*Research Journal of Chemistry and Environment*_________________________________Vol. **30 (1)** January **(2026)**
Res. J. Chem. Environ.

A Combined IFT–TGA Assessment of Anionic Surfactants for Chemical EOR Applications

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Abstract

This study presents a comparative evaluation of five anionic surfactants: Sodium Dodecyl Sulfate (SDS), Alpha-Olefin Sulfonate (AOS), Linear Alkylbenzene Sulfonate (LAS), Petroleum Sulfonates (PS) and Dioctyl Sulfosuccinate Sodium Salt (AOT) with respect to their interfacial tension (IFT) reduction efficiency and thermal stability, under conditions representative of Enhanced Oil Recovery (EOR). IFT measurements were performed using a spinning drop tensiometer at 70 °C in synthetic brine (6000 ppm NaCl), simulating saline reservoir environments. All surfactants showed a decrease in IFT with increasing concentration until reaching their Critical Micelle Concentration (CMC). AOT achieved the lowest IFT (6.9×10^{-2} mN/m at 0.3 w/v%), followed by PS, SDS, AOS and LAS. Thermogravimetric analysis (TGA) further revealed distinct decomposition behaviours linked to surfactant molecular structures. SDS and AOT displayed sharp, clean degradation with negligible residues, indicating minimal risk of solid deposition. PS exhibited the broadest decomposition profile with significant residue (~10–15%), reflecting higher stability but a tendency toward char formation.

AOS and LAS showed intermediate behaviour with minor residues. By integrating IFT and TGA insights. The study identifies AOT as the most promising candidate for high-efficiency EOR due to its superior interfacial activity and clean thermal breakdown, while PS offers robust salinity tolerance and stability despite fouling risks. SDS and AOS represent economical alternatives for moderate conditions, whereas LAS holds potential as a co-surfactant in blended formulations. These findings provide a framework for the rational selection of surfactant systems tailored to reservoir-specific conditions in chemical EOR applications.

Keywords: Interfacial tension, Anionic surfactants, Enhanced oil recovery, Critical micelle concentration, Thermal stability.

Introduction

Enhanced Oil Recovery (EOR) has emerged as a vital technique to extract additional oil from mature and declining reservoirs after primary and secondary recovery methods have been exhausted. Among the various EOR methods, chemical EOR (cEOR), particularly surfactant flooding, is recognized for its potential to significantly improve oil recovery by reducing the interfacial tension (IFT) between crude oil and the displacing aqueous phase[26]. Lowering the IFT facilitates the mobilization of trapped oil by minimizing capillary forces, thereby improving sweep efficiency and overall oil displacement. Surfactants, as surface-active agents, play a crucial role in this process by adsorbing at the oil–water interface and altering the interfacial energy[16]. Anionic surfactants are considered favourable for EOR applications due to their strong surface activity, cost-effectiveness and commercial availability[17].

However, their performance is strongly influenced by multiple factors such as molecular structure, concentration, salinity, temperature and interactions with reservoir rock and fluids[25]. Hence, selecting the right surfactant is essential to ensure effective oil recovery in specific reservoir environments. This study focuses on a comparative analysis of five widely studied and industrially relevant anionic surfactants: Sodium Dodecyl Sulfate (SDS), Sodium Alpha-Olefin Sulfonate (AOS), Sodium Linear Alkylbenzene Sulfonate (LAS), Dioctyl Sulfosuccinate Sodium Salt (AOT) and Petroleum Sulfonates (PS).

These surfactants represent distinct molecular architectures and functional groups which directly influence their surface activity and stability under reservoir-like conditions.

In addition to interfacial performance, the thermal stability of surfactants is a critical parameter for their successful application in high-temperature reservoirs. At elevated temperatures, surfactants may undergo degradation, leading to a loss in efficiency and adverse interactions with reservoir fluids[22,28]. Thermogravimetric analysis (TGA) serves as a valuable technique to evaluate the thermal decomposition behavior of surfactants, providing insights into their stability window and suitability under reservoir conditions. By analyzing weight loss patterns as a function of temperature, TGA enables the identification of thermal degradation stages, onset temperature of decomposition and residual stability[19].

Therefore, this research not only compares the IFT reduction efficiency of these surfactants using the spinning drop method but also investigates their thermal stability through TGA analysis, thereby providing a comprehensive evaluation to identify the most promising candidates for field-scale EOR deployment.

https://doi.org/10.25303/301rjce064070

Material and Methods

Materials used: The anionic surfactants SDS, AOS, AOT, PS and LAS were purchased from Sigma Aldrich. The brine 6000 ppm was prepared by NaCl to match the reservoir salinity. The crude oil was collected from oil fields of Oil India Limited and collected crude oil specifications are shown in table 1.

