup was coupled together, and five pore volume (PV) of crude oil was injected through the sand pack to irreducible water saturation and the oil initially in place (OIIP) was calculated based on the produced formation brine. Thereafter, four pore volume of formation brine was injected through the cell to displace oil until residual oil saturation was reached and oil production ceased. One pore volume of surfactant solution at a concentration above the CMC (0.3 v/v%) was injection injected through the cell and additional four pore volume of formation brine was then injected for further oil displacement. All the flooding was conducted using 0.5 ml/min flow rate and the displacement test was conducted at ambient temperature of 25 °C.

III. RESULTS AND DISCUSSION

The composition and functional groups of the molecular structure of the synthesised surfactant was identified through the Fourier transform infrared spectroscopy analysis and the result of this analysis is presented in Fig. 1. The -OH stretching vibration at 3365 cm^{-1} constitute the main vibrational peaks and it indicate the presence of hydrophilic group in the synthesised surfactant. The narrow peaks at 2959 and 2926 cm^{-1} show the presence of -CH_2 group while the peak 2855 cm^{-1}shows the presence of -CH_3 group. These indicate of the presence of alkanes in surfactant. Also prominent in the surfactant is the presence of carboxylic group such as fatty acid that is indicated by C=O at 1636 cm^{-1}. This is a major contributor to the hydrophobic component of the surfactant. The presence of a sulfonate group is observed by the small absorption bands at 1177 and 1125 cm^{-1}[11]. The result of this analysis shows that the synthesised surfactant has both hydrophilic and hydrophobic functional groups that are necessary for its interfacial interactions.

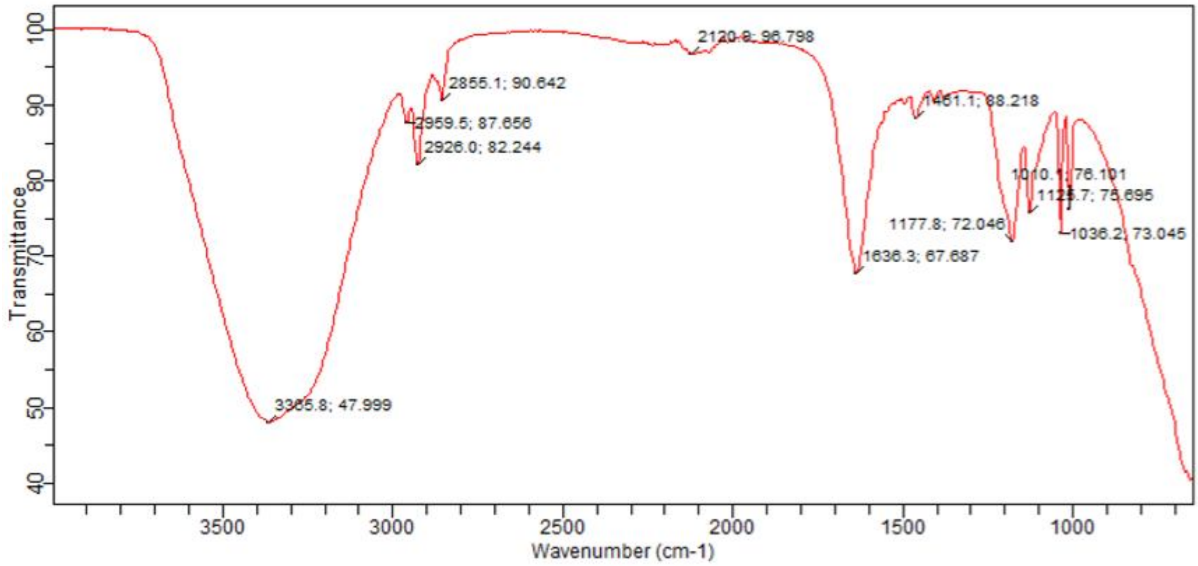

Fig. 1. FT-IR spectra chart of the synthesised dodecyl benzene sulfonate surfactant.

