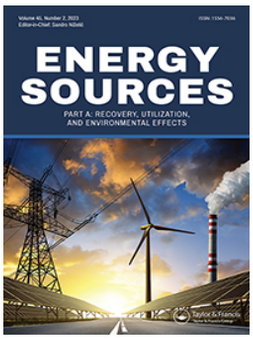

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Comparative performance evaluation of modified red onion skin extract as surface active agents for tertiary oil recovery

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ABSTRACT

Biomass-based recovery agents are fast becoming an innovative, novel solution to the increasing need for eco-friendly, cost-effective chemical agents as the need to cut production cost becomes imperative. Recent studies showed that certain natural materials if modified can suitably replace synthetic chemicals. Red Onion Skin Extract (ROSE) was chemically modified using furfuraldehyde (ROF) and urea (ROFU) and evaluated to determine its oil displacement efficiency at reservoir conditions by evaluating the fluid compatibilities. Two synthetic brine was formulated to replicate the formation of brine with divalent ions present. Compatibility test of the aqueous solution produced highly soluble, compatible fluids at varying temperatures. Type I microemulsion was observed in both surfactants. Sandstone core analysis was performed to ascertain how effective the individual modified derivatives are in recovering bypassed oil at reservoir temperature (90 °C) and pressure (9000 psi). An additional recovery of 22.7% OIIP and 11% OIIP was attained during ROF and ROFU flooding, respectively. The ROSE derivatives show good performance in displacing heavy oil even at reservoir conditions.

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Red onion skin extract; surfactant flooding; furfuraldehyde; chemical enhanced oil recovery; recovery factor

Introduction

Production from hydrocarbon reservoirs (either carbonate or sandstones) mainly occur in three different stages namely Primary, secondary and enhanced oil recovery (Gbadamosi et al. 2022 However, about 50% of the oil originally in place is still retained in the reservoir even after primary and secondary recovery process (Ahmadi and Shadizadeh 2018). Primary recovery which uses inherent reservoir forces accounts for about 20% recovery while secondary recovery methods such as water flooding and/or gas injection can increase oil recovery to an average of 40% (Al Azani et al. 2022). Enhanced oil recovery (EOR) methods increase oil production up to 30% to 60% depending on certain reservoir and fluid properties (Alutbi 2020). The selection of an appropriate EOR method for a specific reservoir is indeed a challenging task as noted by Syafitri et al. (2022) because the choice of the method is dependent on various input factors such as type of formation, reservoir rock properties, oil saturation, fluid properties and the associated cost. Chemical enhanced oil recovery (CEOR) involves the injection of chemicals such as polymers, surfactants and alkalis for the purpose of increasing the capillary number, decreasing the mobility ratio, attaining an ultra-low interfacial tension values between both fluid phases, mobilization of bypassed oil, altering formation rock wettability and oil emulsification (Kamal, Hussein, and Sultan 2017; Sheng 2013). Due to the heterogenous complex nature of hydrocarbon reservoirs comprising of immiscible fluids (gas, water, oil) in which rock-fluid and fluid-fluid interactions is pertinent in ascertaining the oil displacement efficiency, a proper design or screening of the

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fluids to ensure compatibility is pertinent. Laboratory studies and field applications have shown how effective the chemical flooding process is, however, certain factors limit its application, such as the interaction between these chemicals and divalent metals which often require reconditioning the formation. Most often, this process is ineffective and capital intensive. Al Kalbani et al. (2021) reported that interaction of divalent ions in the formation brine with the alkaline chemicals often results in insitu mineral precipitation. Other challenges include the high cost of chemicals (Zulkifli et al. 2020), environmental concerns especially with disposal of produced water and chemical solution, which are harmful to human and aquatic lives. Researchers have demonstrated the efficiency of some natural extracts chemical recovery agents (Ahmadi and Shadizadeh 2018; Nowrouzi, Mohammadi, and Manshad 2021; Obuebite et al. 2020). These natural materials are usually plant-based with special interest in agro-waste biomass. Biomass extracts contain chemicals that act as surfactants, biopolymers and alkalis with similar displacement mechanism as the synthetic counterparts and are advantageous due to their lower toxicity, biodegradability and availability (Gudina et al. 2015). Several plant extracts have been investigated as surfactants for chemical EOR including extract of myrtle, bitter leaf, Eucalyptus, chamomile, quinoa, and recently red beet and red onion skin (Imuetinyan et al. 2022; Norouzpour et al. 2022, 2023; Nowrouzi, Mohammadi, and Manshad 2021; Obuebite, Eke, and Udoh 2022; Sami et al. 2022). In earlier studies, the surface-active plant extracts were mostly used in their crude state. However, chemical derivatives of these natural products exhibit superior performance as EOR agents compared to the crude extracts (Obuebite, Eke, and Udoh 2022). In this present work, novel derivatives of red onion skin extract were prepared and evaluated. Onions (*Allium cepa*) is one of the most widely consumed vegetables (Hanci 2018) with an annual global production of 93 million tons (Big 2021). Onion skin (the inedible outermost skin layer) is a ubiquitous agricultural waste inevitably generated during the handling of the onion bulbs. Red onion skin is a nontoxic and biodegradable and renewable source of natural polyphenolics notably quercetin, a plant flavonol (Ifesan 2018). Quercetin with a melting point of 316 °C is insoluble in water but soluble in alkaline-rich aqueous solutions. Several studies (Biesaga 2011; Chaaban et al. 2017; Wang and Zhao 2016) have shown that the stability of flavonoids is a function of certain factors ranging from pH, extraction method and solvent, temperature, presence of oxygen, and type of flavonoid. The use of red onion skin (quercetin) has been reported in several industries such as the textile industry, food processing, pharmaceutical, and cosmetic industry (Pucciarrini et al. 2019. Recently, red onion skin extract (ROSE) has begun to receive attention as a potential eco-sustainable resource in the hydrocarbon industry (Bamidele et al. 2019; Galo et al. 2021). In their novel work, Obuebite, Eke, and Udoh (2022) compared the efficiency of pristine ROSE and glutaraldehyde – modified ROSE as surface-active oil recovery agents in recovering medium crude. They reported that the chemically modified ROSE performed better than the unmodified ROSE. However, its effectiveness in recovering heavy oil under high salinity, high-temperature sandstone reservoirs is yet to be ascertained. The main objective of this study was to evaluate the effectiveness of the quercetin-rich chemical derivative as a natural surfactant at reservoir conditions. This paper reports the extraction and preparation of ROSE derivatives by chemical modification with furfuraldehyde and urea and its evaluation as chemical EOR agent in sandstone formations under reservoir conditions as such becoming a possible substitute to synthetic and toxic surfactant chemicals presently used in the oil industry.

