Synthesis and assessment of Gemini cationic surfactants as inhibitors for corrosion of carbon steel in hydrochloric acid

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ABSTRACT
Novel mono, di and tetra cationic surfactant (CS) molecules were synthesized by quaternization reaction of diamide with cetyl-2-chloroacetate with different ratio 1:1, 1:2 and 1:4. The chemical structures of the synthetic compounds were proven by FTIR and 1H NMR. The synthetic cationic surfactants were examined as corrosion inhibitors for carbon steel (CSt) in 1.0 M HCl solutions using chemical and electrochemical measurements. Some surface-active properties were determined and linked to the inhibition process. The inhibition efficiency increases with increasing concentration of CS molecules and decreasing temperature. Potentiodynamic polarization technique showed that the three CS molecules are classified as mixed inhibitors. The inhibition process was explained by its spontaneous adsorption on the surface of CSt, according to Langmuir isotherm. The results confirmed that the cationic surfactants successfully inhibited the corrosion of CSt in the investigated corrosion medium and the inhibition efficiency reached 96.08%.

1. Introduction
The corrosion of carbon steel (CSt) in an acidic medium and reducing its risk is an important topic must be studied in depth because CSt is used in many industries. Hydrochloric acid is used to remove grease and fats from the surface of steel, but unfortunately, it corrodes, which leads to huge disasters in industry, it costs governments a lot of money and affects the economy of any country’s government (1, 2). Scientists tended to solve this problem and reduce the risks of corrosion in several ways, among which is the use of corrosion inhibitors. Corrosion inhibitors reduce the corrosion rate of steel by adsorbing on its surface (3–5). There are different types of inhibitors, which reduce the corrosion of metals. One of the most efficient inhibitors are organic inhibitors, which contain heteroatoms such as ‘nitrogen,
oxygen, sulfur atoms, unsaturated bonds, and aromatic cycles (6–14).

In previous years, scientists tended to use surfactants as organic corrosion inhibitors to reduce and control steel corrosion in acidic media (15–22). Surfactants are compounds that lower surface tension and are composed of hydrophilic group ‘polar head’ attached to hydrophobic tail ‘non-polar tail’ connected by a flexible or rigid spacer (15, 16). The surfactants were synthesized based on the fatty acid obtained from Juagafa seeds wastes, which gave an appropriate yield of palmitic acid, followed by esterification and reduction processes to cetyl alcohol (23). On the other hand, surfactants are economically profitable because they are cheap, safe, not harmful to health and easy to prepare and give high inhibition efficiency (20). Cationic surfactants are corrosion inhibitors for different metals besides other applications such as detergents, wetting agents, emulsifiers and dispersants (24, 25).

The fundamental target of this work is to inhibit the corrosion of CSt in 1.0 M HCl solution by newly synthesized mono, di, and tetra cationic surfactants. The inhibitory activity of these compounds was determined by chemical and electrochemical techniques. The effect of increasing temperature on the dissolution of CSt in 1.0 M HCl solution containing 0.005 M of mono, di, and tetra cationic surfactants was studied and some activation thermodynamic parameters of activation were determined and explicated. The relationship between the surface properties and the inhibition efficiency has also been clarified.

2. Experimental

2.1. Materials

Nicotinic acid, methanol, sulfuric acid, hydrochloric acid, ethanol, toluene, chloroform, chloroacetic acid, p-toluene sulphonic acid and cetyl alcohol were obtained from AL-Nasr Chemical Company. Triethylenetetramine was purchased from Merck.

2.2. Synthesis of cationic surfactants

2.2.1. Synthesis of methyl nicotinate

Nicotinic acid (12.3 g, 0.1 mol) was esterified by refluxing with 50 ml of methylated mixture (6% conc. H₂SO₄ in methanol) in a water bath for about a 15 h. Then cooled and neutralized with 15% sodium bicarbonate solution and extracted with chloroform. The chloroform was distilled off to give white crystalline product (yield 76.6% and m. p. 38°C) (26).

2.2.2. Synthesis of diamide

Diamide was prepared by the reaction of methyl nicotinate (2.74 g, 0.02 mol) with triethylenetetramine (1.46 g, 0.01 mol) through fusion technique in the sand bath for about 2 h, then cooled overnight to obtain the final product as pale yellow wax (Scheme 1) (yield 82%, m. p. 80°C). The chemical structure of the diamide was proven by FTIR and 1HNMR (27).

2.2.3. Synthesis of cetyl -2-chloroacetate

A mixture of cetyl alcohol (12.1 g, 0.05 mol), chloroacetic acid (4.72 g, 0.05 mol) in dry toluene and in the presence of 0.01% p-toluene sulphonic acid as catalyst, was refluxed. Using Dean–Stark till the calculated amount of water 0.9 ml (0.05 mol) was separated. The reaction was equalized with sodium bicarbonate and washed with bidistilled water, dried with anhydrous sodium sulphate. The solvent was distilled off to obtain white crystalline solid (Scheme 1) (yield 80%, m. p. 38°C) (23).

2.2.4. Synthesis of cationic surfactants

Cationic surfactants were synthesized by quaternization of the produced diamide with cetyl-2-chloroacetate using ethanol as a solvent for 90 h in molar ratios of 1:1, 1:2 and 1:4. The solvent was distilled off to produce cationic surfactants CSᵢ, CSᵢᵢ and CSᵢᵢᵢ (Scheme 2) (28). The chemical structure of the cationic surfactants was proven by FTIR and 1HNMR.

The percentage yield of compounds CSI, CSII and CSIII are 85.3, 83.5 and 87.6%, respectively, and their melting points are 38–40°C, 72–74°C, and 66–68°C, respectively.

2.3. Carbon steel (CSt)

CSt coupons or rods had the chemical composition (wt %) applied in the measurements: C = 0.38, Cr = 0.90, Mo = 0.15, Si = 0.17, Mn = 0.501 and the rest is Fe. Cst coupons with dimensions 1.4 × 1.2 × 0.5 were used in weight loss measurements. A cylindrical rod immersed in araldite with an exposed surface area of 0.48 cm² was employed in electrochemical measurements. Before any experiment, a pretreatment of the surface of the specimen is performed. The surface of the steel coupon or rod was mechanically polished with some sand paper and washed with distilled water and acetone and then dried.