Table 1
Properties of crude oil

Property	Crude oil
Sp. gravity of crude oil @ 60ºF	0.929
Acid no. of crude oil, mg KOH/g	0.19
Wax content, % (w/w)	2.2
Asphaltene content, % (w/w)	4.12
Resin content, % (w/w)	9.22
Pour point, ºC	15º

IFT determination: The surfactant concentration was prepared from 0.01 to 1.5 w/v % and each surfactant was dissolved in 6000 ppm brine simulating the average salinity of the depleted reservoir in the Assam Shelf basin and to get the homogenous mixture rotated in rotospin for 24 hrs. IFT was measured in the spinning drop tensiometer shown in fig. 1. The mathematical equation behind the instrument is the Vonnegut's equation. As the tube spins, the centrifugal force causes the drop to elongate along the tube's axis. The balance between interfacial tension (which resists elongation) and centrifugal force (which promotes elongation) determines the final shape of the drop. Diameter of the CO drop captured through motic image software, can be read directly from the software and IFT can be calculated by equation 1.

$$\text{IFT}, \gamma\ (\text{mN}, \text{m}) = 1.44 \times 10^{-7} \times \Delta\rho\ (\text{kg}/\text{m}^3) \times\ (\text{D}^3)(\text{mm}) \times \theta\ (\text{rpm}) \qquad (1)$$

where Δρ = Density difference between formulated Slug and CO, D= Diameter in mm read directly from software motic images plus and θ = Rotation in rpm read directly from instrument.

Thermogravimetric analysis: The thermal stability of the surfactants was evaluated using a Perkin Elmer STA-8000 simultaneous thermal analyzer. Each sample was placed in an alumina crucible and subjected to heating under a nitrogen atmosphere to prevent oxidative degradation. The temperature was increased from 35 to 500 °C at a constant scan rate of 20 °C/min. The weight loss (%) and corresponding derivative thermogravimetric (DTG) curves were continuously recorded. From these data, the onset decomposition temperature (T_onset), the maximum degradation temperature (T_max) and the residual mass at 500 °C were determined.