Materials and methods

Materials

The natural agent (ROSE) was obtained from the local stores. Acetone, furfuraldehyde, urea, sodium hydroxide, distilled water, sodium chloride, potassium chloride, calcium chloride, and magnesium chloride were purchased from a Sigma Aldrich chemical distributor and the chemical reagents were of analytical grade, thus they were not subjected to further processing. The oil sample was drilled from an identified oil well around south–south Nigeria and the physical properties determined. Apparatus used include a dean and stark trap, heating mantle, water bath, rotational viscometer, stirrer, thermometer, pipettes, rotary evaporator, core flooding apparatus, conductivity meter, pH meter, filter paper, sandstone core plug, and glass tubes.

Methods

The methodology used during this research work include formulation of synthetic brine, extraction of red onion skin, modification of the extract, characterization of heavy crude, core sample analysis, phase experiments, and core flooding test.

Formulation of synthetic brine

In a bid to imitate formation water, brine solutions were produced with deionized water and reagent-grade salts each having composition and salinity typical of connate water in the reservoir. The first solution was composed of varied NaCl, KCl, $CaCl_2{\cdot}2\ H_2O$ and $MgCl_2{\cdot}6\ H_2O$ concentration as outlined in Table 1 totaling 35.0 g/L TDS with 4,000 ppm assigned as calcium and magnesium chloride concentration. At 20°C, the magnetic stirrer was used to properly stir the brine solution. Thereafter, upon filtration, the brine solution was kept in an airtight container, which was tagged "hard brine." Similarly, the second brine composed only of sodium and potassium chloride was formulated and labeled "soft brine" as outlined in Table 1.

Extraction of ROS

The well selected red onions skin was sun-dried for 5 hours. Thereafter, it was ground and macerated in acetone for 24 hours and properly sieved. It was put into a rotary evaporator and concentrated, while acetone was recovered into a vacuum. The obtained extract was placed into an oven at 55°C temperature and allowed to dry, kept in an airtight container and tagged ROSE.

ROSE modification

The prepared derivatives were chemically modified via a one-pot condensation reaction with varying molar ratios of furfuraldehyde and urea to ROSE, respectively, in the presence of an alkaline catalyst. For ROF, a reaction mixture of ROSE and furfuraldehyde (2:1 mole ratio) was charged into a pre-weighed reactor vessel and a catalytic amount of 1% w/v NaOH was added based on ROSE. At 120°C, the mixture was gradually heated with continuous magnetic stirring under reflux for 60 min. For ROFU, a reaction mixture of furfuraldehyde and urea (2:1 mole ratio respectively) was charged into a pre-weighed reactor vessel and the solution mixture was refluxed for 30 min at a temperature of 70°C. Afterward, ROSE (2-mol ratio) and NaOH (the catalyst, 1% w/v) were added, and the mixture was refluxed for 60 min with continuous stirring at the same temperature. 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, and the product was weighed. Using the desiccator, the product was dried and then kept in secured containers labeled ROSE-furfuraldehyde (ROF) and ROSE-Furfuraldehyde-Urea resin (ROFU) resins respectively. The prepared ROSE-furfuraldehyde (ROF) and ROSE-Furfuraldehyde-Urea resin (ROFU) resins were dark purple in color and were characterized using its FTIR spectra. The proposed synthetic route for the resins is presented in Figures 1 and 2.

Properties of core plug

Core sample obtained from water wet sandstone reservoir was analyzed, and the bulk volume, pore volume, and porosity (using the saturation method) were computed.

Table 1. Composition of Formulated brines.

Chemical ions	Concentration (g/L) of hard brine	Concentration (g/L) of soft brine
Na^+	25.0	25.0
K^+	6.0	10.0
Mg^{2+}	2.0	
Ca^{2+}	2.0	
TDS	35.0	35.0

Note: N/B: 35 g/L is equivalent to 35,000 ppm.

