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Laboratory evaluation of red onion skin extract and its derivative as biomass-based enhanced oil recovery agents

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ABSTRACT

The use of natural alternatives as oilfield chemicals is gradually gaining attention among researchers due to their eco-friendly nature. The aim of this study was to determine the efficiency of red onion skin extract (ROSE) at recovering residual oil using the mechanism of surfactant flooding in sandstone reservoirs at reservoir conditions and compare its effectiveness in its pristine and modified state. ROSE was obtained by solvent extraction of the waste biomass (red onion skin) using acetone. The extract was chemically modified using glutaraldehyde. Phase behavior analysis in the presence of divalent ions at high temperatures (80 °C) and sandstone core flooding were performed to determine the fluid compatibility and displacement efficiency. Results show high compatibility and solubility of pristine (unmodified) and modified ROSE in soft and hard brine. Core flooding analysis showed a higher recovery of 32.1% and 36.5% original oil in place (OOIP) for 0.3 wt.% modified ROSE as compared to a recovery factor of 31.8% and 35.0 % OOIP for 0.5% unmodified ROSE in soft and hard brine respectively. It further reveals an increase in additional recovery at surfactant concentration in hard brine above critical micelle concentration (CMC). Results of statistical significance test showed that modified ROSE exhibited superior performance and a higher recovery relative to unmodified ROSE especially in hard brine. This is a novel work as red onion skin extract was derivatized with glutaraldehyde and successfully recovered additional residual oil under hard brine and reservoir temperature making them potential surface-active agents for chemical enhanced oil recovery.

Introduction

Surfactants also referred to as surface-active agents, are substances that adsorb onto the surfaces or interfaces of the system, altering the degree of surface or interfacial free energies. Interfacial free energy is the minimum amount of work required to create or expand a unit area of the interface [1]. These wetting agents are amphiphilic in nature consisting of a hydrophilic (head) group and a lipophilic (tail) group in a single molecule. This dual character allows surfactant concentrate at a surface or interfaces and can alter surface properties and lowers interfacial tensions resulting in solubilisation of immiscible components.

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Based on the ionic charge of the hydrophilic group, surfactants are classified into four main groups namely: anionic, cationic, non-ionic, and zwitterion or amphoteric surfactants. Anionic surfactants, which include petroleum soap, are the most common type of surfactants. They are widely used in chemical flooding due to their high clay stability, low cost and low adsorption rate on sandstones as opposed to carbonates. The surfactant molecule ionizes in aqueous solution and the head group carries a negatively charge [2]. The phase behavior of anionic surfactant is sensitive to high salinity and to divalent ions concentration. Examples include alkyl benzene sulfonates, alkoxylate alkyl-phenol sulfonates, sulfates and phosphates. Cationic surfactants have a positively charged polar group and are highly adsorbed on the negative charged surfaces of sandstone rocks making it unsuitable for chemical flooding in sandstones. Cationic surfactants such as Dodecyl trimethyl ammonium bromide are more likely to be used in carbonate rocks and have the tendency to alter wettability from oil to water wet. They are excellent emulsifiers but are highly sensitive to high salinity. Zwitterion or amphoteric surfactants such as amino carboxylic acids have pH dependent polar groups. They are positively charged at a low pH and negatively charged at a high pH thus containing both charges. They are salinity and temperature tolerant but are seldom used in Enhanced Oil Recovery (EOR) process probably due to their extremely high cost. Non-ionic surfactants are devoid of ionic charge yet display hydrophilic tendencies due to the presence of polymerized glycol ether or glucose units in their structure [3]. The absence of ionic charge implies that their polarized head group is not electrically charged as such they do not ionize in water. Their polarity is gotten from the oxygenated portion at one end of the molecule. The oxygen generates a dense electron cloud that creates a negative environment; this allows the polar group to form hydrogen bonds with water, thus exhibiting surfactant properties. They serve as co surfactants to improve system phase behavior, as they are used in enhancing the behavior of the anionic surfactants. They are more tolerant of high salinity than anionic or cationic surfactants [4]. These group of surfactants have been used in various applications ranging from food industry, healthcare, as laundry detergents [5–7] and most recently as EOR agents [8]. Examples of non-ionic surfactants include alkoxylated fatty acids and alkylphenols, fatty alcohol polyglycol ether etc.

Surfactant flooding is a type of chemical EOR that is effective in recovering trapped residual oil via the introduction of synthetic surfactant. The surfactant is placed at the displacement interface near optimum conditions where it washes out the trapped oil and recovers residual oil by reducing the capillary forces thereby attaining an ultra-low interfacial tension (10^{-3} dynes/cm) between oil and aqueous phase. The lower the ultra-low interfacial tension, the higher the capillary number, [$N_c = \frac{\mu v}{\sigma \cos\theta}$] . An ultra-low interfacial tension can only be achieved through the synergistic effect of the insitu surfactant and the synthetic surfactant. An ultra-low interfacial tension releases the trapped oil droplets and allows it flow easily through the pore throat to form a continuous oil bank [9]. In order to be a good candidate for chemical EOR, a surfactant should exhibit the following properties: tolerance to high salinity/divalent ions; thermal stability at reservoir temperatures; ability to attain an ultra-low interfacial tension of about ∼0.01–0.001 dynes/cm under reservoir conditions; effectiveness at low surfactant concentrations (0.1–0.3%); low adsorption on reservoir rock ($<$ 1 mg/g rock); high compatibility and solubility with other chemicals used during EOR (alkalis, polymers, nanoparticles etc.); available in commercial quantities at reasonable cost and lastly environmentally friendly, non-toxic substitute. The high cost and their environmental threat owing to the toxic and non-biodegradable nature of these synthetic surfactants has greatly affected the success rate of surfactant flooding process. With the increasing cost of surfactants, particularly anionic surfactants which are commonly used during chemical EOR, recent studies on the application of non-ionic surfactants and natural materials during chemical flooding has gradually gained researchers attention and is fast becoming acceptable [10]. They are surfactant gotten from plants and materials such as fatty alcohols and esters. According to Chiabuotu et al. [11], alcohol also has high tolerance for divalent ions. These fatty alcohols which acts as co-solvents during surfactant flooding, enhances the performance of surfactants, impedes the formation of emulsions, helps in attaining optimum salinity, eliminates polymer-surfactant incompatibility, reduces emulsion coalesce time and help in achieving an ultra-low IFT. In their study [12,33] confirmed the ability of natural surfactants obtained from plants in reducing interfacial tension and improving oil recovery in sandstone reservoirs. Asides their efficiency in improving oil recovery, their biodegradable and environmentally friendly nature will avert negative ecological impacts to life on land and under water in line with sustainable development goals (SDG) 14 and 15. The commercial use of these plant-derived surfactants will promote economic growth by turning waste to wealth, create more jobs, reduce poverty and encourage responsible production of a low-cost green alternative in a bid to achieve sustainable development goals 1, 8, 9 and 12. The efficiency of these natural surfactants derived from plants in reducing IFT and recovering additional oil in carbonate reservoirs was also reported by [34,35]. Ogolo et al. [26] in comparing the efficiency of foreign and local (natural) recovery agents, recommended the modification of the natural agents for an improved displacement efficiency to enable them serve as a substitute to conventional (synthetic) surfactants. However, the effect of certain challenging conditions such as formation brine, reservoir temperature on oil recoverability using these natural surfactants is yet to be ascertained.

