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Optimized Guerbet Alkoxy Carboxylate Surfactant Formulations for EOR in Carbonates Under Harsh Conditions

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Abstract

Surfactant flooding is a proven chemical flooding technique with limited applications in carbonates, especially in the Middle East, due to prevailing conditions of high temperature, high salinity (HTHS), and mixed-to-oil wettability. Under such conditions, surfactants break down or become inefficient, limiting their effectiveness for enhanced oil recovery (EOR) applications. This study evaluates the efficiency and stability of superior chemistry carboxylate-based anionic surfactant blends for EOR applications in Middle East HTHS carbonate reservoirs. The study employed a range of tests to identify optimal surfactant blends for HTHS carbonate conditions, including thermal and aqueous stability tests and phase behavior analyses for salinity optimization. Both carboxylate and internal olefin sulfonate surfactants were utilized at elevated temperatures and salinities, up to 120°C and 170 kppm, respectively. Stable formulations were selected based on their performance under these representative field conditions. Interfacial tension was measured using a spinning drop tensiometer and verified using Huh correlation during phase behavior studies. The screening was further supported by surfactant retention to ensure efficiency and economic viability through both static and dynamic studies. Moreover, a coreflooding experiment was conducted to evaluate incremental oil recovery through this optimized surfactant formulation.

The study demonstrated that specific blends of alkyl ethoxy carboxylate surfactants with internal olefin sulfonate co-surfactants are highly effective in terms of thermal and aqueous stability. These blends consistently maintained transparent, homogeneous solutions without any noticeable turbidity, even when exposed to rigorous reservoir conditions characterized by elevated temperature and salinity. However, for reservoirs with higher salinity, seawater pre-flush is recommended to condition the formation before surfactant injection. The surfactant blends also demonstrated ultra-low interfacial tensions in the order of 10^{-3} at their optimal salinity levels, close to seawater salinity (43 kppm). This was confirmed by spinning

drop measurements and Huh correlation. In parallel, contact-angle measurements showed a shift from strongly oil-wet (~161 °) to water-wet (~69°) conditions, confirming that the formulations induce favorable wettability alteration alongside IFT reduction. Additionally, the surfactant blends exhibited low adsorption onto carbonate rock surfaces, with retention values within the generally accepted economic viability range (~0.1 to 0.2 mg/g-rock), underscoring their suitability and promise for practical EOR applications in harsh, high-temperature, and high-salinity carbonate reservoir environments. Coreflooding experiments further validated the effectiveness of the optimized surfactant blend, achieving a significant incremental oil recovery of 22.9% OOIP (≈ 76 % of S_{orw}) —16.5 % OOIP from the surfactant slug (≈ 55 % of S_{orw}) and a further 6.4 % OOIP from the salinity-gradient post-flush (≈ 21 % of S_{orw}). This study expands the envelope of surfactant flooding EOR applications to Middle East HTHS carbonate reservoirs. By introducing a holistic evaluation framework integrating thermal and aqueous stability, interfacial tension, phase behavior, and salinity optimization, this research highlights the potential of surfactant-based EOR for harsh reservoir conditions. Although further research is necessary to address all challenges associated with surfactant-based EOR in carbonates, the insights gained establish a foundation and pave the way for possible future field-scale applications.

Introduction and Background

Carbonate reservoirs contain an estimated 60% of the world's oil reserves, with many giant carbonate oil fields located in the Middle East. These reservoirs are typically characterized by high temperature, high salinity (HTHS), mixed-to-oil wettability conditions, and are highly heterogeneous. These conditions are, in general, very challenging for EOR applications.

Chemical-enhanced oil recovery (CEOR) methods, particularly surfactant flooding, have shown significant potential to mobilize trapped residual oil by achieving an ultra-low oil-water interfacial tension (IFT). However, extending surfactant EOR to HTHS carbonate reservoirs has historically been challenging due to chemical instability and precipitation issues (Mogensen and Masalmeh, 2020). Subsequent research efforts increasingly focused on the development of anionic surfactants, which demonstrated efficacy in substantially reducing interfacial tensions. However, their application has often been hampered by precipitation and stability issues associated with divalent cations prevalent in carbonate brines (Hirasaki and Zhang, 2004).

A practical mitigation strategy is to inject a lower-salinity water (seawater) pre-flush to dilute formation brine and minimize divalent-ion interactions before the surfactant slug is introduced (Al-Shalabi et al., 2015). Traditional surfactants such as sulfates hydrolyze at temperatures above approximately 60°C, significantly reducing their effectiveness in carbonate reservoirs (Adkins *et al*., 2010). Moreover, carbonate formations containing divalent ions (Ca^{2+}, Mg^{2+}) cause precipitation or adsorption of conventional anionic surfactants, severely compromising chemical efficiency and leading to economic infeasibility (ShamsiJazeyi *et al*., 2014).

A significant breakthrough emerged with surfactants derived from Guerbet alcohols, providing large branched hydrophobic tails essential for maintaining surfactant stability in harsh brine environments (Adkins *et al*., 2010). Initially, Guerbet alkoxy sulfate surfactants showed promising ultra-low IFT performance and phase stability in saline brines. However, sulfate-based surfactants faced severe thermal stability issues, decomposing at temperatures exceeding 60°C under neutral pH conditions (Adkins *et al*., 2010). This critical limitation prompted the development of more thermally stable headgroups, such as carboxylates. Replacing sulfate groups with carboxylate headgroups substantially enhanced thermal stability, extending operational temperature limits beyond 120°C without degradation (Adkins *et al*., 2012; Lu *et al*., 2014). Guerbet Alkoxy Carboxylate (GAC) surfactants feature tailored ethylene oxide (EO) and propylene oxide (PO) content, tuned to achieve ultra-low IFT values (~10^{-3}–10^{-4} mN/m) even under harsh carbonate conditions with extremely high salinity (>150,000 ppm) and high divalent ion concentrations

(Solairaj *et al.*, 2012). The EO and PO segments synergistically enhance aqueous solubility, stabilize microemulsions, improve interfacial penetration, and minimize surfactant precipitation, rendering them ideal for harsh carbonate reservoir conditions (Panthi and Mohanty, 2024). Despite progress in surfactant design, most formulations fail in HTHS carbonate reservoirs due to either thermal degradation, precipitation with divalent ions, or high adsorption, limiting EOR efficacy. This study addresses these gaps through comprehensive laboratory testing and optimization of various GAC/IOS surfactant blends, achieving the stability, ultra-low IFT, wettability alteration, and oil-recovery performance required for Middle-Eastern HTHS reservoirs (up to 120 °C and 170,000 ppm salinity).

These Guerbet Alkoxy Carboxylate (GAC) surfactants have provided novel pathways to overcome the longstanding challenges in carbonates (Adkins *et al*., 2012; Lu *et al*., 2014). Unlike sulfate-based surfactants, GAC surfactants contain carboxylate headgroups coupled with large branched hydrophobic tails derived from Guerbet alcohols and tailored ethylene oxide (EO) and propylene oxide (PO) units. The unique molecular structure of these surfactants provides excellent thermal stability, allowing reliable performance at temperatures of 120°C or higher. Additionally, this architecture imparts strong resistance to precipitation or chemical degradation, even in highly saline and hard brine environments, without the need for alkaline additives (Solairaj *et al*., 2012). The specifically tailored EO/PO composition plays a crucial role in stabilizing microemulsions, significantly lowering interfacial tensions, and minimizing surfactant adsorption onto carbonate mineral surfaces. Collectively, these properties markedly surpass those of previous surfactant generations, establishing GAC surfactants as particularly advantageous for chemical enhanced oil recovery (CEOR) in challenging high-temperature, high-salinity carbonate reservoir environments (Lu *et al*., 2014; Panthi and Mohanty, 2024).

For a clearer depiction of the inherent structural differences and corresponding features of sulfate-based, sulfonate-based (IOS), and GAC-based surfactants, Table 1 provides a detailed comparison of their molecular structures. The tailored EO/PO segments, distinctive hydrophilic headgroups, and hydrophobic tails are highlighted, emphasizing why GAC surfactants exhibit superior stability, minimal adsorption, ultra-low interfacial tension (IFT), and improved wettability alteration under harsh carbonate reservoir conditions (Lu *et al*., 2014; Adel *et al*., 2023; Panthi and Mohanty, 2024).