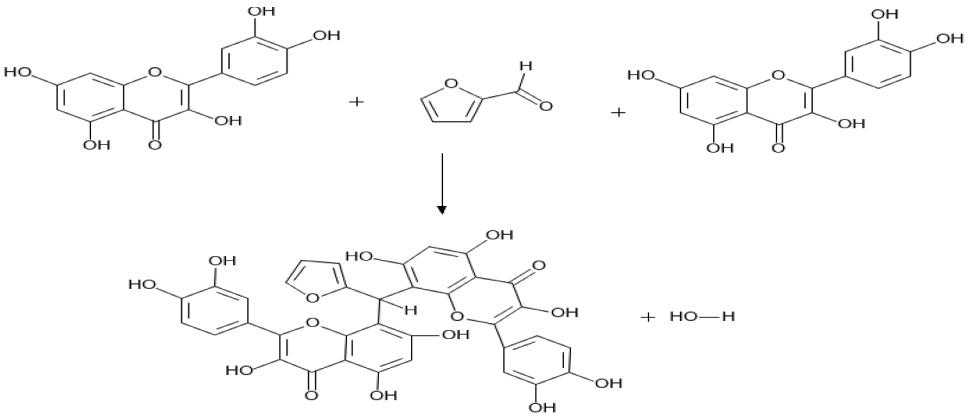

Figure 1. Proposed reaction of ROSE with Furfuraldehyde in 2:1 molar ratio.

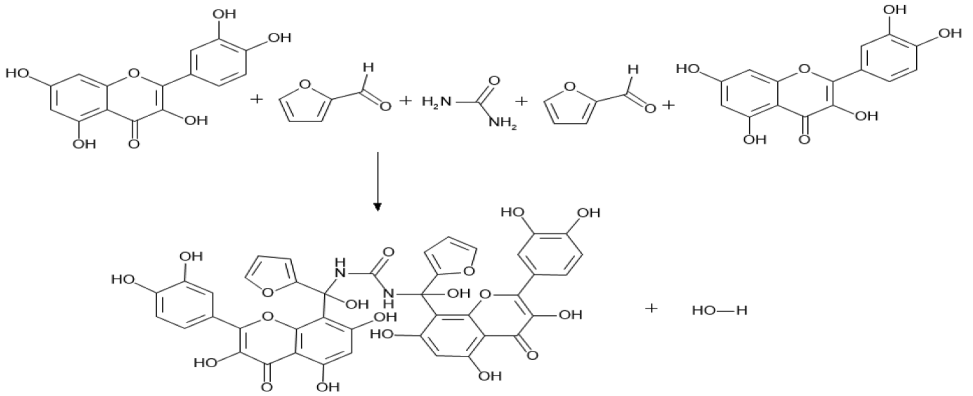

Figure 2. Proposed reaction of ROSE with Furfuraldehyde and Urea in 2:2:1 molar ratio.

Phase behaviour analysis

First, the viscosity, conductivity, potential of hydrogen, and pH of the modified natural surfactant agents were determined. Afterward, the compatibility of the fluids in the aqueous phase was ascertained. Varied concentration (0.5%, 1.0%, 2.0%) of the natural surfactant was mixed into different beakers, each containing the different brines and vigorously stirred using a stirrer. Cloudy samples containing precipitates were unsuitable for the test. All the tests were conducted at laboratory conditions and later subjected to a temperature of 90°C. A further test to determine the salinity tolerant of the natural surfactant at varying electrolyte concentrations in both brines was conducted. The CMC of the natural surfactant was kept constant, while brine salinity was varied.

Pipette Test: A phase separation test was carried out to understand fluid–fluid interaction and determine the microemulsion type present. Compatible aqueous (surfactant +brine) and oil systems were injected into an array of 5 ml borosilicate pipettes. Each pipette contained 2 ml of the aqueous solution at varying salinities and an equal volume of oil. Samples were tightly sealed to avoid evaporation or oxygen inflow and carefully inverted to ensure proper mix of both phases. Fluid interfaces were recorded and samples in the pipettes were observed for micro-emulsion formation at two distinct temperatures (25°C, 90°C) at an equilibration period of 24 days. Afterward, level readings for each of the phases were recorded at different equilibration times. Optimal salinity was calculated for solutions that formed Type III microemulsion.

Core flooding analysis

All experiments were carried out under reservoir temperature and pressure of 90°C and 9000 psi, respectively, and a flow rate of 1 cc/min was maintained all through the experiment. Three flooding experiments (drainage, imbibition, and EOR) were performed on the sandstone core plug to establish the amount of oil that can be recovered using these modified natural surfactants. The core flooding experiment began with the displacement of the brine using crude oil until the first drop of oil is seen, and a stabilized pressure profile is obtained. Start time, oil breakthrough time, and end time of the drainage process were recorded. The volume of displaced brine was recorded as the original-oil-in-place (OIIP). Water flooding using hard or soft brine as the displacing fluid was used to displace crude oil till the first drop of brine was seen and no more oil was recovered. This phase was conducted at a constant flow rate afterward and the amount of residual oil was computed. Chemical slug consisting of the natural surfactant solution was injected to retrieve the bypassed oil. For each phase of the core flooding, the produced oil and water cut were monitored, while residual oil saturation and oil recovery factor were calculated.

Results and discussion

Characterization of ROF and ROFU

The characterization of both extracts with the aid of Fourier transform infrared spectrophotometer within the range of 4000 cm^{-1} to 650 cm^{-1} was performed and the spectra of furfuraldehyde and urea with ROSE are presented in Figure 3, while Figure 4 shows the spectra of the derivatives: ROSE-furfuraldehyde resin (ROF) and ROSE-furfuraldehyde-urea resin (RFU). The broad absorption peak observed at 3272 cm^{-1} corresponds to the phenolic O – H stretch vibrations in the quercetin structure. The strong absorption peaks at 2851 cm^{-1} and 2918 cm^{-1} occurring as doublet are characteristic quercetin absorption peaks and correspond to the aromatic C – H and C=O stretch vibrations, respectively. Aryl conjugated – C=C – C=O stretch vibrations occurring at 1622 cm^{-1} and 1562 cm^{-1} are a mix of C=C and C=O stretch vibrations. The medium absorption bands which occur at 1462 cm^{-1} and 1443 cm^{-1} match aromatic C=C and =C – H stretch vibrations, while those observed at 1380 cm^{-1} and 1339 cm^{-1} match a combination of aryl O – H deformation and C – O stretch vibrations.