A. SURFACE TENSION TEST

Fig. 2 shows the result of the surface tension measurements of the synthesised surfactant at varied concentrations. An initial rapid decrease in surface tension was observed with increase in concentration of surfactant in the solution, but a steady or no significant decrease was observed at high surfactant concentration. This signifies interfacial saturation of surfactant adsorption and initiation of aggregation of surfactant molecules otherwise known as micelle formation. The concentration at which micelle formation is initiated is commonly referred to as critical micelle concentration (CMC). The CMC of this surfactant was determined by the intersection between the descending slope and the constant horizonal line in the surface tension plot against surfactant concentration. The CMC of surfactant was found to be 0.1 v/v% and the surface tension at this concentration is 31.74 mN/m. This is comparable to commercial anionic surfactant of similar composition that is reported to be 0.6 mM with surface tension of 33.7 mN/m [12].

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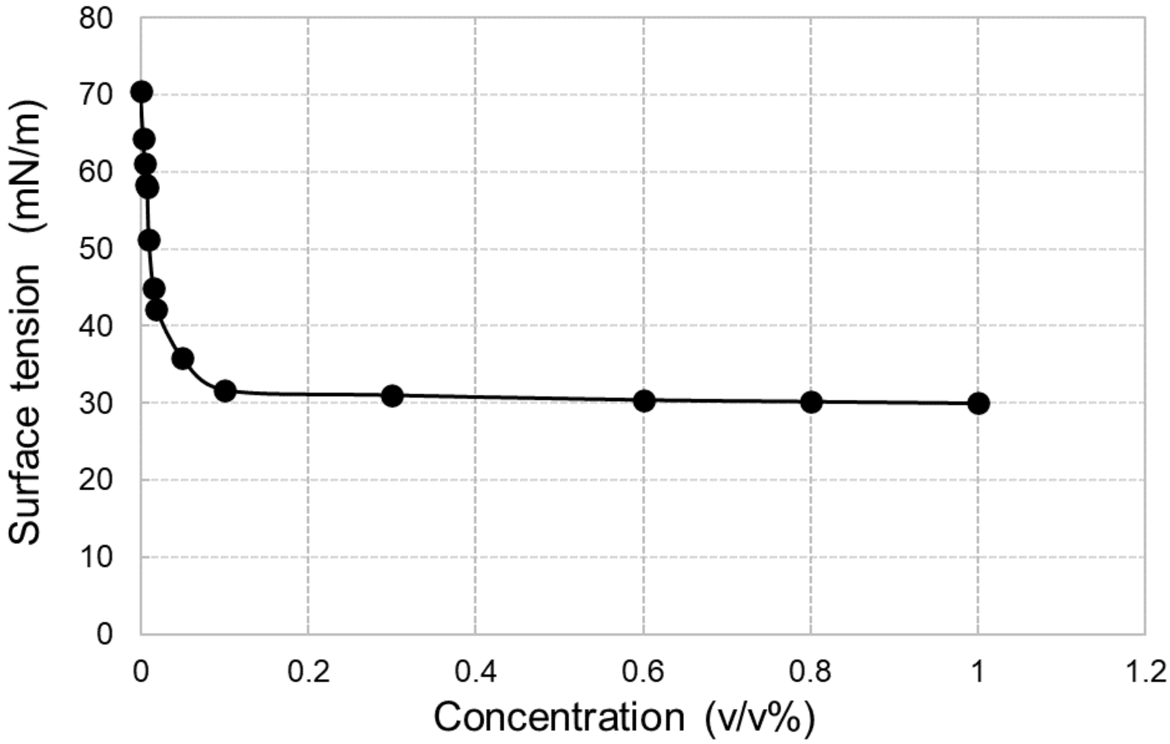

Fig. 2. Surface tension of surfactant aqueous solutions at varied surfactant concentrations.

B. INTERFACIAL TENSION TEST

The interfacial tension test was successfully carried out with fixed concentration of surfactant (0.3 v/v%) in varied saline solutions (0, 10%, 50% and 100% formation brine.). Fig. 3 presents the results of the effect of varied brine salinities on the interfacial activity of the synthesised surfactant. A general decrease in IFT was observed in crude oil and brines system relative to the crude oil and water (zero salinity) system. The observed IFT at 0%, 10%, 50%, and 100% salinity were found to be 20.73 mN/m, 0.63 mN/m, 0.33 mN/m and 0.27 mN/m respectively. This shows that the IFT decreases with increase in brine salinity. This is attributable to interfacial facial activities of the salt ions in the solution. This is consistent with the previous study that shows that brines with very high concentration of sodium chloride (NaCl) demonstrate high surface activities [13]. The brine used in this study has 98% of its compositions made of NaCl. It was seen that the surfactant was able to reduce the interfacial tension of crude oil and brine at an efficiency of 98%, from 20.73 mN/m to 0.33 mN/m after which there was very little or insignificant change observed. This shows that this surfactant can reduce oil-brine IFT irrespective of the salinity level of the injection brine. To better establish a relationship between the oil-brine interfacial tension and brine salinity, the plot in Fig. 4 was generated. With a polynomial regression, an equation that establishes a relationship between them was generated and is presented as Equation 1. Where σ is oil-brine interfacial tension and s is brine salinity.

