



Research article

Structural insights into pyridinium-based dicationic surfactants at harsh conditions: Influence of spacer groups on thermal stability and surface properties

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ABSTRACT

The structural properties of surfactants are essential for understanding their behavior and sustainability under extreme conditions, such as high temperatures and varying salinities. In this study, four pyridinium-based dicationic surfactants with different hydrophilic and hydrophobic spacer groups were synthesized and structurally characterized. Thermogravimetric analysis (TGA) and surface tension measurements were conducted to investigate the influence of spacer groups on thermal stability and surface properties. The results demonstrated that all four surfactants demonstrated remarkable solubility in various aqueous environments-seawater (SW), deionized water (DW), and formation water (FW)-at both ambient and elevated temperatures (90 °C), with no phase separation or cloudiness observed after three weeks. TGA results revealed high thermal stability, with decomposition temperatures close to 300 °C, highlighting their robustness for applications requiring sustainable materials with extended lifespans. Surface tension and critical micelle concentration (CMC) measurements showed that surfactants with hydrophilic spacers achieved lower surface tension and more efficient micelle formation than those with hydrophobic spacers. Notably, the dicationic surfactant with a hydroxy spacer exhibited the lowest CMC, indicating a tightly packed micelle structure, advantageous for efficient resource utilization. The lowest surface tension value of 31.790 mNm⁻¹ was obtained for GS-NH. These findings provide valuable insights into the structural design of dicationic surfactants for sustainable engineering, particularly for applications like CO₂ storage and enhanced oil recovery, where thermal resilience and salt tolerance are critical.

1. Introduction

Over the past two decades, the global demand for oil and gas has dramatically increased due to heightened population growth and industrial development [1–4]. Simultaneously, the majority of oilfield reserves approach their maturity stage. In this context, increasing production through the implementation of advanced techniques is crucial. Around 60 % of reservoirs worldwide show

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intricate features and are characterized by oil-wet properties in carbonate formations [5,6]. Furthermore, these formations have enormously harsh reservoir conditions, with high concentrations of divalent ions like Mg^{2+} and Ca^{2+} , temperatures exceeding $100\text{ }^{\circ}C$ and salinities of up to 240,000 ppm. There are several complications to overcome in order to surge oil recovery in these complex, oil-wet reservoirs. Conventional waterflooding is unproductive improving oil recovery under these conditions. Therefore, to overcome all of these obstacles and improve oil recovery in a reservoir with strong oil-wet characteristics, significantly advanced technology is required. One of the most promising technological approaches is known as chemical-enhanced oil recovery (cEOR), which involves inserting chemicals to enhance oil recovery by altering the interfacial forces at the rock-oil-brine and oil-brine interfaces. In this context, several chemicals, including surfactants, polymers, alkalis, nanoparticles were applied to improve the oil recovery. Mechanistically, they supported altering the capillarity, oil-water interfacial tension, and rock wettability, which triggered the untapped or leftover oils to be displaced in the direction of the production well [7,8]. Surfactants and alkalis improve the microscopic efficiency of the injected slug, lowering the interfacial tension between the injected slug and the trapped crude oil while also improving the reservoir rock's water-wetting property [9,10]. Choosing an appropriate surfactant for specific application in a reservoir depends upon different factors such as type of surfactant, and reservoir, as well as the reservoir's pH, salinity, and temperature conditions [11].

Dicationic, also referred to as gemini surfactants, are a distinctive type of organic compound that features two non-polar tails and two polar head groups linked by a spacer [12]. Dicationic surfactants, in contrast to monomeric ones, possess incredible physico-chemical properties, including excellent thermal stability, pronounced solubility, remarkably reduced critical micelle concentration (CMC), enhanced interfacial activities and the capacity to produce special aggregation structures [13]. Owing to their unique physicochemical characteristics, dicationic surfactants have gained widespread application in different industries, including coatings, paints, pharmaceuticals, nanomaterials, homes, cosmetics, detergents, and numerous oilfield applications such as enhanced oil recovery [14]. In recent decades, significant attention has been received by amido-amine and pyridinium-based dicationic surfactants, due to their low cost [15] and high performance in oilfield applications [16,17]. Given the importance of dicationic surfactants, researchers in the petroleum industry have conducted extensive research on their applications for enhanced oil recovery [18–23]. Special physicochemical characteristics in dicationic surfactants can be achieved via proper structure design. For instance, the solubility of the surfactant decreases with an increase in the length of the lipophilic tail group. Nevertheless, inserting the ethoxy units into the lipophilic tail of dicationic surfactants can lead to enhanced water solubility [24,25]. Simultaneously, the amide functional group in surfactants makes them environmentally benign and biodegradable [26]. Similarly, the introduction of oleyl tail groups enables the attainment of a low value of CMC due to the rigidity of the hydrophobic tail [27]. Extensive studies have demonstrated that the physicochemical behavior of dicationic surfactants is significantly influenced by the spacer's nature [28,29]. The spacers may be hydrophilic (ether linkage or hydrocarbon chain with hydroxy/amine functional group) [30], and hydrophobic (long hydrocarbon chain) [13].