Aromatic =C – H in-plane deformation vibration and out-of-plane C – H deformation within the furan ring were observed at 1272 cm^{-1} and 1175 cm^{-1} respectively confirming the bond formation between ROSE and furfuraldehyde. The weak band at 1052 cm^{-1} is due to the ether C – O stretch vibration, while that at 1019 cm^{-1} corresponds to the =C – H stretch vibrations in the furan ring. The strong to weak absorption bands that occurred at 888 cm^{-1} and 784 cm^{-1} are due to aromatic and out-of-plane C – H stretching and deformation (due to isolated H atoms) vibrations, while the 724 cm^{-1} corresponds to O – H out-of-plane bending vibrations. The disappearance of the characteristic C=O stretch vibrations of the aldehydic group of furfuraldehyde at 1782 cm^{-1} and 1670 cm^{-1} further confirms bond formation between ROSE and furfuraldehyde.

Overlapping broad absorption peaks seen at 3350 cm^{-1}, 3290 cm^{-1} and 3134 cm^{-1} coincides to the N – H and phenolic O – H stretch vibrations in the ROSE-furfuraldehyde-urea resin structure (Figure 4). The characteristic quercetin doublet absorption peaks at 2851 cm^{-1} and 2918 cm^{-1} thus conforming to aromatic C – H and C=O stretch vibrations, respectively. Aryl conjugated – C=C – C=O stretch vibrations that occurred at 1622 cm^{-1} and 1562 cm^{-1} is a blend of C=C as well as C=O stretch vibrations. However, the band at 1592 cm^{-1} corresponds to the N – H deformation and C – N stretch vibration, while the appearance of a sharp peak at 1465 cm^{-1} corresponds to the asymmetric N–CO–N stretch vibration, which confirms the occurrence of an amide bond within the ROSE-furfuraldehyde-urea resin structure. Aromatic C=C and =C – H stretch vibrations in the furan ring occurred at 1443 cm^{-1}, while aryl O – H deformation and C – O stretch vibrations for the flavone ring occurred at 1387 cm^{-1}. Medium doublet peaks noted at 1357 cm^{-1} and 1328 cm^{-1} occur based on C – N stretch vibrations. Aromatic =C – H in-plane deformation vibration was observed at 1279 cm^{-1}, while weak absorption bands due to ether C – O stretch vibrations in the furan and flavone rings occurred at 1264 cm^{-1}, 1223 cm^{-1}, 1197 cm^{-1}, 1179 cm^{-1}, 1127 cm^{-1} and 1096 cm^{-1},

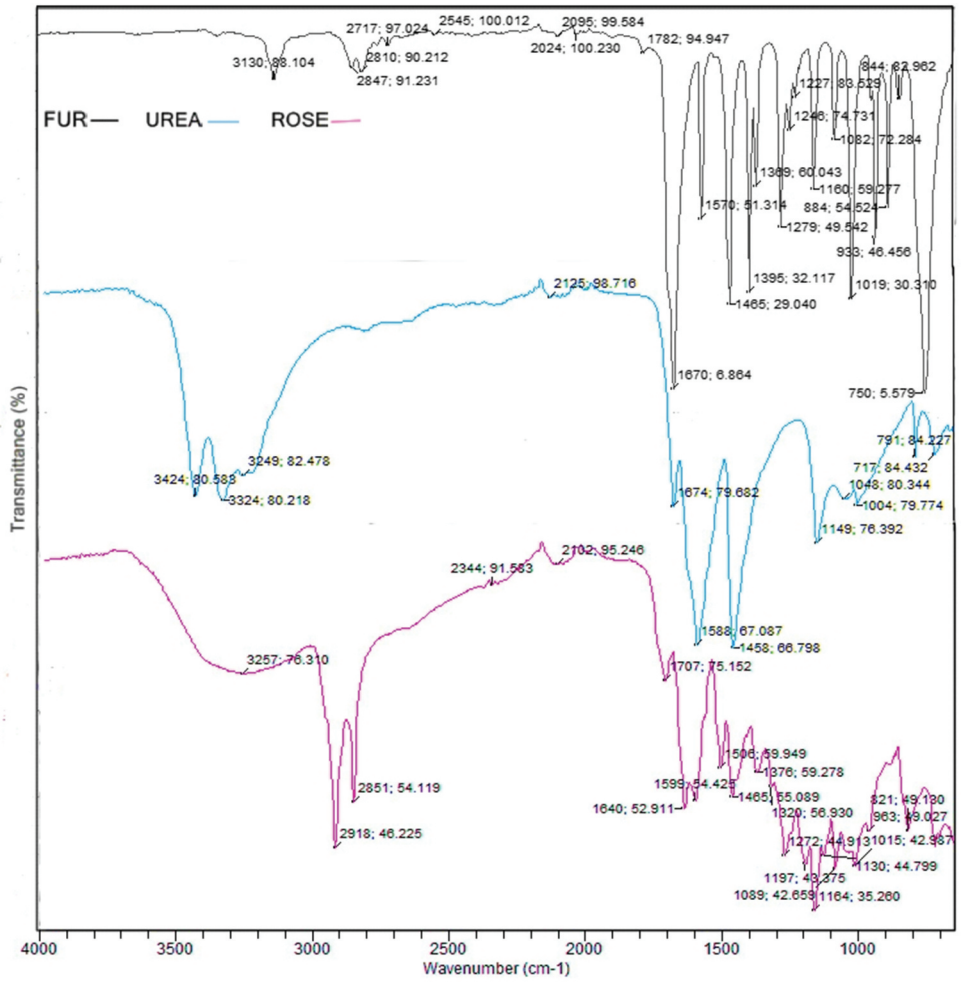

Figure 3. FTIR spectra of furfuraldehyde (FUR), urea and red onion skin extract (ROSE).

respectively. Methine C – H deformation vibration and aromatic =C – H stretch vibrations in the furan and flavone rings occurred at 1071 cm^{-1} and 1015 cm^{-1}, respectively.