Table 1—Summary of molecular structure and features of surfactant classes for CEOR in carbonate reservoirs

Surfactant Class	Molecular Structure & Features
Sulfate-Based Surfactants (e.g., Alkyl Sulfates)	**Headgroup:** Sulfate ($–O–SO_3^-$ Na^+) **Tail:** Linear alkyl (C12–C18) **EO/PO:** Typically absent
Sulfonate-Based Surfactants (IOS)	**Headgroup:** Sulfonate ($–SO_3^-$ Na^+) **Tail:** Linear/branched alkyl (C15–C28) **EO/PO:** Usually absent or minimal EO units
Guerbet Alkoxy Carboxylate (GAC)	**Headgroup:** Carboxylate ($–O–(EO)x–(PO)y–COO^-$ Na^+) **Tail:** Branched Guerbet alcohol (C24–C45) **EO/PO:** Tuned EO/PO units

Data Sources: Zhao *et al*. (2008), Adkins *et al.* (2010, 2012), Solairaj *et al*. (2012), Lu *et al.* (2014), Levitt *et al.* (2009), Maubert *et al*. (2018), Panthi and Mohanty (2024).

Table 2 summarizes the comparative strengths and limitations of sulfate, sulfonate, and carboxylate-based surfactants under high-temperature, high-salinity carbonate conditions, clearly highlighting why GAC surfactants are strategically advantageous for this study. The novelty and significance of this research lie in demonstrating the comprehensive effectiveness and practical viability of optimized GAC surfactant blends under these challenging Middle Eastern carbonate reservoir conditions. These findings provide a robust

technical foundation for advancing chemical EOR operations, ultimately unlocking substantial additional oil recovery from carbonate reservoirs historically viewed as chemically infeasible.

Table 2—Comparative properties of surfactant classes for Chemical EOR in carbonate reservoirs

Property / Performance Metric	Sulfate-Based Surfactants	Sulfonate-Based Surfactants (IOS)	Carboxylate-Based Surfactants (GAC)
Thermal Stability (°C)	≤60°C (limited by hydrolysis)	~90–100°C (moderate stability)	≥120°C (excellent stability)
Chemical Stability (pH)	Requires alkaline conditions	Stable across wide pH range	Stable across broad pH range
Salinity Tolerance (ppm TDS)	Moderate (<50,000 ppm)	Good (50,000–150,000 ppm)	Excellent (>150,000 ppm)
Hardness Tolerance (Ca^{2+}, Mg^{2+})	Limited (precipitates readily)	Moderate (possible precipitation)	High (minimal precipitation risk)
Wettability Alteration Ability	Limited	Moderate	Good (effective wettability alteration)
IFT Reduction Capability (mN/m)	Good (10^{-2} to 10^{-3} mN/m)	Good (10^{-2} to 10^{-3} mN/m)	Excellent (10^{-3} to 10^{-4} mN/m)
Adsorption & Retention (mg/g-rock)	High (>2 mg/g-rock)	Moderate (0.5–2 mg/g-rock)	Low (0.1–0.5 mg/g-rock)
Cost & Availability	Moderate cost (standard synthesis)	Low cost (commodity production)	Moderate-high (complex synthesis)
Recommended Field Application	Not recommended for typical Middle East carbonate conditions (>80°C, >100,000 ppm TDS)	Possible (with stabilization measures)	Highly recommended (optimized for HTHS conditions)

Data Sources: Zhao *et al.* (2008), Adkins *et al.* (2010), Solairaj *et al.* (2012), Lu *et al.* (2014), Panthi and Mohanty (2024).

Recent coreflooding studies have shown that GAC surfactants can successfully mobilize and recover over 90% of residual oil from carbonate formations under severe conditions of high temperature and salinity, while concurrently exhibiting notably low retention values around 0.2 mg/g-rock. This performance is attributed to their branched structures and the steric hindrance provided by EO/PO chains, significantly reducing adsorption on carbonate surfaces (Lu *et al.*, 2014; Panthi and Mohanty, 2024). These promising coreflooding results underscore the substantial potential of GAC-based surfactant formulations to be successfully scaled up for field implementation, particularly addressing the persistent challenges posed by Middle Eastern carbonate reservoirs.

The synergistic blending of Guerbet Alkoxy Carboxylate (GAC) surfactants with internal olefin sulfonates (IOS) has recently emerged as a highly effective strategy, yielding significant performance improvements. IOS surfactants themselves are recognized for their cost-effectiveness, broad salinity tolerance, and moderate ability to lower interfacial tension (IFT). When carefully combined with GAC surfactants, these blends display an expanded operational salinity range, enhanced aqueous-phase stability, and notably reduced optimal salinity levels. This combined effect considerably surpasses the performance achievable with either surfactant individually (Zhao *et al.*, 2008; Lu *et al.*, 2014). Such synergistic behavior stems from the complementary roles each surfactant type plays: IOS surfactants primarily enhance stability within the aqueous phase and widen the operational salinity window, whereas the GAC surfactants contribute significantly to reducing interfacial tensions through their robust interfacial activity (Panthi and Mohanty, 2024).

Achieving meaningful wettability alteration in carbonate reservoirs strongly depends on the interactions between surfactant molecules and the positively charged surfaces of carbonate minerals. Recent research has indicated that the adsorption behavior of GAC surfactants and their IOS blends effectively transitions the wettability conditions toward water-wet states. This alteration occurs as surfactant monolayers gradually replace the previously adsorbed oil films on the carbonate surfaces (Lu *et al.*, 2014; Panthi and Mohanty,

2024). Additionally, the ethylene oxide (EO) and propylene oxide (PO) segments incorporated into the surfactant structures are critical, as they help mitigate electrostatic interactions between the surfactants and calcite surfaces, thus significantly reducing the affinity of surfactant molecules for carbonate surfaces and ultimately minimizing the extent of surfactant retention.

Table 3 benchmarks recent coreflooding studies conducted under HTHS carbonate-reservoir conditions with optimized GAC/IOS surfactant blends. The comparative data underscore two key advantages of these formulations: (i) high incremental oil recovery and (ii) consistently low surfactant retention—even in tight (≈10 mD) carbonates—supporting their viability for field-scale deployment. Notably, although the blends are qualified to remain stable at reservoir temperatures near 100 °C and formation-brine salinities approaching 170,000 ppm TDS, they are actually injected as lower-salinity slugs (in this study, seawater ≈ 43 373 ppm TDS) after a seawater pre-flush, thereby delivering competitive–to-superior performance while minimising chemical usage under harsh conditions.

Table 3—Coreflood Benchmarking of GAC/IOS Surfactant Systems in Carbonate Reservoirs

Reference	Core Perm	Temp (°C)	Formation Salinity (ppm)	Slug Salinity (ppm)	Surfactant Formulation	Cosolvent Alkali Polymer	Incremental CEOR Rec. (%OOIP)	Total Rec. (%OOIP)	Retention (mg g^{-1})
Lu et al. 2014	Estaillade limestone / 10 mD	100	117 000	43 000	1.0 % GAC C28-25PO-55EO 0.25 % IOS C15-18 0.15 % IOS C19-23	TEGBE 1 % – –	≈ 30	≈ 80	0.30
Parra et al. 2016	Silurian dolomite / 45 mD	78	100 000	60 000	0.5 % GAC C28-25PO-45EO 0.20 % IOS C15-18 0.30 % IOS C19-28	– Na_2CO_3 3 % –	≈ 28	≈ 91	–
Maubert et al. 2018	Indiana limestone / 26 mD	83	58 000	58 000	0.5 % GAC C28-35PO-20EO 0.25 % IOS C15-18 0.25 % IOS C19-23	IBA-3EO 1 % NaOH 0.3 % HPAM	35–40	99.2	0.15
Ghosh & Mohanty 2019	Indiana limestone / 29 mD	80	90 000	90 000	0.5 % GAC C23-35PO-40EO 0.25 % IOS C15-18 0.15 % IOS C19-23	Phenol-5EO 0.25 % – HPAM	30–35	98.2	0.29
Abalkhail et al. 2020	Indiana limestone / 25 mD	100	60 000	60 000	0.5 % GAC C28-35PO-65EO 0.25 % IOS C15-18 0.25 % IOS C19-28	DIPA-10EO 1 % NH_3 0.75 % HPAM	≈ 30	93.6	0.11
Mejía et al. 2021	Texas Cream limestone / 23 mD	78	116 000	60 000	0.5 % GAC C28-25PO-45EO 0.20 % IOS C15-18 0.30 % IOS C19-23	– Na_2CO_3 2 % + NaOH 0.5 % –	≈ 22	52.0	0.11
Adel et al. 2025 (This Study)	Indiana limestone / 27 mD	100	167 000	43 373	0.5 % GAC-4 0.25 % IOS C15-18 0.25 % IOS C20-24	ethoxylated-phenol 0.5 % – –	22.9	92.8	0.16