In this study, four new pyridinium-based dicationic surfactants such as 1, 4-dibromobutane (GS-4), Bis(2-bromoethyl) ether (GS-Et), 1,3-dibromo-2-propanol (GS-OH), and Bis(2-chloroethyl) amine hydrochloride (GS-NH), were prepared and analyzed using NMR, and FT-IR spectroscopy. The special focus was to determine the effect of different types of spacer on the surfactant properties, including water solubility, thermal stability, and surface properties of the synthesized pyridinium-based dicationic surfactants. The solubility tests were performed by dissolving the surfactants in DW, SW, and FW, and they were aged for 21 days at $90\text{ }^{\circ}C$ temperature. The thermal stabilities of the surfactants were measured with the help of TGA. Furthermore, surface properties including critical micelle concentration, surface tension at CMC, and maximum surface access were also measured. Overall, this work mainly concentrates on the synthesis of new dicationic surfactants and their detailed characterization, along with thermogravimetric analysis, salt tolerance, and surface property analysis.

2. Chemicals and methods

2.1. Chemicals

Glycolic acid (Mn \sim 700) purity (98.5 %), 4-amino pyridine (99 %), 1,4-dibromobutane (99 %), 2-Bromoethyl ether (98 %), 1,3-Dibromo-2-hydroxypropane (97 %), Bis(2-chloroethyl) amine hydrochloride (97 %) were purchased from Aldrich company (Missouri, United States). $CaCl_2$, Na_2SO_4 , $NaCl$, $MgCl_2$, and $NaHCO_3$ were procured from commercial retailers Panreac (Barcelona, Spain) and used as-is for the preparation of FW and SW. The concentrations of the aforementioned salts in both FW and SW are described in Table 1.

Table 1
The proportion of different mono and divalent ions in formation water (FW) and seawater (SW).

Ions	FW (gL^{-1})	SW (gL^{-1})
Na^+	59.5	18.3
Ca^+	19.1	0.7
Mg^+	2.5	2.1
SO_4^+	0.4	4.3
Cl^-	132.1	32.2
HCO_3^-	0.4	0.1
Total	214	57.7

2.2. Structure confirmations

NMR ($^1\text{H}/^{13}\text{C}$) and FTIR spectroscopy were used to elucidate the chemical structure of all newly synthesized dicationic surfactants. A 600 MHz Jeol 1500 (Jeol, Tokyo, Japan) spectrometer was used to measure ^{13}C and ^1H /NMR spectra. A PerkinElmer instrument 16 F model (PerkinElmer, Waltham, MA, USA) was used for the FTIR analysis, and values were recorded in cm^{-1} .

