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Experimental Investigation of the Synergistic Effect of Two Nonionic Surfactants on Interfacial Properties and Their Application in Enhanced Oil Recovery

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ABSTRACT: In chemically enhanced oil recovery (EOR), surfactants are conventionally used to lower the interfacial tension (IFT) at the water−oil interface, alter the rock wettability, and help in the emulsification of trapped oil after primary and secondary modes of recovery. A mixture of surfactants is usually more effective than a single surfactant with enhanced surface or interfacial properties. The primary objective of this study is to examine the synergistic effects of two nonionic surfactants (Tergitol 15-S-12 and PEG 600) on surface properties, such as surface tension, IFT, and wettability alteration, in the context of EOR. The optimum composition of the surfactant mixture was obtained by surface tension measurement, and it has been found that the Tergitol 15-S-12 and PEG 600 mixture shows better synergistic effect with a minimum surface tension value of 30.3 mN/m at 225 ppm concentration of Tergitol 15-S-12 and 1 wt % of PEG 600. The surfactant mixture with optimum composition shows an ultra-low IFT of 0.672 mN/m at optimum salinity. The wettability alteration study was conducted in a goniometer by observing the change of the contact angle of an oil-wet sandstone rock in the presence of the formulated chemical slugs at different concentrations, and the results show a shift in the wettability of rock from the oil-wet to the water-wet region. The wettability alteration behavior of oil-wet rock is established using X-ray diffraction analysis of sandstone rock and zeta potential measurements of the chemical slugs. The efficacy of the optimized chemical slug for EOR was checked by a core flooding experiment, and an additional recovery of 17.73% of the original oil in place was observed.
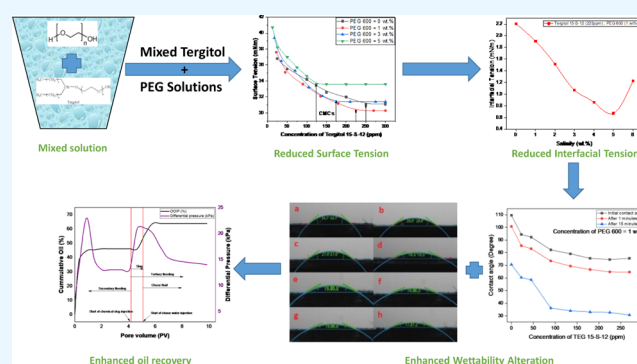
1. INTRODUCTION

The increase in consumption and demand for petroleum and petroleum-derived products has prompted the oil industry to employ improved recovery techniques to access residual oil. The petroleum industry currently pursues the implementation of environmentally acceptable and commercially viable technologies to improve residual oil recovery from subsurface reservoirs.[1]

Oil wells go through three distinct cycles of life, during which several strategies are used to keep crude oil production at high levels. There are three stages of development for specific oil fields: primary recovery, secondary recovery, and tertiary recovery or enhanced oil recovery (EOR). The primary recovery processes rely on natural energy to drive oil from the reservoir, and recovery is 10−30%, depending on the formation rock and fluid properties. Secondary recovery processes, such as water flooding and gas flooding, improve oil recovery, but they leave more than half of the original oil in place (OOIP) in the reservoir.[2] Chemical, thermal, and miscible EOR methods are tertiary EOR approaches that can further increase oil recovery by up to 60%.[3] The present

economics, reserve oil, and crude oil price have a significant impact on EOR projects. Chemical EOR techniques comprising the injection of different formulated chemicals to lower the interfacial tension (IFT) between the reservoir oil and the injected fluid or increase the injected fluid's sweep efficiency.[4] To begin with, the injected chemicals are intended to change forces within the pore spaces of petroleum reservoir rocks to mobilize and displace oil. It is primarily accomplished by lowering the IFT between fluids in the pore network and modifying the wettability of the rock surface helpfully.[5] Among the chemicals utilized, the most common chemical system is a polymer, which is used to improve the viscosity of injected water. Polymer flooding has proven to be a viable method to enhance macroscopic sweep efficiency by viscosifying the
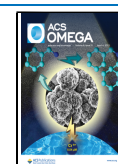
injection water.[6] However, some researchers claim that some specific polymers also increase the microscopic displacement efficiency.[7,8] Surfactant solutions are used to reduce capillary forces and increase the capillary number (N_c), which characterizes the relationship between viscous and capillary forces and is the critical predictor of oil displacement. The capillary number is defined by eq 1 given below

$$N_c = \frac{\mu v}{\gamma} \tag{1}$$

where μ is the viscosity of displacing fluid, mPa s; v is the linear flow velocity, m/s; γ is the IFT between oil and displacing fluid, mN/m.

The capillary number in a typical water flooding operation is in the range of 10^{-7} to 10^{-6}, where capillary forces retain a large amount of oil in the pores after water flooding. A capillary number may be increased by at least four orders to mobilize entrapped oil after water flooding and minimize residual oil saturation. This can be accomplished by lowering the IFT between the water and oil phases and increasing the displacing fluid's viscosity. Various techniques, such as surfactant flooding, miscible CO_2 flooding,[9] use of nanoparticles as biosynthesized nanocomposites as dispersing agents,[10,11] ionic liquids,[12] and so forth mobilizes residual primarily by lowering the IFT of the crude oil system. Studies have been conducted to blend surfactant with other chemicals to design hybrid injection fluids, like low salinity surfactant nanofluids, where the surfactant is used to disperse the nanoparticles in an aqueous medium uniformly.[13] Nanoparticles/surfactant solution can also be utilized in the carbon geo-sequestration by sorption trapping of CO_2 in shale formation.[14]

Surfactants, also called surface-active agents, solely operate by accumulating on the interface and altering the interactive forces. Because of the amphiphilic nature, it is aligned in a manner such that its hydrophobic end is in oil and its hydrophilic part is in water. Depending on the charges on the head group, these are further classified into anionic, cationic, and zwitterionic surfactants. Both zwitterionic and cationic materials are quite expensive to produce, and their use is entirely based on the project economics. The selection of surfactants for their application in EOR is very crucial.

Anionic surfactants have usually higher critical micelle concentration (cmc), poor salt tolerance, and are environmentally hazardous due to the larger pollutants emitted during its production and processing the anionic surfactants.[15,16] The nonionic surfactant, in comparison, has excellent tolerance to salt, greater compatibility with different surfactants, good temperature resistance, lower cmc values, and hardly gets influenced by strong acids and bases.[17,18] Nonionic surfactants are relatively nontoxic, and different green nonionic surfactants have been synthesized to deal with shallow water zones and marine environment[19] It can be used both in sandstone and carbonate reservoirs and have better emulsifying property compared to ionic surfactants.

