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Enhancing oil recovery of sandstone core samples using an innovative surfactant blend fighting severe reservoir conditions

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Abstract. Surfactants are a vital component of enhanced oil recovery, offering the potential to significantly increase oil production from mature and challenging reservoirs. This study examined the use of nonylphenol ethoxylate (NPE) and its modified version, which is blended with 2-butoxyethanol (butyl glycol), for enhancing oil recovery (EOR). Results showed that butyl glycol enhances NPE's efficiency and stability under challenging reservoir conditions. Where the blend significantly reduced the interfacial tension (8.5 mN/m vs. 12 mN/m for NPE alone). Using two sandstone reservoir rock slices, the contact angle for the blend was lower (27.7° & 30.5°) than that of the surfactant alone (42° & 39.6°) for both tested samples. This means the rock wettability is modified into stronger water-wet characteristics. Tertiary flooding of sandstone core samples confirmed these improvements, yielding (38.1 % S_{or}), compared to (30 % S_{or}) with NPE alone. This study demonstrates the potential of this novel, cost-effective surfactant blend to effectively extract more oil under challenging reservoir conditions.

1. Introduction

Enhanced oil recovery (EOR) is essential for maximizing production from mature reservoirs, where conventional waterflooding leaves a significant portion (approximately 60%) of the original oil in place (OOIP) [1, 2]. Surfactant flooding, a cornerstone of chemical EOR, aims to mobilize trapped oil by reducing interfacial tension (IFT) and altering rock wettability [3, 4]. While numerous studies have demonstrated the potential of various surfactants, including anionic [5] [6] , cationic [7] [8], and nonionic types [9], a persistent challenge remains: performance degradation under the harsh temperature and salinity conditions prevalent in many sandstone reservoirs. Traditional surfactants often fail to maintain their effectiveness in these extreme environments, creating a critical research gap. This necessitates the development of novel, cost-effective surfactant formulations capable of withstanding these conditions. Nonylphenol ethoxylates (NPEs) are widely used due to their broad applicability, but their stability under extreme conditions can be further enhanced [10].

This study introduces a novel surfactant blend of nonylphenol ethoxylate (NPE) with ethoxylated butyl glycol (EBG), representing an innovative approach to improve EOR in challenging reservoirs. The innovation lies in the synergistic effect of EBG, which is hypothesized to enhance the thermal and chemical stability of NPE, thereby ensuring sustained effectiveness in high-temperature and high-salinity environments. Unlike prior studies that focused on individual surfactant types or nanoparticle additions, this research explores the potential of a specific binary blend to address the critical issue of surfactant stability. The primary objective is to evaluate the blend's ability to enhance oil extraction efficiency under simulated harsh reservoir conditions. Specifically, we aim to demonstrate that the addition of EBG to NPE improves the blend's thermal and chemical stability, thereby ensuring sustained effectiveness in high-temperature and high-salinity environments. By quantifying the impact on IFT, wettability, and oil recovery through core flooding experiments, we seek to validate the potential of this novel blend for practical application in challenging sandstone reservoirs. Extracting additional and reasonable quantities of oil using the current effective surfactant blend encourages the oil recovery industry to retrieve as much remaining oil from reservoirs as possible. This, in turn, could lead to economic growth for all parties involved in the petroleum industry.

2. Lab-Experiments

2.1. Materials That Used

Nonylphenol ethoxylate (≥ 99%, Sigma-Aldrich), ethylene glycol butyl ether (≥ 99%, Sigma-Aldrich), soda ash (sodium carbonate) (powder, ≥ 99.5%, Sigma-Aldrich), distillate water (prepared in the lab), salts of calcium chloride, and sodium chloride (99.9 % pure, Merck), crude oil, subsurface sandstone core plugs, toluene (purity (99.89 %), Merck), and methanol (purity (99.89 %), Merck). This study utilized a synthetic formation water with a total salinity of 18 wt% (180,000 ppm). The water was formulated with a calcium chloride to sodium chloride ratio of 20:80.