2.3. Thermogravimetric analysis

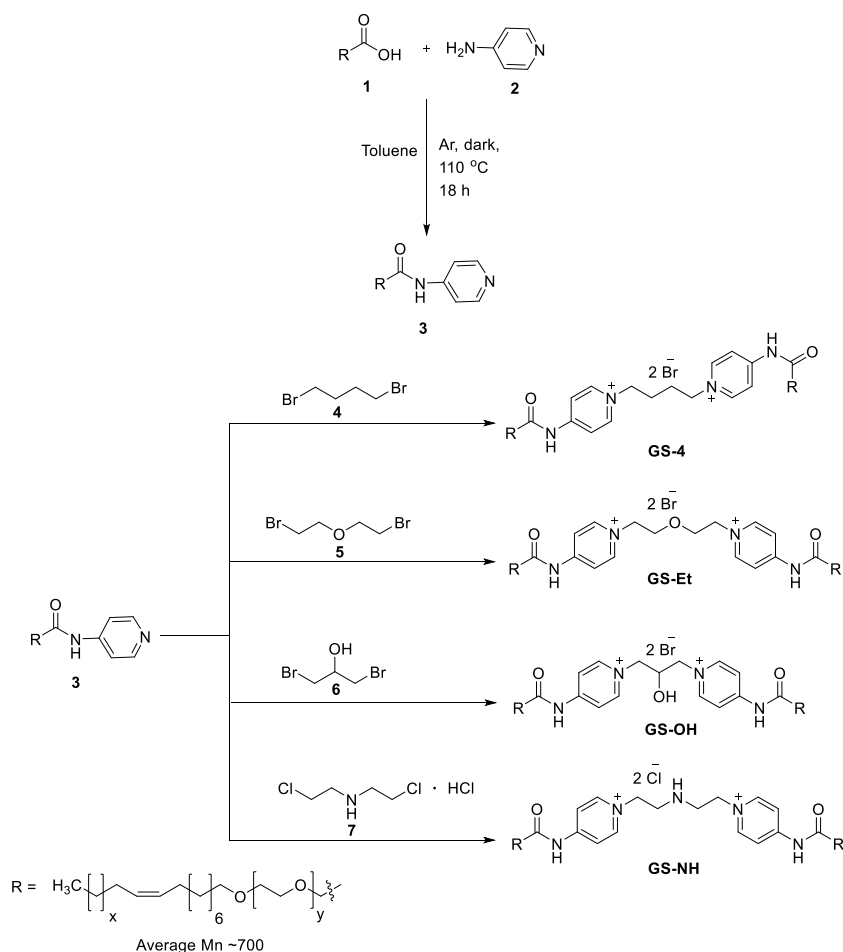
Thermogravimetric analysis, commonly referred to as TGA, is used to measure the heat stability of a material. SDT Q600 machine from TA instruments (New Castle, DE, USA) was used to perform the Thermogravimetric analysis. The temperature ranges from 25 °C to 1000 °C, with a constant supply of nitrogen gas.

2.4. Solubility test

0.25 wt% solutions of **GS-4**, **GS-Et**, **GS-OH**, and **GS-NH**, were prepared in deionized water, seawater, and formation water. These transparent solutions were then kept at a temperature of 90 °C for 21 days. After three weeks (21 days), transparent solutions were observed, demonstrating that **GS-4**, **GS-Et**, **GS-OH**, and **GS-NH** are compatible and soluble in all types of water.

2.5. Surface tension analysis

A platinum Wilhelmy plate (Sigma 702, Biolin Scientific, Gothenburg, Sweden) was used to measure the surface properties of **GS-4**, **GS-Et**, **GS-OH**, and **GS-NH** using a force tensiometer. In order to obtain accurate readings, the Wilhelmy plate was washed with distilled water before each test. All tests were performed at 25 ± 1 °C. Before the start of the experiment the instrument was calibrated with deionized water and the surface tension was obtained in range of 70–72 mNm^{-1} . In our study, each point is an average of five



Scheme 1. Synthetic route for the synthesis of pyridinium-based dicationic surfactants (**GS-4**, **GS-Et**, **GS-OH**, **GS-NH**).

measurements, with a standard deviation of $\pm 0.06 \text{ mNm}^{-1}$, demonstrating high precision and reproducibility.

2.6. Synthesis

2.6.1. General procedure for the synthesis of pyridinium-amide intermediate (3)

The synthetic pathway for synthesizing intermediate **3** is described in [Scheme 1](#). Glycolic acid (25 g, 35.7 mmol), 4-amino pyridine (4.7 g, 50 mmol) and 25 mL of toluene were added to a 250 mL round bottom flask equipped with a magnetic bar under an Argon atmosphere. The mixture was then heated to 110 °C for 18 h under dark conditions. Any excess water formed during the reaction was removed using a Dean-Stark apparatus. After the reaction was completed, a rotary evaporator was used to remove the solvent. The resulting crude mixture was then dissolved in cold acetone filtered, and dried under a high vacuum, yielding the desired intermediate **3**.