While several published corefloods (e.g., Lu *et al.,* 2014; Ghosh & Mohanty, 2019; Abalkhail *et al.,* 2020) do investigate surfactant flooding at high temperature and high salinity, most rely on North-American crudes, moderate-permeability plugs, or do not couple wettability alteration, adsorption, and injectivity in a single workflow. The present study advances the state of knowledge by evaluating a Middle-East-specific GAC/IOS system under fully integrated conditions—carbonate core aged in representative crude oil at reservoir temperature, 170,000 ppm formation brine, seawater-slug injection, and a full suite of rock-fluid tests. The tests include thermal and aqueous stability screening, salinity-scan phase behavior, ultra-low IFT measurements, wettability testing, static/dynamic adsorption, and high-temperature coreflooding. The coreflood achieves 22.9 % OOIP incremental recovery (≈ 76 % of S_{orw}) with only 0.16 mg g^{1} retention —showing a balanced performance envelope that is directly applicable to Middle-East carbonate fields.

Nonetheless, prior to recommending field-scale implementation, the full workflow will be repeated on preserved reservoir core plugs to confirm surfactant performance under true mineralogy, connate-fluid composition, and in-situ wettability.

Materials and Methods

Materials

This subsection includes a description of different materials used in this work and their properties, including surfactants and surfactant formulations, brines, crude oil, and rock samples.

Surfactants and Chemicals. The primary surfactants evaluated were Guerbet Alkoxy Carboxylates (GAC) and Internal Olefin Sulfonates (IOS). GAC surfactants included long-chain (C24, C28) and short-chain (C13, C18) variants and were obtained from Ultimate EOR Services. An ethoxylated-phenol co-solvent used to enhance phase behavior and reduce equilibration times was also sourced from Ultimate EOR Services. IOS15–18 and IOS20–24 were obtained from Stepan Company. Sodium chloride (NaCl), calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$), magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$), sodium sulfate (Na_2SO_4), and sodium bicarbonate ($NaHCO_3$) for brine preparation were purchased from Sigma-Aldrich.

Surfactant Formulations. Five optimized surfactant formulations (SF0–SF4) were systematically evaluated in this study. All formulations included carboxylate-based anionic surfactants (Guerbet Alkoxy Carboxylates (GAC)), internal olefin sulfonates (IOS), and an ethoxylated-phenol co-solvent (0.5 wt%). Specific formulations are defined below (all concentrations by weight percent, wt%):

- **SF0**: 0.5 % GAC-4 + 0.5 % IOS15 + 0.5 % ethoxylated-phenol co-solvent
- **SF1**: 0.5 % GAC-1 + 0.25 % IOS15 + 0.25 % IOS20 + 0.5 % ethoxylated-phenol co-solvent
- **SF2**: 0.5 % GAC-2 + 0.25 % IOS15 + 0.25 % IOS20 + 0.5 % ethoxylated-phenol co-solvent
- **SF3**: 0.5 % GAC-3 + 0.25 % IOS15 + 0.25 % IOS20 + 0.5 % ethoxylated-phenol co-solvent
- **SF4**: 0.5 % GAC-4 + 0.25 % IOS15 + 0.25 % IOS20 + 0.5 % ethoxylated-phenol co-solvent

GAC series (GAC-1 → GAC-4) : Branched alkoxy-carboxylates with progressively longer Guerbet tails (short → long). GAC-1 to -3 are PO-rich (PO > EO); GAC-4 has PO = EO, giving the highest HLB.

IOS series: IOS15 (C15–18 internal-olefin sulfonate) and IOS20 (C20–24) have identical head-groups; IOS20's longer tail broadens oil-solubilisation at high salinity. These blends were selected to systematically probe the impact of carboxylate tail length and PO/EO balance on aqueous stability, optimum salinity, ultralow IFT, wettability alteration, and surfactant retention at 100 °C and 170 kppm conditions representative of Middle-Eastern carbonate reservoirs.

Brines. Synthetic seawater (SW) and synthetic formation water (FW) were prepared. SW had a salinity of 43,373 ppm, hardness of 2,122 ppm, density of 1.044 g/cm^3, and viscosity of 1.08 cP. FW had a salinity of 167,301 ppm, hardness of 10,696 ppm, density of 1.166 g/cm^3, and viscosity of 1.25 cP. All density and viscosity values were measured at room temperature (~25 °C). Both brines were prepared without bicarbonate and sulfate ions to maintain ionic strength and avoid precipitation issues.

Crude Oil. Stock tank crude oil from a Middle Eastern carbonate reservoir in Abu Dhabi was used. The crude oil had a density of 0.85 g/cm^3 (API gravity ~35°) and a viscosity of 5.34 cP at 25°C. No additional acid number treatments were required due to its low acid number, indicating minimal natural acids. The crude oil was filtered (5 μm filter) and centrifuged prior to use to remove any solids or water. The same crude oil was utilized for aging core samples, ensuring consistent initial wettability conditions.

Rock Samples. Outcrop Indiana limestone was employed as an analog core material, given its mineralogical similarity with Abu Dhabi carbonates (calcite content >98%). The porosity of the core utilized in this study was approximately 18%, and its measured air permeability was about 27 mD. Prior to experiments, cores underwent Soxhlet extraction (methanol/ethanol) and drying to ensure purity. Crushed Indiana limestone (grain size: 63–250 μm) and crushed reservoir rock cuttings (grain size: 125–250 μm) were used for static adsorption tests.

Methods

This subsection includes a description of different experiments conducted in this work, including aqueous and thermal stability tests, interfacial tension (IFT) measurements, phase behavior tests, contact angle measurements, static adsorption tests, coreflooding experiment for oil recovery and dynamic retention, and HPLC analytical measurements for determining surfactant concentrations.

Aqueous and Thermal Stability Tests. To evaluate thermal stability, surfactant solutions were prepared at 1 wt% using synthetic brines with varying salinity levels. These solutions were then sealed in transparent ampoules and subjected to a temperature of 100°C for one month. Throughout this duration, periodic visual assessments were carried out, carefully noting any signs of instability such as changes in color, formation of precipitates, or the appearance of turbidity, thereby ensuring precise detection of any thermal instability issues.

Aqueous stability was determined by quantifying each formulation's cloud point or precipitation limit as a function of salinity. Each surfactant formulation (1 wt% total active matter) was prepared by incrementally increasing brine salinity until the solution turned visibly turbid. The highest salinity at which the surfactant remained a clear, single-phase solution at 100°C was recorded as the aqueous stability limit. Stability at lower salinities was also observed, though low-salinity stability was generally not challenging due to inherent surfactant solubility; the primary challenge was stability at high salinities typical of reservoir conditions. These stability tests ensured the chosen formulations would remain stable upon contact with high-salinity formation water during coreflooding, representing the conditions likely encountered during actual reservoir flooding processes.