In this study, Red Onion Skin (ROS) which is an agro-waste biomass was selected to serve as a natural recovery agent. This agricultural waste is a rich source of polyphenolics [13,14] and has a high content of anthocyanins and flavanols, notably quercetin, which has been extensively exploited (either as pure compounds or crude extract) as an antioxidant in biological systems, and to a lower extent in industrial processes [14–18]. The effectiveness of the phenolic-rich ROSE as a surface-active agent for recovering additional oil under challenging conditions was investigated and the results obtained at laboratory scale were upscaled to field scale. ROSE was modified with glutaraldehyde in aqueous sodium hydroxide. The performance of the pristine (unmodified) and modified ROSE was evaluated in brine-saturated sandstone core and their recoverability was compared to ascertain the possibility of replacing foreign (synthetic) surfactants.

Table 1
Composition of formulated brine.

Brine component	Concentration (ppm)
NaCl	20,000
KCl	4,000
$MgCl_2$	3,000
$CaCl_2$	3,000
TDS	30,000

Materials and methods

Materials

Red onion skin was sourced locally from Mile one market (4.7918°N, 6.9986°E) in Port Harcourt LGA, Rivers State. Acetone, distilled water, sodium chloride, calcium chloride and magnesium chloride were purchased from local suppliers. The reagents used were analytical grade. The crude oil used was obtained from an oil field in the Niger Delta. The methods used during this experimental study include: preparation of agro waste sample, preparation of brine sample, extraction of the samples, modification of the extract, crude oil characterization, preparation of the porous medium, phase behaviour analysis and coreflooding analysis.

Extraction of ROS

The outer inedible scales of red onions (red onion skin) were properly selected, sun-dried at an average temperature of 29 °C for 5 hours. The dried red onion skin extract (ROSE) was extracted from a pre-weighed amount of pulverished red onion skin (ROS) as described by [29,30] with slight modification by maceration in acetone for 24 hours. The extract was filtered off and transferred to the rotary evaporator. The extract was concentrated and the solvent recovered for reuse in vacuo. The extract was dried in an oven at 55 °C to obtain ROSE powder. The product was stored in airtight bag labelled ROSE for later use.

Preparation of brine sample

Synthetic brine was prepared to replicate the formation brine using distilled water. Two different types of brines was formulated, the first brine contained varying concentrations of sodium chloride, potassium chloride, calcium and magnesium chloride having a total dissolved solids (TDS) of 30,000 ppm with 6,000 mg/l being total concentrations of calcium and magnesium chloride, as outlined in Table 1 and reported by [27] where it was noted that the TDS of most formation water in Niger Delta reservoirs vary between 14,537 and 31,761ppm with its composition in the order of Na > Ca > Mg > K. The brine solution containing distilled water and varying salts was measured in a 1 litre beaker and stirred continuously using a magnetic stirrer at 20°C temperature until the solution was completely dissolved. The brine solution was filtered using a filter paper, stored into an airtight vacuum flask and labelled 'hard brine'. The same procedure was performed on the second type of brine composed of sodium and potassium chloride with total dissolved solids of 30,000 ppm and labelled 'soft brine'.

Modification of ROSE

The modification of ROSE was carried out via a polycondensation reaction with glutaraldehyde under similar conditions as described by [31]. A solution containing ROSE extract (5 g, 2 mol) and Glutaraldehyde (0.83 g, 1 mol) was charged into a pre-weighed 250 ml round bottom flask (the reactor vessel) and connected to a Dean-Stark trap fitted to a condenser on a retort stand and placed on a hotplate equipped with a mechanical stirrer. The mixture was heated to a temperature of 120 °C and the catalyst (2 ml of 1% w/v NaOH) was added followed by refluxing for 1 h under magnetic stirring. At the end of the reaction (when the volume of water condensed in the dean and stark trap is constant), the flask was allowed to cool, the product weighed using an analytical weighing balance, placed in a desiccator to dry, and stored in an airtight container and labelled as ROSE-GLUT.

Crude oil characterization

Kinetic viscosity of the crude oil at 30.5 °C was determined using a rheometer. Relative density and specific gravity of the crude was also determined using a hydrometer according to ASTM D1298 -12b. The measure of the amount of carboxylic acid, total acid number (TAN) present in the crude oil was measured using the non-aqueous titration method and then calculated using Eqs. 1 and 2 respectively.

$$KOH\ vol\left(\frac{mol}{l}\right) = \frac{(KHP\ solution.grams) * (KHP\ concentration)}{KOH\ concentration} \quad (1)$$

$$Acid\ number = (A - B) * M * \frac{56.1}{W} \tag{2}$$

Where:
A = volume of KOH solution used in the titration to the last inflection endpoint, ml
B = Volume corresponding to A for blank titration, ml
M = KOH Concentration, mole/L
W = Mass of oil Sample, grams.