Recently, there has been a shift in trend toward combining different surfactants in the petroleum sector, as the IFT obtained from such combinations is significantly low. Anionic/cationic surfactant mixtures have cmc values that are considerably lower than the individual surfactants.[20] The lower cmc is attributed to the formation of microstructure arising from electrostatic interaction between the opposite head charges of surfactants.[21] On the contrary, strong synergistic interactions between cationic/nonionic and anionic/nonionic binary surfactant mixture has been observed, thus lowering the cmc considerably as compared to antagonism found in the cationic/nonionic binary surfactants.[22] The polyoxyethylenated nonionic surfactant is found to have greater molecular interaction with an anionic surfactant as compared to the cationic surfactant with the same hydrophobic group.[23] The synergy between the synthesized anionic/nonionic binary surfactant mixture has been established with micellization behavior study, including surface tension and viscosity studies.[24,25] Few studies have been conducted on the utilization of these synergies in EOR processes with a reported adsorption behavior and oil mobilization potential.[26−29] It is apparent that the careful design of combinations, such as cationic/anionic, anionic/nonionic, and cationic/nonionic, have the potential to work synergistically when mixed in the appropriate proportion. Such mixing facilitates better salt tolerance in addition to achieving minimum IFTs with a lesser concentration of surfactants, thus improving the economics of EOR projects.

The efficiency of mixed surfactant systems mainly depends on the mutual interaction among the surfactants. The dominance of molecular interaction between two surfactants of different molecular structures in the mixture than in unit component causes the synergistic effect on their interfacial properties. It is reported that nonionic surfactant mixtures are usually more effective than a single surfactant.[8] After cmc, the surfactants form micelles in the bulk water phase, and the micelles of mixed surfactant systems can alter the physicochemical properties of the system significantly. Further, the synergistic effects of mixed surfactants are often influenced by salinity, pH, temperature, and so forth.

Thus, in the present work, an attempt has been made to explore the synergistic effects of two nonionic surfactants, viz. Tergitol 15-S-12 and PEG 600, on their physicochemical properties, which are crucial for their application in EOR. Under dynamic conditions, the surface tension and IFT values of the mixed chemical slugs at different compositions were investigated. The changes of wettability of oil-wet sandstone rock to water-wet were studied in the presence of an optimized solution of a surfactant mixture. The core flooding experiment was also done with the formulated chemical slug to find additional recovery after conventional water flooding.

2. MATERIALS AND METHODS

2.1. Materials. The nonionic surfactant, Tergitol 15-S-12 (99% purity) and NaCl, were procured from Sigma-Aldrich (Germany). Polyethylene glycol, PEG-600, was purchased from TCI Chemicals. The crude oil has been acquired from the Ahmedabad asset, ONGC, and its API gravity was 41° API at 30 °C. Distilled water was used to make all aqueous solutions.

The chemical formula of Tergitol 15-S-12 is $C_{12-14}H_{25-29}O[CH_2CH_2O]_{12}H$ with an ethylene oxide number (EON) number of 12, a molecular weight of 738, and a HLB value of 14.7. For this study, Tergitol 15-S-12 was selected because it has outstanding wetting properties, has high thermal resistivity, is highly water soluble, is an efficient emulsifier, has excellent detergency properties, and has excellent foamability. It is readily biodegradable and can rapidly wet and spread on the hard surfaces. The micelle size of Tergitol 15-S-12 is larger compared to other surfactants because of its higher ethylene oxide number. The favorable entropy and enthalpy of micellization allow the formation of

stable micelles. Thus, it can produce microemulsion quite easily and be able to produce ultra-low IFT and higher additional recovery. The chemical formula of PEG 600 is $H(OCH_2CH_2)_nOH$ with an average molecular weight of 570–630. PEG 600 is molecularly stable, completely soluble in water, and has lower toxicity.

2.2. Experimental Methods.

2.2.1. XRD Analysis of Sandstone Rock.
The X-ray diffraction (XRD) analysis of the sandstone rock used under this study was done to gain insights into the mineral composition of the rock. The XRD patterns were recorded using a Bruker D8 ADVANCE Powder X-ray Diffractometer. The generated spectra were then processed using the Diffraction software.

2.2.2. Crude Oil.
Crude oil used in this study was taken from Cambay basin of India. The Fourier transform infrared (FTIR) spectra of crude oil samples were measured using a PerkinElmer Spectrum-2 FTIR spectrophotometer in the 400 to 4000 cm^{-1} range. FTIR analysis is also used to analyze the functional groups present in the crude oil sample.

Figure 1 depicts the oil sample's FTIR spectrum, which contains peaks due to the presence of specific oil components.
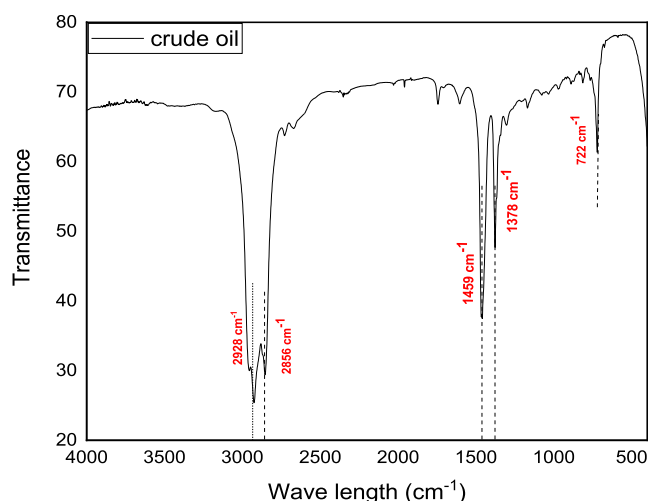

Figure 1. FTIR of the crude oil sample.

The presence of an aliphatic group, like methylene, is confirmed by asymmetric stretching of methylene at a wavenumber band of about 2928 cm^{-1}. Usually when CH_3 is attached to the aromatic rings, it causes asymmetric stretching of CH_3 at 2928 cm^{-1}. The symmetric bending vibration of methyl, also known as the umbrella mode, is detected by vibrational stretching at 1378 cm^{-1}. Generally, the C–H out of plane bending vibrations of aromatic rings contribute mainly to the band spectra of 900–700 cm^{-1}. The aromatic rings with four isolated hydrogen (di-substituted) may be confirmed at 722 cm^{-1}.[30]

2.2.3. Surface Tension.
The Easy Dyne K20 Tensiometer (KRÜSS Germany) was used to quantify the surface tension of the mixture of surfactants in aqueous solutions. The surfactant solutions of different concentrations of Tergitol 15-S-12 (25–300 ppm) were prepared in distilled water, keeping the wt % of PEG-600 constant. Four such sample sets were prepared by varying the concentration of PEG-600 as 0, 1, 3, and 5 wt %. Prior to each measurement, the platinum ring was cleaned with acetone and flame-dried, then used for surface tension measurement. The curve was plotted between the surface tension and concentration of respective surfactant solutions to determine the cmc of the mixed solutions. The results were accurate within the limits of ±0.1 mN/m.

2.2.4. IFT Study.
The IFT values between the crude oil and nonionic surfactant (mixture) solutions were measured at different concentrations in an SVT20 tensiometer using the spinning drop technique for different solutions. The crude oil was injected into a capillary tube consisting of an aqueous solution of the surfactant system as the surrounding phase, and this whole system was then rotated at 6000 rpm. The IFT is determined by profile fitting the drop for each condition. The capillary was rinsed with toluene or benzene before any experiment to remove the remaining crude oil and further cleaned with acetone to remove salt/surfactant traces and then left to dry. The IFT between nonionic mixed surfactant solutions was measured with varying salinities and concentrations. Triplicate measurements were taken for each experiment.