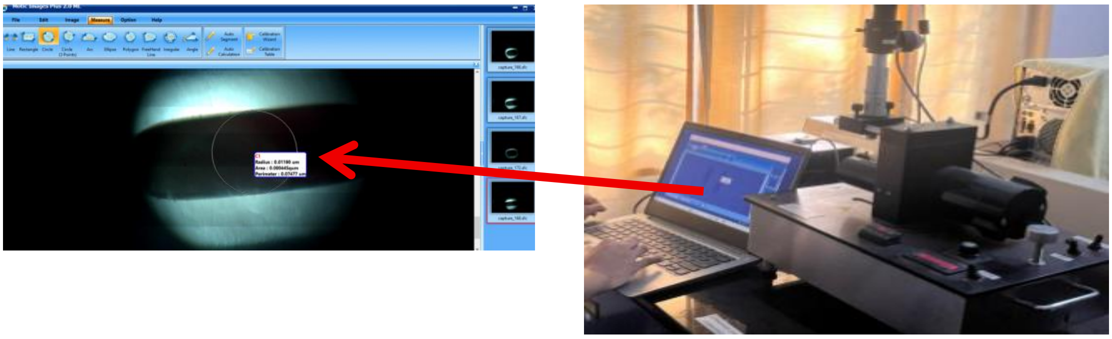

Fig. 1: Spinning drop tensiometer

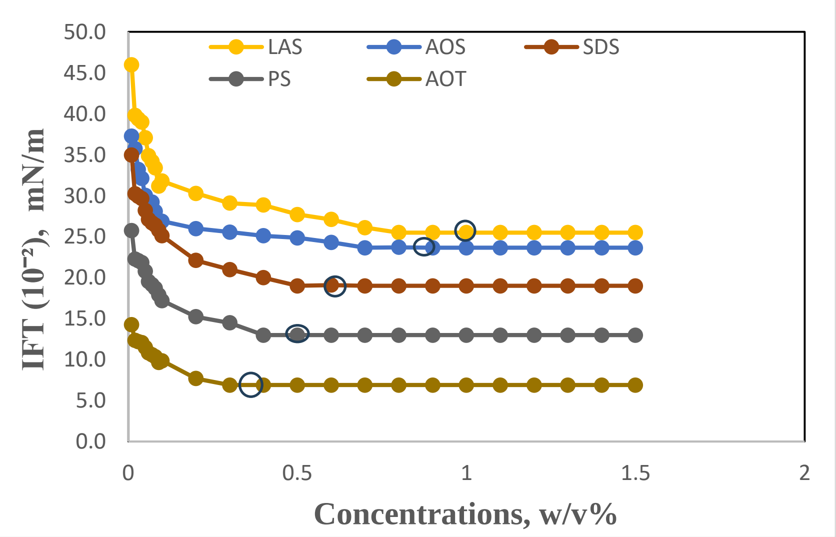

Fig. 2: IFT Reduction vs concentration of surfactants

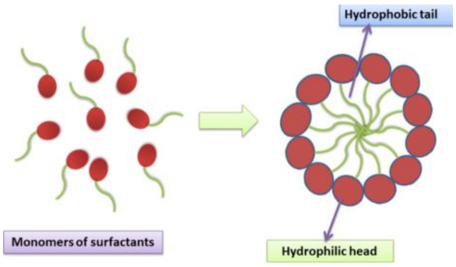

Fig. 3: Monomers to Micelle

Results

IFT Reduction Performance: Fig. 2 presents the results demonstrating the Interfacial Tension (IFT) reduction performance with increasing surfactant concentration. It was observed that IFT decreases as the surfactant concentration increases, up to a certain point beyond which no significant change occurs. This specific concentration is known as the Critical Micelle Concentration (CMC), where surfactant molecules begin to aggregate and form micelles, as illustrated in fig. 3. CMC is defined as the minimum concentration of a surfactant at which micelles start forming in solution. Below the CMC, surfactant molecules exist primarily as individual monomers, while above it, they organize into micelles. Beyond the CMC, further increases in surfactant concentration do not result in a significant reduction in IFT.

The minimum IFT values obtained for each surfactant were as follows: LAS – 25.25 × 10^{-2} mN/m at 0.8 w/v%, AOS – 23.65 × 10^{-2} mN/m at 0.7 w/v%, SDS – 19.1 × 10^{-2} mN/m at 0.5 w/v%, PS – 13.09 × 10^{-2} mN/m at 0.4 w/v% and AOT – 6.9 × 10^{-2} mN/m at 0.3 w/v%. Among these, AOT achieved the lowest IFT followed by PS, SDS, AOS and LAS in increasing order of IFT values.

TGA analysis: The TGA results for the five surfactants revealed distinct decomposition behaviours that reflected their molecular structures. SDS (Curve 1) exhibited an onset of decomposition at ~80 °C, with complete degradation by ~130 °C. The profile showed a sharp, single-step weight loss (nearly 100% → 0%) and negligible residue, which is characteristic of the clean breakdown of a simple alkyl sulfate structure (Fig. 4a). AOS (Curve 2) began decomposing near 100 °C and was fully degraded by ~170 °C. Its curve was broader than that of SDS, with a minor residual fraction, most likely due to the variation in chain lengths within the olefinic mixture (Fig. 4b). LAS (Curve 3) showed an onset at ~90 °C and decomposition up to ~160 °C, with a minor two-step shoulder and a small residue. The aromatic ring in LAS likely accounts for this multi-phase degradation behaviour (Fig. 4c).

PS (Curve 4) displayed the broadest and most complex decomposition profile, initiating between 70–80 °C and continuing up to ~250 °C. Multiple weight-loss steps were observed, leaving behind a significant residue of ~10–15%, consistent with its heterogeneous composition and the partial carbonization of heavier aromatic and branched fractions (Fig. 4d). AOT (Curve 5) showed decomposition onset at ~90 °C with a sharp main weight-loss step between 120–150 °C, followed by a secondary shoulder. Decomposition was nearly complete, leaving minimal residue. This two-step behavior corresponds to breakdown of the sulfosuccinate backbone followed by degradation of the branched dioctyl chains (Fig. 4e).

Comparatively, PS demonstrated the highest apparent thermal stability, with decomposition spanning the broadest temperature range, but its relatively large residue (~10–15%) indicates a risk of char formation and potential pore fouling under reservoir conditions. In contrast, SDS and AOT underwent clean, well-defined decomposition steps with negligible residues, suggesting minimal risk of solid deposition.