Preparation of core sample

Cylindrical core plugs which served as a porous media were obtained from a clastic (sandstone) reservoir at a depth of 2136-2539 m with lithological properties ranging from very fine, well-sorted, moderately cemented grains. They were used in determining the residual oil recovery factor of ROSE and ROSE-GLUT with respect to displacement efficiency and incremental oil recovery. In the Petroleum Engineering laboratory of the University of Port Harcourt where the core flooding experiments were conducted, the core sample was cleaned using a Soxhlet extractor and toluene as solvent. The core was then dried, weighed and then fully saturated in brine for 24 hours and re-weighed afterwards. The length and diameter of the core was measured using a caliper and micrometer screw gauge. The pore volume was estimated as the ratio of weight difference between the saturated and the dry core to the density of the brine (liquid saturation method).

The bulk volume was determined using the formula of the volume of a cylinder due to the shape of the core

$$V_b = \pi r^2 h. \tag{3}$$

Where,
V_b = Bulk volume
r^2 = Radius of the core h = Length of the core
Porosity was calculated using the saturation method as the ratio of pore volume to bulk volume, expressed in percentage.

Aqueous stability test

To determine the compatibility of the fluids at different concentrations, a compatibility test was performed on ROSE and ROSE-GLUT using both formulated brine solutions at varying concentrations ranging from 0.1 to 1.0%. The brine-surfactant solution was mixed into a glass beaker and stirred vigorously with the aid of a magnetic stirrer. This was carried out at ambient temperatures and at an elevated temperature of 80°C with the aid of a water bath.

Critical micelle concentration (CMC)

The value of CMC was determined to ascertain the optimum concentration of the surfactants. Electrical conductivity (as a physical property) of both surfactants in deionized water was measured using a conductivity meter and plotted against varying surfactant concentration. The point of inflection on the plot was the CMC.

Phase behavior test

Phase behavior test was performed to ascertain the compatibility of the aqueous and oleic phase. First, a scan of salinity ranges of ROSE and ROSE-GLUT was conducted using different concentration of brine to ascertain their salinity tolerance. This was performed by measuring a constant volume of the surfactant at its CMC into various glass tubes while varying the brine concentration. The pH was measured using a pH meter. Afterwards, equal volumes of aqueous solution (at different concentrations) and crude oil was measured in a glass pipette, the enclosed pipettes were carefully inverted to ensure a proper mix of the two phases and left for observation at laboratory and reservoir temperature of 80 °C for an equilibration period of 10 days. Only solutions containing Type III microemulsion which is indicative of an ultra-low interfacial tension was selected. Finally, level readings obtained for the aqueous, oleic and microemulsion were recorded and solubilization ratio was calculated and plotted against salinity values to obtain an optimum salinity.

Oil displacement test

Physical properties of the sandstone cylindrical core were calculated, and the oil displacement analysis was conducted using the core sample as the porous medium while ROSE and ROSE-GLUT respectively served as the chemical recovery agents. A CFS-700 core flooding apparatus was used to carry out the oil displacement experiment at reservoir conditions of 80 °C and 7000 psi. Fig. 1 shows a schematic diagram of the core flooding process. The displacement efficiency and recovery factor of the modified and unmodified natural surfactant in both brines was calculated. The oil displacement test followed a sequence from drainage, imbibition and chemical flooding.

Drainage

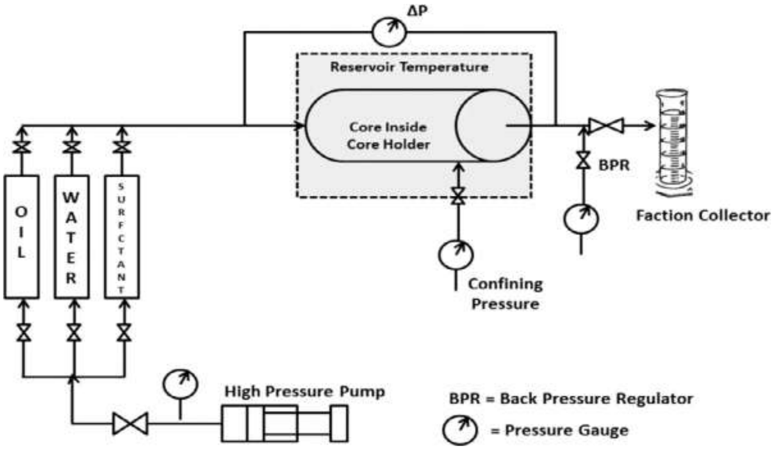

Fig. 1. Schematic diagram of the core flooding process [25].

The saturated sandstone core sample was placed into core holder and pressurized. Using crude oil as the displacing fluid at 1.4PV, brine was completely displaced till an initial drop of oil was observed. The volume of the displaced brine was measured and recorded as the OOIP. The initial oil saturation and irreducible water saturation was determined.

Imbibition (Secondary Flooding)

Formulated brine at 10 pore volume (PV) was deployed to completely displace oil until oil was no longer produced. The collected volume of displaced oil was measured, and the residual oil saturation was calculated.

Surfactant Flooding

A solution of ROSE-GLUT in hard brine at 2PV was injected into the core to enhance recovery of the residual oil at reservoir temperature. Similar test was performed in soft brine. Surfactant flooding continued until an oil cut of less than 1% was recorded. The recovery factor and oil displacement efficiency were calculated. A repeat experiment was performed using ROSE in both hard and soft brine. Results obtained from the laboratory experiment were up scaled to field scale.

Statistical significance test

A two-tailed paired t-test (statistical test) was conducted on the experimental data obtained from the displacement efficiency and recovery factor analysis of pristine (unmodified) ROSE and ROSE-GLUT (modified ROSE) respectively using Microsoft Excel. The probability value (p-value) was computed for each group of data to determine the statistical significance of the measured improvement in the performance of the ROSE derivative (ROSE-GLUT) relative to ROSE, with the null hypothesis that there was no significant difference in the displacement efficiency and recovery factor of ROSE-GLUT and ROSE in soft and hard brine respectively. A p-value less than 0.05 was considered statistically significant and implied that the null hypothesis be rejected and the alternative hypothesis which is that the derivative exhibited improved performance as an EOR agent be accepted.