2.4. Weight loss (WL) technique

CSt coupons were washed, dried, and weighed thoroughly and then the coupons were immersed in a
solution containing blank 1 M HCl and with the addition of specific concentrations ranging between $5 \times 10^{-3}$ and $1 \times 10^{-5}$ M of the synthesized cationic surfactants for 24 h. After the immersion time, the samples are washed, dried, and weighed accurately.

2.5. Electrochemical techniques

For electrochemical techniques, we use a glass cell containing three electrodes and they are Pt counter electrode and saturated calomel electrode (SCE) as a reference and CSt as working electrode. Before each experiment, the CSt electrode remains in the examined solution until the electrode potential remains constant (about 40 min). The potentiodynamic polarization (PDP) technique was acquired using scan rate of 2 mV/s at 27 ± 0.5°C. The electrochemical impedance spectroscopy (EIS) technique was carried out at open circuit potential with AC signals of 5 mV peak-to-peak at open circuit potential in the frequency range of 100 kHz to 10 mHz. Measurements were performed at a constant temperature of 27°C utilizing a super circulating thermostat.

2.6. Determination of the inhibition efficiency

The inhibition efficiency ($IE\%$) and the degree of surface coverage ($\Theta$) of the investigated CS molecules from the WL, PDP and EIS techniques were computed by utilizing the subsequent equation (29):

$$IE\% = [1 - \frac{\partial}{\beta}] 100$$  

$$\Theta = [1 - \frac{\partial}{\beta}]$$  

Scheme 1. Synthesis of diamide.
where $\partial$ and $\beta$ symbolizes the values of corrosion rate (CR) and $I_{corr}$ in the case of WL and PDP techniques in the presence of examined cationic surfactants and in the blank 1.0 M HCl solutions, respectively. But in EIS technique the opposite happens, $\alpha$ and $\beta$ symbolizes the charge transfer resistances ($R_{ct}$) in the blank 1.0 M HCl solutions and in the presence of the examined CS molecules, respectively.

### 2.7. Structural demonstration of the synthesized CS compounds

The chemical structures of the CS were demonstrated by:

1. FTIR spectra: The FT-IR spectra of the compounds were characterized by an FT-IR spectrometer (Thermo scientific Nicolet iS10)
by using KBr as a dispersant, which ranged from 400 to 4000 cm$^{-1}$.

2. $^1$HNMR: The $^1$HNMR spectra of samples were characterized by Switzerland, Bruker Avance.

2.8. Surface active properties of synthesized CS molecules

The surface tension ($\gamma$) values of CS molecules were measured by a Tensiometer-K6 processor by applying ring way. All the measurements were performed at 293 k. Surface active parameters such as critical micelle concentration(CMC), effectiveness ($\pi_{CMC}$), maximum surface excess ($\Gamma_{max}$), minimum surface area ($A_{min}$) and free energy of micellization ($\Delta G_{mic}$) were determined as previously described (30).

3. Results and discussion

3.1. Structural confirmation of diamide ‘N, N’-((ethane-1, 2-diylbis(azanediyl)) bis (ethane-2,1-diyl)) dinicotinamide’

The FT-IR spectra identify the predictable functional groups in the synthesized diamide (Figure 1) by appearing bands at 3289 cm$^{-1}$ (vNH stretching), 3027 cm$^{-1}$ (vCH aliphatic chain), 1649 cm$^{-1}$ (vC=O amide), 1597 cm$^{-1}$ (vNH amide bending), 1550 cm$^{-1}$ (vC = C aromatic stretching), 1473 cm$^{-1}$ (vCH$_2$ bending), 1313 cm$^{-1}$ (vC-$\text{N}$ aryl stretching), 1164 cm$^{-1}$ (vC-$\text{N}$ alkyl stretching), 833, 709 cm$^{-1}$ (three adjacent hydrogen in pyridine ring).

The results of $^1$H-NMR spectra demonstrate the predictable hydrogen proton distribution in the synthesized diamide (Figure 2) δ (ppm): 1.24 (s, 2H, CONHCH$_2$CH$_2$NHCH$_2$CH$_2$NHCH$_2$CH$_2$NHCO), 2.7(t,4H,CONHCH$_2$CH$_2$NHCH$_2$CH$_2$NHCH$_2$CH$_2$NHCO),2.89(t,4H,CONHCH$_2$CH$_2$NHCH$_2$CH$_2$NHCH$_2$CH$_2$NHCO), 7.44–8.6 (d, 8H, NHCOC$_5$H$_4$N pyridine protons) and 9.009(s,2H, CONH of amide proton) (31).

3.2. Structural confirmation of C$_5$I cationic surfactant

The FT-IR spectra demonstrate the predictable functional groups in the C$_5$I molecule (Figure 1) by appearing bands at 3447 cm$^{-1}$ (vNH stretching), 2920 and 2851 cm$^{-1}$ (vCH aliphatic chain), 1745 cm$^{-1}$ (vC=O ester), 1647 cm$^{-1}$ (vC=O amide), 1549 cm$^{-1}$ (vC = C aromatic stretching), 1468 cm$^{-1}$ (vCH$_2$ bending), 1377 cm$^{-1}$ (vCH$_3$ bending), 1313 cm$^{-1}$ (vC–N aryl stretching),1033cm$^{-1}$ (vC–N alkyl stretching), 829, 713 cm$^{-1}$ (three adjacent hydrogen in pyridine ring) and 630 cm$^{-1}$ (ionizable chloride ion).

The results of $^1$H-NMR spectra demonstrate the predictable hydrogen proton distribution in the C$_5$I molecule δ (ppm): 0.85 (t, 3H, C$_3$H$_4$N$^+$H$_2$COOCH$_2$CH$_2$(CH$_2$)$_3$CH$_3$), 1.23 (m, 2H, C$_5$H$_4$N$^+$H$_2$COOCH$_2$CH$_2$(CH$_2$)$_3$CH$_3$), 1.38 (m, 2H, C$_5$H$_4$N$^+$H$_2$COOCH$_2$CH$_2$(CH$_2$)$_3$CH$_3$).
3.3. Structural confirmation of CSII cationic surfactant.