Interfacial Tension (IFT) Measurements. IFT between the crude oil and surfactant formulations was measured using two complementary methods:

1. *Spinning Drop Tensiometry* was used for accurately measuring ultra-low IFT values (~10^{-3} mN/m). A surfactant-rich aqueous droplet was injected into a rotating capillary tube filled with crude oil. At high rotational speeds, the droplet elongates due to density differences. The equilibrium droplet shape allowed the determination of IFT via the Vonnegut equation (Vonnegut, 1942). This relationship links the centrifugal elongation of the drop to the IFT and is widely adopted in modern spinning-drop tensiometry. Spinning drop measurements were performed at varying temperatures (25–90°C), and IFT values were extrapolated to reservoir-relevant temperatures (100°C).
2. *Pendant Drop Tensiometry* was utilized for baseline (high) IFT measurements at ambient conditions. A droplet of crude oil was formed at the tip of a needle immersed in seawater without surfactant, and the droplet shape was analyzed to determine IFT. Baseline IFT between crude oil and seawater (without surfactant) averaged 21.5 mN/m (at 25°C) over three repeat runs.

All ultra-low IFT measurements obtained by spinning drop tensiometry were further validated by calculating IFT from measured solubilization ratios at optimum salinity using the established empirical relationship known as Huh's correlation (Huh, 1979):

$$\sigma^* = \frac{0.3}{R^{*2}} \quad (1)$$

where σ* represents the interfacial tension at optimum conditions (mN/m), and R* represents the optimal solubilization ratio (volume of oil or water solubilized per volume of surfactant). The empirical constant (0.3) used in Huh's correlation has been extensively validated through experimental data and remains widely accepted in surfactant-enhanced oil recovery (EOR) literature (Huh, 1979; Sheng, 2011; Green and Willhite, 2018).

Phase Behavior Experiments. Phase behavior studies were conducted to determine each surfactant formulation's optimum salinity and corresponding solubilization ratios. Two ml of crude oil and surfactant solutions (1:1 oil-to-water ratio) were mixed in sealed transparent pipettes (5 mL volume) and equilibrated at the reservoir target temperature (100°C). For each surfactant formulation (SF0–SF4), a salinity scan was performed: a series of samples were prepared at incrementally varied brine salinities (from ~10,000 ppm up to the precipitation limit near 100,000 ppm NaCl) while maintaining a constant total surfactant concentration (1.0 wt% active surfactant). All blends also contained phenol-ethylene-oxide cosolvent, which lowers microemulsion interfacial rigidity, reduces phase viscosity, and enhances mass-transfer across the oil–water interface. These effects dramatically shorten the time required to reach thermodynamic equilibrium; in the absence of a cosolvent, comparable carbonate formulations have been reported to require many months to equilibrate (Lu *et al.,* 2014). The samples were allowed to equilibrate for a minimum of 30 days at 100°C. Additional samples were intermittently inspected throughout the equilibration period to confirm equilibrium.

From these measured volumes, the solubilization ratios for oil (R_o) and water (R_w) were calculated at equilibrium. The solubilization ratio is defined as the volume of oil or water solubilized in the middle microemulsion phase per unit volume of surfactant. At optimum salinity (S_{opt})—characterized by a Winsor Type III microemulsion system—the oil and water solubilization ratios are equal ($R_o = R_w$), correlating with ultra-low IFT according to Huh's correlation (Huh, 1979). Optimum salinity is identified as the salinity at which the volume of the middle-phase microemulsion was maximized, and equal excess oil and water volumes were observed, indicating optimal balance. The lower and upper salinity limits bounding the Winsor Type III region (three-phase microemulsion existence) were noted for each formulation as indicators of robustness and practical applicability. Furthermore, visual assessments regarding the transparency, cloudiness, or any noticeable phase changes of the surfactant solutions under different salinity and temperature conditions were systematically documented. These observations served as an additional validation check for the aqueous stability limits previously determined.

Contact Angle Measurements. Contact angle measurements were conducted to assess the wettability alteration potential of the surfactant formulations. Indiana limestone chips (aged for two weeks at 100°C in reservoir crude oil) were utilized in these measurements. Measurements were performed using an Attension Theta tensiometer (Biolin Scientific) under ambient laboratory conditions. For comparison, each limestone chip was submerged separately in either seawater brine (baseline condition without surfactant) or the optimized surfactant formulation (SF4). Contact angles were measured using the sessile-drop method (aqueous droplet on oil-aged rock surface) with careful imaging and software-based angle determination.

To ensure measurement reliability, each test scenario (seawater and SF4) was repeated 3 times, with reported values representing the average results. Although these ambient-condition tests provided valuable qualitative insights regarding wettability alteration potential, more accurate evaluation under actual reservoir conditions (100°C, reservoir pressures) would require specialized high-temperature and high-pressure instrumentation, which is recommended for future studies.

Static Adsorption Tests. Static adsorption tests were conducted to measure and quantify surfactant retention onto carbonate rock surfaces under controlled laboratory conditions. Experiments utilized crushed rock samples, specifically Indiana limestone (grain sizes: 63–250 μm) and reservoir rock cuttings (grain sizes: 125–250 μm). The tests employed a solid-to-liquid ratio of 1:10, where precisely weighed rock samples

(1.0 g each) were equilibrated with surfactant solution (10 mL total volume) at two distinct temperature conditions: ambient laboratory temperature (~25°C) and high temperature (100°C). For tests conducted at ambient temperature, rock-surfactant mixtures were placed in sealed stainless-steel tubes and gently agitated using a laboratory tumbler for 24 hours to reach adsorption equilibrium. In contrast, high-temperature adsorption experiments were performed by placing sealed tubes in a temperature-controlled heating bath at 100°C, maintaining continuous agitation over the same 24-hour duration to facilitate equilibration.

Once equilibrium conditions were achieved, the aqueous phase was rapidly separated from the rock particles through high-speed centrifugation. The surfactant concentration remaining in the solution was then accurately quantified using High-Performance Liquid Chromatography (HPLC) coupled with an Evaporative Light Scattering Detector (ELSD). Adsorption values were determined based on the difference between the initial surfactant concentration and the concentration measured at equilibrium, calculated using the following equation:

$$\text{Adsorption}\left(\text{mg} \;/\; \text{g}-\text{rock}\right) = \frac{\left(C_0 - C_{eq}\right) \times V}{m} \tag{2}$$

where C_0 and C_{eq} represent the initial and equilibrium surfactant concentrations (mg/mL), respectively, V is the solution volume (mL), and m is the rock mass (g).

Each adsorption test was carried out in duplicate to ensure the reliability and reproducibility of the results. Control experiments using rock-brine mixtures without surfactants were also performed to check for potential interference from dissolved minerals, and these control tests confirmed that no significant interference was present in the analytical measurements.

Coreflooding Experiment - Dynamic Adsorption and Oil Recovery. A coreflooding experiment was conducted to comprehensively evaluate surfactant performance under dynamic flow conditions, providing data on incremental oil recovery and surfactant retention behavior. The test utilized an Indiana limestone core (3 inches in length, 1.5 inches in diameter, 18.2% porosity, and 27 mD air permeability) securely mounted in a stainless-steel core holder under 1200 psi confining pressure, representing typical reservoir stress conditions, and a backpressure of 200 psi. Core temperature was maintained precisely at reservoir conditions (100°C) within a controlled oven chamber throughout the experiment. The coreflood involved multiple sequential stages detailed below:

- *Initial Saturation and Wettability Alteration.* The core was first evacuated under vacuum conditions and fully saturated with synthetic formation brine (167,301 ppm TDS) to establish 100% water saturation. A two-step drainage procedure established initial reservoir oil saturation:
  - First, Primol (a refined mineral oil) was injected to displace brine and establish irreducible water saturation (S_{wi}). Primol was chosen to prevent stable crude oil/brine emulsions during initial displacement.
  - Subsequently, reservoir crude oil was injected to displace Primol. To achieve representative wettability conditions, the core was aged in crude oil at 100°C for 14 days.
- *Water Injection.* Following aging, forced imbibition was performed using synthetic seawater (43,373 ppm TDS) at an elevated injection rate (7 cc/min) to ensure the true residual oil saturation (S_{or}) was reached. Approximately two pore volumes (PVs) of seawater were injected until no oil production was observed (~0% oil cut), thus clearly establishing a baseline for residual oil saturation after waterflooding.
- *Surfactant Slug Injection (SF / Tertiary Recovery).* After achieving residual oil saturation (S_{orw}), an optimized surfactant formulation (SF4: 0.5% GAC-4, 0.25% IOS15, 0.25% IOS20, and 0.5% ethoxylated-phenol co-solvent) was injected as a surfactant slug (0.8 PV slug size, dissolved in 43,373 ppm TDS seawater) at an injection rate of approximately 1 ft/day (0.25 cc/min).