Results and discussion

Characterization of ROSE and ROSE-GLUT

The extracts were characterized by Fourier transform infrared spectrophotometry (FTIR) scanning in the range 4000 cm^{-1} to 650 cm^{-1}. The FTIR spectra of the ROSE and ROSE-GLUT are shown in Figs. 2&3 respectively. The broad absorption peak observed at 3272 cm^{-1} in the spectrum of the derivative as seen in Fig. 3 is due to the phenolic O–H stretching vibrations. Strong peaks observed at 2851 cm^{-1} and 2918 cm^{-1} which occurred as a doublet corresponds to a combination of aromatic C–H and C=O stretching vibrations, while that at 1562 cm^{-1} is a combination of C=C and C=O stretching vibrations. Aromatic C=C and =C–H stretching vibrations were observed at 1462 cm^{-1} and 1443 cm^{-1}, while those observed at 1380 cm^{-1} and 1335 cm^{-1} correspond to aryl O–H deformation and C–O stretching vibration interactions. Medium to weak bands observed at 1264 cm^{-1} and 1205 cm^{-1} correspond to C–O stretching vibrations for cyclic ethers, those observed at 1171 cm^{-1}, 1115 cm^{-1} and 1048 cm^{-1} correspond to out-of-plane and in-plane C–H deformation vibrations respectively, while that at 784 cm^{-1} is due to aromatic out-of-plane O–H bending vibrations.

Properties of core sample

The initial reservoir pressure at the depth where the core sample was obtained was 6500 psi with a horizontal air permeability (k_{air}) of 417mD and the reservoir temperature is about 90 °C. Table 2 shows the calculated properties of the

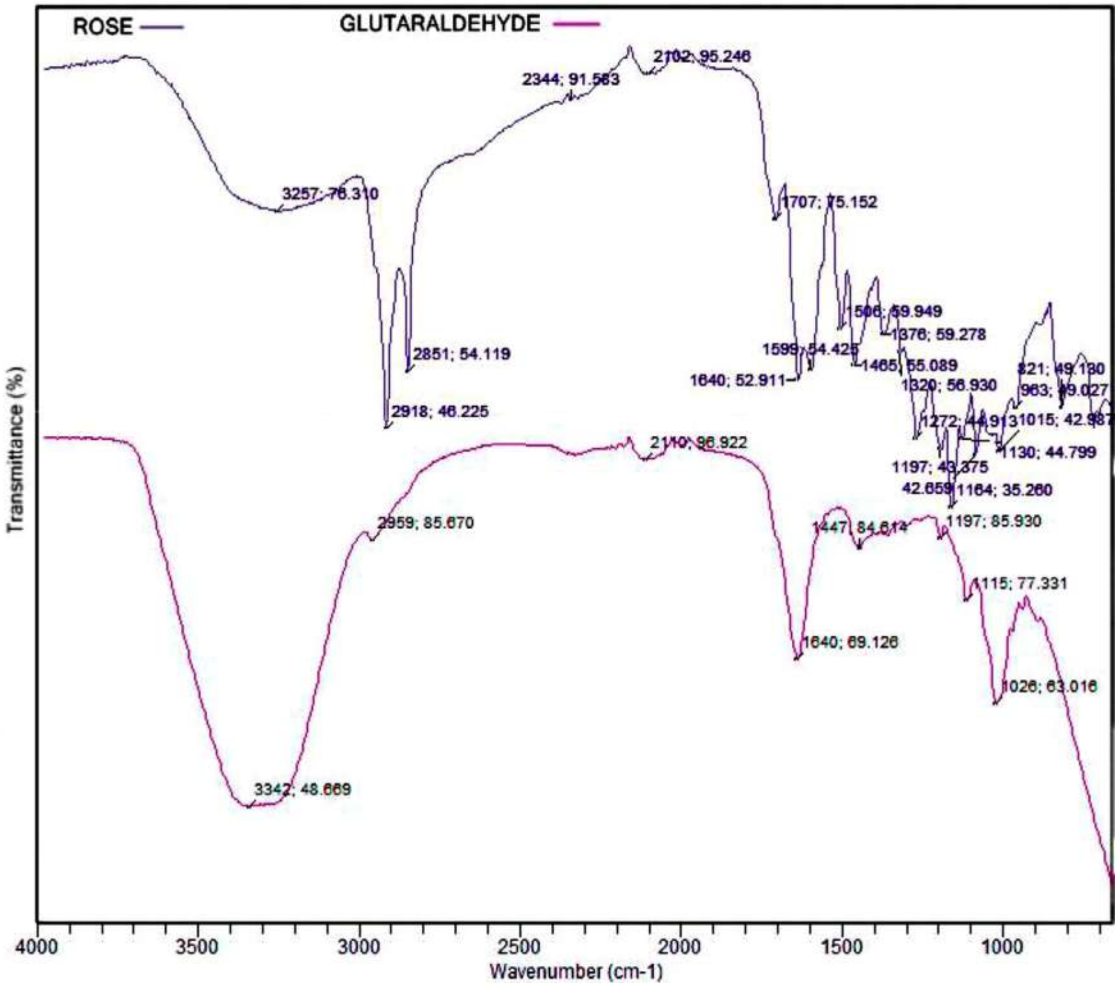

Fig. 2. FTIR spectrum of unmodified ROSE and ROSE-glutaraldehyde.

Table 2
Properties of Core Sample.

Core Length (cm)	Core Plug Diameter (cm)	Bulk Volume (cm^3)	Dry Sample mass (g)	Saturated Sample mass (g)	Mass of Brine (g)	Brine density (g/cm^3)	Pore Volume Vp (cm^3)	Porosity (%)
5.8	3.4	52.66	128.54	143.159	14.62	1.02	14.32	27.31

sandstone core sample with a pore volume and absolute porosity of 14.32 cm^3 and 27.3% respectively, this is in line with the findings of [28] for the range of porosity values of Niger Delta reservoirs.