LAS and AOS exhibited intermediate stability, with broader curves than SDS/AOT but still leaving only minor residues. Overall, all five surfactants remained thermally stable at temperatures far exceeding the simulated reservoir condition of 70 °C. Considering both IFT performance and thermal stability, AOT emerges as the most promising candidate, offering strong IFT reduction combined with clean thermal decomposition. PS, despite its excellent IFT performance, requires careful consideration due to its higher char yield and associated fouling potential.

Table 2 summarizes the TGA results of the five surfactants, highlighting clear differences in their thermal stability and decomposition patterns. PS showed the broadest decomposition range and the highest apparent stability but left a significant residue (~10–15%), indicating potential risks of char formation and pore plugging despite its advantage in high-temperature applications. In contrast, SDS and AOT decomposed in sharp one- to two-step profiles with negligible residues (<3%), reflecting clean breakdown and low risk of formation damage. LAS and AOS exhibited intermediate stability, with low residues and moderately broader curves, suggesting that they are operationally clean though less suited to ultra-high temperature conditions.

Importantly, all five surfactants remained stable well above the reservoir temperature of 70 °C, confirming their suitability for chemical EOR. When combining thermal stability with IFT performance, AOT and PS emerge as the most promising: PS offers strong IFT reduction but with fouling risk, whereas AOT combines low IFT with clean thermal decomposition, making it more balanced and reliable candidate for field applications.

Practical Implications for EOR

The practical application of these surfactants in EOR operations requires a balance between performance, cost and environmental compatibility. AOT and petroleum sulfonates, while more expensive, deliver ultra-low IFT values, making them ideal for high-efficiency recovery in mature or tight reservoirs[10,15]. Their strong performance under high salinity and elevated temperatures indicates suitability for deep or offshore reservoirs with challenging conditions.