2.2.5. Measurement of Contact Angle.
The contact angle was measured by placing a drop of the mixed surfactant solution on the sandstone rock surface. It is a measure of the wettability characteristics of the rock. The sessile drop method was used to measure the contact angle in a KRÜSS Drop Shape Analyzer DSA25S, Germany, with a reliability of ±0.3°. The sandstone rock samples were aged in crude oil for 15 days to change their wettability to oil-wet and utilized for determining contact angle values. For varying concentrations of the surfactant solutions, the contact angles were measured very carefully by dropping a small drop of 5 μL sample solutions through the needle tip with a diameter of 0.5 mm on the rock surface; the variation of the contact angle at 30 °C was identified with respect to time.

2.2.6. Zeta Potential Measurement.
The potential difference between the bulk solution and the solid surface is referred to as the zeta potential. It measures the particle's electrical charge while suspended in an aqueous phase.[31] Zeta potentials of the powdered adsorbent samples suspended in surfactant solutions were measured by an Anton Paar Litesizer 500 particle analyzer at a temperature of 30 °C. The magnitude of the zeta potential values is related to the wettability and mineralogy of the rock, along with the interfacial properties of the surfactants.[32] Zeta potential was measured by preparing a sandstone suspension by mixing 2.5 g of powdered sandstone in 1000 mL of distilled water. The sonicated sandstone powder suspension was obtained by using a Fisher Band FB15051 sonicator for 30 min. The samples collected after sonication were left for stabilization and then tested with varying concentrations of mixed surfactant solutions. Further, the sandstone powder was aged with crude oil, and the oil-aged sandstone powder particles were then treated with a surfactant solution to investigate their behavioral interactions with surfactant solutions. The reproducibility of the data was also checked by multiple measurements of the samples.

2.2.7. Core Flooding.
In chemical EOR, after the proper screening of the chemical slugs, core flooding experiments are generally performed to check the ability of the chemical slugs for EOR. The primary set of experiments includes the testing of chemical slugs for synergism of the two surfactants used in this study in terms of their ability to reduce IFT, alter the wettability, and improve the mobility ratio. The core-flooding experimental setup comprises a positive displacement syringe pump, fluid injection system, core holder, and fluid collectors. The schematic of the flooding experimental setup has been
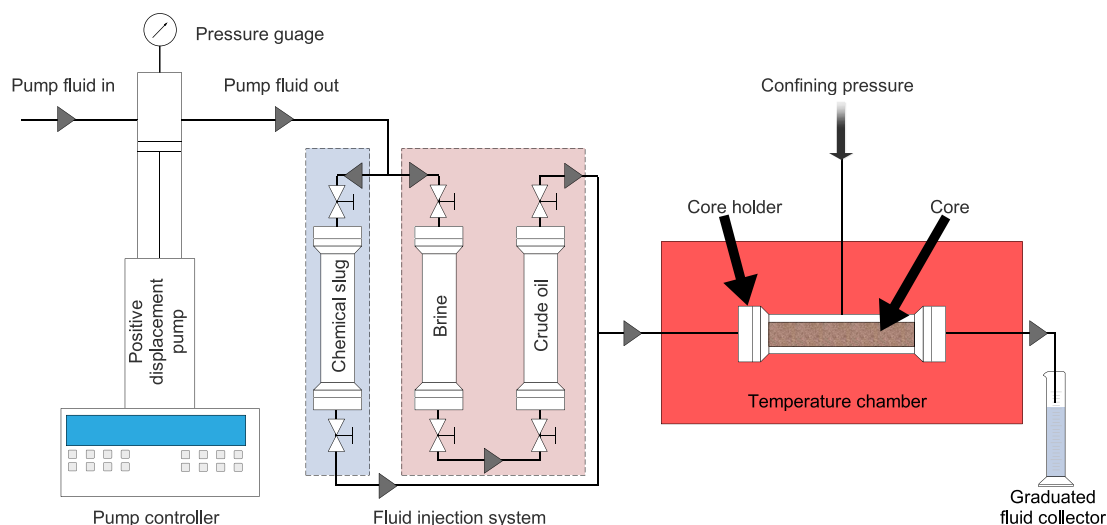
Figure 2. Core flooding experimental setup.

shown in Figure 2. The core sample is first cleaned properly in a Soxhlet apparatus and properly dried. Then, the core was saturated with brine and left for one week for proper brine displacement in the entire core. The water permeability of the core was determined by injecting brine water at 70 °C with different injection rates, and the slope method was used. Darcy's law, as given in eq 2, is used to calculate the permeability.

$$q = \frac{kA}{\mu} \frac{\Delta P}{\Delta x} \qquad (2)$$

where permeability (k) is calculated in Darcy, the flow rate (q) is calculated in cm^3/s, fluid viscosity (μ) is calculated in cP, length of core (l) is calculated in cm, cross-sectional area of core (A) is calculated in cm^2, and pressure differential (ΔP) is calculated in atm.

The crude oil was then injected into the core, initially saturated with water, to the irreducible water saturation level. The irreducible water saturation and initial oil saturation were measured using volume balance. The core, with its initial oil saturation, was aged to equilibrate the rock-fluid interaction. The water was flooded into the core at a constant flow rate of 0.3 mL/min, and the effluent at the outlet was collected in a graduated measuring cylinder. The water flooding is continued until the water content in the produced fluid reached more than 95%. After injection of one pore volume of predesigned chemical slug, chase water is introduced to drive the chemical slug forward, and additional oil recovery was calculated.

3. RESULTS AND DISCUSSION

3.1. Surface Tension. *3.1.1. Effect of Concentration of Surfactant Mixtures on Surface Tension.* Surfactants are widely known for lowering surface tension by getting adsorbed at the liquid–air interface. The most critical factor for surfactants is the cmc, the concentration at which the interface gets saturated by the adsorbed surfactant, and the excess surfactants form micelles inside the bulk of the solution.[33] The surface tension values of mixture surfactant solutions (Tergitol 15-S-12 and PEG 600) at different concentrations were measured while keeping the concentration of PEG 600 constant, as reported in Figure 3. It can be observed that the surface tension values gradually decrease with the increase in
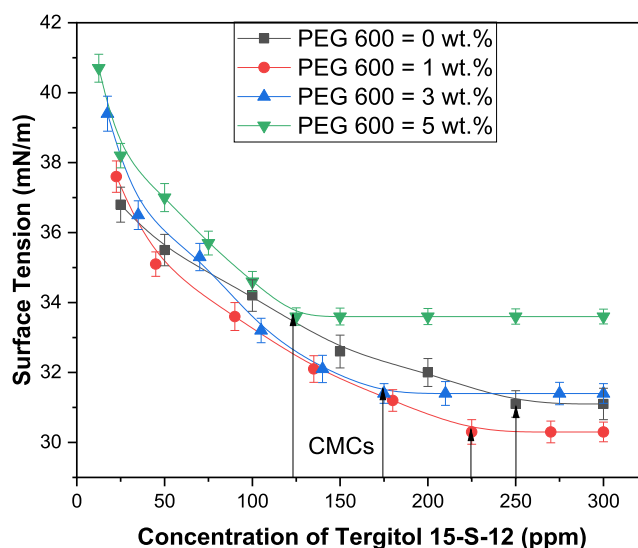