The bands seen at 933 cm^{-1} and 888 cm^{-1} conform to out-of-plane aromatic C – H deformation vibrations (due to isolated H atoms) around the rings, while that observed at 817 cm^{-1} corresponds to ether C – O–C stretching vibrations.

Crude oil properties

The slightly heavy oil obtained from X field in Niger Delta reservoir was studied at ambient pressure and temperatures based on the standard test method (ASTM). Table 2 shows physical properties of the crude oil measured at ambient conditions. The value of the crude oil's viscosity is (61.71 cP). As stated by Sheng (2013), oil viscosity that is higher than 100 cP is not a suitable candidate for surfactant flooding, invariably, this crude oil sample suits surfactant flooding.

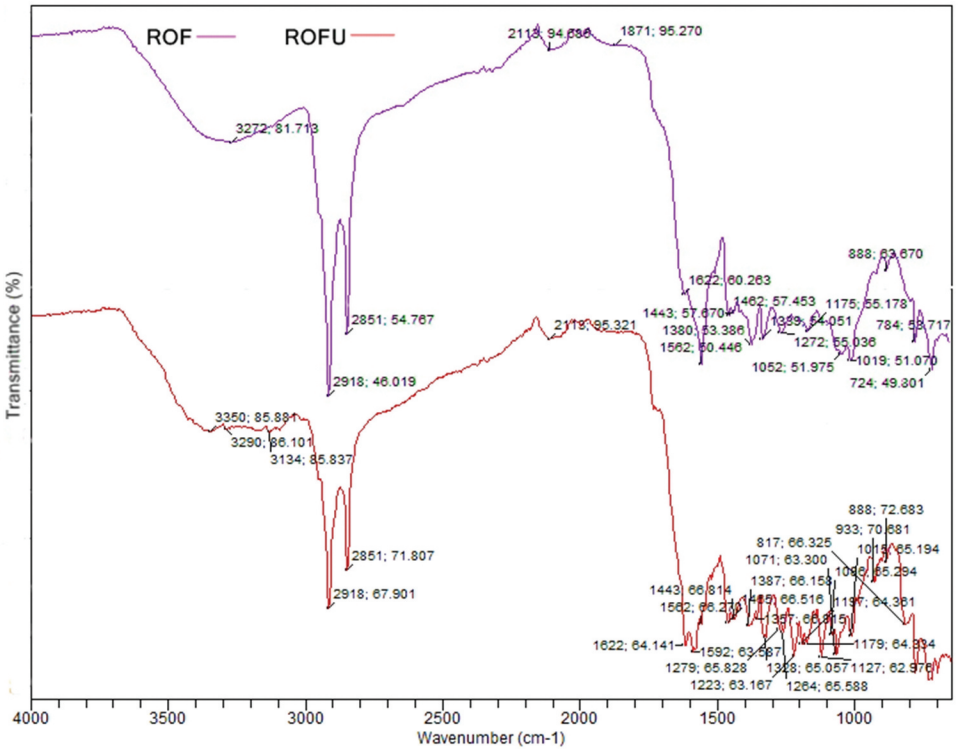

Figure 4. FTIR spectra of ROSE-furfuraldehyde resin (ROF) and ROSE-formaldehyde-urea resin (ROFU).

Properties of core sample

The mineralogy of sandstone core sample determined by X-ray diffraction analyses is 95% Quartz, 3% Feldspar, 1% rock fragments, clay-rich matrix, and cement composed of silica material as obtained from the petrographic data of the well. Certain core plug properties were estimated at ambient conditions and presented in Table 3. The result validates that of Guo (2019) who reported that the porosity of sandstone formations ranges between 5% and 40% (Guo 2019).

Viscosity values

The dynamic viscosities of ROF and ROFU at varying concentrations are presented in Figure 5. The viscosity of a surfactant may not be an imperative factor during oil recovery because interfacial tension reduction between oil and aqueous solution is the principal function of surfactants. However, Liu et al. (2018) reported that surfactants, especially nonionic surfactants, can reduce the viscosity of viscous crude oil through the formation of stable oil-in-water emulsions.

Table 2. Physical Properties of Crude Oil.

Physical Properties	Values
Specific gravity	0.924 g/cm^3
API Gravity	21.6°
Dynamic viscosity at 25°C	61.71 cP
Pressure	14.7 psia
Wax content	15.2 wt.%
Total Acid Number	0.4 mg KOH/g

Note: *API- American Petroleum Institute.

Table 3. Properties of Core Sample.

Parameter	Value
Core length (cm)	6.50
Core diameter (cm)	3.80
Pore volume (cm^3)	16.2
Porosity (%)	22.0

The results showed viscosity values ranging between 4 and 5.8 cP for ROF and 3.5 to 5 cP for ROFU at 25 °C indicating a more viscous ROF compared to ROFU. It was observed that an increase in surfactant concentration resulted in a direct increase in the viscosity of the surfactant solution as noted by Obuebite, Eke, and Udoh (2022). In their study of mechanism of reduction of viscosity of heavy oil, Liu et al. (2018) reported that nonionic surfactants have greater viscosity reduction effect than other surfactants, thus the higher the viscosity of the surfactants, the higher the reduction in viscosity of viscous crude and the easier the flow or recovery of oil. In line with these findings, Esteves, Onukwuba, and Dikici (2016) also stated that the viscosity of nonionic and biodegradable surfactants is higher than that of anionic surfactants, and these natural, biodegradable surfactants (ROF and ROFU) showed a higher viscosity value than most synthetic anionic surfactants such as sodium dodecyl sulfate (SDS).