2.2. Preparation of surfactant slugs

Two composite solutions were prepared for chemical core flooding. The first solution consisted of the nonionic surfactant nonylphenol ethoxylate slug. It was created by dissolving 8 g of sodium carbonate in 300 ml of cold water and 2 g of nonylphenol ethoxylate in 200 ml of hot water (60 ºC) under regular higher stirring. The solutions were then combined with thorough stirring to ensure complete dissolution of the component. The second one was a blend of nonylphenol ethoxylate and ethylene glycol butyl ether (1 g nonylphenol ethoxylate- 1 g ethylene glycol butyl ether) by adding butyl glycol to a homogeneous surfactant solution and mixing this solution for a half hour.

2.3. Test Techniques of Characterization

Some tests were performed to study and analyze the effect of ethylene glycol butyl ether on the performance enhancement of the nonylphenol ethoxylate in EOR as follows:

2.3.1. Interfacial Tension Studies

IFT is the force that acts at the interface between two immiscible liquids. This force is instigated by the imbalance of intermolecular forces at the interface, where the molecules of the two substances interact with each other [11, 12].

The interfacial tension (IFT) force between the crude oil and liquid phases (formation water, nonylphenol ethoxylate slug, and the chemical blend slug) was studied by using K6 Force Tensiometer prepared with a ring of Platinum–Iridium DuNouy ring.

2.3.2. contact angle test

Wettability alteration was assessed by measuring contact angles using the sessile drop method with an optical tensiometer. Thin rock sections, prepared and used without cleaning to simulate reservoir conditions, were used as the substrate. Four 8 μL droplets of crude oil, formation water, nonylphenol ethoxylate slug, and chemical blend slug were placed on each sample at different locations. Contact angles were measured and analyzed using dedicated software at room temperature until equilibrium was reached.

2.4. API of crude oil determination

API gravity (American Petroleum Institute) measures the density of fossil oil relative to water. It is commonly used as an indicator of the quality and type of crude oil [13-15]. The API gravity scale was developed by the American Petroleum Institute as shown in Equation 1.

$$°API = (141.5/SG) - 131.5 \qquad \text{(Eq.1)}$$

The specific gravity (SG) is the density (ρ) of the oil relative to the ρ of water at the same temperature The ρ of oil is the mass (M, gm) of a substance per unit volume (V, cc) (Equation 2).

$$\rho = M / V \qquad \text{(Eq.2)}$$

A pycnometer was used to determine the volume and mass of crude oil hence the density of it. First, we weighed the empty pycnometer with a known volume and then filled it with crude oil. Finally, we weighed it again. The difference in weight was the weight of oil. By dividing the mass by the volume, we obtained the ρ of oil and, consequently, the API of the oil at ambient temperature. To determine the ρ of crude oil at reservoir temperature, we filled a pycnometer with crude oil and placed it in a water bath set to reservoir temperature. We observed that the oil expanded and some came out of the pycnometer. After the oil had expanded at this temperature, we weighed the pycnometer. By dividing the new mass by the constant volume, we obtained the ρ of the oil and, consequently, the API of the crude oil at reservoir temperature.

2.5. Viscosity of petroleum determination

Viscosity measures a fluid's resistance to flow at a given temperature. The kinematic viscosity of crude oil at 67 °C (reservoir temperature) was determined in centistokes (cSt) using a U-tube viscometer immersed in a water bath set at the same temperature. The dynamic viscosity of crude oil in centipoise (cP) was found by multiplying its kinematic viscosity by its specific gravity (SG).