2.6.2. Synthesis of (GS-4, GS-Et, GS-OH, and GS-NH)

The resulting intermediate **3** (5.0 g, 6.4 mmol) was refluxed with 1,4-dibromobutane (3.1 g, 14.72 mmol) in 5 mL dry ethanol for 24 h. Afterwards, the volatiles (excess 1,4-dibromobutane, bp. 63–65 °C) were removed by rotary evaporator and dried under high vacuum without additional purification which acquired the corresponding product (GS-4). Surfactants GS-Et, GS-OH, and GS-NH were prepared using the same method by treating intermediate **3** with 2-Bromoethyl ether, 1,3-Dibromo-2-hydroxy propane, and Bis(2-chloroethyl) amine hydrochloride respectively.

3. Results and discussion

Four pyridinium-based dicationic surfactants (GS-4, GS-Et, GS-OH, and GS-NH) were prepared by reacting acid (**1**) with amine (**2**) in dry toluene under dark conditions with an argon atmosphere. While in the second step, the intermediate (**3**) was reacted with different spacers i.e. 1,4-dibromobutane, Bis(2-bromoethyl) ether, 1,3-Dibromo-2-hydroxy propane, and Bis(2-chloroethyl) amine hydrochloride, to obtain of (GS-4, GS-Et, GS-OH, GS-NH).

3.1. Structure elucidation

Spectroscopic techniques including ^1H , ^{13}C NMR, and FTIR, were employed to characterize the structures of the newly prepared surfactants. The chemical structure of GS-4 is demonstrated here, whereas the data for GS-OH, GS-Et, and GS-NH are discussed in the synthesis section. In [Fig. 1](#), the ^1H NMR spectra of GS-4 are presented, highlighting a triplet peak at δ 0.87 ppm which indicates the presence of the methyl (CH_3) group in the surfactant tail, while a multiplet peak at δ 1.28–1.15 ppm represents the characteristic methylene (CH_2) groups in the long tail. An intense multiplet peak appeared at δ 3.63–3.54 ppm, which can be attributed to the ethoxy units ($(\text{CH}_2)_2\text{-O-(CH}_2)_2$). The presence of the methylene groups next to the quaternary pyridine nitrogen ($-\text{N}^+\text{CH}_2-$) and the methylene

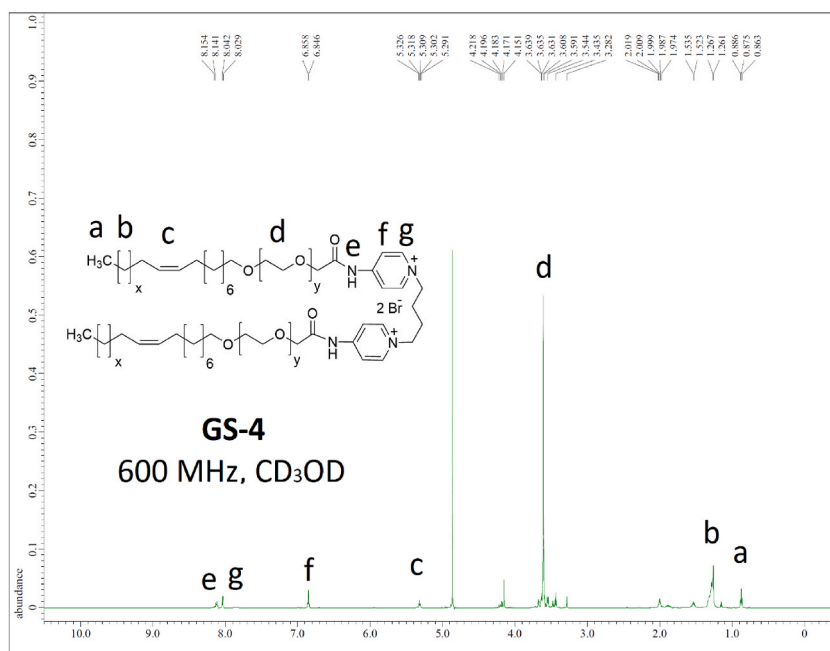


Fig. 1. GS-4 ^1H NMR spectra.