$$\sigma = 7e^{-5}s^2 - 0.0117s + 0.74 \qquad (1)$$

C. COMPATIBILITY TEST

The characteristic compatibility as evident by solubility of the surfactant was also experimentally investigated. It was observed that the higher the salinity concentration the less soluble the surfactant was found to be in the solution. When the surfactant was first added the 10% brine salinity, it was observed that the resultant solution was transparently clear as the surfactant was completely dissolved in the solution. This was not the case for the remaining 50% and 100% brine salinities as an opaque, chalky, and unclear resultant solutions were formed after the surfactant was added. In other words, the surfactants precipitated in these saline environments.

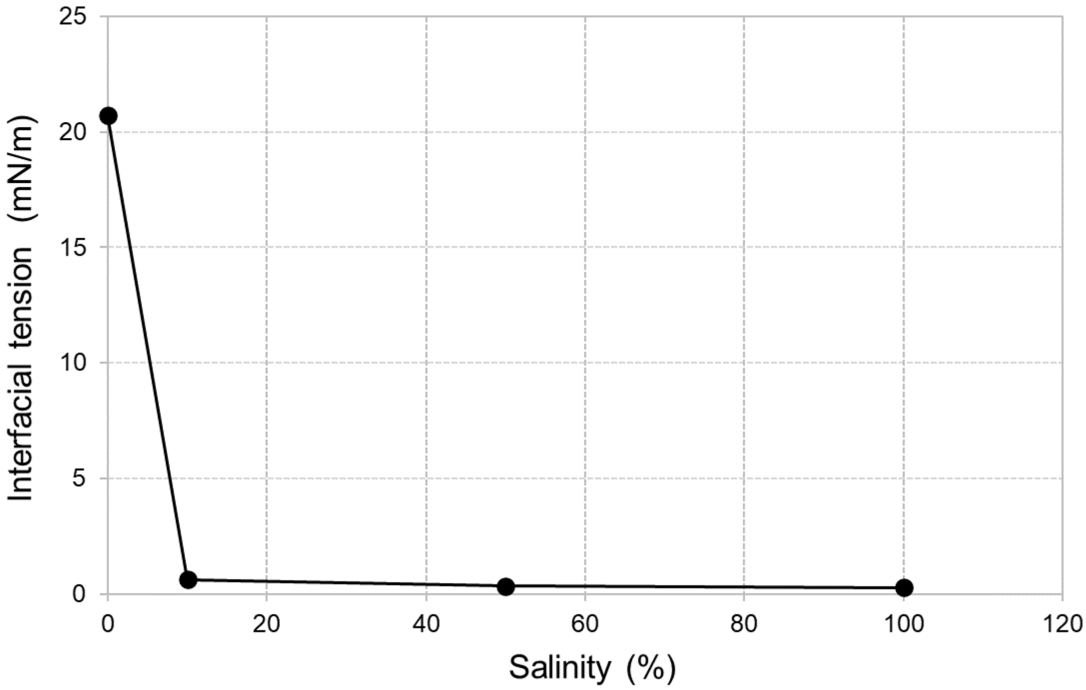

Fig. 3. Interfacial tension of surfactant at different salinity.