The FT-IR spectra demonstrate the predictable functional groups in CSII cationic surfactant (Figure 1) by appearing bands at 3419 cm\(^{-1}\) (\(\nu\)NH stretching), 3069 cm\(^{-1}\) (\(\nu\)CH aromatic stretching), 292 and 2851 cm\(^{-1}\) (\(\nu\)CH aliphatic chain), 1748 cm\(^{-1}\) (\(\nu\)C=O ester), 1671 cm\(^{-1}\) (\(\nu\)C=O amide), 1550 cm\(^{-1}\) (\(\nu\)C=C aromatic stretching), 1467 cm\(^{-1}\) (\(\nu\)CH\(_2\) bending), 1368 cm\(^{-1}\) (\(\nu\)CH\(_3\) bending), 1315 cm\(^{-1}\) (\(\nu\)C=N aryl stretching), 1059 cm\(^{-1}\) (\(\nu\)C=N alkyl stretching), 831, 720 cm\(^{-1}\) (three adjacent hydrogen in pyridine ring) and 617 cm\(^{-1}\) (ionizable chloride ion).

The results of \(^1\)H-NMR spectra demonstrate the predictable hydrogen proton distribution in the CSII molecule \(\delta\) (ppm): 0.89 (t, 6H, C\(_5\)H\(_4\)N + CH\(_2\)COOCH\(_2\)CH\(_2\)\(_{12}\)CH\(_3\)), 1.25 (m, 48H, C\(_5\)H\(_4\)N + CH\(_2\)COOCH\(_2\)CH\(_2\)\(_{12}\)CH\(_3\)), 1.54 (m, 4H, C\(_5\)H\(_4\)N + CH\(_2\)COOCH\(_2\)CH\(_2\)\(_{12}\)CH\(_3\)), 1.62 (m, 4H, C\(_5\)H\(_4\)N + CH\(_2\)COOCH\(_2\)CH\(_2\)\(_{12}\)CH\(_3\)), 3.05-3.69(m, 24H, CONH(CH\(_2\)CH\(_2\)NH\(_3\))

\(\text{δ}(\text{ppm}): 0.89\text{ (t, 6H, C}_5\text{H}_4\text{N + CH}_2\text{COOCH}_2\text{CH}_2\text{CH}_2(CH_2)_{12}\text{CH}_3), 1.25\text{ (m, 48H, C}_5\text{H}_4\text{N + CH}_2\text{COOCH}_2\text{CH}_2\text{CH}_2(CH_2)_{12}\text{CH}_3), 1.54\text{ (m, 4H, C}_5\text{H}_4\text{N + CH}_2\text{COOCH}_2\text{CH}_2\text{CH}_2(CH_2)_{12}\text{CH}_3), 1.62\text{ (m, 4H, C}_5\text{H}_4\text{N + CH}_2\text{COOCH}_2\text{CH}_2\text{CH}_2(CH_2)_{12}\text{CH}_3), 3.05-3.69(m, 24H, CONH(CH}_2\text{CH}_2\text{NH}_3)\)
4.01 (t, 4H, C₅H₄N⁺CH₂COOCH₂CH₂CH₂(CH₂)₂CH₃), 4.19 (s, 4H, NHCH₂COOCH₂CH₂CH₂(CH₂)₁₂CH₃), 7.5 and 8.23–9.62 (d, 8H, NHCO₅H₄N) (26). 8.23 (s, 2H, CONHCH₂ of amide proton) and 7.5–9.62 (d, 8H, -CH₂-NHCO₅H₄N pyridinium protons) (24).

### 3.4. Structural confirmation of CS₃ cationic surfactant

The FT-IR spectra demonstrate the predictable functional groups in the synthesized CS₃ molecule (Figure 1) by appearing bands at 3417 cm⁻¹ (νNH stretching), 3070 cm⁻¹ (νCH aromatic stretching), 2921 and 2851 cm⁻¹ (νCH aliphatic chain), 1747 cm⁻¹ (νCO ester), 1674 cm⁻¹ (νC = O amide), 1554 cm⁻¹ (νC = C aromatic stretching), 1466 cm⁻¹ (νCH₂ bending), 1364 cm⁻¹ (νC–N aryl stretching), 1056 cm⁻¹ (νC–N alkyl stretching), 827, 722 cm⁻¹ (three adjacent hydrogen in pyridine ring) and 612 cm⁻¹ (ionizable chloride ion) (27).

The data of ¹H-NMR spectra confirm the expected hydrogen proton distribution in the synthesized CS₃ molecule (Figure 2) δ (ppm): 0.86 (t, 12H, NHCH₂COOCH₂CH₂CH₂(CH₂)₁₂CH₃), 1.25 (m, 96H, NHCH₂COOCH₂CH₂CH₂(CH₂)₁₂CH₃), 1.54 (m, 8H, NHCH₂COOCH₂CH₂(CH₂)₁₂CH₃), 1.64 (m, 8H, NHCH₂COOCH₂CH₂(CH₂)₁₂CH₃), 3.12 (m, 4H, CONHCH₂), 3.63 (m, 4H, NHCH₂CH₂NH), 4.05 (t, 8H, NHCH₂COOCH₂CH₂(CH₂)₁₂CH₃), 4.18 (s, 4H, NHCH₂COOCH₂CH₂(CH₂)₁₂CH₃), 5.99 (s, 4H, C₅H₄N⁺CH₂), 7.6 (s, 2H, NHCH₂COOCH₂CH₂(CH₂)₁₂CH₃) and 8.22–9.636 (d, 8H, NHCO₅H₄N pyridinium protons)) (32, 33).

### 3.5. WL technique

Figure 3 represents the WL-time curves for CSt in free 1.0 M HCl solution and with some concentrations of the CS molecules (CS₁, CS₂ and CS₃). The figure shows that WL of CSt decreases than the free solution, showing that, the inhibitory activity of the three tested cationic surfactants. Obviously the linear curves of Figure 3 can be explained by the construction of protection layer on the CSt surface in presence of cationic surfactants. This results from the adsorption of surfactants molecules on the CSt surface and the absence of the insoluble layer formation in acid-free solution. This protection layer on the CSt surface, reduces the contact between the CSt surface and the acidic solution, thus reducing the effect of aggressive medium on the CSt surface (34).