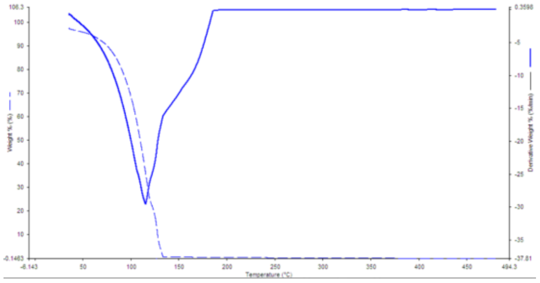

Fig. 4a: TGA curve-1 for SDS

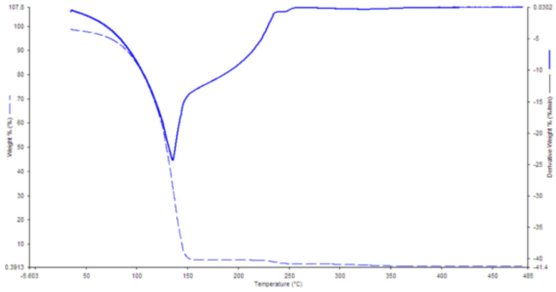

Fig. 4b: TGA curve- 2 for AOS

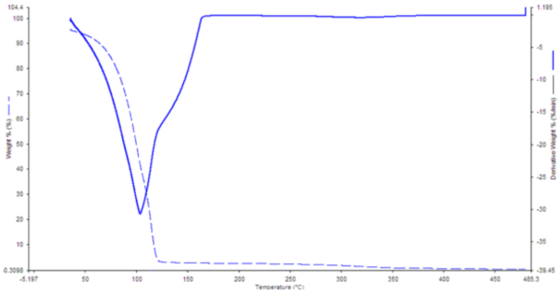

Fig. 4c: TGA curve -3 for LAS

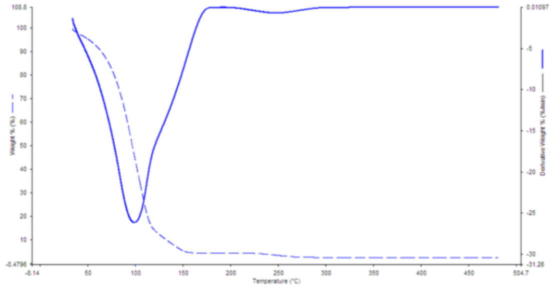

Fig. 4d: TGA curve -4 for PS

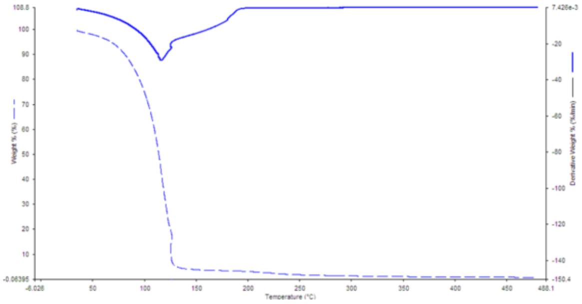

Fig. 4e: TGA curve -5 for AOT

Table 2
TGA summary table of five surfactants

Surfactant	Moisture loss ≤120 °C (%)	Tonset (°C)	Tmax (°C, DTG peak)	Major mass-loss interval (%)	Residue @600 °C (%)	Remarks
SDS (Curve 1)	~2	~80–90	~110–120	80–150 °C: ~95%	~1–2	Clean, sharp one-step decomposition, almost no residue.
AOS (Curve 2)	~2	~100	~130–140	100–170 °C: ~90%	~2	Slightly broader DTG due to chain distribution.
LAS (Curve 3)	~1.5	~90–100	~120 & 150 (shoulder)	90–160 °C: ~90%	~3	Two-step feature from alkyl vs aromatic breakdown.
PS (Curve 4)	~3–4	~70–80	~110 & 180–200 (broad)	80–250 °C: ~80%	~10–15	Broad, multi-step decomposition, significant residue (aromatic/ heavy).
AOT (Curve 5)	~2	~90	~130 & 170	90–200 °C: ~95%	~2–3	Two-step breakdown (succinate → alkyl), low residue.

Table 3
Minimum IFT values achieved by each surfactant under test conditions

Surfactant	Minimum IFT (10^{-2}), mN/m	CMC, w/v%	Remarks
AOT	6.9	0.3	Excellent performance; ideal for tight reservoirs[21]
PS	13.09	0.4	Industry standard; high salinity tolerance[6]
SDS	19.1	0.5	Economical; suitable for lab-scale/pilot use[1]
AOS	23.65	0.7	Stable under salinity and heat[14]
LAS	25.25	0.8	Cost-effective; moderate EOR utility[18]

SDS and AOS, on the other hand, offer a cost-effective solution for shallow or moderately saline reservoirs[15]. Although they require higher concentrations to achieve competitive IFT values, their widespread availability and ease of formulation make them attractive for pilot-scale and commercial operations[3].

LAS, being economically favourable, may serve as a blending component in mixed-surfactant formulations to reduce overall cost while maintaining reasonable performance[11]. Table 2 summarizes the minimum IFT values achieved by each surfactant under test conditions. Ultimately, the selection of a surfactant for field application should consider reservoir conditions (temperature, salinity, lithology), economic constraints and regulatory/ environmental standards. This study provides essential comparative insights that can guide oilfield engineers and decision-makers in formulating tailored EOR chemical packages for specific reservoir challenges.

Discussion

The experimental results highlight significant differences in the IFT reduction capabilities of the tested anionic surfactants, reflecting the critical influence of surfactant molecular structure, concentration and physicochemical interactions in aqueous media under EOR-relevant conditions. Among the five surfactants examined AOT, PS, SDS, AOS and LAS. AOT demonstrated the highest efficiency, achieving an IFT of 6.9 × 10^{-2} mN/m at only 0.3 w/v%. This superior performance can be attributed to its unique double-tailed sulfosuccinate structure, which promotes tight packing at the oil–water interface and effectively lowers interfacial energy[9]. The branched structure of AOT facilitates rapid adsorption, micelle formation and strong interaction with crude oil, even under high salinity (6000 ppm NaCl) and elevated temperatures (70 °C), conditions often encountered in depleted or mature reservoirs[24].

PS also performed strongly, achieving 13.09 × 10^{-2} mN/m at 0.4 w/v%. Its well-documented salinity tolerance and favorable adsorption kinetics[4,24] reaffirm its status as a benchmark EOR surfactant. The amphiphilic balance and diversity of hydrocarbon chain lengths in PS enable effective interaction with crude oil, especially in brine-rich environments[27]. However, batch-to-batch variability and complex formulation requirements remain practical limitations in field-scale applications. SDS and AOS delivered moderate IFT reductions 19.1 × 10^{-2} mN/m and 23.65 × 10^{-2} mN/m respectively. Their linear single-chain structures limit packing density compared to AOT, leading to higher residual IFT values[8,12]. Despite this, their low cost, wide availability and ease of formulation make them attractive for pilot projects or moderate-depth reservoirs where conditions are less extreme.