During surfactant injection, effluent samples were systematically collected at 0.1 PV intervals. Produced oil and water volumes were continuously monitored to quantify incremental oil recovery, and effluent surfactant concentrations were analyzed using HPLC-ELSD to monitor surfactant breakthrough and retention.

- *Low-Salinity Waterflood (Salinity Gradient Post-Flush).* To maximize oil recovery and investigate surfactant desorption from rock surfaces, a gradient-salinity flush was conducted immediately after surfactant injection:
  - Initially, 0.4 PV of intermediate-salinity brine (20,000 ppm TDS) was injected.
  - Followed immediately by 1.2 PVs of low-salinity brine (10,000 ppm TDS) to promote surfactant desorption and further incremental oil recovery. Effluent samples continued to be systematically collected and analyzed throughout this stage, providing robust data on surfactant and oil recovery profiles.
- *Measurement and Analysis of Dynamic Surfactant Retention.* Dynamic surfactant retention within the core was calculated using material balance analysis by comparing total surfactant injected and cumulative surfactant recovered in effluent fractions (surfactant slug effluent and subsequent low-salinity flush effluent). The difference represented surfactant retained within the core, normalized by total rock mass to yield dynamic retention values (mg-surfactant/g-rock). The low-salinity flush step allowed differentiation between temporarily retained (reversible) and permanently adsorbed (irreversible) surfactant, providing more accurate quantification of true surfactant retention. Dynamic retention was obtained from a material-balance integral:

$$R_{dyn} = \frac{C_{slug}V_{slug} - \sum_{j=1}^{N} C_{out,j}V_{out,j}}{m_{rock}} \tag{3}$$

where C_{slug} and V_{slug} are the surfactant concentration and volume of the injected slug, $C_{out,j}$ and $V_{out,j}$ are the concentration and volume of effluent fraction j (including the surfactant-slug effluent and the subsequent low-salinity flush), N is the total number of collected fractions, and m_{rock} is the oven-dry mass of the core.

HPLC Analytical Measurements. Surfactant concentrations in both static adsorption solutions and coreflood effluent samples were quantified using High-Performance Liquid Chromatography (HPLC) coupled with an Evaporative Light Scattering Detector (ELSD). Given the anionic nature of the surfactants evaluated (GAC and IOS) and their typically weak UV absorbance characteristics, ELSD detection provided superior sensitivity, accuracy, and reliability.

An optimized gradient elution method—adapted from the procedure developed by Upamali et al. (2018) — was used to achieve clear peak separation and resolution between carboxylate and sulfonate surfactants. Minor adjustments were implemented to enhance analytical resolution. The optimized elution method included the following gradient conditions:

- The initial mobile-phase composition (85% aqueous ammonium acetate buffer and 15% acetonitrile) was maintained for 5 minutes.
- Linear gradient shift to 10% buffer and 90% acetonitrile over a 15-minute period, effectively eluting all surfactant species.
- The final mobile-phase composition (10% buffer, 90% acetonitrile) was maintained for an additional 20 minutes to guarantee complete surfactant elution from the column.
- Re-equilibration back to initial conditions for 5 minutes was performed between the runs.

Calibration curves were prepared daily, utilizing fresh standard solutions of the surfactant formulations covering a concentration range of 0–5000 ppm. All calibration curves consistently demonstrated strong

linear relationships, with regression coefficients (R^2 values) around 0.99 in all cases, underscoring the reliability and robustness of the analytical method employed. The amount of surfactant adsorbed onto the rock was calculated by comparing the initial surfactant concentration with the measured equilibrium concentration after adsorption. This difference represented the adsorbed surfactant amount, normalized by the mass of the rock to yield adsorption capacity (mg-surfactant/g-rock).

For coreflooding experiments, dynamic surfactant retention was determined using a similar normalization approach but based on cumulative pore volumes (PVs) injected and the rock mass of the core plug. The cumulative surfactant mass retained within the core was calculated through the integration of surfactant concentrations measured from the effluent profiles. This retained mass was normalized by the total core rock mass, yielding dynamic retention values (mg-surfactant/g-rock).

Results and Discussions

Thermal Stability

All candidate GAC/IOS formulations were first confirmed to be thermally stable up to 120 °C in seawater salinity (43,373 ppm TDS); subsequent aqueous–stability and phase–behavior tests were therefore conducted at 100 °C to mimic reservoir conditions.

Aqueous Stability and Phase Behavior Studies

Ensuring aqueous stability is essential for the effective delivery of surfactants into carbonate reservoirs without causing precipitation or undesirable phase separations. Stability typically depends on the surfactant's hydrophilic-lipophilic balance (HLB), which is mainly influenced by its ethylene oxide (EO) and propylene oxide (PO) content. Generally, formulations containing higher EO content exhibit improved aqueous stability because of their increased hydrophilicity, whereas increased PO units typically have a destabilizing effect on the surfactant solutions (Lu *et al*., 2014; Panthi and Mohanty, 2024).

In this study, surfactant formulation SF0 showed an initial aqueous–stability threshold of around 105,000 ppm TDS. However, when IOS20 was introduced into subsequent formulations (SF1–SF4), stability fell to 75,000 ppm TDS—about a 25 % reduction—yet this limit still sits well above the highest salinity the slug will meet in practice (seawater ≈ 43,373 ppm TDS plus any residual mixing with formation brine). This 25% decrease in stability can be primarily attributed to the greater hydrophobicity imparted by IOS20. These results closely match observations reported in earlier studies, which similarly documented reduced aqueous stability upon the addition of IOS20 co-surfactants, despite improvements in other properties such as interfacial activity and broader salinity compatibility (Zhao *et al*., 2008; Lu *et al*., 2014; Panthi and Mohanty, 2024). Moreover, this trend aligns well with the consensus in the literature that enhanced EO content tends to stabilize surfactants under challenging reservoir conditions (Maubert *et al*., 2018).

Identifying the optimum salinity (S_{opt}) is particularly important, as it represents the conditions at which surfactants minimize interfacial tension (IFT) and produce stable Winsor Type III microemulsions. These microemulsions are vital for effectively mobilizing trapped oil (Huh, 1979; Tagavifar *et al*., 2017). Table 4 provides a comprehensive overview of the tested surfactant formulations, summarizing their aqueous stability limits, optimal salinities, solubilization ratios, and corresponding IFT results.

Table 4—Phase Behavior and IFT Summary

Formulation	Aqueous Stability (ppm)	Middle Phase Range (ppm)	S^* (ppm)	R^* (cc/cc)	σ^* (mN/m)	σ-SW (mN/m)
SF0	105,000	85,000 – 95,000	88,400	9	3.62×10^{-3}	2.50×10^{-2}
SF1	50,000	20,000 – 45,000	37,000	7	6.12×10^{-3}	4.20×10^{-3}
SF2	60,000	30,000 – 45,000	40,000	9	3.70×10^{-3}	2.58×10^{-3}
SF3	70,000	30,000 – 50,000	45,000	9.5	3.32×10^{-3}	3.07×10^{-3}
SF4	75,000	30,000 – 55,000	44,000	12	2.08×10^{-3}	1.93×10^{-3}

Temperature = 100ºC, S^* = Optimal Salinity, R^* = Solubilization Ratio at Optimal Salinity, σ^* = Huh IFT at Optimal Salinity σ-SW = spinning drop IFT at 100 °C using Seawater

Formulation SF0 initially exhibited an optimum salinity of 88,400 ppm TDS, significantly higher than the intended injection salinity (43,373 ppm TDS). The addition of IOS20 (SF1–SF4 formulations) progressively shifted optimum salinity downward, enhancing practical applicability for typical seawater injection conditions. Notably, SF4 demonstrated an optimum salinity of 44,000 ppm TDS and the highest solubilization capacity (12 cc/cc), correlating longer hydrophobic chains and balanced EO/PO ratios with improved oil solubilization into microemulsions. These findings support literature highlighting the efficacy of IOS co-surfactants in adjusting optimal salinity downward and broadening operational salinity windows (Zhao *et al*., 2008; Panthi and Mohanty, 2024).