Critical micelle concentration (CMC)

This was obtained from the measure of conductivity of the aqueous phase. Figure 6 shows that the critical micelle concentration of the modified natural surfactants is determined from a plot of surfactant concentration and the conductivity of the surfactant. From the plot, a CMC value of 1% and 1.5% was obtained for ROF and ROFU, respectively. According to Szutkowski et al. (2018), the lower the CMC value, the better the solubilization of the hydrophobic group in aqueous solution. Ideally, a lower CMC implies that a lower surfactant concentration will be required to solubilize and emulsify at the interface. Invariably, ROF is a more preferred surfactant than ROFU based on their findings. The brine containing divalent ions (hard brine) was used for the conductivity measurement because its composition represents a typical formation brine. Having obtained the CMC for each of the surfactant, salinity scan and phase separation test were performed to determine the effect of varying salinity and temperature on the surfactants and the type of microemulsion formed.

Aqueous stability

ROSE-furfuraldehyde derivative (ROF) in both brines produced highly compatible solution at ambient (25°C) and elevated (50 °C and 90 °C) temperatures, respectively, indicating the high solubility of

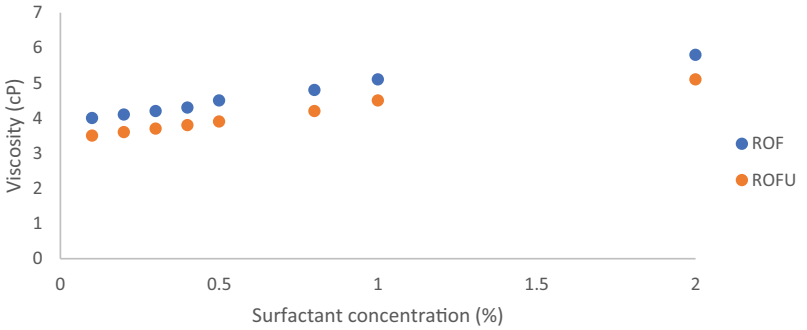

Figure 5. Viscosity values of ROF and ROFU as a function of concentration at ambient temperature.

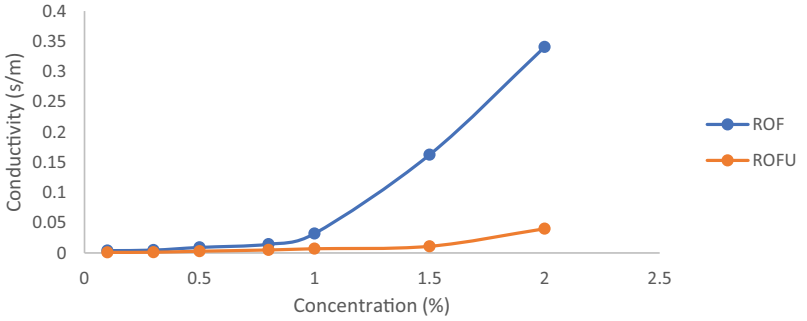

Figure 6. CMC of ROF and ROFU in hard brine.

ROF even in the formation of brine typical of sandstone reservoirs, which contain divalent ions. As pH values increased from 5.8 to 6.5, a direct proportional relationship was observed between the concentration of ROF-brine solution and pH as shown in Figure 7. A slight decrease in pH value was observed as electrolytes were introduced into the solution. The addition of calcium and magnesium ions further decreased the surfactant-brine alkalinity. According to Obuebite, Victor-Oji, and Eke (2022), the pH of the unmodified ROSE in hard brine ranges between 7.6-8. This affirms their findings, wherein they reported that the modification of ROSE reduced the alkalinity of the surfactant solution. Similarly, solutions of ROSE-furfuraldehyde-urea derivative (ROFU) in both brines also resulted in high compatibility under varied temperatures with slightly lower pH values (see Figure 7). An increase in pH was observed as the solution changed from deionized water to brine. For both brine types, the pH value and the concentration of the solution increased accordingly. Results also showed that ROF has a higher alkalinity than ROFU and a further increase in the concentration of ROF will yield an alkaline pH value. However, Wang and Zhao (2016), reported that increasing pH value from 6.0 to 7.5 under reservoir temperature of 100 °C completely degrades quercetin, thereby making it unstable. This implies that the stability of ROSE is dependent on pH and temperature. Thus, the result shows that the higher the concentration of ROF and ROFU, the higher the pH and the faster the rate of its degradation.