2.6. Core preparation

The two sandstone reservoir core samples (#C & #D), each with a diameter of 1.5 inches, underwent cleaning using the Soxhlet extraction technique with toluene followed by methanol to remove oil and salts, respectively. After drying in an oven (for 24 hours), the cores were weighed. Bulk volume (BV) was determined using a digital Vernier caliper, while grain volume (GV) was obtained from a helium porosimeter. This allowed the calculation of pore volume (PV) and porosity (Ø) using Equation 3. We also calculated the grain density of the samples using Equation 4.

$$\emptyset = \frac{\mathrm{PV}}{\mathrm{BV}} = \frac{\mathrm{BV-GV}}{\mathrm{BV}} \qquad \text{(Eq.3)}$$

$$\text{Grain density} = \frac{\text{Dry wieght}}{\mathrm{GV}} \qquad \text{(Eq.4)}$$

2.7. Experimental flooding test

The plugs underwent a four-hour vacuuming followed by saturation with an 180000 ppm salinity brine solution at 2500 psi for a day to ensure complete saturation. The cores were reweighed post-saturation to confirm full brine saturation. Utilizing a stainless-steel core holder, the fully saturated core samples were subjected to 67°C temperature and 3600 psi confining pressure (reservoir conditions). Porosity at reservoir conditions was determined using the pipette method. Original oil in place (OOIP) was estimated by crude oil flooding a fully brine-saturated core. Residual oil saturation was assessed through secondary flooding with formation water till no more oil was displaced from the sample. Lastly, plug samples were chemically flooded with nonylphenol ethoxylate surfactant and its blended form, showing varied additional oil recoveries.

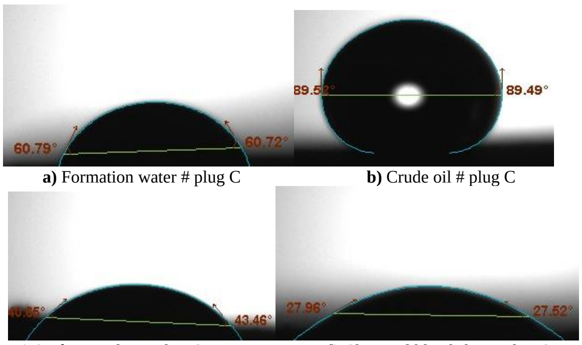
3. Results and Discussion

3.1. Interfacial Tension Measurements

In this study, IFT measurements were conducted under ambient conditions between crude oil and different solutions. The results indicated that the interfacial tension (IFT) values were 27 mN/m for oil and formation water, 12 mN/m for oil and nonylphenol ethoxylate solution, and 8 mN/m for oil and the blend solution. The significant reduction in IFT observed with the blend slug solution demonstrates that the addition of ethylene glycol butyl ether enhances the effectiveness of nonylphenol ethoxylate in lowering the IFT between the injected water and crude oil. Where ethylene glycol butyl ether modifies the hydrogen bond network in water, reduces intermolecular cohesion, and improves the solubility and mobility of nonylphenol ethoxylate molecules. Additionally, it decreases the viscosity of the solution, allowing nonylphenol ethoxylate to distribute more effectively at the interface and form micelles more efficiently. This combined effect leads to a greater reduction in surface tension than either component could achieve alone.

3.2. Contact Angle Test

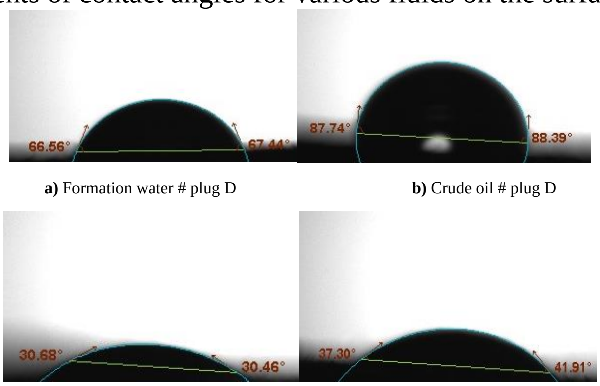
Contact angle measurements help understand how wettability is altered in oil reservoirs, a key factor in mobilizing trapped residual oil from rock pores [16]. Contact angle measurements revealed a marked shift from oil-wet to water-wet conditions upon treatment with two surfactants especially in the case of modified form. The contact angle of the studied rock samples (Figures (1&2)) shows that the crude oil-rock contact angle is about 60.75° in the case of sample #C and about 67° in the case of sample #D, which means oil-wetting rock nature. On the other hand, the formation water-rock contact angle nearly approaches 90°, which points to neutral water-wetting rock properties. When the two core samples (#C and #D) were treated with nonylphenol ethoxylate the contact angle became 42° and 39.6°, respectively and when they were treated with the modified form the contact angle became 27.7° and 30.5°, respectively. It can be concluded that, the two surfactant slugs have the effectiveness to entirely change the oil-wetting rock properties into strong water-wet affinity, especially in the case of the blend composite.