Crude oil properties

The medium crude oil used in this study was obtained from a Niger Delta oilfield. It was characterized and its properties are summarized in Table 3. The dynamic viscosity of the crude (≈50 cP) is less than 100 cP, this implies that it is suitable for surfactant flooding as reported by Sheng, 2011 [4]. The total acid number of the crude oil is 0.6 mg KOH per gram, this is not high and does not pose a corrosion risk, as TAN greater than 1.0 are considered high [32]. Furthermore, via the process of saponification, the presence of sodium hydroxide as a catalyst (during the modification process) and the acid content in the oil, an insitu surfactant can be formed.

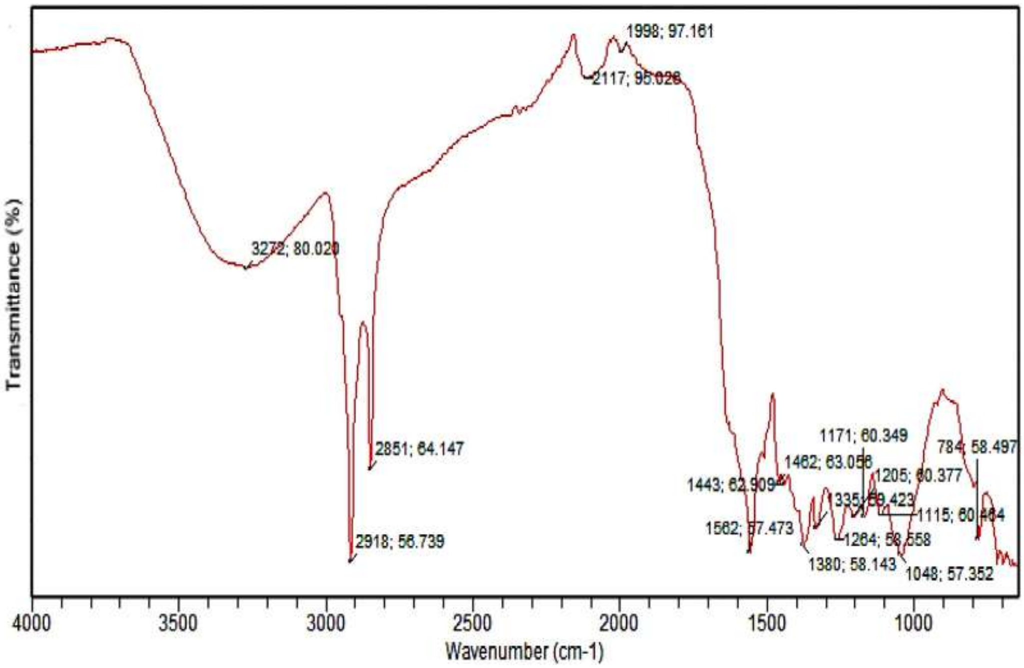

Fig. 3. FTIR spectrum of ROSE-glutaraldehyde derivative.

Table 3
Physical Properties of Crude Oil.

Physical Properties	Values
Density @ 27°C	0.92 g/cm^3
API Gravity	22.7°
Viscosity	49.64 cP @ 30.5 °C
Colour	Brownish Black
pH	6.2
Total Acid Number	0.6 mg KOH/g

Aqueous stability test

Results from compatibility study of ROSE in soft brine and hard brine resulted in clear, compatible aqueous solution at laboratory and reservoir temperatures. With pH values ranging from 6.3 to 7.6, a decrease in the pH value of surfactant-brine solution was observed as the concentration of the solution increased from 0.5 wt.% to 2.0 wt.%. It was also noted that ROSE solution in hard brine had higher pH values than the soft brine solution, thus the presence of divalent ions, increases alkalinity of the solution. Likewise, ROSE-GLUT in soft and hard brine also produced clear, compatible fluid at varying temperatures with pH values ranging from 4.6 to 5.4 as shown in Fig. 4. The modification of ROSE reduced the pH value of the solution in comparison with the unmodified ROSE. For both brines with ROSE-GLUT, a direct relationship was observed between the pH value and the concentration of the solution with the pH value increasing as the surfactant concentration increased.

Critical micelle concentration (CMC)

The critical micelle concentration (CMC) of the ROSE in each brine was determined by measuring the electrical conductivity of the natural surfactant-brine solution at varying concentrations. The CMC of ROSE was 0.5% in soft brine and hard brine respectively (Fig. 5). Similar test carried out on ROSE-GLUT in soft and hard brine gave a CMC of 0.5% and 0.3% respectively. Figure 6 shows CMC results of ROSE-GLUT in hard brine. A surfactant with the lowest critical micelle concentration enough to reduce the surface tension at the interfaces is always recommended [9,19] as this indicates that it is more effective and cost effective due to the lower concentration (quantity). Based on the CMC results, ROSE-GLUT in hard brine with the lowest CMC (0.3%) is a better candidate than unmodified ROSE.

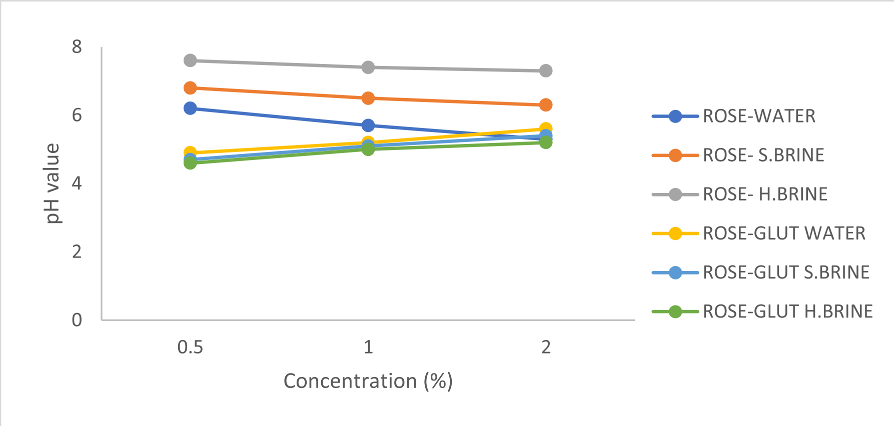

Fig. 4. Plot of pH values against surfactant concentration.