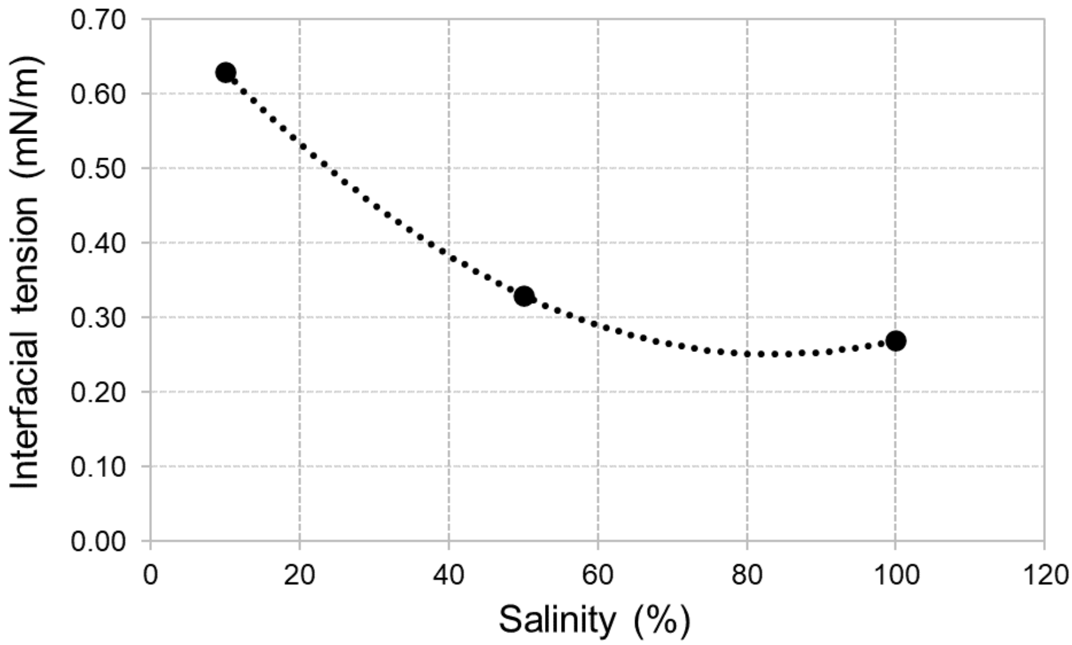

Fig. 4. Relation between oil-brine interfacial tension and brine salinity.

D. CONTACT ANGLETEST

The results of contact angle measurements conducted using varied brine salinities in the absence and presence of surfactant are presented in Fig. 5. There seems to be no significant effect of brine salinity variations on the wettability of the surfaces when the brines alone were used. The contact angles ranged between 54^o and 57^o which is water wetness according to the wettability classification by Treiber and Owens, 1972 [14]. Addition of surfactant to each of the solution modified the wettability of the surfaces towards increased water wetness with more significant effect been seen in lower salinity brines. This shows that the synthesised surfactant has the wettability potential of the rock surfaces toward increased water-wetness which invariably favors increased oil recovery. The observed surface wettability alteration potential of the surfactant is attributable to its adsorption on the solid surfaces with the polar components oriented away from the surface.

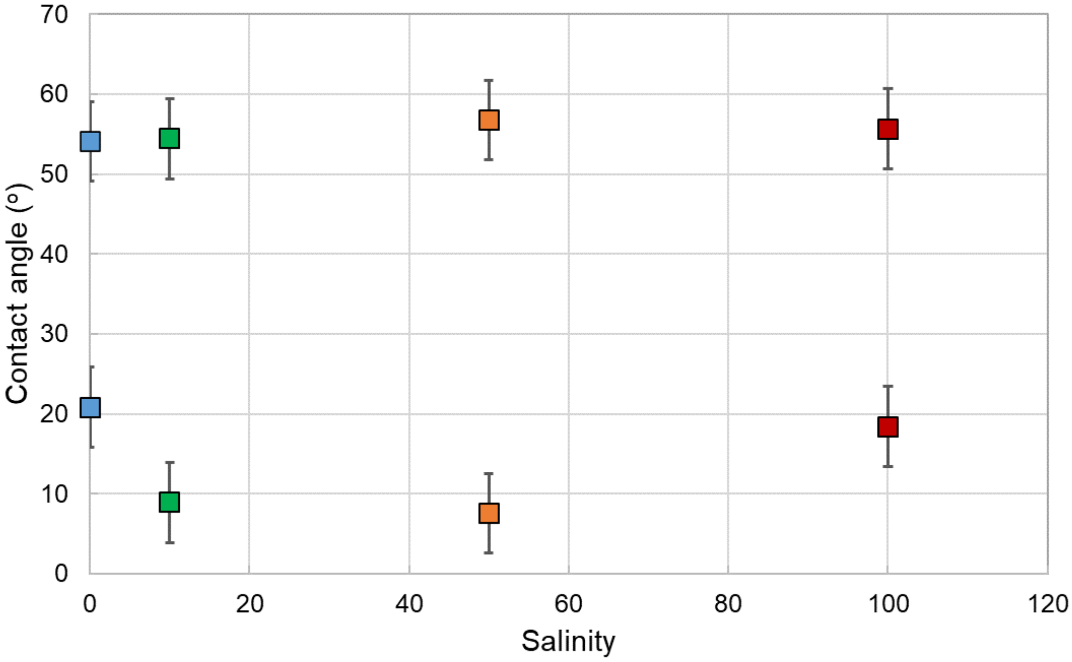

Fig. 5. Relation between contact angle and varied brine salinities in absence and presence of surfactant.