a) Formation water # plug C **b)** Crude oil # plug C

c) Surfactant slug # plug C **d)** Chemical blend slug # plug C

Figure 1. Measurements of contact angles for various fluids on the surface of core sample #C.



a) Formation water # plug D **b)** Crude oil # plug D

c) Surfactant slug # plug D **d)** Chemical blend slug # plug D

Figure 2. Measurements of contact angles for various fluids on the surface of core sample #D.

3.3. Experimental Results of Reservoir Core Plugs

3.3.1. Water flooding secondary recovery

The physical characteristics of brine (formation water) and crude (Tables 1 & 2) illustrate severe reservoir conditions where the salinity of formation water is 181000 ppm and API of crude oil at reservoir temperature is about 26 which means heavy crude oil. The petrophysical characteristics of the tested plugs are displayed in Table 3. The results of water flooding (secondary recovery) (Table 4) at reservoir conditions, displayed that the residual oil that was left in the two tested core samples was 47.61% OOIP for sample #C and 49.41% OOIP for sample #D. The significant residual oil in the two

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core samples suggested some factors hindering oil recovery, such as a high IFT between the oil and injected water, along with the oil-wet nature of the samples.

Table 1. Physical properties and ions concentration of injection brine.

Physical properties	
Conductivity, mohs/cm at 25 °C	15.12 x 10^{-2}
Salinity, mg/l	181000
pH at 25 °C	6.08
Density, g/ml	1.099
Specific gravity	1.22517
Ion's concentration	
Total Dissolved Solids, mg/l	175305.04
Ca^{++}	7064.25
Cl^{-}	102573
Mg^{++}	1443.56
K^{+}	287.55
Na^{+}	60241.37
Sr^{++}	328.84
HCO_3^{-}	162.67
SO_4^{-}	3203.8

Table 2. Crude oil physical properties at reservoir temperature.

Test	**Result**
Oil viscosity, cp (67 °C)	11.40
Oil density, gm/cm^3	0.896
Oil API, gravity	26.39
Asphaltene, wt%	0.15
Flash point, °C	<-15

Table 3. The petrophysical characteristics of the tested plugs.

Parameters	**#C**	**#D**
Length, cm	4.70	4.73
Diameter, cm	3.81	3.81
Area, cm^2	11.40	11.41
Bulk volume, cc	52.86	52.46
Pore volume, cc	14.45	14.20
Grain volume, cc	38.41	38.27
Dry weight, gm	102.53	102.63
Grain density, g/cc	2.67	2.68
Porosity (%)	27. 3	27.1
Air permeability (Ka), mD	283	235

Table 4. Results of water flooding secondary recovery and flooding conditions.

Parameters	**#C**	**#D**
Original oil in place (OOIP), cc	8.4	8.5
Original oil in place, % Pore volume (P.V.)	58.13	59.86
Initial water saturation (S_{wi}), cc	6.05	5.7
S_{wi}, % Pore volume (P.V.)	41.87	40.14
Residual oil saturation (S_{or}), cc	4	4.2
Oil recovery of water flooding, cc	4.4	4.3
Oil recovery of water flooding % Pore volume	30.44	30.28
Oil recovery of water flooding % Original oil in place	52.38	50.58
S_{or}, % Pore volume	27.68	29.57
S_{or}, % Original oil in place	47.61	49.41
Flooding Conditions		
Flooding temperature, °C	67	
Confining pressure, psi	3600	
Brine salinity, ppm	181000	