groups adjacent to the carbonyl are confirmed by an overlapping multiplet peak at δ 4.18–4.15 ppm. A characteristic peak at δ 5.31–5.28 ppm represents the internal double-bond protons in the long tail. Furthermore, two doublet peaks at δ 8.03 ppm and δ 6.85 ppm represent the aromatic ring ($-\text{ArCH}-$) protons, while the doublet peak at δ 8.12 ppm corresponds to the characteristic amide NH proton. According to the ^{13}C NMR spectra of **GS-4** (Fig. 2) the CH_3 and CH_2 groups of the unsaturated tail appear at δ 13.1 ppm and 22.4–67.8 ppm, respectively. The ether moieties in the long aliphatic chain ($-\text{CCH}_2\text{O}-\text{CCH}_2-$) could be resonated at δ 69.4–71.0 ppm. The aromatic carbon ($-\text{CH}=\text{CH}-$) adjacent to the amide bond is indicated by the downfield peaks at δ 108.8 ppm and δ 109.5 ppm, while the peaks at δ 139.5 ppm and δ 142.6 ppm are associated with aromatic carbon near the quaternary nitrogen of pyridine. The internal olefin ($-\text{C}=\text{C}-$) peak can be attributed to the signal resonating at δ 129.5 ppm. Peaks at δ 160.6 ppm and δ 171.4 ppm are associated with the aromatic carbon directly linked with NH of amide and the amide carbonyl, respectively.

The FTIR spectra of **GS-4** (Fig. 3) display an adsorption band of amide NH at 3344 cm^{-1} . The asymmetric and symmetric vibrations of the methylene units in the long unsaturated tail could be assigned to peaks at 2923 cm^{-1} and 2854 cm^{-1} , respectively. Furthermore, the characteristic stretching vibrations of carbonyl ($\text{C}=\text{O}$) are found at 1650 cm^{-1} and 1535 cm^{-1} , corresponding to the amide I and II [31]. Simultaneously, an adsorption band at 1461 cm^{-1} , represents the bending vibration of CH_2 , while the band at 1350 cm^{-1} is assigned to the bending vibrations of CH_3 in the tail. Moreover, a sharp peak appearing at 1095 cm^{-1} confirms the existence of ether units ($-\text{CH}_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_2-$) in the tail [32].

3.2. Surfactant solubility

The surfactant's solubility in both seawater and reservoir brine is a prerequisite for its possible oilfield applications. It was observed that the surfactant's solubility is directly associated with the length of the hydrophobic tail group; as the tail length increases, the solubility decreases. However, the incorporation of ethoxy units (EO) in the tail group of the surfactant can enhance its aqueous solubility [33]. The current findings indicate that incorporating special (EO) units into the hydrophilic tail of the synthesized surfactants (**GS-4**, **GS-Et**, **GS-OH**, and **GS-NH**) can remarkably increase their solubility. This enhancement in solubility may be due to strong hydrogen bonding present among the water molecules and ethoxy moieties in the tail. The solubility of surfactants in high salinity conditions and their tolerance to the presence of divalent ions are both enhanced by the addition of ethoxy units, as shown by Kathel & Mohanty [34]. According to their findings, the aqueous stability increases as the number of EO groups increases. Liu et al. (2023) observed similar results in their study, highlighting that the salt tolerance of the system improved as the number of EO units increased. This improvement can be attributed to the enhanced hydrophilicity achieved with the addition of more EO units. This stronger solvation effect not only stabilizes the system in high-salinity environments but also makes it more resistant to the destabilizing effects of salts, underscoring the critical role of EO units in enhancing the performance of such systems [35].

We tested the solubility of all the newly synthesized pyridinium-based dicationic surfactants by dissolving them in DI, SW, and FW at room temperature as well as at $90\text{ }^\circ\text{C}$. All four dicationic surfactants exhibited excellent solubility at both room temperature and $90\text{ }^\circ\text{C}$ (for three weeks) with no phase separation, precipitation, or cloudiness detected (Figures S1-S3).