The decrease in weight was recorded. The weight loss (ΔW, in grams) is given by the following equation:

\[ \Delta W = (W_X - W_Y) \]

where \( W_X \) and \( W_Y \) are the weight of the specimen before and after the reaction, respectively. The corrosion rate (CR, in mg cm⁻² d⁻¹) was determined due to the following equation (34):

\[ CR = \frac{\Delta W}{S t} \]

where \( \Delta W \) is the weight loss of CSt coupons, \( S \) is the surface area of the coupons, and \( t \) is inundation time. The inhibition efficiencies (IE %) were determined as described in Equation (1).

CR and IE% values were computed and registered in Table 1. The data in Table 1 show that CR values decrease with increasing concentration of CS molecules and the order of decreasing follows the sequence:

\[ CS_1 < CS_2 < CS_3 \]

Figure 4 shows the relationship between the IE % values and the concentrations of the three CS
molecules at different times. The figures show that the \( \text{IE\%} \) increases with increasing the concentration of CS molecules and the sequence of \( \text{IE\%} \) increase as follows:

\[
\text{CS}_1 > \text{CS}_II > \text{CS}_III.
\]

This behavior is explained by the adsorption and coverage of CS compounds on the surface of CSt. This adsorption reduces surface wear of CSt by blocking the wear sites, thus with increasing concentration of CS particles, WL decreases and the inhibition efficiency increases.

This behavior is explained by the adsorption and the coverage of CS compounds on the surface of CSt. This adsorption reduces corrosion of the surface of CSt by blocking the corrosion sites, thus with increasing concentration of CS molecules, the WL decreases and the inhibition efficiency increases. This adsorption can be explained by an electrostatic attraction between the positive center in the CS molecules and the charged sites on the CSt surface (33). The high inhibition efficiency of the examined inhibitors is 96.07% at 5 \( \times 10^{-3} \) M.

### 3.6. PDP technique

Figure 5 shows the representative PDP curves of CSt in 1.0 M HCl solution alone and with some concentrations of the three CS molecules. From this figure, it is clear that there is a transition region in which the current slowly changes to a positive or negative direction (anodic and cathodic polarization curves). After this region, the potential increases rapidly with the current (the Tafel region). Corrosion kinetics parameters, e.g. corrosion potential (\( E_{corr} \)), cathodic and anodic Tafel slopes (\( \beta_a \) & \( \beta_c \)), corrosion current density (\( I_{corr} \)) achieved from the extrapolation of the anodic and cathodic polarization curves, corrosion rate (CR) and inhibition efficiency.
The parameters listed in Table 2 reveal that, with the increase in the concentration of the three CS molecules, the values of the Tafel slopes ($\beta_a$ and $\beta_c$) altered slightly. This demonstrated that CS molecules influence both the anodic dissolution of CSt and the cathodic $H_2$ evolution reactions. The CS molecules block the cathodic and anodic sites without variation in the corrosion mechanism and no change was observed in the value of $E_{corr}$.

These data confirmed that the three CS molecules are classified as mixed inhibitors (36, 37). The values of $I_{corr}$ decrease resulting in a rise of $IE \%$ values. All values of these parameters confirmed the inhibitory impact of the tested CS molecules by blocking the surface of the steel by adsorbing of the CS molecules through the active centers present in its structure.

### 3.7. EIS technique

Figure 6 displays the Nyquist plots for CSt in 1.0 M HCl solution in the absence and presence of various concentrations of the three CS molecules (CSI, CSII and CSIII) ranging from $(5 \times 10^{-3}$ to $1 \times 10^{-5}$) M at $25^\circ$C ± 1. It is clear from this figure that the impedance pattern does not show perfect semicircles and this due to the frequency dispersal as a result of the roughness and asymmetry of the CSt surface (38). The impedance plots show a similar trend (one capacitive ring). Thus, the diameter of this capacitive ring increases with increasing concentration of the CS molecule, which reduces the corrosion rate and indicates the strengthening of the inhibitory layer formed on the surface of CSt. The semicircular appearance is observed in both the absence and presence of different concentrations of CS particles, indicating that the corrosion of CSt in 1.0 M HCl is mainly controlled by the charge transfer process (39–41).

The EIS spectra of the Nyquist plots were analyzed by matching the experimental results with an equivalent circuit model. The parameters determined and reported in Table 2 reveal that, with the increase in the concentration of the three CS molecules, the values of the Tafel slopes ($\beta_a$ and $\beta_c$) altered slightly. This demonstrated that CS molecules influence both the anodic dissolution of CSt and the cathodic $H_2$ evolution reactions. The CS molecules block the cathodic and anodic sites without variation in the corrosion mechanism and no change was observed in the value of $E_{corr}$.

### Table 2. PDP data of CSt in 1 M HCl solution and with certain doses of the three CS molecules.

| Conc. M | $\beta_a$ (V/dec) | $\beta_c$ (V/dec) | $E_{corr}$ (V, SCE) | $I_{corr} \times 10^{-4}$ (A/cm²) | CR (mm/year) | $\theta$ | $IE \%$ |
|---------|------------------|------------------|---------------------|-------------------------------|--------------|--------|--------|
| Blank 1 M HCl | 0.121 | 0.147 | 0.438 | 6.180 | 7.18330 |
| CSI     | 0.00001 | 0.087 | 0.105 | 0.421 | 0.703 | 0.87172 | 0.8862 | 88.62 |
|         | 0.0001 | 0.075 | 0.091 | 0.419 | 0.608 | 0.70670 | 0.9016 | 90.16 |
|         | 0.0005 | 0.090 | 0.091 | 0.416 | 0.460 | 0.5346 | 0.9255 | 92.55 |
|         | 0.001  | 0.080 | 0.093 | 0.428 | 0.383 | 0.44516 | 0.9380 | 93.80 |
|         | 0.005  | 0.083 | 0.104 | 0.418 | 0.260 | 0.30219 | 0.9579 | 95.79 |
| CSII    | 0.00001 | 0.135 | 0.097 | 0.407 | 0.715 | 0.83104 | 0.8843 | 88.43 |
|         | 0.0001 | 0.138 | 0.091 | 0.412 | 0.533 | 0.61950 | 0.9137 | 91.37 |
|         | 0.0005 | 0.100 | 0.134 | 0.416 | 0.497 | 0.57766 | 0.9195 | 91.95 |
|         | 0.001  | 0.083 | 0.118 | 0.415 | 0.415 | 0.48235 | 0.9328 | 93.28 |
|         | 0.005  | 0.076 | 0.116 | 0.428 | 0.340 | 0.39518 | 0.9449 | 94.49 |
| CSIII   | 0.00001 | 0.138 | 0.139 | 0.438 | 1.60  | 1.85968 | 0.7411 | 74.11 |
|         | 0.0001 | 0.161 | 0.163 | 0.422 | 1.25  | 1.45287 | 0.798 | 79.77 |
|         | 0.0005 | 0.157 | 0.149 | 0.420 | 1.10  | 1.27853 | 0.822 | 82.20 |
|         | 0.001  | 0.101 | 0.181 | 0.440 | 0.818 | 0.95076 | 0.868 | 86.76 |
|         | 0.005  | 0.178 | 0.159 | 0.452 | 0.665 | 0.77292 | 0.892 | 89.24 |
circuit model shown in Figure 7. It includes the solution resistance \( R_s \) and the double-layer capacitance \( C_{dl} \), which is placed in parallel to the charge transfer resistance \( R_{ct} \). The values of \( R_{ct} \) can be obtained by intercepts of the semicircle with the axis of the real component. \( C_{dl} \) values were determined from the angular frequency \( \omega = 2\pi f \) at the maximum virtual component and \( R_{ct} \) due to the subsequent equation:

\[
C_{dl} = \frac{1}{\omega_{max} R_{ct}} \frac{1}{2\pi f_{max} R_{ct}} 
\]

where \( f \) is the frequency, \( \omega \) is the angular velocity. The values of \( R_s, R_{ct}, C_{dl} \) and \% IE were registered in Table 3.

![Figure 6](image)

Figure 6. Nyquist diagrams of CSt in 1M HCl solution and with certain concentrations of (A) CSI, (B) CSI, and (C) CSIII.

![Figure 7](image)

Figure 7. The equivalent circuit model used to fit the experimental results.

It is obvious that from Table 3, with the increase in the concentration of CS molecules, the \( C_{dl} \) values decreased significantly, due to the exchange of more water molecules on the CSt by CS molecules, and the area exposed to the steel for corrosive HCl solution decreases. \( R_{ct} \) values rise and therefore, IE \%and \( \theta \) values increase due to its vigor adsorption on the steel surface. The CS molecules can first be adsorbed and cover some sites on the steel surface by forming of a coating layer on the steel surface. The IE \%values increase in the following sequence: \( \text{CSI} > \text{CSI} > \text{CSIII} \)

3.8. Influence of temperature

The influence of high temperature (from 398 to 343 K) on the dissolution of CSt in the blank 1M HCl solution and containing 0.005M of three CS was studied using PDP technique. Figure 8 represents the PDP plots for CSt electrode in 1M HCl alone and in the existence of \( 5 \times 10^{-3} \)M of the three CS molecules at different temperatures. Some corrosion kinetics parameters, e.g. \( \beta_c, \beta_a, E_{corr}, I_{corr}, C_R \) and IE \% were determined and recorded in Table 4.

Inspection of Table 4 reveals that, with increasing of temperature, the values of \( E_{corr} \) unaffected, but the values of \( I_{corr} \) and IE \% increase and thus the values of IE \%increases in the presence of CSI and CSII, which demonstrates the inhibition effectiveness of the two CS molecules due to the formation of an adsorbed physical layer on the steel surface (42). While, in the presence of CSIII, the IE\% values increase, which indicates adsorption of this compound on the steel surface is chemical (43).

3.9. Kinetic parameter

The Arrhenius equation and alternative transition state equation are applied to determine the activation parameters such as activation energy \( (E_a) \), enthalpy of

| Conc. M | \( R_s \) (\( \Omega \)) | \( R_{ct} \) (\( \Omega \)) | \( C_{dl} \) | IE\% |
|---------|-----------------|-----------------|---------|------|
| Blank   | 2.340           | 52              | 112     | --   |
| CSI     | 0.00001         | 1.437           | 517     | 98   | 89.94 |
|         | 0.0001          | 1.997           | 670     | 87   | 92.24 |
|         | 0.005           | 2.001           | 871     | 81   | 94.03 |
|         | 0.01            | 2.029           | 1033    | 74   | 94.97 |
|         | 0.005           | 2.519           | 1294    | 66   | 95.98 |
| CSII    | 0.00001         | 0.647           | 429     | 94   | 87.88 |
|         | 0.0001          | 0.758           | 463     | 85   | 88.77 |
|         | 0.005           | 0.937           | 746     | 78   | 93.03 |
|         | 0.01            | 1.043           | 972     | 69   | 94.65 |
|         | 0.005           | 1.953           | 1049    | 58   | 95.04 |
|         | 0.00001         | 0.507           | 159     | 101  | 67.29 |
| CSIII   | 0.0001          | 1.563           | 194     | 93   | 73.19 |
|         | 0.005           | 1.836           | 251     | 88   | 79.28 |
|         | 0.001           | 2.055           | 318     | 82   | 83.65 |
|         | 0.005           | 2.699           | 354     | 76   | 85.31 |
Activation ($\Delta H^*$) and entropy of activation ($\Delta S^*$) for CS in the 1 M HCl solution as well as in the existence of $5 \times 10^{-3}$ M of CS molecules at various temperatures ($44, 45$):

$$C_r = A e^{(-E_a/RT)} (6)$$

$$\ln \left( \frac{CR}{T} \right) + \left( \frac{\Delta H^*}{RT} \right) = \left[ \ln \left( \frac{R}{N_A h} \right) + \left( \frac{\Delta S^*}{R} \right) \right] (7)$$

where $A$ is the Arrhenius constant, $R$ is the gas constant, $T$ is the absolute temperature, $h$ is the Plank's constant and $N_A$ is the Avogadro's number.

Figure 9 represents the Arrhenius plots (ln CR vs. 1/T) for CS in free 1 M HCl solution and includes $5 \times 10^{-3}$ M of CS molecules. Straight lines are obtained with a linear regression coefficient of approximately one demonstrating the corrosion of CS in 1.0 M HCl solution devoid of and including CS molecules obeys Arrhenius equation.