The inclusion of IOS20 significantly lowered the optimum salinity from an initial 88,400 ppm TDS (SF0) down to 44,000 ppm TDS (SF4), aligning closely with the target injection salinity of seawater (43,373 ppm TDS). Although this adjustment reduced the aqueous–stability ceiling by ≈ 30,000 ppm (25 %), the resulting 75,000 ppm threshold remains comfortably higher than the maximum salinity that the surfactant will encounter along the flow path, ensuring adequate operational margin. Consequently, the substantial reduction in optimum salinity, combined with improved surfactant adaptability and notably lower interfacial tension (IFT), represents a major advantage. This trade–off introduces a reduction in stability that does not compromise the formulation's practical applicability or efficiency. Table 4 also shows that the IFT values predicted from Huh's correlation (using the measured solubilisation ratios) agree closely with those obtained by spinning–drop tensiometer at 100 °C, confirming the reliability of both measurement approaches for SF4. These results align well with previous studies, reinforcing IOS20's effectiveness in optimizing surfactant performance under challenging reservoir conditions (Zhao *et al*., 2008; Panthi and Mohanty, 2024).

Based on these findings, formulation SF4 emerged as the optimal surfactant formulation due to its superior combination of aqueous stability, reduced optimal salinity, high solubilization ratio, and consistently low IFT. SF4 was therefore selected for further detailed analyses, including contact angle, static adsorption, and coreflooding experiments (dynamic adsorption and oil recovery).

Impact of Surfactant Chain Length and EO/PO Ratios on Formulation Performance. Surfactant chain length and EO/PO ratios significantly influenced aqueous stability, optimum salinity, middle-phase microemulsion range, solubilization ratio, and interfacial tension (IFT) (Table 4). Shorter hydrophobic chains (SF1: C18) required lower optimum salinities and showed limited solubilization capacity due to weaker oil-phase interactions (Levitt *et al*., 2009; Lu *et al*., 2014). Increasing the chain length from C18 (SF1) to C24 (SF2) and further to C28 (SF3, SF4) systematically raised optimum salinity and improved solubilization ratios, reflecting enhanced lipophilicity and oil interaction (Tagavifar *et al*., 2017). Formulation SF4 (C28 with higher EO/PO) achieved the highest optimum salinity, the widest middle-phase range, the best aqueous stability, the highest solubilization ratio, and the lowest IFT. These results highlight

the critical role of increased EO/PO content in stabilizing microemulsions, broadening salinity adaptability, and significantly reducing IFT, consistent with previous literature findings (Solairaj *et al*., 2012; Maubert *et al*., 2018; Panthi and Mohanty, 2024).

Interfacial Tension (IFT) Measurements

Baseline interfacial tension (IFT) measurements performed between crude oil and seawater (in the absence of surfactants) resulted in an average value of approximately 21.53 mN/m at ambient laboratory temperature (25°C). Ultra-low IFT measurements (~10^{-3} mN/m or lower), critical for enhanced oil recovery (EOR), were obtained using spinning drop tensiometer and validated through Huh's correlation (Huh, 1979). The spinning drop technique yields precise IFT data due to the distinct elongation of droplets induced by strong centrifugal forces within the instrument. Huh's correlation estimated ultra-low IFT values based on microemulsion solubilization ratios at optimum salinity conditions. Table 4 summarizes measured IFT values for each formulation (SF0–SF4) at seawater salinity (~43,373 ppm TDS) and reservoir temperature (100°C). Notably, formulation SF4 demonstrated the lowest measured IFT, aligning with its optimized EO/PO ratio and superior phase behavior characteristics.

To assess temperature dependence, comparative IFT measurements for formulations SF0–SF4 were performed at 60, 70, 80, and 90°C. Given the maximum operational limit of the measurement equipment at 90°C, IFT results at the reservoir temperature of interest (100°C) were reliably determined by extrapolation using best-fit regression analyses, which consistently yielded high correlation coefficients ($R^2 \approx 0.99$). Figure 1 presents these comparative trends, clearly illustrating a steady decline in IFT values with increasing temperature, thereby confirming enhanced surfactant performance under realistic reservoir conditions.

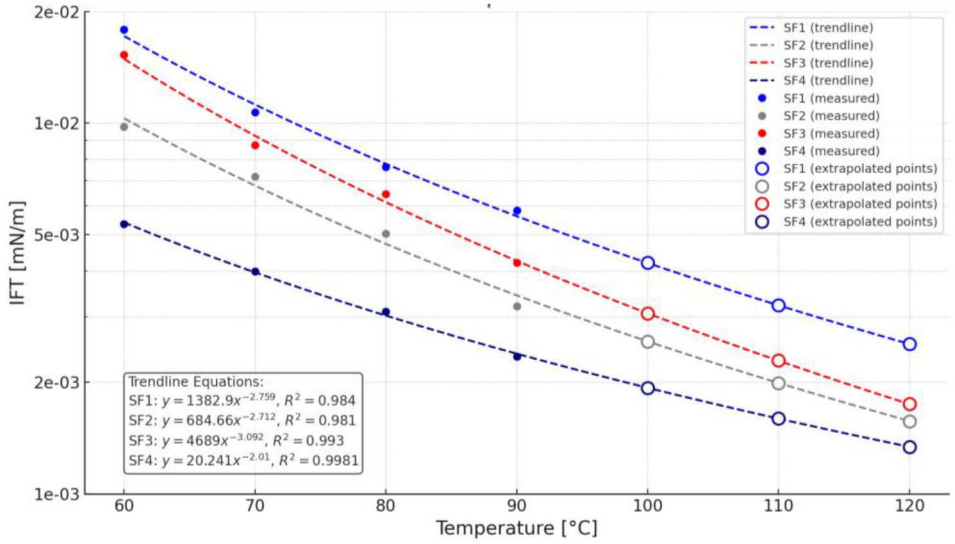

Figure 1—Comparative IFT Measurements vs. temperature for SF1–SF4 using Spinning Drop Tensiometer.

Contact Angle Measurements

Contact angle measurements provided direct evidence of the wettability alteration capability of the optimized surfactant formulation (SF4). The measured contact angle of aged Indiana limestone immersed in seawater was initially 161°, confirming strongly oil-wet conditions typical for carbonate reservoirs after aging (Okasha and Al-Shiwaish, 2010). Upon exposure to formulation SF4, the contact angle significantly decreased to 69°, clearly indicating substantial wettability alteration toward water-wet conditions. The observed shift from strongly oil-wet (161°) to distinctly water-wet conditions (69°) demonstrates the robust effectiveness of SF4 in altering wettability, a critical factor for enhanced oil recovery (EOR) in carbonate reservoirs (Hirasaki and Zhang, 2004; Lu *et al*., 2014).

Static Adsorption Test

Static adsorption tests evaluated the extent of surfactant retention onto carbonate rock surfaces using crushed Indiana limestone and reservoir rock samples at ambient (~25°C) and elevated (100°C) temperatures. Results clearly demonstrated the temperature sensitivity of surfactant adsorption. At ambient temperature, measured static adsorption values for the optimized formulation (SF4) were 1.20 ± 0.04 mg/g-rock for Indiana limestone and 1.08 ± 0.07 mg/g-rock for reservoir rock. The slightly higher adsorption observed with Indiana limestone is consistent with its higher surface homogeneity and mineralogical purity, known to enhance ionic and polar interactions between the surfactant and rock surfaces (Tagavifar *et al*., 2017).

At reservoir temperature (100°C), surfactant adsorption noticeably decreased, measuring 0.87 ± 0.06 mg/g-rock for Indiana limestone and 0.78 ± 0.03 mg/g-rock for reservoir rock. This significant temperature-induced reduction in adsorption aligns with the literature, as increased thermal energy reduces interactions between surfactant molecules and carbonate surfaces, resulting in lower surfactant retention (Austad *et al*., 2012; Lu *et al*., 2014).