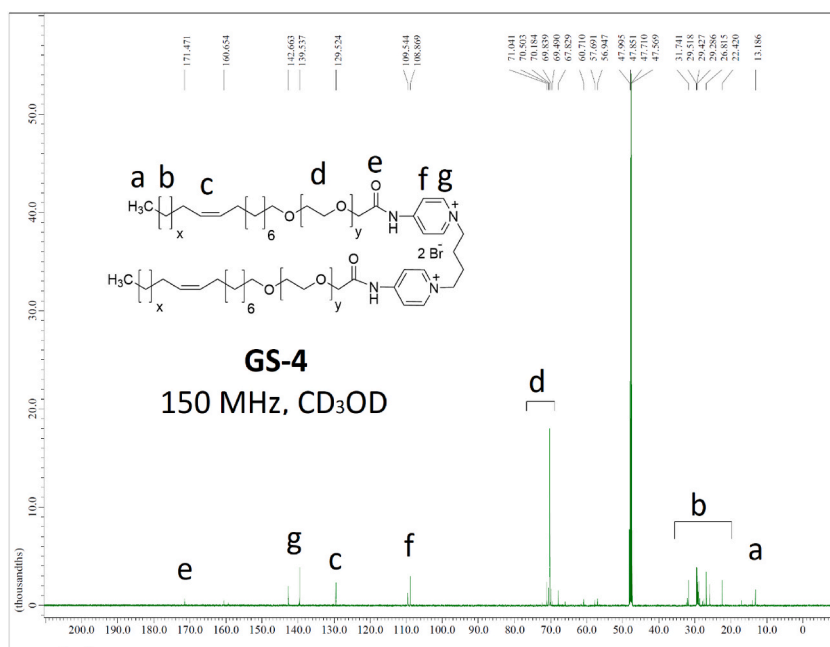


Fig. 2. **GS-4** ^{13}C spectra.

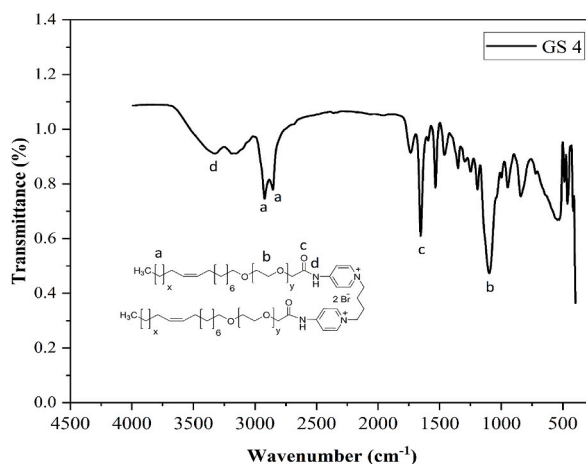


Fig. 3. FTIR spectrum of GS-4 surfactant.

3.3. Thermal stability

Thermal stability for any kind of surfactant is one of the most crucial features for its possible usage in oilfields. Surfactants have a long residence time in oil reservoirs, and the high temperature (90 °C) can cause their degradation. In this study, we investigated the heat tolerance of **GS-4**, **GS-Et**, **GS-OH**, and **GS-NH** surfactants with the help of TGA. According to the TGA graph (Fig. 4), the initial weight loss noticed was 10 %, 12 %, 15 %, and 6 % for **GS-4**, **GS-Et**, **GS-OH**, and **GS-NH**, respectively. The evaporation of moisture and solvent content in the surfactant causes this weight loss. A significant loss in weight was observed at 282 °C (**GS-4**), 280 °C (**GS-Et**), 270 °C (**GS-OH**), and 295 °C (**GS-NH**), demonstrating the impact of temperature on the decomposition of each surfactant structure. All four dicationic surfactants contain similar pyridinium head groups with the same hydrophobic unsaturated tail, each having the same number of ethoxy units. They differ from one another based on their respective spacer groups. Therefore, there is no significant difference in thermal decomposition; though, **GS-NH** which has a secondary amine spacer, revealed relatively higher thermal stability. In a nutshell, it was concluded that these surfactants exhibit higher decomposition temperatures than the real reservoir temperature, and the type of spacer has an insignificant impact on their heat stabilities.