LAS, while being least effective with a minimum IFT of 25.25 × 10^{-2} mN/m at 0.8 w/v%, still has potential as a co-surfactant in blended formulations. Its bulky benzene ring likely hinders interfacial packing[5] and its poor salinity tolerance[13,29] further restricts its standalone application, but it remains valuable for cost reduction strategies. A consistent trend across all surfactants was the sharp IFT decrease until the CMC, after which further increases in concentration produced no significant changes. This classical behavior confirms that monomeric surfactants dominate interfacial activity, while micelles mainly stabilize the solution without further lowering IFT[7,20,23].

The thermal stability results from TGA further highlight important operational considerations. SDS degraded in a single, clean step (~80–130 °C), leaving negligible residue, while AOT decomposed in two distinct stages associated with breakdown of its sulfosuccinate backbone and branched tails. AOS and LAS showed broader decomposition ranges with minor residues, whereas PS exhibited the most complex behavior, gradually degrading up to ~250 °C with a char yield of 10–15%. Although PS is thermally stable, its residue formation suggests a risk of pore blockage during reservoir application. In contrast, the clean decomposition of SDS and AOT minimizes this risk, making them better suited for high-temperature environments.

When both IFT reduction and TGA stability are considered together, AOT emerges as the most promising surfactant, combining excellent interfacial activity with clean thermal decomposition. PS remains a strong candidate for saline and high-temperature reservoirs but requires attention to its residue-forming tendency. SDS and AOS balance moderate efficiency with economic viability, while LAS has limited standalone utility but can reduce costs when used in blends.

Overall, the findings demonstrate that no single surfactant is universally optimal. AOT and PS are most suited for challenging high-temperature, high-salinity (HTHS) reservoirs requiring ultra-low IFT. SDS and AOS fit better in moderate-depth, cost-sensitive settings, while LAS may be integrated into hybrid systems where economics outweigh performance trade-offs. These results provide a solid foundation for tailored surfactant selection and chemical package optimization in EOR. Looking ahead, synergistic surfactant blends, nanoparticle–surfactant hybrids and eco-friendly biosurfactants could overcome current limitations and expand the applicability of chemical EOR.

Conclusion

This study provides a comparative evaluation of five anionic surfactants AOT, PS, SDS, AOS and LAS for their suitability in EOR, considering both IFT reduction and thermal stability (TGA analysis).

- AOT emerged as the most promising surfactant, achieving the lowest IFT (6.9×10^{-2} mN/m at 0.3 w/v%) and demonstrating clean two-step thermal decomposition with negligible residue. Its branched sulfosuccinate structure enhances interfacial activity, making it highly effective in tight and mature reservoirs, particularly under high-temperature and brine-rich conditions.
- PS also showed excellent performance with an IFT of 13.09×10^{-2} mN/m at 0.4 w/v%, alongside broad thermal stability up to ~250 °C. However, its relatively high char residue (10–15%) highlights potential risks of pore fouling, warranting careful consideration during field implementation despite its strong salinity tolerance and proven industrial record.
- SDS and AOS achieved moderate IFT reduction (19.1×10^{-2} and 23.65×10^{-2} mN/m respectively) with clean decomposition profiles and minimal residues. Their balance of cost-effectiveness, availability and practical stability makes them suitable for pilot-scale or moderate-depth reservoirs with less severe salinity and temperature stress.
- LAS demonstrated the least IFT reduction efficiency (25.25×10^{-2} mN/m at 0.8 w/v%) and showed multi-phase degradation with a small residue, reflecting its limited performance in EOR-like conditions. Nonetheless, its low cost and commercial availability make it a potential co-surfactant for blended formulations where economic trade-offs are critical.

Overall, the findings highlight that no single surfactant can universally satisfy all reservoir conditions. Instead, molecular structure, concentration, salinity tolerance and thermal stability must be jointly considered when designing optimized surfactant packages. While AOT offers superior performance, its cost and regulatory aspects may limit large-scale use. PS provides a robust alternative with proven stability, whereas SDS and AOS remain practical, economical options. LAS, though less effective alone, retains potential value in hybrid formulations.

By integrating both IFT and TGA insights, this study establishes a framework for tailored surfactant selection in EOR projects. Future work should focus on synergistic blends, nanoparticle-surfactant hybrids and environmentally benign formulations to overcome current limitations and expand applicability across diverse reservoir environments.

Acknowledgement

The authors would like to express their sincere gratitude to the Dibrugarh University for providing the excess of institutional facilities and resources to carry out the work without which this work would not have been possible. The authors also would like to express sincere thanks to Oil India Limited for providing the reservoir rock and fluid samples to carry the academic research.

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(Received 02nd September 2025, accepted 04th October 2025)