Figure 3. Surface tension vs. concentration of the mixed surfactant solutions at 30 °C.

concentration of Tergitol for all sets of solutions with constant PEG 600 concentration. At lower concentrations, the surfactant molecules move from the bulk solution to the air–water interface. With increasing concentration, the surfactant molecules occupy the vacant spaces at the air–water interface, thus reducing the surface tension. With further increase in concentration, the air–water interface gets saturated, resulting in the accumulation of molecules in the bulk solution to form micelles.[34] The cmc values of four different solutions are shown by an arrow mark in Figure 3. It has been found that the solution with 1 wt % PEG shows a better synergistic effect on surface tension with a minimum value of 30.3 mN/m at a cmc of 225 ppm of Tergitol.

3.1.2. Effect of Temperature on the Surface Tension of Surfactant Mixture. When surfactant solution is injected into the reservoir, its compatibility must be checked at the reservoir temperature. The surface tension values of the all the surfactant mixture solutions were performed at 30, 50, and 70 °C as shown in Figures 3–5 respectively. It may be observed from the figures, the surface tension of surfactant
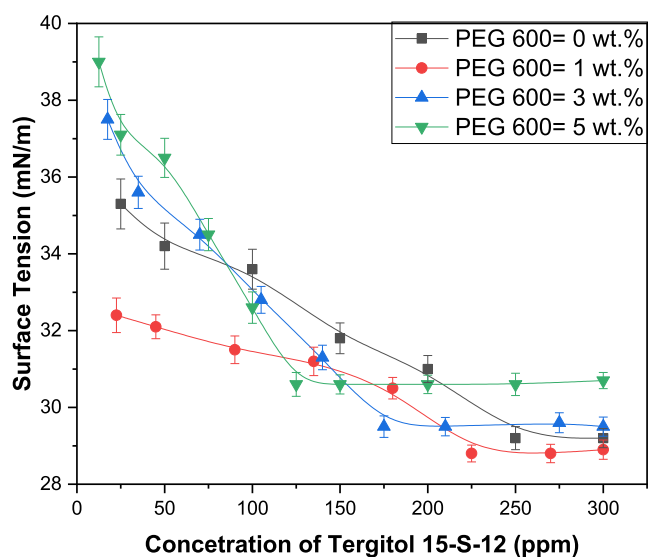
Figure 4. Surface tension vs. concentration of the mixed surfactant solutions at 50 °C.
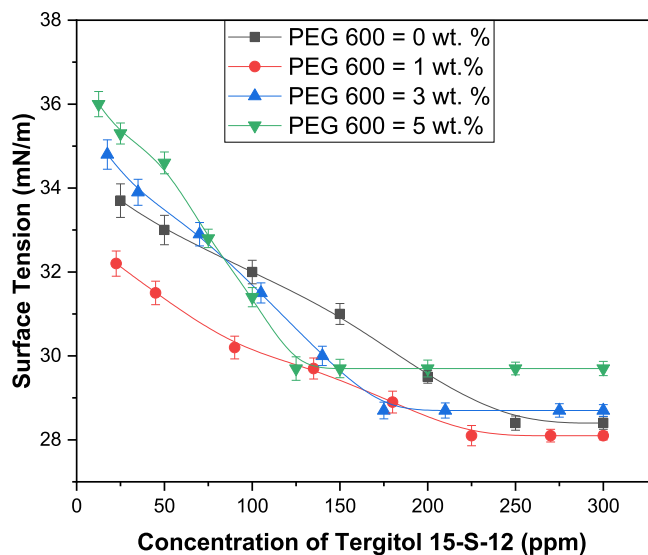

Figure 5. Surface tension vs. concentration of the mixed surfactant solutions at 70 °C.

solutions reduces with increasing temperature. This is due to the surfactant's increased solubility and the breaking of hydrogen bonds between water molecules and the surfactant's hydrophilic head. As the temperature of the surfactant solution rises, the hydrophobic interaction between surfactant molecules becomes more critical, boosting the rate of adsorption of surfactant monomers and forming a tight arrangement at the interface, resulting in decreased surface tension.[35] Temperature changes do not affect the cmc value of mixtures. The mixture surfactant solutions with 1 wt % of PEG 600 show the lowest surface tension values at all temperatures (30.3 mN/m at 30 °C, 28.8 mN/m at 50 °C, and 28.1 mN/m at 70 °C), as shown in the figures. As the minimum value of surface tension is achieved for surfactant solution with 1 wt % of PEG 600, it was maintained for further studies.

3.2. Interfacial Tension. The mobilization of trapped residual oil in the smaller pores is induced by the addition of surfactants in the injected fluid. The interaction of the surfactant solution with the crude oil lowers the IFT value at the interface and minimizes the capillary force that is required to flush the residual oil from the smaller pores. This raises the capillary number (N_c) to a desired value for efficient displacement of oil by injecting fluid. The performance of mixed surfactant solution in the reduction of IFT depends on the degree of adsorption of surface-active agents at the crude oil−water interface. The adsorption of surfactants at the interface is influenced by the nature of surfactant, concentration, temperature, and other factors.

3.2.1. Effect of Concentrations on IFT between Crude Oil and Surfactant Solutions. The concentration-dependent IFT values of solutions of Tergitol 15-S-12 with 1 wt % PEG 600 solutions are shown in Figure 6. The figure shows that the IFT
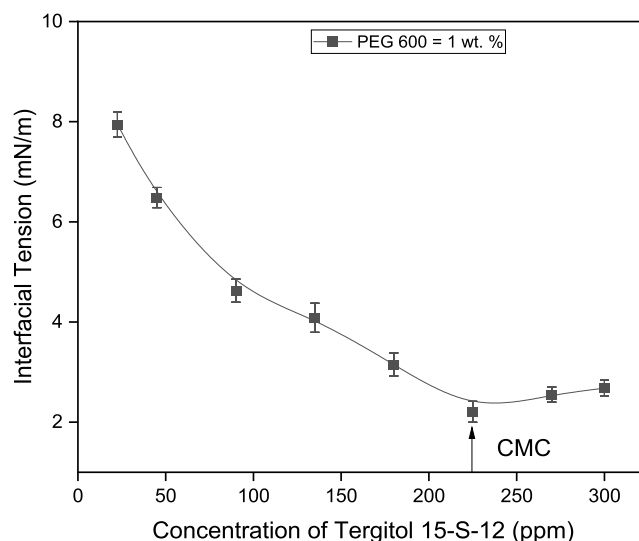

Figure 6. IFT with varying concentrations of Tergitol 15-S-12. ($T =$ 30 °C).

value decreases with increasing Tergitol concentration until 225 ppm, and further increasing the concentration results in the IFT value increasing as well. At lower concentrations, molecules of surfactant are preferentially adsorbed on the interface of oil−water in aqueous surfactant solutions. Hence, the IFT of solutions starts to decline. After that, the oil−water interface becomes saturated with surfactant monomers, and the IFT values reduce to a minimum. This surfactant concentration related to the minimum IFT is the cmc. Any surfactant added after cmc changes the size or structure of micelles and increases the total number of micelles, reducing the effective surfactant concentration, owing to micelle solubilization in the aqueous phase and surfactant molecule reduction at the interface, both of which cause the IFT to increase.[36] The minimum IFT value attained at 225 ppm of Tergitol is 2.20 mN/m.