3.4. Surface tension measurement

The newly prepared Pyridium-based dicationic surfactants (**GS-4**, **GS-Et**, **GS-OH**, **GS-NH**) demonstrated pronounced water solubility, resulting in clear and stable solutions across all tested concentrations. Fig. 5 illustrates the air-water interface data (surface data) plotted against bulk concentration, representing the relation between surface concentration and interfacial tension. The addition of surfactant continuously decreases the surface tension until it reaches the breakpoint, known as the CMC. Beyond the CMC, the addition

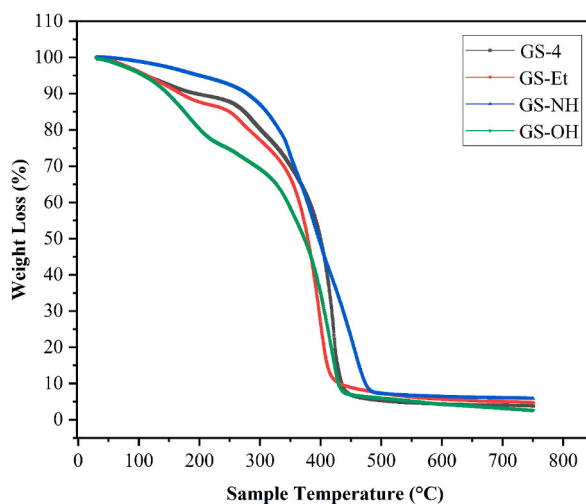


Fig. 4. TGA thermograph of **GS-4**, **GS-Et**, **GS-OH**, and **GS-NH**.

of more surfactants results in negligible changes to the surface tension. Surface properties, including CMC, γ_{cmc} and other properties, were studied with respect to the effects of different spacers.

The CMC values of dicationic surfactants (**GS-4**, **GS-Et**, **GS-OH**, **GS-NH**) were determined to be 0.019 mmol/L, 0.016 mmol/L, 0.013 mmol/L and 0.017 mmol/L, respectively. Surfactants with the hydrophobic spacer group were found to have the highest γ_{cmc} compared to surfactants with the hydrophilic spacer group. The variation of the cmc with the number of hydrophilic spacer groups has been shown in Fig. 6. Nevertheless, the γ_{cmc} increased by changing from hydrophobic to hydrophilic spacer. All the surfactants have structurally identical lengths of tail groups but differ only in their spacer groups. The hydrophilic spacer (ether, hydroxy, and secondary amine functional group) makes the surfactant more hydrophilic and increases its tendency to self-assemble, contributing to lowering the CMC. It was observed that modifying the chain length or changing the spacer group's characteristics from hydrophobic to hydrophilic can remarkably improve the CMC. The influence of the spacer nature on the CMC was principally described for the olea tail while in this work all surfactants have ethoxylate oleyl ether tail [36]. The developed dicationic surfactants exhibit lower CMC compared to other pyridinium-based cationic surfactants such as cetyl pyridinium chloride in the literature [37,38].

Based on surface tension measurements, other surface properties such as critical micelle concentration (CMC), maximum surface access (Γ_{max}), surface tension at CMC (γ_{cmc}), surface tension lowering (π_{cmc}), and minimum surface per molecule (A_{min}) were also determined.

These surface properties were determined with the help of the following equations.

$$\pi_{max} = \gamma_0 - \gamma_{cmc}$$

$$\Gamma_{max} = -\frac{1}{2.303 nRT} \left(\frac{d\gamma}{d \ln C} \right)_T$$

$$A_{min} = 10^{18} / N_A \Gamma_{max}$$

In this equation, γ_0 represents the surface tension of solvent in the absence of surfactant, R denotes the gas constant, T refers to the temperature in absolute terms, NA is Avogadro's number, and $d\gamma/d \log C$ indicates the slope beneath the CMC. Both π_{cmc} and Γ_{max} increased when moving from hydrophobicity (nonpolar spacer) to hydrophilicity (polar spacer), however, A_{min} decreased when moving from hydrophobicity to hydrophilicity. When comparing the influence of different spacer types on surface properties, it was noticed that the surfactants with a polar spacer i. e. secondary amine spacer (**GS-NH**) revealed a lower γ_{cmc} compared to those of **GS-4**, **GS-Et**, and **GS-OH** (Table 2). The γ_{cmc} values followed the order of **GS-4** > **GS-Et** > **GS-OH** > **GS-NH**, signifying that the secondary amine spacer in **GS-NH** enhances its tendency for adsorption at the interface. These results indicate that the presence of a secondary amine spacer notably improves the surfactant's efficacy in lowering surface tension at CMC and producing micelles.