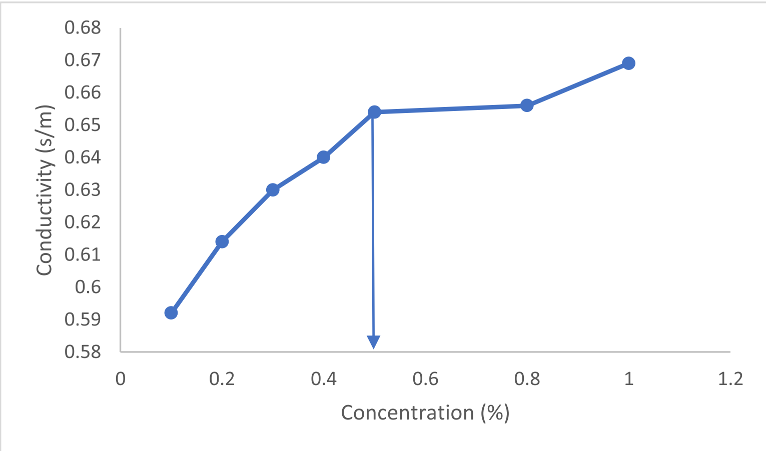

Fig. 5. Critical micelle concentration of ROSE in hard brine.

Results of phase separation test

Phase separation test was performed on the two natural surfactants in both brines and crude oil. Firstly, equal volumes of clear aqueous solution (containing 0.5% ROSE in soft brine at varying salinities) and crude oil in pipettes produced a Type I or Lower phase microemulsion across varying salinity range under laboratory and reservoir temperatures of 80 °C. Similar test was performed in hard brine and oil which also resulted in Type I microemulsion.

Phase separation test was then conducted on aqueous solution containing 0.3% ROSE- GLUT in hard brine and oil and afterwards same test was carried out on the crude oil with solutions containing 0.5% ROSE - GLUT in soft brine. All the results produced Type I micro emulsions at laboratory and increased temperature of 80 °C. This indicates that an optimum salinity was not achieved as such an ultra-low interfacial tension (IFT) was not obtained due to the absence of a Type III microemulsion. An ultra-low IFT is achieved via the interaction between a surfactant and alkaline [4].

Results of oil displacement test

Oil displacement test was conducted on the two surfactant agents at reservoir temperature and pressure of 7000 psi and 80 °C with a sandstone core sample acting as the porous medium. The two formulated brines (soft and hard brine) were used at separate times with each natural surfactant agent during secondary recovery. The surface-active agents were used to flood individually, and their displacement efficiency and recovery factors were determined. The core flooding analysis was performed first on the unmodified ROSE in soft and hard brine, followed by the ROSE-GLUT also in both brines. The experiment commenced with the drainage process where medium crude was used as the displacing fluid to displace brine from the core sample fully saturated with soft brine. Afterwards, 10PV soft brine was injected into the reservoir to displace oil at an injection rate of 0.107 ml/sec for 2 hours and 25mins. Tertiary flooding or enhanced oil recovery using the natural surfactant was carried out. 2PV of unmodified ROSE at critical micelle concentration of 0.5 wt.% was injected at the same

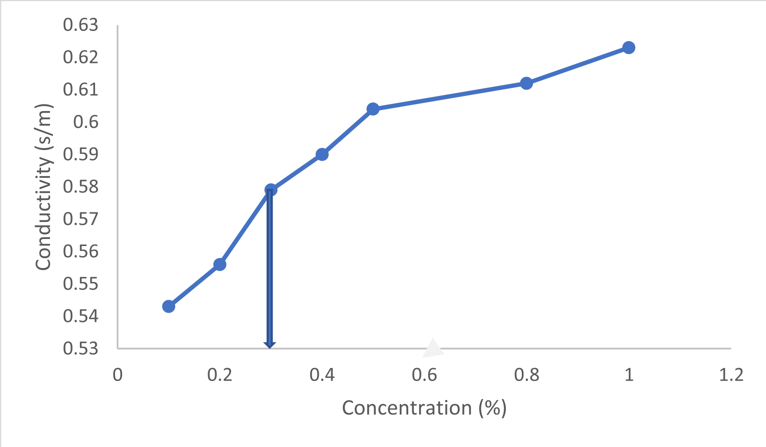

Fig. 6. Critical micelle concentration of ROSE-GLUT in hard brine.

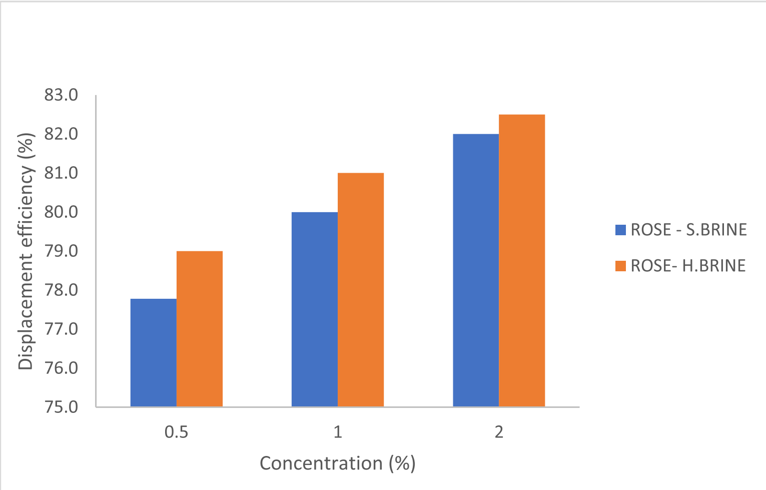

Fig. 7. Displacement Efficiency of ROSE in soft and hard brine.

rate for about 1 hour and 59 mins. A repeat experiment was conducted using hard brine as the displacing fluid during imbibition followed by EOR process using the unmodified ROSE at the same concentration and pore volume. It was observed that at CMC of 0.5%, the unmodified ROSE performed slightly better in the presence of divalent ions with a displacement efficiency of 79% (Fig. 7) as compared to flooding with soft brine which resulted in a displacement efficiency of 77.8%. This corroborates the work of Obuebite *et al.* [20] which reported a slightly higher additional recovery for the natural surfactant, *AlkaSurf X (22.7%)* than SDS (20%) in the presence of divalent ions indicating that most anionic synthetic surfactants are more susceptible to the effect of divalent cations as their presence in the reservoir or formation water inhibit IFT reduction and causes surfactant retention by blocking the pore throats, restricting oil flow and in turn reduces reservoir permeability [4,24].