Table 4. Corrosion parameters of CS in 1 M HCl solution in absence and presence of ($5 \times 10^{-3}$) M of the CS molecules at various temperatures.

| $T$   | $\beta_a$ (V/dec) | $\beta_c$ (V/dec) | $E_{corr}$ (V/SCE) | $I_{corr} \times 10^{-4}$ (A/cm²) | CR (mm/year) | IE%  |
|-------|-------------------|-------------------|--------------------|-----------------------------------|--------------|------|
| Blank | 303               | 0.104             | 0.180              | -0.418                            | 6.18         | 7.1833 |
|       | 313               | 0.156             | 0.084              | -0.418                            | 9.30         | 10.809 |
|       | 328               | 0.091             | 0.168              | -0.412                            | 11.80        | 13.715 |
|       | 343               | 0.123             | 0.114              | -0.432                            | 15.50        | 18.016 |
| CS_I  | 303               | 0.092             | 0.145              | -0.3924                           | 0.26         | 0.3022 |
|       | 313               | 0.124             | 0.117              | -0.4067                           | 0.70         | 0.8136 |
|       | 328               | 0.108             | 0.099              | -0.4305                           | 1.10         | 1.2785 |
|       | 343               | 0.091             | 0.107              | -0.4335                           | 1.70         | 1.9759 |
| CS_{II}| 303               | 0.099             | 0.147              | -0.4207                           | 0.34         | 0.39518 |
|       | 313               | 0.126             | 0.123              | -0.4304                           | 0.80         | 0.9298 |
|       | 328               | 0.111             | 0.121              | -0.4405                           | 1.20         | 1.3948 |
|       | 343               | 0.084             | 0.117              | -0.4544                           | 1.90         | 2.2084 |
| CS_{III}| 303              | 0.155             | 0.127              | -0.4148                           | 0.665        | 0.7729 |
|       | 313               | 0.136             | 0.103              | -0.437                            | 1.05         | 1.2204 |
|       | 328               | 0.139             | 0.080              | -0.4383                           | 1.50         | 1.7435 |
|       | 343               | 0.102             | 0.075              | -0.4433                           | 1.99         | 2.3130 |

Figure 8. PDP curves of CS in the 1 M HCl solution alone and with $5 \times 10^{-3}$ M of the three CS molecules at different temperatures, (A) blank, (B) CS_I, (C) CS_{II} and (D) CS_{III}.
$E_a$ values were determined from the slopes of linear Arrhenius plots, which equal to 16.72 kJ.mol$^{-1}$ for 1 M HCl solution and equal to 29.95, 29.17 and 15.41 kJ.mol$^{-1}$ for CSI, CSII and CSIII, respectively. Clearly, the values of $E_a$ in the presence of CSI and CSII molecules are higher than those acquired in the HCl solution. This supports the physical adsorption of the two molecules on the Cst surface (22). The rise in $E_a$ and the decrease in $CR$ due to the formation of the adsorbed layer on the surface of the steel, which acts as an energy barrier for the steel dissolution. On the other hand, $E_a$ in the presence of CSIII molecule are lower than that obtained in the free 1M HCl solution. This confirms that the type of adsorption of CSIII on the surface of the steel is chemical.

The values of $\Delta H^*$ and $\Delta S^*$ are computed from the relation between ln($CR/T$) vs. $1/T$ for CSt in a free 1 M HCl solution as well as included $5 \times 10^{-3}$ M of CS molecules. Straight lines were obtained with slope $- (\Delta H^*/R)$ and the intercept of ln($R / N_Ah$) + $(\Delta S^*/R)$. The values of $\Delta H^*$ and $\Delta S^*$ were determined from the slopes and intercepts of the straight lines. The positive values of $\Delta H^*$ reflect the endothermic nature of the corrosion process and demonstrate that the presence of CS molecules reduces the corrosion of CSt. The negative signs of $\Delta S^*$ indicate that the activated complex in the rate-limiting step denotes a binding rather than disengaging which leads to more stable and a transition from the reactant to the activated complex (46).

3.10. Adsorption isotherm

CS molecules inhibit the corrosion of CSt in 1M HCl solution by adsorbing it on the surface of the CSt. The adsorption process can be initiated through the exchange operation between the CS molecule in the aqueous phase and the water molecule adsorbed on the steel surface.

$$CS(aq) + zH_2O_{(surf)} = CS_{(surf)} + zH_2O_{(aq)}$$

where z is the amount of adsorbed water molecules that are exchanged by one CS molecule.

The adsorption intensity relies on the kind and the structure of the surfactant applied as inhibitor, the type and concentration of the aggressive acidic solution, hydrogen ion concentration, temperature and other factors. The values of surface coverage (θ) for some doses of CS molecules from the PDP technique were entered into some isotherms, and we choose the best isotherm that coincides with the current paper. We concluded that the best adsorption isotherm is Langmuir by
applying the subsequent equation:

\[ C - \frac{C}{\theta} = K_{ads}^{-1} \]  

(9)

where \( C \) is the concentricity CS molecule, \( K_{ads} \) is the equilibrium constant of the adsorption.

Figure 10 represents the relationship of Langmuir isotherm (\( C/\theta \) vs \( C \)). Straight lines were acquired with a correlation coefficient (R²) of approximately one and slope equal to one. This elucidates that the adsorption of CS molecules onto the surface of the CSt in 1M HCl solution is subject to Langmuir isotherm. This isotherm postulates, monolayer adsorbed molecules on the steel surface and no any interaction between the adsorbed species. Moreover, the values of \( K_{ads} \) were determined from the intercept of the plots of the Langmuir isotherm and equal to 88,977.45, 88,977.45 and 41,673.26 M⁻¹ for CS, CSII and CSIII molecules, respectively. The high values of \( K_{ads} \) indicate the vigor adsorption of the CS molecules on the steel surface through the formation of a stable layer on it through a coordination bond between the CS molecules and the d-orbital of iron atom on the surface of CSt via a lone pair of electron of hetero atoms.

The free energy of absorption (\( \Delta G_{ads}^{\circ} \)) was assessed from the next equation:

\[ \Delta G_{ads}^{\circ} = -RT \ln (55.5K_{ads}) \]  

(10)

where the value (55.5) is the molar concentration of water in solution in molarity units (mol L⁻¹).