3.3.2. Surfactant flooding (enhanced oil recovery)

Following the core water flooding the surfactant flooded using nonylphenol ethoxylate for sample (#C) and the blend composite (nonylphenol ethoxylate with ethoxylate butyl glycol) for sample (#D). The results are shown (Tables 5 & 6), and represented graphically (Figures (3 & 4)) and indicate positive economics for enhanced oil recovery through two composites of nonylphenol ethoxylate and its modified form (nonylphenol ethoxylate with ethoxylate butyl glycol) where they achieve a recovery factor of 38.1 %S_{or} in the case of monoanionic surfactant and 30 %S_{or} in the case of modified composite from the remaining oil. These results support the results of ITF and wettability tests.

Table 5. Cumulative oil recovery as a function of pore volume injected in the case of NPE.

Slug injected,	**Tertiary oil recovery,**	**Tertiary oil recovery,**	**Tertiary oil recovery,**
%, Pore volume	**%, Residual oil saturation**	**%, Original oil in place**	**%, Pore volume**
10	1.25	0.60	0.35
20	2.50	1.19	0.69
29	3.75	1.79	1.04
39	5.00	2.38	1.38
48	5.75	2.74	1.59
58	8.75	4.17	2.42
67	10.00	4.76	2.77
76	11.25	5.36	3.11
85	12.50	5.95	3.46
94	17.50	8.33	4.84
119	22.50	10.71	6.23
144	25.00	11.90	6.92
169	27.50	13.10	7.61
193	30.00	14.29	8.30
264	30.00	14.29	8.30

Table 6. Cumulative oil recovery as a function of pore volume injected in the case of modified surfactant

Slug injected, %, Pore volume	Tertiary oil recovery, %, Residual oil saturation	Tertiary oil recovery, %, Original oil in place	Tertiary oil recovery, %, Pore volume
10	2.38	1.18	0.70
20	4.76	2.35	1.41
29	9.52	4.71	2.82
39	16.67	8.24	4.93
48	21.43	10.59	6.34
58	23.81	11.76	7.04
67	26.19	12.94	7.75
76	28.57	14.12	8.45
85	30.95	15.29	9.15
94	33.33	16.47	9.86
119	35.71	17.65	10.56
144	36.90	18.24	10.92
169	38.10	18.82	11.27
193	38.10	18.82	11.27
264	38.10	18.82	11.27

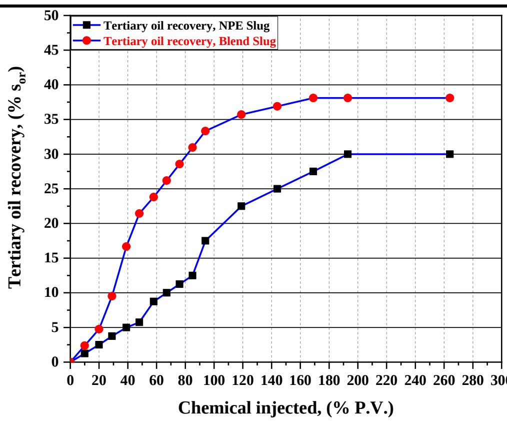

Figure 3. Oil recovery percentage (%) S_{or} by NPE and blend (NPE & EBG) composites.

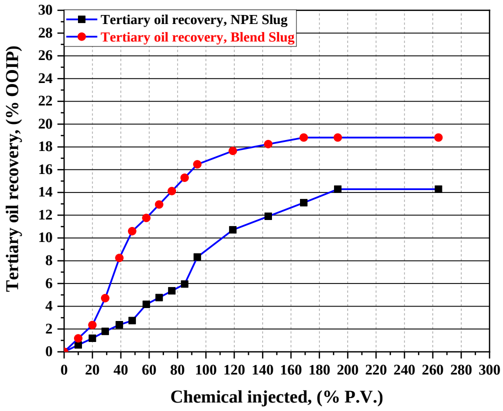

Figure 4. Oil recovery percentage (%) OOIP by NPE and blend (NPE & EBG) composites.