Phase separation

A salinity scan was performed on ROF and ROFU in both soft and hard brine at varying temperatures. At fixed surfactant CMC with a range of brine salinities being altered (1.0–3.5%), clear and consistent solutions were observed for ambient and reservoir temperatures. Figures 8 and 9 analyzes the impact of brine salinity (with or without divalent metals) on the pH of the derivatives. The modified agents in soft brine showed an increase in pH value as the brine salinity increased. The presence of divalent ions in the aqueous solution

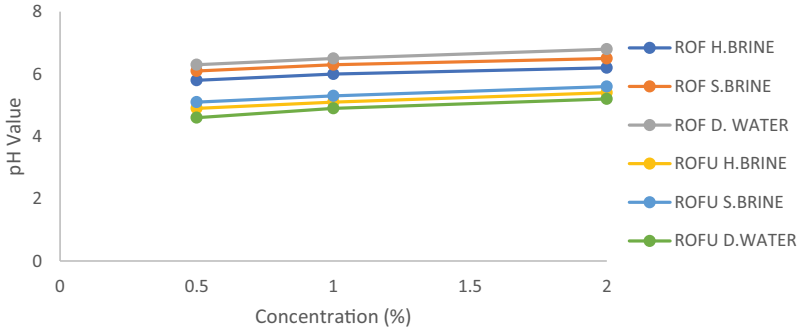

Figure 7. Relationship between pH values and surfactant concentration during compatibility test.

had little or no effect as similar result when using soft brine was also obtained with hard brine wherein the pH value was directly proportional to the brine salinity as seen in Figure 10. This indicates that further increase in the salinity of the brine will result in surfactants with alkaline properties (pH > 7).

Phase separation was carried out on both derivatives (ROF and ROFU) in hard brine and heavy oil. Visual assessment of the glass pipettes containing equal volumes of oil and ROFU-hard brine solution at varied salinities resulted in oil in water microemulsion (see Figure 10a); thus, optimum salinity was not attained. Similarly, ROF-brine and oil produced Lower phase microemulsion system where the surfactant forms an oil-in-water microemulsion in the aqueous phase. However, at higher salinities of 3.0% and 3.5%, it was observed that a microemulsion phase -forms at the middle of the oil and water phase (see Figure 10b) as the temperature increased to 90 °C. This is largely attributed to the higher pH value (alkalinity) of the surfactant solution at salinities greater than 3.0% (see Figure 9) as well as thermal effect on the heavy crude. Due to the absence of a middle-phase microemulsion (indicative of an ultra-low IFT) in all the range of salinities (Bera and Mandal 2015), optimal salinity could not be calculated but a brine salinity of 3.5% was adopted.

Displacement efficiency

The formulated brine containing divalent ions (hard brine) was used to flood during secondary recovery. For the three phases of the experiment, a steady state displacement was assumed; volume of oil injected = volume of water recovered. Therefore, OIIP = volume of water recovered during drainage (ml). The experiment started with the displacement of brine from the saturated core using heavy oil. Oil initially in place (OIIP) and initial water saturation was measured as 11 ml and 5.2 ml, respectively. Oil cut during secondary flooding was high and reduced to zero at the late stage with 5 ml of oil produced after the injection of 10PV of hard brine at 3.5% salinity and a recovery factor of 45.4% after brine flooding. Results of surfactant flooding at reservoir temperature and pressure using 1.0% ROF at brine salinity of 3.5 wt.%

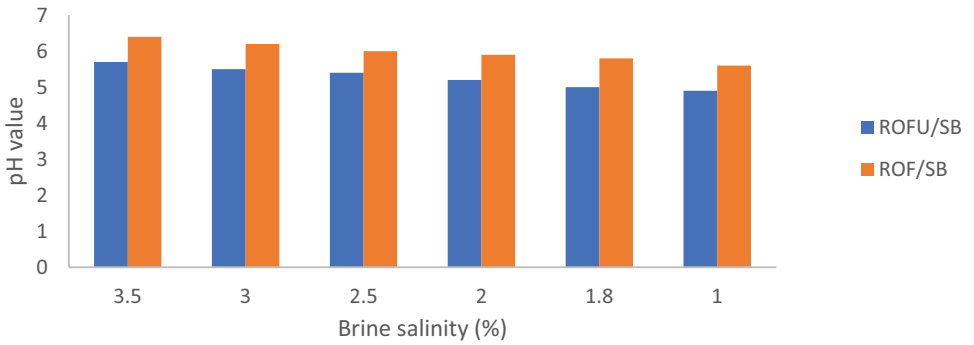

Figure 8. A variation of soft brine salinity against pH value.

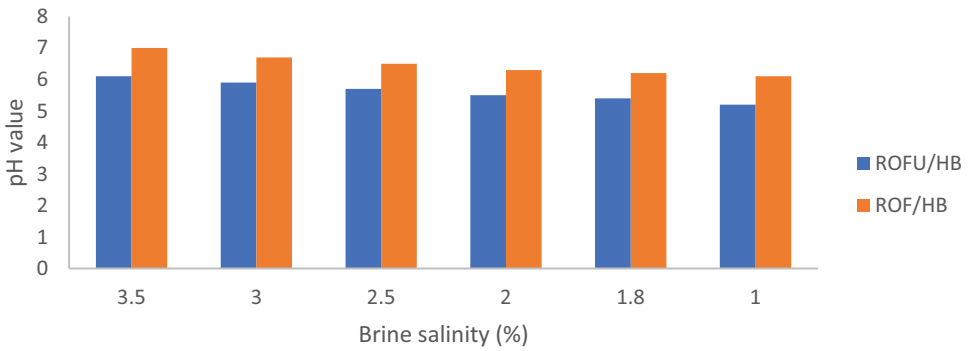

Figure 9. A variation of hard brine salinity against pH value.