The values of \( \Delta G_{ads}^{\circ} \) are equal to −38.18, −37.73 and −36.30 kJ/mol for CSI, CSII and CSIII molecules, respectively. In general, when the value \( \Delta G_{ads}^{\circ} \) is up to −20 kJ mol⁻¹ or less convenient with the physical adsorption mechanism which demonstrates that the interaction between the CS molecule and the CSt surface is electrostatic. When it is about −40 kJ mol⁻¹ or higher that indicative of a chemical adsorption mechanism. This means that a share or transfer a lone pair of electrons from the additive molecules to the steel surface to form a co-ordinate type of bond (47). The calculated values for \( \Delta G_{ads}^{\circ} \) in the presence of the investigated CS molecules are negative and range from −36.3 to −38.18 KJ mol⁻¹. This indicates that the spontaneous adsorption of the CS molecules on the surface of CSt and the type of adsorption is a combination of physical and chemical adsorption.

### 3.11. Surface active properties

The surface-active properties of the synthesized CS molecules, such as \( \gamma \), CMC, \( \pi_{CMC} \), \( \Gamma_{max} \), \( A_{min} \) and \( \Delta G_{mic} \) were calculated and recorded in Table 5. Figure 11A displays the relationship between \( \gamma \) and the logarithm of the concentration of CS molecules. A sharp reduce in \( \gamma \) values is noted as a concentration of the CS molecules increases and then the curves break rather quickly at relatively low concentrations and continue to decline slowly with increasing concentrations. CMC was computed from the intersection points in the \( \gamma - \log C \) curves (48). From the data recorded in Table 5, it is obvious that the values of \( \gamma \) are reduced by the addition of the CS molecules. The CMC values increase by increasing the alkyl chain length, this may be attributed to the large size of the molecule makes its movement more difficult and hardly migrate to the surface.

Inspection of the data in Table 5, it is obvious that the values of \( \gamma \) are reduced by the addition of the CS molecules, due to the emigration of the CS molecules to the surface and the hydrophobicity of fatty chain lengths in the CS molecules. \( \pi_{CMC} \) values are defined as the difference between the surface tension at CMC (\( \gamma_{CMC} \)) and that for the bi-distilled water (\( \gamma_o \)) at a constant temperature. The surface tension values (\( \gamma \)) at CMC were utilized to compute values of the surface pressure (effectiveness) from equation:

\[ \pi_{CMC} = \gamma_o - \gamma_{CMC} \]  

(11)

where \( \gamma_o \) is the measured surface tension of pure water at the adequate temperature. From the values of \( \pi_{CMC} \) in Table 5, it is obvious that the CSI molecule is more effective CS molecules due to the lower values of \( \gamma \) and \( \pi_{CMC} \) (48). Maximum surface excess (\( \Gamma_{max} \)) is defined as the adsorption efficiency at an interface. \( \Gamma_{max} \) was determined from the slope of the straight line in the surface tension diagram (\( d\gamma/d\log C \)) below CMC, utilizing Gibb’s equation (52):

\[ \Gamma_{max} = \frac{-(d\gamma/d\log C)\gamma}{2.303nRT} \]  

(12)

where \( n \) is a constant that depends on the number of surfactant molecules adsorbed at the interface. The values of \( \Gamma_{max} \) were determined and recorded in Table 5. It is clear that increasing the hydrophobic character of CS molecules shifts \( \Gamma_{max} \) to lower concentrations (48).

The minimum surface area (\( A_{min} \)) is the area occupied by each CS molecule at the air/water interface and

### Table 5. Surface active properties of the CS molecules.

|       | \( \gamma \) | \( \pi_{CMC} \) | \( \Gamma_{max} \times 10^{-4} \) | \( A_{min} \times 10^{-7} \) | \( \beta \) | CMC | \( \Delta G_{mic} \) |
|-------|-------------|-----------------|-----------------|-----------------|-----|-----|-----------------|
| CSI   | 37          | 30.86           | 6.809           | 2.438           | 0.084| 0.00125| -31.19          |
| CSII  | 39.5        | 33.36           | 4.440           | 3.738           | 0.195| 0.00187| -29.38          |
| CSIII | 42          | 35.86           | 2.115           | 7.846           | 0.283| 0.00250| -25.06          |
computed according to the subsequent equation (51):

$$A_{\text{min}} = 10^{14} / N \Gamma_{\text{max}}$$  \hspace{1cm} (13)$$

where $\Gamma_{\text{max}}$ is the maximum surface excess. The values of $\Gamma_{\text{max}}$ increase with the increase in the length of the hydrophobic portion of three CS molecules which increases the tendency towards adsorption of CS molecules, thus $\Gamma_{\text{max}}$ increases, indicating higher surface concentration and more CS molecules number at the surface. Parameters in Table 5 signalize that the values of $\Gamma_{\text{max}}$ decreases with increasing $A_{\text{min}}$ of the CS molecules (48). The specific conductivity ($K$) measurements of the CS molecules were performed to assess the degree of counter-ion dissociation ($\beta$). $K$ is linearly related to the CS concentration in both the premicellar and in the postmicellar regions. The ratio of the slopes of the postmicellar region to those in the premicellar region donates the dissociation of a counter ion ($\beta$) which is recorded in Table 5. The relationship between conductivity and concentration of CS molecules is illustrated in Figure 11(B). The results showed that for CS molecules, the degree of dissociation of the CS molecules increases with an increase in the length of the carbon chain due to the difference in the electronic charge density on the hetero atoms, which relies on the positive inductive effect of the alkyl group and bulk of cation (48).

The values of $\Delta G_{\text{mic}}$ are set from the next equation and registered in Table 5:

$$\Delta G_{\text{mic}} = (2 - \beta)RT \ln \Gamma_{\text{CMC}}$$  \hspace{1cm} (14)$$

Negative signs of $\Delta G_{\text{mic}}$ indicate that the micellization is a spontaneous process and that CS molecules immigrate to the interface or collect in micelles to reduce the repulsion process. The free energy change associated with the transfer of a methylene group from aqueous solutions to the interior of the micelle is negative, thus favoring micellization (49).