3.2.2. Effect of Salinity on IFT. The presence of salt in surfactant solutions can affect the distribution of surface-active components from the oil phase to the aqueous phase. Several researchers have examined the influence of salt on IFT.[37] More surface-active agents tend to concentrate at the fluid interface in the saline environment and thus help in IFT reduction. In Figure 7, the effect of salt that is NaCl on the reduction of IFT was evaluated in the presence of Tergitol 15-S-12/PEG 600 mixed surfactant solutions at their respective cmc by plotting the IFT value against the salt concentration. NaCl concen-
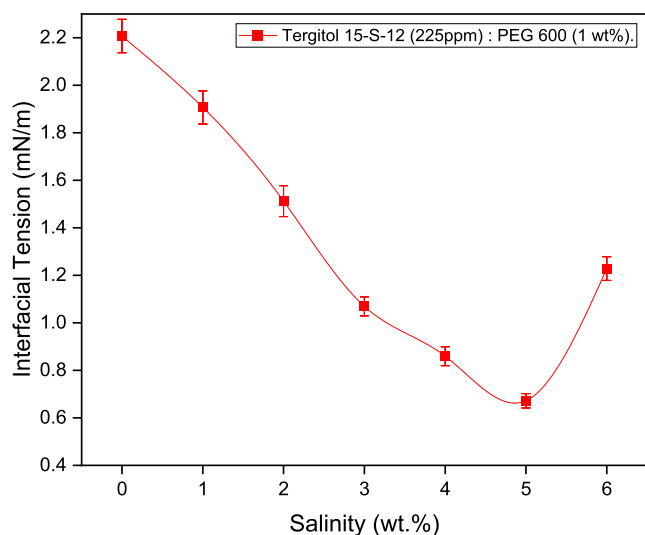
Figure 7. IFT of the Tergitol−PEG mixture with varying salt concentrations. (T = 30 °C).

tration was varied up to 6 wt % and showed its influence on IFT between surfactant solution and crude oil. IFT is observed at a minimum of 0.672 mN/m at 5 wt % NaCl. This is mainly due to the presence of salt, which decreases crude oil surface energy with surfactant solution.[38] With the increasing concentration of NaCl, the IFT values decline and attain the lowest value at some optimal salt concentration. Further increases in concentration beyond this optimal salt concentration increase the IFT value steadily. For Tergitol 15-S-12, the lowering in IFT caused by the addition of NaCl is due to the loosening of hydrogen bonds.[34]

3.3. Thermodynamics of Micellization and Adsorption. Understanding surfactant adsorption and micellization characteristics is critical in determining the optimal surfactant concentration and predicting beneficial applications. Various adsorption and micellization parameters are calculated for mixed surfactant solutions and reported in Table 1. Negative values of ΔG_{ads} and ΔG_{mic} indicate the occurrence of both processes, namely surfactant adsorption at the air−liquid interface and micelle formation in the bulk phase. The greater magnitude of ΔG_{ads} than ΔG_{mic} for each surfactant ratio at all temperatures suggests spontaneous adsorption rather than micellization. The addition of PEG 600 to Tergitol 15-S-12 reduces the Gibbs aggregation energy (ΔG_{mic}). Lower aggregation values reflect the greater capacity of surfactant

combinations to bind with water, thereby reducing the hydrophobic nature of the mixture. For all the mixing ratios, ΔG_{mic} values show a step increase in magnitude, indicating a significant increase in the hydrophobicity of the mixture. With the rising temperature, ΔG_{ads} values tend to become increasingly negative, implying that increased energy in the form of heat facilitates greater surfactant adsorption at all proportions. Surfactant concentration ratios of about 1 wt % provide the highest negative values G_{ads} for each temperature, showing the greatest synergy when blended in that proportion.

Increasing the concentration of PEG 600 in the Tergitol 15-S-12 for a fixed temperature causes a decrease in the value of A_{min} indicating an increase in surface activity and the adhesive force between air and the surfactant mixture. The increased adhesiveness seems to have enlarged the interfacial curvature and thus reduces the IFT.

The difference between interfacial concentration and concentration in the interior of the volume phase results in excess surface concentration. τ_{max} can be approximated by interfacial surfactant concentrations as the surface concentration is way too high compared to bulk concentration. The decrease in A_{min}, due to the increased PEG 600 concentration in the surfactant mixture, allows for a greater surfactant concentration at the interface. However, as the mixing ratio approaches 3 wt %, no substantial increase in τ_{max} is observed as surface activity cannot be further enhanced appreciably by the synergistic action of both nonionic surfactants and more surfactant mixtures are going to reside in the bulk phase.

Further, the role of temperature on the synergistic performance of both ionic surfactants can be interpreted from the increase in the Π_{cmc} for all the mixing ratios. The mixing ratio of 1 wt % has the greatest Π_{cmc} value of all the proportions, demonstrating the efficacy of the interaction between these two surfactants at that exact proportion.

3.4. Contact Angle. *3.4.1. Effects of Concentration of Chemical Slugs on the Contact Angle.* The majority of the world's oil reservoirs are intermediately wet.[39] In the reservoir, as crude oil remains in contact with the formation rock for long time asphaltenes, resins and other polar components of the oil get deposited on the rock surface, making the rock oil-wet or intermediate.[40] The recovery of oil from oil-wet or intermediate reservoir is difficult due to poor microscopic displacement efficiency.[41] The injection of surfactant alters the rock wettability by preferential adsorption on the rock surface. However, depending on the rock mineralogy proper selection of the surfactant is very much important.[12]

Table 1. Thermodynamic Parameters of Micellization and Adsorption

temp. (°C)	Tergitol/PEG 600 (wt %)	γ_{cmc} (mN/m)	Π_{cmc} (mN/m)	τ_{max} (10^{-6} mol/m^2)	A_{min} (10^{-6} m^2/molecule)	ΔG_{mic} (kJ/mol)	ΔG_{ads} (kJ/mol)
30	0	31.1	40.9	0.98	170.18	−30.24	−72.16
	1	30.3	41.7	1.22	136.62	−30.18	−64.49
	3	31.4	40.6	1.35	123.14	−30.07	−60.18
	5	33.6	38.4	1.15	143.97	−29.97	−63.26
50	0	29.2	42.8	0.90	184.23	−32.24	−79.72
	1	28.8	43.2	0.65	256.74	−32.18	−98.97
	3	29.5	42.5	1.20	138.93	−32.06	−67.62
	5	30.6	41.4	1.24	134.38	−31.95	−65.45
70	0	28.4	43.6	0.77	215.63	−34.23	−90.85
	1	28.1	43.9	0.70	236.77	−34.17	−96.76
	3	28.7	43.3	0.89	187.52	−34.04	−82.94
	5	29.7	42.3	0.90	184.98	−33.92	−81.05