Dynamic adsorption values for Indiana limestone cores were estimated based on static adsorption measurements and typical BET surface area ratios (crushed rock ~2 m²/g vs. cores ~0.5 m²/g; Fathi and Austad, 2010; Austad *et al*., 2012). Using BET surface areas reported in the literature, dynamic adsorption onto Indiana limestone cores at 100°C was preliminarily estimated to be approximately 0.22 mg/g-rock. Although these values serve as helpful initial approximations, direct BET surface area measurements of the actual test samples are recommended for more accurate confirmation. Subsequent coreflooding experiments provided direct, precise measurements of dynamic adsorption under realistic reservoir conditions.

Coreflooding Experiment (Dynamic Adsorption and Oil Recovery)

The coreflood employed an Indiana limestone core (2.97″ length, 1.48″ diameter) characterized by 18.2% porosity and absolute permeability of 21.7 mD (K_w at S_w =1) and effective oil permeability of 19.4 mD measured at the initial water saturation (K_o at S_{wi} = 28.5%). The core dry mass was 184 g, and experiments were conducted at reservoir-relevant conditions (100°C). Synthetic seawater (43,373 ppm TDS) and lower-salinity brines (10,000–20,000 ppm TDS) were used, with initial saturations of 28.5% water (S_{wi}) and 71.5% oil (S_{oi}). The coreflooding experiment provided comprehensive insight into surfactant performance under dynamic flow conditions representative of reservoir environments (Table 5 and Figure 2).

Table 5—Summary of coreflooding results for tertiary surfactant flooding with salinity gradient post-flush

Stage	PV inj.	Cum. Rec. (% OOIP)	Incremental (% OOIP)	% Sorw Mobilised	So (%)	Retention (mg g-¹)
Waterflood	2.0	69.9	–	–	30.1	–
Surfactant slug	0.8	86.4	16.5	55 %	13.5	0.23
Post-flush	1.6	92.8	6.4	21 %	7.2	0.16

The initial forced–imbibition waterflood recovered 69.9 % OOIP, as the high injection rate (7 cc/min) established a realistic residual–oil saturation (S_{orw} = 30.1 %) consistent with centrifuge benchmarks.

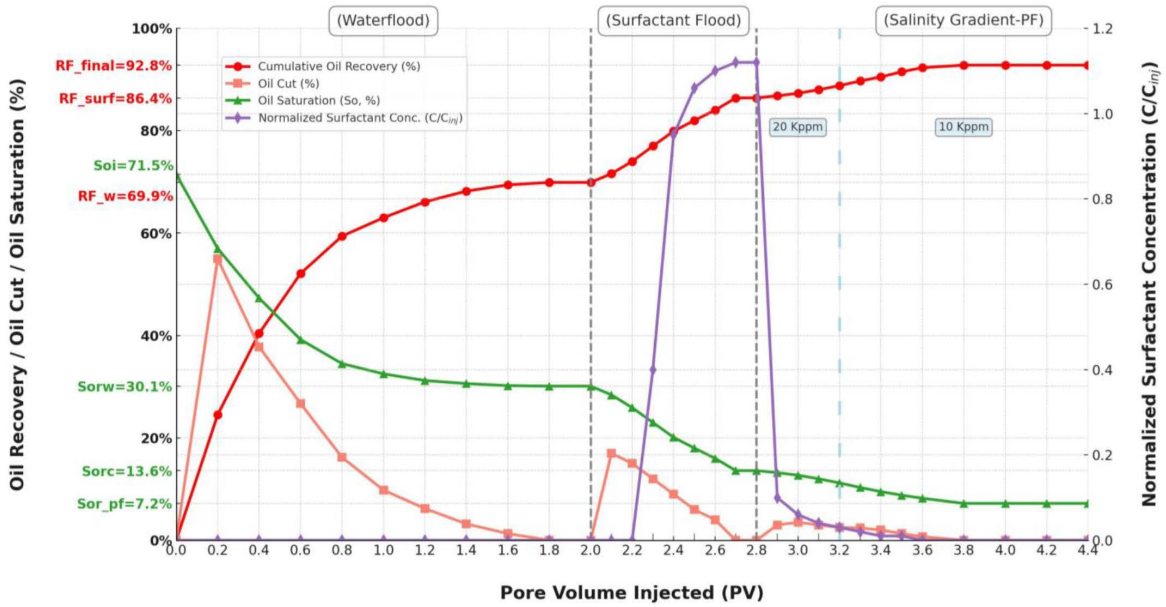

Figure 2—Coreflood effluent analysis illustrating cumulative oil recovery, oil cut, oil saturation, and normalized surfactant concentration versus injected pore volumes (PVs).

As the surfactant slug advances, it could be mixing with some of the connate water brine and simultaneously picking up Ca^{2+}/Mg^{2+} ions released from calcite surfaces, slightly increasing the in-situ salinity just enough to cross the narrow optimum-salinity window (S*) centred at 44,000 ppm TDS for SF–4 to Type II microemulsion. The brief 2–3 psi hump at 2.3 PV (Figure 3) can be attributed to the passage of a viscous Type II micro-emulsion bank, which temporarily raises flow resistance as it displaces oil (Hirasaki et al., 2011; Levitt *et al.,* 2016). Confirming the detailed in-situ salinity phase behaviour transitions will still require effluent-salinity profiling (conductivity and ion analysis) and an activity–phase-diagram analysis. Once the viscous bank exits, ΔP settles at 0.8–1 psi for the remainder of the surfactant flood, and SF–4 leads to an incremental recovery of 16.5 % OOIP (≈ 55 % of S_{orw}). The subsequent salinity-gradient post-flush (20,000 → 10,000 ppm TDS) leaves ΔP flat, indicating no formation damage, yet contributes a further 6.4 % OOIP (≈ 21 % of S_{orw}) of extra recovery, and the total recovery reaches 92.8 % OOIP. The incremental recovery is most plausibly linked to surfactant desorption during the low-salinity flush: as ionic strength drops, charge screening weakens, electrostatic repulsion between anionic head-groups and the carbonate surface increases, more surfactant stays in the aqueous phase, ultralow IFT is preserved, wettability shifts toward water-wet, and residual oil is mobilised (Hirasaki *et al*., 2011; Levitt *et al.*, 2016).

Surfactant desorption during the salinity gradient is primarily governed by ionic strength reduction, weakening electrostatic adsorption bonds between anionic surfactants and carbonate surfaces. Reduced ionic strength increases electrostatic repulsion, liberating adsorbed surfactants back into solution, thereby maintaining lower interfacial tensions and extending tertiary recovery efficiency (Hirasaki *et al*., 2011; Montes et al., 2018).

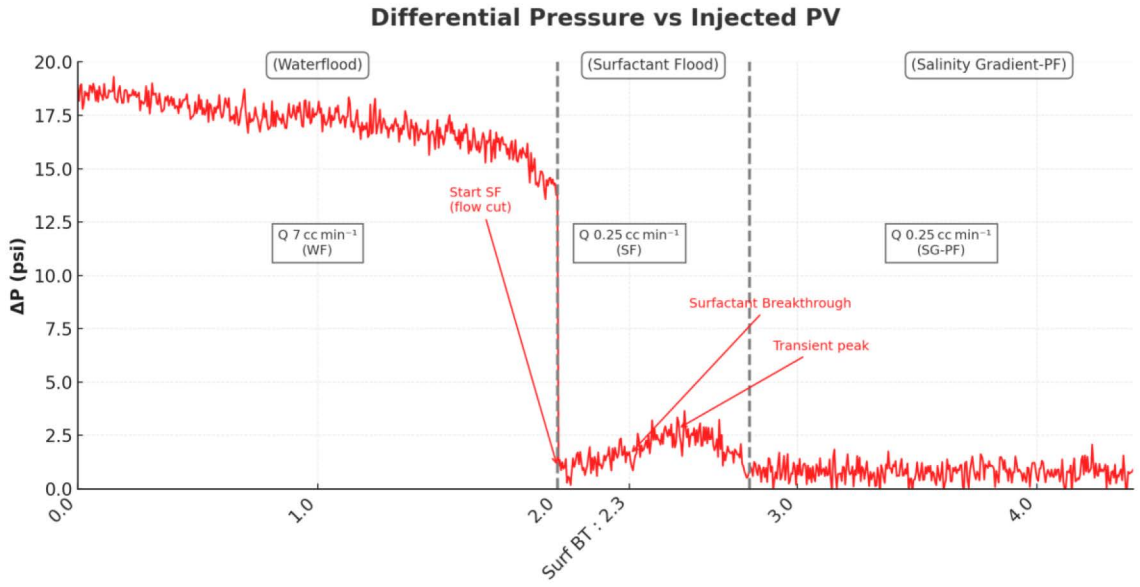

Figure 3—Coreflood differential pressure versus injected pore volumes (PVs)