3.12. Mechanism of inhibition

The inhibition action of CSt in 1M HCl solution using synthesized CS molecules was inspected using WL, PDP and EIS techniques. All the corrosion parameter like a decrease in WL, $I_{\text{corr.}}$, $R_{\text{ct}}$ and increase the value IE %, in addition to, surface parameters such decrease in $\gamma$, $\pi_{\text{CMC}}$, $\Gamma_{\text{max}}$ supports the inhibition of CS molecules. The inhibition vigor of CS molecules is due to its spontaneous adsorption on the steel surface where the $\Delta G_{\text{ads}}^0$ values are negative. The adsorption is mixed between physical and chemical mechanism. The investigated CS molecules have different adsorption centers to accelerate the inhibition efficiency such as conjugated rings, hetero atoms, unsaturated bonds ($\sim C = O \sim$) and positively charged centers ($N^+$). In physisorption, the electrostatic interaction between the charged CS molecule and the charged steel surface helps the CS molecules to be adsorbed onto the steel surface. While in chemisorption, the donor-acceptor interactions arise from the presence of $\pi$-electrons of multiple bonds, free electron pairs of hetero atoms, and a pyridine group with vacant d-orbitals of iron surface atoms. The values of $\Delta G_{\text{ads}}^0$ are more negative than $\Delta G_{\text{mic}}$. This demonstrates that these CS molecules prefer adsorption at the interfaces rather than the micellization in the bulk of their solution. It is expected that these CS molecules may be used as an interfacial agent such as emulsifiers, corrosion inhibitors and phase transfer catalysts (50).

The addition of CS molecules reduces the $\gamma$ values due to the emigration of the CS molecules to the surface and due to the alkyl group of fatty chain lengths (CH2) in the synthesized CS molecules, the values of $\gamma$ increases by increasing the alkyl group number, this may be due to the large size of the molecule makes its movement more difficult and it hardly travels to the surface (23). We note from Table 5 that the largest decrease in the values of $\gamma$ and $\pi_{\text{CMC}}$ for CSI molecule more than in CSII and CSIII molecules. This is in good agreement with the highest IE % of CSI molecule. The IE % values computed from the different techniques increase as the hydrophobicity of fatty chain lengths decreases. This is due to the fact that the large size of molecules increases with the increase in the number of alkyl group, which makes the movement of the molecule
more difficult and leads to crowding (stearic hindrance), along with the rotation of molecules and interaction between fatty chains decline the coverage of the metal surface by the inhibitor. This implies that the adsorbed molecule may make the surface more difficult for else molecule to adhere to an adjacent site, the distances between molecules increase and the value of θ decreases. Also, multilayer adsorption may occur. CS̃ molecule has a lower number of alkyl group and the highest inhibition efficiency, while the CS³ molecule has a higher alkyl group number and a lower inhibition efficiency. The IE % of CS molecules increases in the following sequence: CS₁ > CS₂ > CS³. This sequence is the inverse of the y values where the CS₁ is the lowest values and is a more effective inhibition than CS₂ and CS³. Therefore, the solubility of the CS molecules increases in the following sequence: CS₁ > CS₂ > CS³. The CS₂ molecule has more hetero atoms (free electron pairs) attached with fatty chain length and less alkyl group than CS₁ and CS³ and the IE % is linked with solubility.

### 3.13. Comparisons with previous studies

Table 6 presents a comparative investigation of the inhibition efficiency of mono-, di- and tetra- cationic surfactant molecules (CS) with other cationic surfactants (51–55). From the data obtained in this table, it was found that the CS molecule used in the present study is more inhibition efficiency than that observed in Schiff base cationic surfactants (51), tricationic surfactants (52) and cationic surfactants such as cetylpyridinium bromide (CPB) and Cetyltrimethylammonium bromide (CTAB) (54). On the other hand it is nearly to Bis (p-N,N,N-decyl-2-1(2hydroxybenzylideneamino)pyridinium bromide) (53) and three new synthesized Gemini surfactants (namely, A312, A314, and A316) of the type 4,4-[1,4phenylenebis(azanylylidene)-bis (N,N-dimethyl-N-alkylaminium) bromide (55). The inhibition efficiency of these compounds depends on the type of carbon steel used, the concentration of the HCl solution or the pH of the solution and the temperature.

| Table 6. Comparison of the inhibition efficiency of the present work with the previous studies. |
|---------------------------------------------------------------|
| Schiff base cationic surfactants | Carbon steel | 1.0 M HCl | 1200 ppm | 88.4–92.1 | (51) |
| **Tri-cationic surfactants** | carbon steel | 1.0 M HCl | 5 x 10⁻³ | 89.3 | (52) |
| Bis(p,N,N,N-decyl-2-1(2hydroxybenzylideneamino)pyridinium bromide) | Carbon steel | 1.0 M HCl | 5.0 mM | 94.09 | (53) |
| Cationic Surfactants | Carbon steel | 1.0 M HCl | 150 ppm | 88.3 | (54) |
| Gemini surfactants | Carbon steel | 1.0 M HCl | 200 ppm | 89.69–94.23 | (55) |
| CSI | Carbon steel | 1.0 M HCl | 0.005 M | 95.79 | Present Work |
| CSII | Carbon steel | 1.0 M HCl | 0.005 M | 94.49 | Present Work |
| CSIII | Carbon steel | 1.0 M HCl | 0.005 M | 89.24 | Present Work |

4. Conclusion

1. The synthesized CS molecules are considered as efficient inhibitors for the corrosion of CST in 1 M HCl.
2. The PDP measurements indicated the CS molecules are mixed-type inhibitors.
3. The inhibition efficiency increases with increasing the inhibitors concentration and with lowering temperature.
4. The performance of inhibition of these CS molecules is due to their adsorption on the surface of CST.
5. The adsorption obeyed the Langmuir isotherm model.
6. The computed surface parameters coincide with the inhibition efficiency of the CS molecules.

### Acknowledgement

The authors express their gratitude to Princess Nourah bint Abdulrahman University Researchers for their support project number [PNURSP2022R94]. Also, the authors would like to thank the Deanship of Scientific Research at Umm Al-Qura University for supporting this work with a grant [Grant number 22UQU4320006DSR02].

### Disclosure statement

No potential conflict of interest was reported by the author(s).

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