Among the various parameters responsible for wettability alteration, the mineral composition of the rock sample is sought to be important factor driving the wetting character of the rock sample when exposed to the environment of surfactant solutions. The XRD analysis of the rock sample (sandstone) is shown in Figure 8, where the different observed
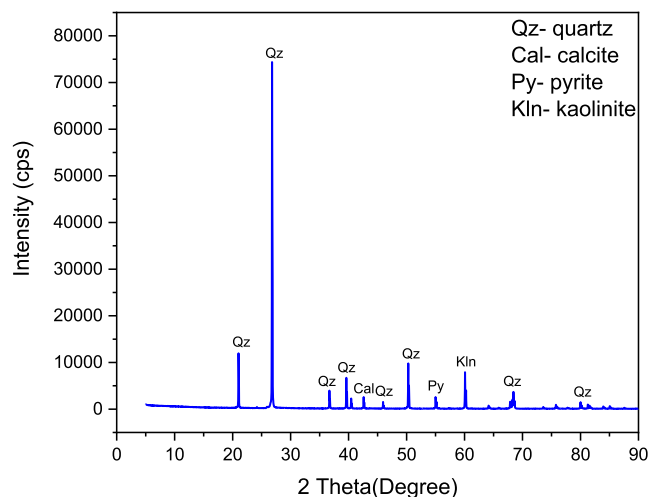

Figure 8. XRD of sandstone rock.

peaks are attributed to the presence of different minerals. Although multiple peaks are obtained at 21.7, 40.7, 50.9, 60.8, and 68.6, quartz is believed to be the dominant constituent of the rock specimen, with maximum peak intensity obtained at 21.7. XRD analysis indicated the presence of other minerals such as calcite, kaolinite, and pyrite. The contact angle of surfactant solution drop on the oil-wet rock specimen is measured against exposure time and shown in Figure 9. The
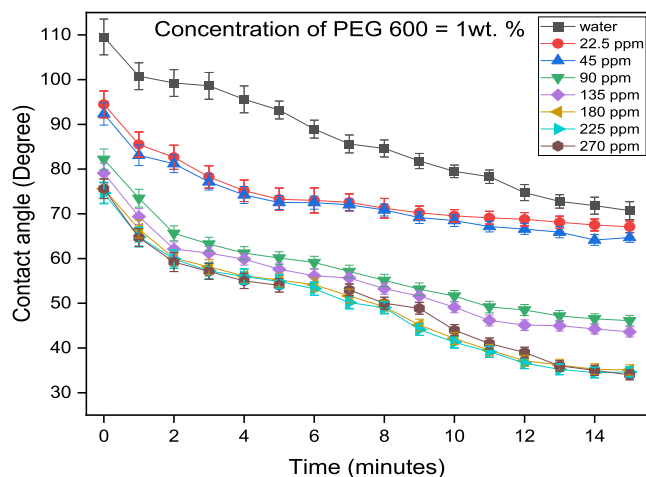

Figure 9. Variation of the contact angle with the concentration of Tergitol 12-S-15 and 1 wt % of PEG 600.

initial and final contact angles of surfactant solution drops at different concentrations and times are shown in Figure 10. The change of contact angle from initial measurement of 109.5° to 15 min measurement of 70.7° indicates the wetting preference to intermediate oil-wet. The contact angle decreases significantly as the concentration of surfactant is increased up to cmc. After the cmc concentration, the final contact angle obtained is almost constant, around 34°. The interaction
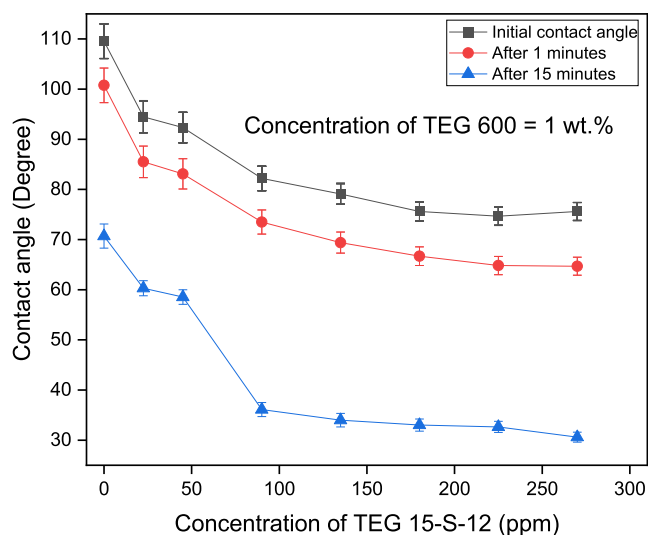

Figure 10. Variation of the contact angle with the concentration of mixed surfactant solutions at different times.

between the hydrophilic head of the surfactants and the adsorbed crude oil on the rock surface results in the formation of ion-pairs and influences the wettability alteration toward more water-wet wettability.[32,42] It was also shown that surfactant molecules co-adsorbed with the acid in crude oil exhibit a significant hydrophobic–hydrophobic interaction. Hence, the wetting characteristics have altered to be more water wet.[43] As shown in Figure 10, the contact angle of a solution drop of different surfactant concentrations, started measuring at $t = 0$ min, decreases as the surfactant concentration increases. It indicates that instant surface activity behavior of surfactant upon interaction with the rock surface, modifying its wettability behavior. Figure 11 shows images of a droplet of surfactant solution on a sandstone surface at various concentrations after 15 min. These images give a vivid depiction of the wettability alteration caused by the surfactant solution, showing its efficacy to alter the wetting characteristics to water-wet.
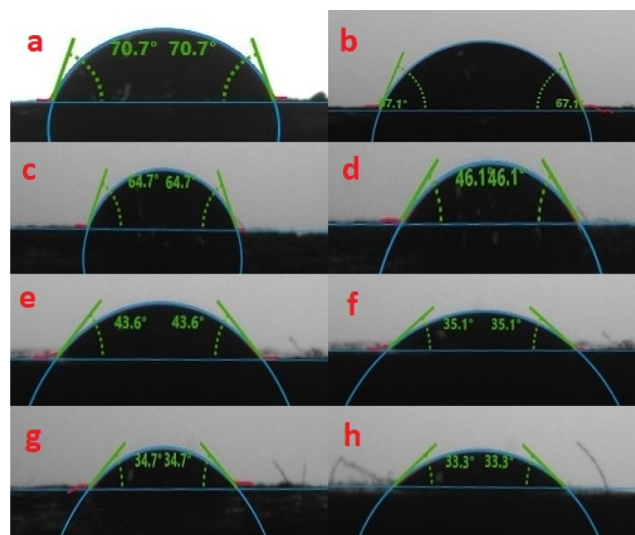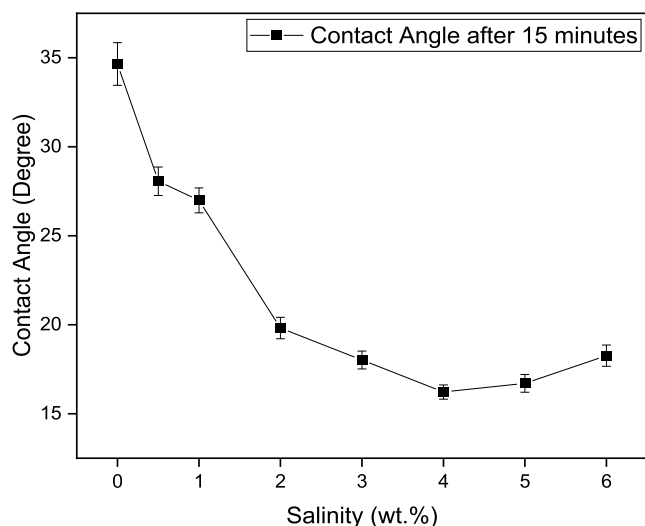