Dynamic surfactant retention was quantified through material balance. The total injected surfactant mass was 121.8 mg (0.8 PV at 1.0 wt%), with approximately 79 mg recovered during the surfactant slug injection stage. Initial dynamic retention was thus 0.23 mg/g-rock. Salinity gradient post-flush produced a secondary surfactant peak (~ 21 mg), matching the 0.07 mg g-¹ drop in calculated retentions, subsequently reducing retention to 0.16 mg/g-rock due to desorption. This post-flush retention value (0.16 mg/g-rock) represents a significant improvement, which falls within the generally accepted economic threshold (~0.1 to 0.2 mg/g-rock) for large-scale applications (Liu et al., 2010). Thus, future optimization should include novel retention-reducing additives or alkalis (e.g., ammonium hydroxide or sacrificial agents), which effectively minimize retention without adverse interactions common with conventional alkalis such as sodium carbonate (Hirasaki *et al*., 2011).

Overall, these coreflooding results clearly confirm the effectiveness and viability of the optimized SF4 formulation and its potential for enhancing oil recovery in challenging Middle Eastern carbonate reservoirs. Despite slight challenges with retention, the optimized approach substantially improved final oil recovery to 92.8% OOIP, demonstrating significant potential even in the absence of polymer-induced mobility control. The critical insights gained underscore key opportunities for further surfactant formulation and injection strategy optimization to achieve economically feasible field-scale EOR implementation. Nonetheless, prior to recommending field-scale implementation, the full workflow will be repeated on preserved reservoir core plugs to confirm surfactant performance under true mineralogy, connate-fluid composition, and in-situ wettability.

Conclusions and Recommendations

This study comprehensively evaluated optimized carboxylate-based anionic surfactant blends (GAC/IOS) for enhanced oil recovery (EOR) applications in high-temperature, high-salinity Middle Eastern carbonate reservoirs. Based on systematic laboratory evaluations and coreflooding experiments, the following conclusions can be made:

- GAC/IOS surfactant blends are thermally stable to 120 °C in seawater (≈ 43,373 ppm TDS) and remain aqueous-stable to ≈ 75 000 ppm TDS at 100 °C. Consequently, after a seawater pre-flush and slug injection at seawater salinity, they can be deployed in carbonate reservoirs whose formation brines are as saline as 170,000 ppm TDS. Optimized formulation SF4 (0.5% GAC-4 +

0.25% IOS15 + 0.25% IOS20 + 0.5% ethoxylated-phenol co-solvent) achieved the highest aqueous stability, broadest middle-phase microemulsion range, highest solubilization ratios, and lowest interfacial tension (IFT ≈10^{-3} mN/m).

- The molecular structure of the GAC surfactants significantly influenced their overall EOR performance. Increased hydrophobic tail length (C18 to C28) and elevated EO/PO contents systematically improved microemulsion stability, broadened salinity windows, increased solubilization capacity, and reduced interfacial tension, consistent with previous literature (Solairaj *et al*., 2012; Lu *et al*., 2014; Panthi and Mohanty, 2024).
- The optimized surfactant formulation (SF4) demonstrated substantial wettability alteration, shifting the carbonate rock surface conditions from an initial strongly oil-wet state (contact angle ~161°) to a water-wet condition (contact angle ~69°).
- Coreflooding experiments validated the optimized surfactant's effectiveness, achieving a cumulative oil recovery of 92.8% OOIP, including an incremental recovery of 16.5% OOIP from the surfactant flood alone, and a further 6.4% OOIP from subsequent salinity-gradient post-flush.
- Dynamic surfactant retention, directly quantified via coreflood material balance calculations, averaged approximately 0.16 mg/g-rock. This retention value falls comfortably within the generally accepted economic viability range (~0.1 to 0.2 mg/g-rock), highlighting the economic feasibility of the formulation. Nevertheless, continued optimization efforts are recommended to reduce surfactant retention further, potentially enhancing the economic attractiveness of field-scale applications.

Based on the study's findings and detailed analyses, the following recommendations are proposed to enhance surfactant-based EOR processes further in carbonate reservoirs:

- Retention Reduction Strategies: Investigate advanced additives, sacrificial agents, or mild alkaline substances (e.g., ammonium hydroxide) specifically designed to reduce surfactant retention. These substances should minimize adverse reactions with carbonate minerals typically observed with stronger conventional alkalis (such as sodium carbonate).
- Mobility Control Enhancements: Evaluate the compatibility and effectiveness of polymers and other potential mobility-control agents, aiming to improve reservoir sweep efficiency significantly (Hassan *et al.,* 2023a; Hassan *et al.*, 2023b). This approach will enhance the economic viability and overall performance of chemical EOR operations in carbonate reservoirs.
- Perform the experiments using reservoir core material under reservoir conditions.

Overall, the optimized GAC/IOS surfactant formulation and systematic evaluation framework presented in this study provide robust technical foundations and a clear roadmap for future chemical EOR development and implementation in challenging carbonate reservoirs.

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Nomenclature: Symbols

cP	centipoise, dynamic viscosity (mPa·s)
C_o	initial surfactant concentration, mg/mL
C_{eq}	equilibrium surfactant concentration, mg/mL
$C_{out,\,j}$	surfactant concentration in effluent fraction j, mg/mL
C_{slug}	surfactant concentration in the injected slug, mg/mL
kppm	thousand parts per million
m	rock mass in static-adsorption tests, g
m_{rock}	dry mass of core plug, g
mD	millidarcy, permeability
N	total number of collected effluent fractions
ppm	parts per million
R_{dyn}	dynamic surfactant retention, mg/g
R*	total solubilization ratio at optimum salinity cc/cc
R_o	oil solubilization ratio at optimum salinity, cc/cc
R_w	water solubilization ratio at optimum salinity, cc/cc
S*	optimum salinity producing middle phase microemulsion, ppm
S_{oi}	initial oil saturation
S_{or}	residual oil saturation
S_{orc}	residual oil saturation after surfactant flood
S_{or_pf}	residual oil saturation after post-flush
S_{orw}	residual oil saturation after waterflood
S_{wi}	initial water saturation
σ *	interfacial tension at optimum salinity, mN/m
σ–SW	interfacial tension at seawater salinity, mN/m
V	solution volume in static-adsorption tests, mL
$V_{out,\,j}$	volume of effluent fraction j, mL
V_{slug}	total volume of injected slug, mL
wt %	weight percent
NaCl	sodium chloride
NaOH	sodium hydroxide
Na_2CO_3	sodium carbonate
NH_3	ammonia

Abbreviations

API	American Petroleum Institute gravity (°API)
BET	Brunauer–Emmett–Teller specific-surface-area method (m^2/g)
CEOR	Chemical Enhanced Oil Recovery
DIPA	di-isopropanolamine cosolvent
ELSD	Evaporative Light-Scattering Detector (HPLC)
EO	ethylene-oxide group in surfactant
EOR	Enhanced Oil Recovery
FW	formation water
GAC	Guerbet alkoxy carboxylate surfactant
HLB	hydrophilic–lipophilic balance
HPLC	high-performance liquid chromatography

HPAM	partially hydrolysed polyacrylamide polymer
HTHS	high temperature, high salinity
IFT	interfacial tension (mN/m)
IOS	internal olefin sulfonate surfactant
OOIP	original oil in place
PO	propylene-oxide group in surfactant
PV	pore volume
Rec	recovery
rpm	revolutions per minute (spinning-drop tensiometer)
SF0–SF4	surfactant formulations defined in text
SW	seawater
TDS	total dissolved solids (ppm)
TEGBE	triethylene glycol butyl ether cosolvent

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