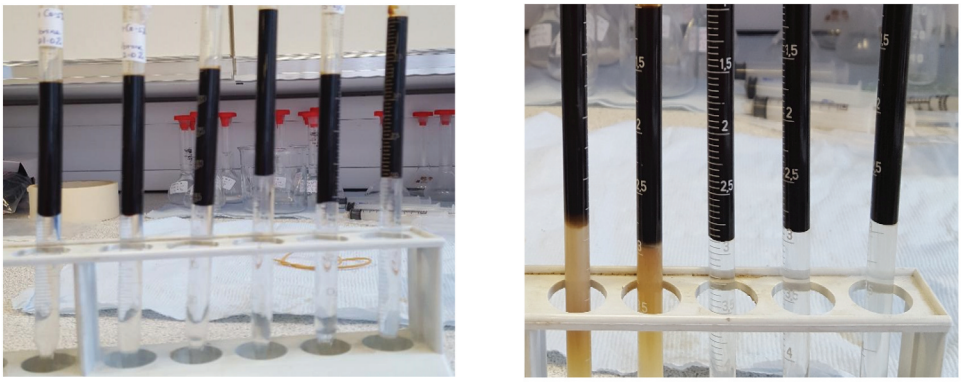

Figure 10. Pipette test between (a) ROF and (b) ROFU in hard brine and crude oil at 90 °C.

displaced additional 2.5 ml of oil. The results of the fluid volumes and recovery efficiencies of both modified surfactants (ROF and ROFU) are outlined in Tables 4 and 5.

The oil displacement test between the two natural modified surfactants ROF and ROFU in hard brine showed that ROF gave a higher recovery factor, 22.7% as opposed to ROFU with 11% additional recovery. This could be attributed to the higher viscosity and higher pH value of ROF, which resulted in the presence of Type III microemulsion at higher salinities, indicative of a lower interfacial tension (IFT) value than ROFU.

To further verify how effective divalent metals are on these natural surfactants in a sandstone reservoir, a repeat core flooding experiment was conducted using 3.5% soft brine. The results outlined in Table 6 reveal that divalent ions have little or no effect on these natural surfactants when compared to results obtained by flooding with hard brine. Core flooding using ROF in hard and soft brine gave an additional recovery of 22.7% and 23.6%, respectively, while ROFU in hard and soft brine resulted in an additional recovery of 11% and 11.7% OIIP, respectively. This implies that these modified natural surfactants have high tolerance in the presence of hard water. Furthermore, the oil displacement efficiency of these natural surfactants (ROF and ROFU) affirms their ability to improve heavy oil recovery under reservoir conditions.

Table 4. Results of Fluid Volumes.

Parameter	Units	ROF	ROFU
Pore volume		16.2	16.2
Original oil in place (OOIP)		11.0	10.0
Brine effluent volume	ml	5.20	6.20
Brine recovery	ml	5.00	5.00
Residual oil volume after imbibition	ml	6.50	5.00
EOR	ml	2.50	1.10
Residual oil after EOR	%	3.50	3.90
Total volume of oil recovered	ml	7.50	6.10

Table 5. Fluid saturation and recovery efficiency.

Parameter	ROF	ROFU
Initial oil saturation (S_{oi})	67.9	61.7
Initial water saturation (S_{wi})	32.1	38.3
Primary & Secondary recovery	45.5	50.0
Residual oil saturation (S_{or})	54.5	50.0
Recovery factor (EOR)	22.7	11.0
Critical oil saturation	31.8	39.0
Total oil recovery	68.2	61.0
Displacement efficiency after EOR (S_{or})	41.6	22.0

Note: *All values are in %.

Table 6. Recovery factor using soft brine under reservoir conditions of 90 °C and 9000 psi.

Parameter	ROF	ROFU
Pore volume (ml)	16.2	16.2
OOIP (ml)	11.4	10.2
Oil recovered during brine flooding (ml)	5.30	5.20
Recovery factor after brine flooding (ml)	46.4	50.9
Residual oil volume (ml)	6.10	5.00
Oil recovered after surfactant flooding (ml)	2.70	1.20
Recovery factor after EOR (%)	23.6	11.7
Displacement efficiency (%)	44.2	24.0

Conclusion

Derivatives of red onion skin extract (ROSE) was modified using furfuraldehyde and urea. The derivatives were analyzed to ascertain their oil displacement efficiency in the presence of heavy crude and formulated formation brines with a TDS of 35,000 ppm. Aqueous stability analysis performed at ambient and reservoir temperatures showed a high compatibility and solubility of the two natural surfactants (ROF and ROFU) in the formulated brines. The viscosity and pH of the surfactant solution is directly proportional to the surfactant concentration. ROSE-furaldehyde (ROF) has a higher viscosity (4.0 to 5.8 cP) and pH value (5.8 to 6.5) compared to ROSE-furfuraldehyde-urea resin (ROFU) having slightly lower viscosity values ranging from 3.5 to 5 cP and pH value between 4.9 and 5.6. More so, ROF produced a lower critical micelle concentration value than ROFU. Phase behavior tests conducted on both surfactants produced Type I microemulsion both at ambient and reservoir temperatures in all salinities except for ROF wherein salinities greater than 3.0% produced Type III microemulsion at 90 °C. An additional recovery of 22.7% OIIP and 11% OIIP was attained while flooding with ROF and ROFU in hard brine under reservoir conditions. A slightly higher recovery factor (23.6% and 11.7% OIIP) for ROF and ROFU, respectively, was obtained for surfactant flooding with brine devoid of divalent ions. Despite the slight decrease in oil recovery in the presence of divalent ions, it is evident that these ROSE derivatives showed good prospects in displacing heavy oil in the presence of divalent ions and under reservoir conditions thus enabling further research studies into the application of quercetin-rich ROSE derivatives for oil field chemicals in the petroleum industry. Further studies on the chemical stability of the ROF and ROFU over a period is recommended. Furthermore, the adsorption mechanism of these natural surfactants on sandstone and carbonate reservoir rocks and its effect on oil recoverability should be investigated.

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Availability of data and material

All data were generated during this study as provided by the authors. This manuscript is an original novel research article.

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