Figure 11. Images of the contact angle after 15 min with surfactant solution droplet concentrations of (a) 0, (b) 22.5, (c) 45, (d) 90, (e) 135, (f) 180, (g) 225, and (h) 270 ppm.

### 3.4.2. Effects of Various Salinity on the Contact Angle.
Figure 12 shows the effect of salinity on the contact angle for

Figure 12. Variation of the contact angle of Tergitol 15-S-12 solution at cmc of 225 ppm and 1 wt % of PEG 600 with salinity.

surfactant solutions of optimized concentration at its cmc on the oil-wet rock sample. It has been observed that there is an optimum salinity level at which the wettability alteration property of the surfactant solution is maximized. As shown in Figure 12, the wettability alteration properties of surfactant improve with increasing salt concentrations up to 4% salinity. This improvement is caused by surfactant molecules escaping from the bulk of the fluid phase and accumulating on the sandstone surface. Furthermore, when salinity exceeds 4%, the contact angle increases due to salt ion deposition on the sandstone surface.[43] Higher salt concentrations have a lower final contact angle than surfactant solution without salt. This suggests that the surfactant affects wettability alteration in a saline reservoir. Figure 13 shows that after 15 min, there is a variation in the contact angle in the 225 ppm surfactant solution with various salinities.

3.5. Zeta Potential. The zeta potential is measured to examine the effect of the optimized surfactant solution (Tergitol 12-S-15 at 225 ppm and 1 wt % PEG 600) and crude oil on sandstone powder and is shown in Figure 14. The zeta potential values are observed for the sandstone powder with and without surfactant solutions to be −30.2 and −35.6 mV respectively. This difference is attributed to the negatively charged sandstone particles suspended in the solution and the charge neutralization of the sandstone particles by hydrogen bonding in presence of nonionic Tergitol surfactant.[44] The zeta potential of crude oil-aged sandstone particles is less negative than that of sandstone particles alone. The variance is accounted for by the adsorption of polar amide groups and asphaltene compounds in the aging process and the alteration of the wettability from water-wet to oil-wet.[45] Crude oil has polar molecules that become physically adsorbed on the sandstone surface. Therefore, it reduces the negative charge. Th interaction of aged rock with a surfactant solution etches some of the crude oil from the rock surfaces so that there is a slight increase in negative charge as compared to crude oil-aged rock. The zeta potentials of crude-oil aged samples of sandstone powder with or without surfactant solution were
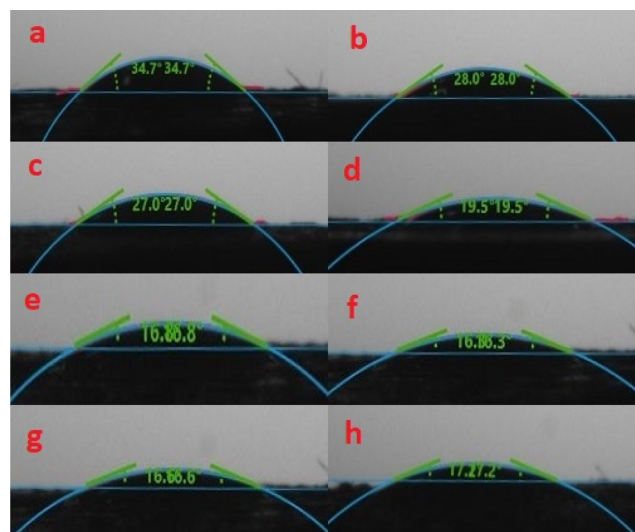
Figure 13. Contact angle after 15 min of 225 ppm surfactant solution droplet with various salinities of (a) 0, (b) 0.5, (c) 1, (d) 2, (e) 3, (f) 4, (g) 5, and (h) 6 wt %.
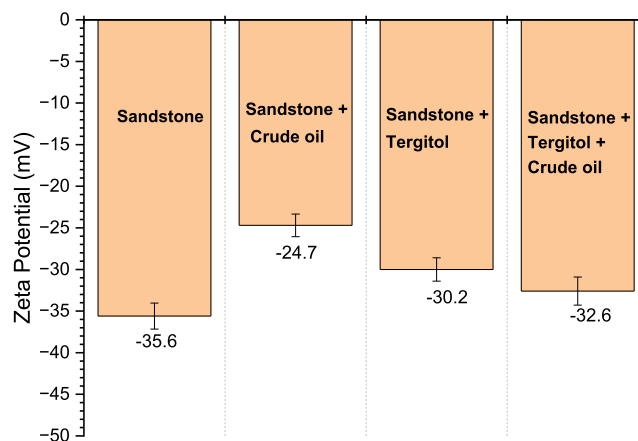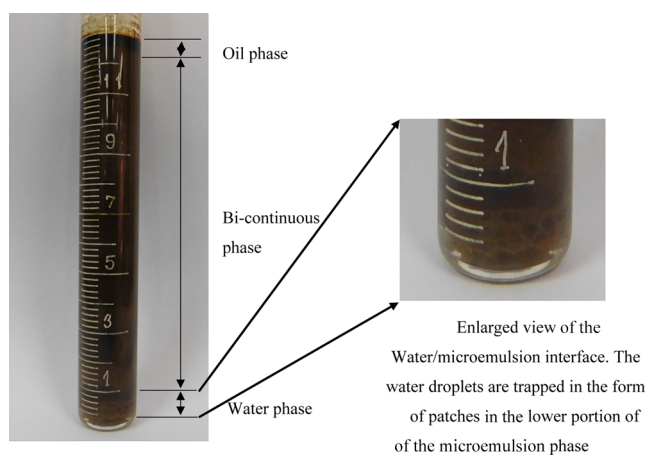

Figure 14. Effect of optimum surfactant solution on the zeta potential of sandstone and crude oil-aged sandstone particles at 30 °C.