The higher displacement efficiency obtained from flooding with formulated brine containing divalent ions (hard brine) found mostly on the rock surfaces indicates that ROSE is more effective in the presence of divalent ions due to its chelating ability which enables it to recover more oil even under harsh conditions. This also agrees with the findings of Wojton et al. [12] which reports that natural surfactants can reduce surface or interfacial tension even in hard waters. Enhanced oil recovery conducted using ROSE-GLUT (Fig. 8) resulted in displacement efficiency of 84% at 0.5 wt.% concentration for both soft and hard brine respectively. This implies that the modification of red onion skin extract (ROSE) with glutaraldehyde produced a surfactant chemical that can improve oil recovery either in the presence or absence of divalent ions, suggesting that ROSE-GLUT is less susceptible to divalent ions which causes surfactant adsorption and/or retention and phase separation. According to Tabary et al. [21], the use of synthetic surfactants in certain conditions such as reservoir temperatures and presence of divalent ions is challenging because surfactant adsorption increases significantly when divalent ion is present in the injection brine. A further investigation on the effect of concentration and salinity showed an increase in displacement

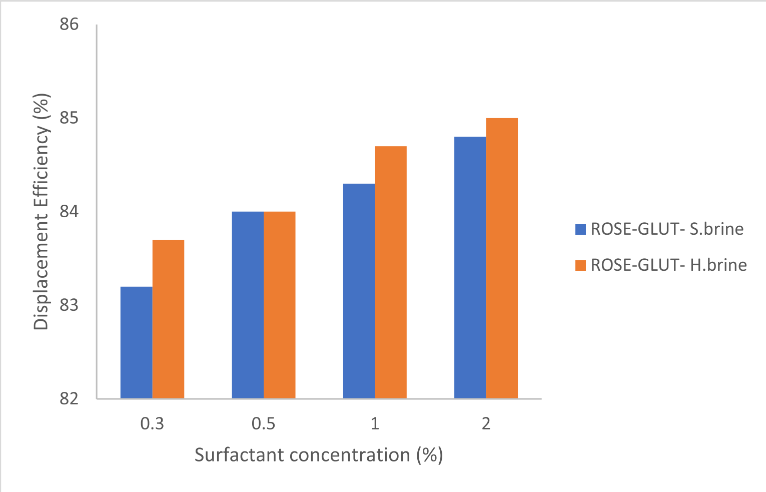

Fig. 8. Displacement Efficiency of modified ROSE-Glutaraldehyde with both brines.

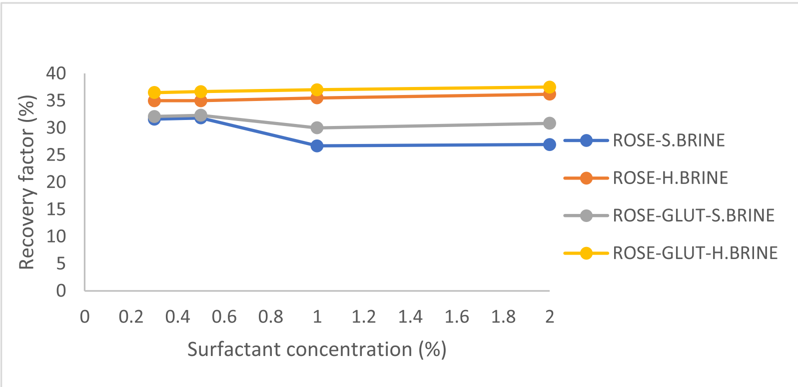

Fig. 9. Plot of Recovery factor against surfactant concentration.

efficiency of oil as surfactant concentration increased. A slight increase in displacement efficiency was observed above the micelle concentration (0.3 %wt.), however the increase (from 0.3 %wt. - 1.0 %wt.) was insignificant with respect to the cost.

Furthermore, the modification process improved the oil displacing properties of red onions skin extract (ROSE) as evident in the results shown in Figs. 7 and 8 where a higher oil displacement efficiency value was obtained when flooding with ROSE-GLUT. This is likely due to the increased number of phenolate groups derived from quercetin in ROSE by mild crosslinking using glutaraldehyde in the presence of NaOH. This is expected to increase the surface-active properties of the derivative with respect to unmodified ROSE.

The recovery factors of ROSE and ROSE-GLUT were calculated and presented (Fig. 9). Core-flood experiments with hard brine showed that 0.5 wt.% ROSE achieved an incremental oil recovery of 35.0 % following waterflooding. This was raised to 36.5 % and 36.6% using 0.3 wt% and 0.5 wt% respectively of ROSE-GLUT, showing improvement in effectiveness of ROSE after derivatization. This is similar to the work of Rezk and Allam [22], where SDS achieved about 16% increase in residual oil recovery after waterflooding. However, the use of 0.2 wt% SDS with 0.05 wt% ZnO nanoparticles increased the recovery to 35%. A maximum recovery factor of 37.5 % OOIP was achieved using 2.0 w% concentration of ROSE-GLUT. It was also observed that increasing the surfactant concentration (0.3 wt%. to 2.0 wt%.) above the critical micelle concentration (0.3 wt%.), resulted in a slight increase in the surfactant efficiency at recovering additional oil. This finding is contrary to the reports of Sheng [4] and Shunhua [23] who maintained that an increase in surfactant concentration beyond a critical concentration, increases the micelle concentration with little or no effect on the monomer concentration or surfactant efficiency.