The summarized experimental data is illustrated in Table 7 and represented graphically (Figure 5). Where the recovery factors (RF) obtained by the secondary method (SM) in the two samples were 52.38 %OOIP (#C) and 50.58 %OOIP (#D) and the recovery factors obtained by the tertiary method (TM) were 14.29 %OOIP (#C) and 18.82 %OOIP (#D). The total recovery factor (RF_{Total}) is obtained by summing up the amounts of oil recovered in each step (secondary and tertiary oil displacement process) so it became 66.67 %OOIP in the case of the sample (#C) and 69.40 %OOIP in the case of the sample (#D). In the end, we can mention the following:

The enhanced oil recovery achieved with the NPE/butyl glycol blend in this study has significant practical implications for field operations. The blend's ability to maintain low interfacial tension and improve wettability under high-temperature and high-salinity conditions indicates that it could be particularly effective in mature sandstone reservoirs, where conventional surfactants often fall short.

To successfully translate these laboratory findings to field-scale applications, careful attention must be paid to injection strategies. This includes optimizing slug sizes and injection rates to ensure efficient contact with the reservoir's oil. Additionally, conducting an economic analysis to compare the cost of the blend with the expected increase in oil production is crucial for determining its commercial viability.

Table 7. Secondary and tertiary recovery factors in the flooding process with two composites.

Parameter		**Value**							
		Plug (# C) (NPE flooding)				**Plug (# D)** (Bend flooding)			
V_o injected, cc		8.4				8.5			
V_o recovered by SM, cc		4.4				4.3			
V_o remain, cc		4				4.2			
Recovered oil by TM, cc		RF_{SM} (%OOIP)		RF_{TM} (%OOIP)		RF_{Total} (%OOIP)		Remaining Oil (%OOIP)	
# C	# D	# C	# D	# C	# D	# C	# D	# C	# D
1.2	1.6	52.38	50.58	14.29	18.82	66.67	69.40	33.33	30.60

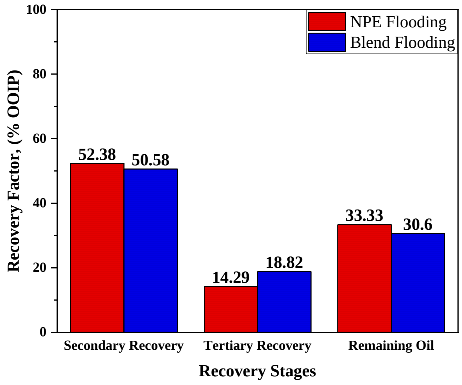

Figure 5. Histogram displaying recovery stages and the remaining oil using NPE and blend composites.

5. Conclusion

In this study, the nonylphenol ethoxylate surfactant and its modified form (nonylphenol ethoxylate with ethoxylate butyl glycol) have been assessed in enhanced oil recovery under reservoir conditions on subsurface core plugs. The physical blending method has been used to mix the ethoxylate butyl glycol with the surfactant. The results from different characterization analyses indicated that the presence of EBG with NPE has a positive and supportive effect on its performance in EOR where it was found that the interfacial tension between crude oil and injected water in the presence of blend form was reduced more than in the presence of NPE alone. Also, EBG enhanced the performance of NPE in altering the wettability of reservoir rock to more water-wet. The results from core flooding experiments confirmed and supported the previous results where the tertiary recovery factor in the case of modified composite was (38.1 $\%S_{or}$) more than the tertiary recovery factor in the case of nonanoic surfactant alone (30 $\%S_{or}$). Finally, we can conclude that the blend of nonylphenol ethoxylate and ethoxylate butyl glycol present a promising advancement in surfactant-based enhanced oil recovery. By leveraging the synergistic effects of both surfactants, this blend offers improved reduction of interfacial tension, altered wettability, and enhanced stability under harsh reservoir conditions. Future research and field trials will be essential in optimizing its application and ensuring its sustainability in EOR operations.

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