−32.6 and −24.7 mV. The increased zeta potential values of surfactant-treated oil-aged sandstone demonstrate crude oil removal from the oil-wet rock surface.

3.6. Emulsification Study. Microemulsion study was performed by mixing surfactants in crude oil and water (water-to-oil ratio of 1) at increasing salinities using the high-energy emulsification process. A succession of Winsor-phase systems was formed for different salinities at 70 °C for evaluating the thermodynamic stability of the microemulsions so formed.

Since 4% wt salinity showed better oil/brine/rock interfacial properties, microemulsions of 4% wt salinity are shown in Figure 15 only. The Winsor III system is formed at 4% wt salinity, with bi-continuous microemulsions in equilibrium with excess oil and water phases. Type III microemulsion has been shown to be suitable for lowering residual oil saturation due to its special characteristics, including ultra-low IFT, thermodynamic stability, and the capacity to solubilize both oil and water. Salinity greater than the optimum level of 4% starts to decrease the oil-microemulsion IFT, trapping surfactant in residual oil (causing surfactant loss) and increase the water-microemulsion IFT, which in turn reduces the mobilization of
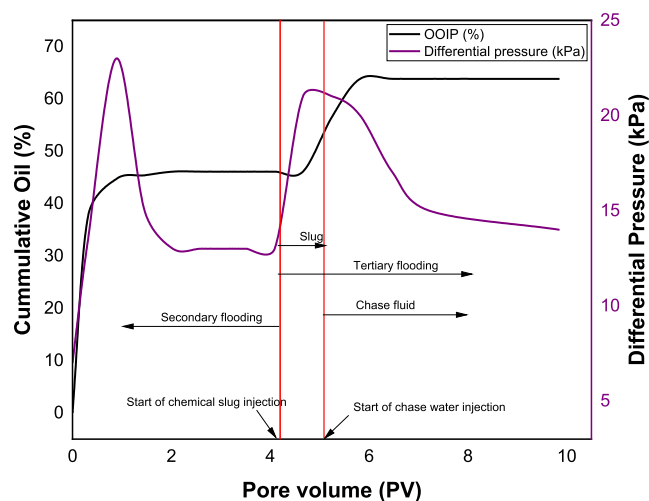
Figure 15. Phase behavior study of the microemulsion formed at 4% wt salinity and 70 °C.

Figure 16. Cumulative oil recovery and pressure differential with injection of water and mixture surfactant slug at 70 °C.

oil. Whereas salinity below 4% raises the oil-microemulsion IFT, which results in the minimization of oil mobilization, and decreases the water-microemulsion IFT to keep the surfactant in the water phase. In addition to that, approximately an equal amount of water and oil is co-solubilized in a microemulsion when kept for 15 days at 70 °C, implying the temperature to be close to an optimal temperature, T^*. Taking 4% wt as optimum salinity and optimum solubilization ratio (σ^*) to be around 430, the IFT of middle phase is calculated using the Chun Huh relation[46] and was found to be around 1.6225×10^{-6} mN/m, which lies in the ultralow IFT region and is favorable to EOR.

3.7. Core Flooding. On the basis of the screening, the optimum chemical formulation (Tergitol 12-S-15 with a concentration of 225 ppm and 1 wt % of PEG 600) was selected for further flooding experiments to ensure the effectiveness of the designed chemical slug solution for field applications. The petrophysical properties of the core and flooding results are summarized in Table 2.

Figure 16 shows the secondary oil recovery during water flooding was 46.09%. After injecting the formulated surfactant slug followed by the injection of chase water, the cumulative oil recovery increased to 68.8% of OOIP with an additional recovery of 17.73% of OOIP. Chemical slugs lower the IFT, which leads to formation of an oil bank and subsequent increase in the mobility of the tapped oil. The chemical slug also alters the wettability of the sandstone core toward more water-wet. The synergistic effects of two nonionic surfactants improve the microscopic displacement efficiency.[47] In Figure 16, pressure drop across the core as a function of pore volume of chemical slug injected in the core was examined. During the water flood injection, differential pressure reaches a maximum and then starts to decrease, ultimately achieving a constant value. The constant differential pressure indicates that the injected flood broke through. Later, the pressure difference rises with the injection of a chemical slug, mainly due to the formation of oil−water emulsions in the presence of the

surfactants, which raises the flooding fluid viscosity and hence the injection pressure.[48] After the injection of the chemical slug, when the chase water is injected, the pressure drops decrease and returns to a constant amount.

The pressure drop during the chase water flooding is still higher than the original water flooding. The reason is that the interaction of chemical agents with the surrounding reservoir environment, leading to their retention, adsorption, and emulsion, increases the residue resistance by blocking portions of the core's high-permeability flow-channels during the migration of emulsified oil droplets.[44,49]

3.8. Conclusions. The formulation and optimization of surfactant slugs according to reservoir conditions ensure their efficiency in EOR. In the present study, a series of experiments are performed at ambient and elevated temperatures to understand the interactions of mixed surfactants (Tergitol 12-S-15 and PEG 600) in aqueous solutions and their effects on surface tension, IFT behavior, and wettability alteration in oil-wet sandstone rock. The surfactants were selected based on their thermodynamic parameters of micellization and adsorption. The Gibbs free energy values of micellization and adsorption of the formulated mixed surfactant solutions indicate that the adsorption of the surfactants at the interface dominates micellization, which is desirable for their application in EOR. The synergism of Tergitol (15-S-12) and PEG 600 on surface tension (30.3 mN/m at cmc) and IFT (0.672 mN/m) is clearly observed, and the minimum values are obtained for the mixture of 225 ppm Tergitol 15-S-12 and 1 wt % of PEG 600. The salinity of the chemical slug plays a vital role as the minimum IFT is obtained at optimum salinity of 5 wt %. At optimum salinity, surfactants are dissolved almost equally in the oil and aqueous phases, which leads to the minimum IFT. The results of reduced surface tension and IFT demonstrate the beneficial effects of both the surfactant in mobilizing oil from sandstone surfaces. The non-ionic surfactant has proven

Table 2. Core Flooding Result

core sample	porosity (%)	absolute permeability (mD)	slug design (injection volume = 1 PV)	secondary oil recovery (%)	additional oil recovery (%)
sandstone	23.22	91.66	Tergitol 15-S-12 of conc. 225 ppm and PEG 600 of 1 wt %; and 0.2% NaCl	46.09	17.73

to efficiently release crude oil from sandstone because of its potential to minimize oil−water IFT and, hence, improve the wettability alteration of oil-wet sandstone rock. The surfactant solutions reduce the contact angle significantly, which is further reduced around the optimum salinity. The surfactants are preferably adsorbed on the sandstone rock surface and expels the adsorbed oil from it, which leads to an improvement in oil recovery, which is also evidenced by the zeta potential values. The efficacy of the optimized chemical slug was tested by core flooding experiments, and an additional recovery of 17.73% OOIP was obtained by injection of 1 pore volume of chemical slug after the conventional water flooding. The increase in differential pressure after injection of surfactant slug during flooding indicates that emulsification is also an important mechanism of additional oil recovery.

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Notes

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