Results of core flooding with soft brine show a decrease in oil recovery as the concentration increased above CMC for both unmodified ROSE and ROSE-GLUT.

Table 4
Results of displacement efficiency tests.

SOFT BRINE Conc. (%)	ROSE (%)	ROSE-GLUT (%)	HARD BRINE ROSE (%)	ROSE- GLUT (%)
0.3	75.7	83.2	77.0	83.7
0.5	77.8	84	79.0	84.0
1.0	80.0	84.3	81.0	84.7
2.0	82.0	84.8	82.5	85.0

Table 5
Results of Recovery factor.

SOFT BRINE Conc. (%)	ROSE (%)	ROSE-GLUT (%)	HARD BRINE ROSE (%)	ROSE-GLUT (%)
0.3	32.0	32.1	33.8	36.5
0.5	32.3	32.3	35.0	36.7
1.0	26.7	30.0	35.5	37.0
2.0	26.9	30.8	36.2	37.5

Table 6
Assumed Parameters of Reservoir Model.

Parameters	Description
Length – Average spacing of well	400 ft.
Thickness	30 ft.
Width	30 ft.
Well pattern	One Injector – One producer
Upscaling factor	2,102.066

Table 7
Up-scaled Model Parameters.

Parameters	Pore Scale	Field Scale
Brine injection rate	143 ml/min (10PV)	25.0 Barrels/day
Chemical Injection rate	28.6 ml/min (2PV)	6.1 Barrels/day

Results of statistical significance test

A set of p-values were computed for unmodified and modified ROSE in both soft and hard brine with p-values less than 0.05 ($p\text{-value} < 0.05$) being considered as statistically significant. Tables 4 and 5 show data obtained during core flooding analysis for displacement efficiency and recovery factor of both surfactant agents. The p-value obtained for displacement efficiency of ROSE and ROSE-GLUT in soft brine and hard brine was 0.0458 and 0.0354 respectively. The results indicate that the difference in displacement efficiency of ROSE-GLUT and unmodified ROSE though statistically significant is only marginal in soft brine. However, there is a high statistical significance in difference of the displacement efficiency of ROSE-GLUT and unmodified ROSE in hard brine. This implies that the performance of ROSE was improved by the chemical modification with glutaraldehyde and that ROSE-GLUT is more effective in hard brine. This results also show that there is a relationship between the varying surfactant concentrations, brine type and additional recovery.

The p-value obtained for the t-test of recovery factor data (Table 5) of ROSE and ROSE-GLUT in soft brine and hard brine was 0.1752 and 0.0110 respectively. The p-value for soft brine was greater than 0.05. This implies that the difference in the recovery factor of ROSE-GLUT and unmodified ROSE in soft brine is not statistically significant as such the null hypothesis is true. On the contrary, p-value obtained using hard brine was less than 0.05 ($p\text{-value} << 0.05$). Therefore, there is a statistically significant difference between the recovery factor of ROSE-GLUT and unmodified ROSE in hard brine.

Upscaling to field scale

The laboratory model was up-scaled to field scale so that parameters from the up-scaled model can be applied to a pilot design and be evaluated on a reservoir scale. The laboratory units were converted to field units. Certain assumed values of the reservoir model were made as shown in Table 6. The average length between two wells was assumed to be 400 ft. with the reservoir having a well pattern of one injector to one producer. The upscaling factor was determined by a ratio of the field length to core length. Table 7 shows the parameters calculated at pore and field scale. The injection rate of the surfactant used during tertiary recovery and that of the brine during imbibition was calculated as a ratio of volume to time and thereafter converted to field units. Recall that the pore volume was calculated to be 14.3 ml (see Table 2). Using the upscaling factor, the brine injection rate and surfactant injection rate was obtained as 25 barrels/day and 6 barrels/day respectively. Since an oil barrel is equal to 158.98 litres, an estimated 954 litres is equivalent to 6 barrels. This implies that an injection rate of 6 barrels per day of the natural surfactant, ROSE-GLUT is needed to achieve a displacement efficiency of 85.4% on a field scale.

Conclusion

Based on the outcome of this study, pristine (unmodified) ROSE and ROSE-GLUT derivative showed a high solubility in formulated brine with or without divalent ions at varying concentrations including at reservoir temperature of 80°C. The critical micelle concentration (CMC) of ROSE-GLUT resulted in a lower value (0.3 wt.%) compared to the CMC of the unmodified ROSE (0.5 wt.%) implying that ROSE-GLUT is a more effective surface-active agent. The modification of red onion skin extract (ROSE) using glutaraldehyde in NaOH solution produced a more effective surface-active agent compared to prisitine ROSE due to the presence of a large number of phenolate groups originating from crosslinkinking of quercetin in NaOH. The 0.3 wt.% ROSE-GLUT gave a higher oil displacement efficiency (85.4%) and additional recovery compared to the 0.5 wt.% ROSE (82.5%). Results from core flooding experiments indicates ROSE performed better in the presence of divalent ions, which implies high tolerance to divalent ions and reduced tendency of surfactant retention. Furthermore, results of statistical test of significance (t-test) showed that ROSE-GLUT (modified ROSE) exhibited superior performance and a higher recovery relative to pristine ROSE (unmodified ROSE) especially in hard brine.The statistical difference in the displacement efficiency of ROSE-GLUT compared to unmodified ROSE is more significant in hard brine, implying that the performance of ROSE was improved by the chemical modification using glutaraladehyde and the resultant derivatives are more effective in brine containing divalent ions. An upscaling of the laboratory units to field scale showed that an injection rate of about 6 barrels of the natural surfactant daily will result in a displacemnet efficency of over 85%. ROSE and ROSE-GLUT have potential as low-cost green surface-active agents for chemical enhanced oil recovery especially when flooding with hard waters.

Declaration of Competing Interest

The authors declare that there is no financial or personal interest or belief that could affect the objectivity of this work or influence the work reported in this paper.

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