E. DISPLACEMENT EXPERIMENT

Having assessed and confirmed the effectiveness of the synthesised surfactant to reduce the oil-brine interfacial tension and modify the solid surface wettability toward increased water wetness, the enhanced oil recovery potential of surfactant was investigated through displacement test. The result of the test is presented in Fig. 6. The oil production was initiated by injection of four pore volume of 100% formation brine. During this process, progressive continuous oil production of oil was observed until a point was reached when oil production ceased and a total 76% OIIP was made. Subsequently, one pore volume of surfactant solution was injection, and no oil production was initially observed, but toward the end of this injection process a batch of oil was produced. The oil production then continued with the injection of additional four pore volume of 100% formation brine until oil production ceased and 100% water cut was attained. At the end of the injection process, a total of 14.89% OIIP additional oil recovery was made. This shows the enhanced oil recovery potential of the synthesised surfactant. The observed increased oil recovery can be attributed to high interfacial activity of the surfactant as demonstrated by its adsorption on fluid-fluid and fluid-rock interfaces. This interfacial adsorption resulted in reduction of interfacial tension between the oil and brine and wettability alteration of the surfaces of the sand grains. These two processes result in oil desorption from sand grains and oil-brine mixture or emulsification that favors residual oil displacement [2].

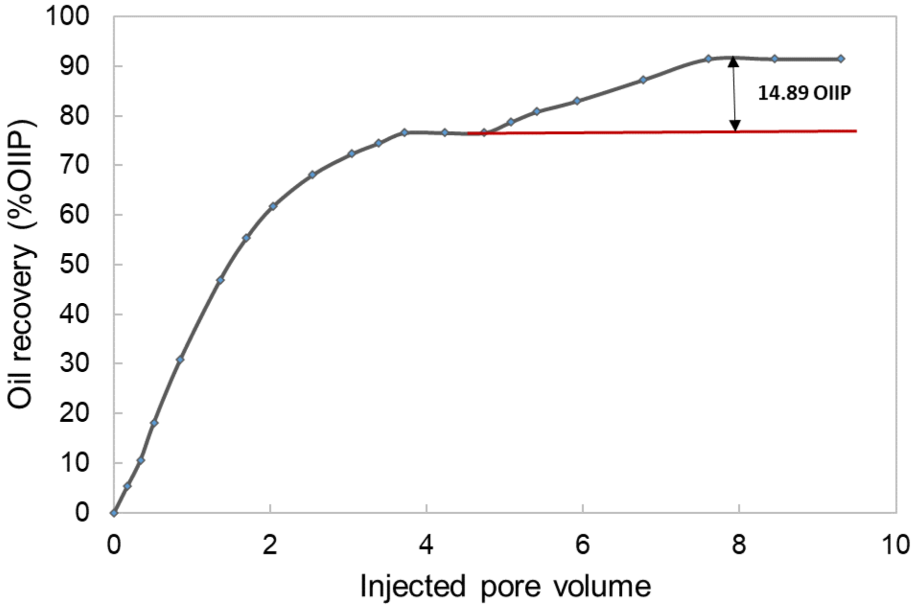

Fig. 6. The enhanced oil recovery application of the surfactant in tertiary phase.

IV. CONCLUSION

In this study, an anionic surfactant was synthesised and characterised for the purpose of enhanced oil recovery application. The critical micelle concentration of the surfactant was determined, and the interfacial activity of the surfactant was investigated in interfacial tension and contact angle tests. The results of the tests showed the synthesis surfactant has high surface activity that makes it a candidate for enhanced oil recovery applications. The potential of the surfactant to improve oil production was then investigated and the result showed that the surface activity of the surfactant can be related to its enhanced oil recovery potential as evidenced by 14.89% OIIP additional oil recovery made over water flooding.

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