4. Conclusion

In the current study, pyridinium-derived dicationic surfactants were synthesized for the application of enhanced oil recovery. The synthesis of the developed surfactants was confirmed by $^1\text{H}/^{13}\text{C}$ NMR, and FTIR spectroscopic techniques. Results indicated that the type of spacer significantly affected the aggregation patterns. These surfactants demonstrated excellent solubility and salt tolerance in all types of water without any precipitation or phase separation. The TGA findings revealed that **GS-NH** demonstrated comparatively higher thermal stability than **GS-4**, **GS-Et**, and **GS-OH**. The thermal degradation temperature of these surfactants was in the order of **GS-NH** (295 °C) > **GS-4** (282 °C) > **GS-Et** (280 °C) > **GS-OH** (270 °C). The surface tension results depicted that the surfactants with a polar spacer i. e. secondary amine spacer (**GS-NH**) revealed a lower γ_{cmc} compared to those of **GS-4**, **GS-Et**, and **GS-OH**. The lowest surface tension value of 31.79 mNm⁻¹ was obtained for **GS-NH**.

CRedit authorship contribution statement

Muhammad Israr: Writing – original draft. **Ahmad Mahboob**: Investigation. **Masooma Nazar**: Formal analysis. **Syed Muhammad Shakil Hussain**: Supervision, Methodology. **Muhammad Shahzad Kamal**: Writing – review & editing, Supervision.

Data and code availability

Not applicable.

Ethical approval

Not applicable.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

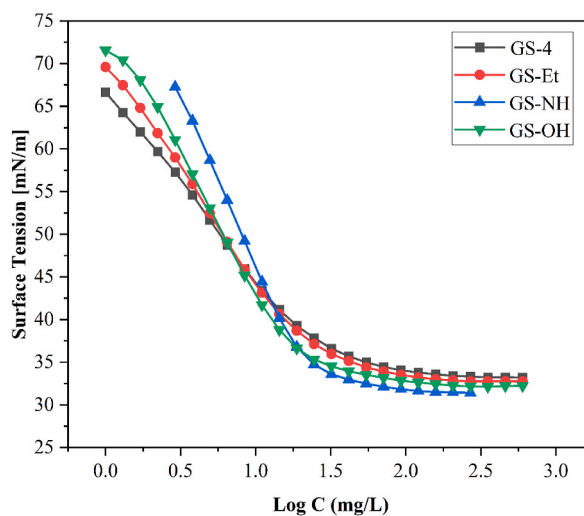


Fig. 5. Surface tension graph of GS-4, GS-Et, GS-OH, and GS-NH in deionized water.

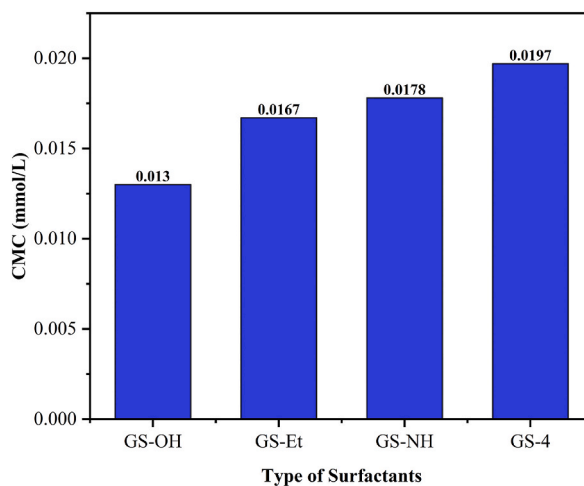


Fig. 6. Variation of the cmc with the number of hydrophilic spacer groups.

Table 2

Surface properties of GS-4, GS-Et, GS-OH, and GS-NH.

Surfactant	T (°C)	cmc (mmol L ⁻¹)	γ_{cmc} (mNm ⁻¹)	Γ_{max} (mol mm ⁻²) × 10 ⁻¹²	π_{cmc} (mN m ⁻¹)	A _{min} (nm ²)
GS-4	25	0.0197	34.156	2.67	37.844	0.4355
GS-Et	25	0.0167	33.223	2.81	38.777	0.3649
GS-OH	25	0.0130	33.165	3.06	38.835	0.2979
GS-NH	25	0.0178	31.790	4.75	39.734	0.2777

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.heliyon.2025.e42625>.

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